

Polymer Material for the Construction of the Membrane with the Various Pore Size

(a Critical Comparison of Various Synthesis
Mechanisms)

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ABSTRACT

The goal of this work was to prepare diblock-copolymer which rapidly changes its solubility in the dependency of the temperature. Appropriate diblock-copolymer should consist of one active (hydrophilic) component, and hydrophobic matrix block. The active component should have the switching temperature as close as possible to the human body temperature. Diblock-copolymer should exhibit sufficient mechanical stability, and the polydispersity index should be as low as possible. The mechanically stable components of the diblock copolymer were, polystyrene (PS) or poly(tert-butylmethacrylate) (PtBMA), while as an active component, poly-(2-(2ethoxy)-ethoxy)methoxy methacrylate (PDEGMA) was used. A polymer required for this purpose should have molar mass of at least 150000 g/mol (in order to possess mechanical stability), and molar ratio of PDEGMA of 0.20–0.40 (in order to get desired structure of hexagonally packed cylinders of PDEGMA in the matrix). The syntheses were performed via different polymerization mechanisms (sequential anionic polymerization, group transfer polymerization, atomic transfer radical polymerization, combination of anionic and atomic transfer radical polymerization). The highest molar masses ($M_n > 20000$ g/mol), lowest polydispersities ($M_w/M_n < 1.1$), and molar amounts of DEGMA exceeding 10% were gained by sequential anionic polymerization. Group transfer polymerization was performed successfully for molar masses up to 22000 g/mol, but no phase separation has been achieved. A PtBMA-PDEGMA random copolymer was achieved employing tetrabutylammoniumbibenzoate (TBABB) as a catalyst, and copolymerization parameters were determined. Atomic transfer radical polymerization has resulted in polymers with molar masses up to 16000 g/mol, and higher polydispersity index compared to the analogous polymers synthesized via sequential anionic polymerization. A combination of anionic and atomic transfer radical polymerization, yielded in copolymers of molar masses up to 25000 g-mol with higher amounts of DEGMA (up to 80 mol%), but with the significant amount (over 20%) of the residual polystyrene macroinitiator.

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LIST OF ABBREVIATIONS

- [A] – Concentration of the free ions
[A⁻C⁺] – Concentration of the ion pairs
aBriBu - Ethyl α -bromoisobutyrate
 α -EiBuBr – α -bromoisobutyrylbromide
ATRP – Atomic Transfer Radical Polymerization
BHT – 2,6-di-tert-butyl-4-methylphenol
 χ – Florry - Huggins interaction parameter
CME – methyl-(α -phenyl-isopropyl) ether
DEGMA – 2-(methoxyethoxy)ethyl methacrylate
DPE - 1,1-diphenylethene
DSC – Differential scanning calorimetry
 ε – Parameter from Kelen and Tudos
 ε_{AB} – Interaction energy between segments A and B
 η – Parameter from Kelen and Tudos
 F – Parameter from Fineman and Ross
 ϕ_i – Volume fraction of the component i
 G – Parameter from Fineman and Ross
 ΔG_m – Free energy of mixing
GTP – Group Transfer Polymerization
GPC – Gel permeation chromatography
 ΔH_m – Enthalpy of mixing
 I – Intensity of primary beam that passes at an angle 0°
 I_0 – Intensity of incident light
[In⁻] – Concentration of the initiator
 k_b – Boltzman constant ($1.38 \cdot 10^{-23}$ J/K)
 K_d – Partition coefficient between the mobile and the stationary phase
 k_i – Rate constant of the initiation
 k_p – Apparent rate constant
 k_{p-} – Propagation rate of the free anions
 k_{p+-} – Propagation rate of the ion pairs
LCST – Lower critical solution temperature
[M] – Concentration of the monomer

$[M]$ – Concentration of all the living chain ends in the reaction system
 $[M_0]$ – starting concentration of the monomer
 M_i – molar mass of the i^{th} polymer chain
 M_n – Number average molar mass
 M_n^{app} – Apparent number average molar mass
 M_n^{theo} – Theoretical number average molar mass (monomer-initiator ratio)
 M_w – Weight average molar mass
 Me_6TREN – Tris[2-(dimethylamino)ethyl]amine
 MMA – Methylmethacrylate
 MTS – Methyl trimethylsilyl dimethylketene acetal
 N_i – number of polymer chains with molar mass M_i
 NMR – Nuclear magnetic resonance spectroscopy
 $[P]$ – Number of polymer chains
 P_n – Degree of polymerization
 PDEGMA – Poly(2-(methoxyethoxy)ethyl methacrylate)
 PMAA – Polymethacrylic acid
 PMDTA – N,N,N',N'',N''' pentamethyldiethylenetriamine
 PS – Polystyrene
 PtBMA – poly(tert-butylmethacrylate)
 PTEGMA – poly(2-(2-(methoxyethoxy)ethoxy) ethyl methacrylate)
 R – Universal gas constant (8.315 J/Kmol)
 r_i – Copolymerization parameter of the component i
 ΔS_m – Entropy of mixing
 T – Temperature
 T_g – glass transition temperature of the polymer
 T_{gi} – glass transition temperature of component i
 τ – Turbidity
 TASHF_2 – Tris(dimethylamino)sulfoniumbifluoride
 TBABB – Tetrabutylammoniumbibenzoate
 tBMA – tert-butylmethacrylate
 TBAOH – Tetrabutylammonium hydroxide
 TEGMA – 2-(2-(methoxyethoxy)ethoxy) ethyl methacrylate
 THF – Tetrahydrofuran
 TMS – Tetramethyl silane

TREN – Tris-(2-aminoethyl) amine

UCST – Upper critical solution temperature

V_0 – volume between the gel particles

V_e – elution volume

V_i – the overall sum of all pore volumes

w_i – Weight fraction of component i in copolymer

x_p – Degree of monomer conversion

Z – Number of nearest segments

1. INTRODUCTION

1.1. MEMBRANES

1.1.1. DEFINITION

In general, a membrane is defined as a layer of a porous material which is a selective barrier between two phases and remains impermeable to specific substances under the influence of a driving force. Components that can pass through a membrane are called permeate, while components that cannot pass through a membrane are called retentate.¹ According to the pore diameter (d_p)², membranes might be classified as:

- microporous ($d_p < 2$ nm)
- mesoporous (2 nm $< d_p < 50$ nm)
- macroporous ($d_p > 50$ nm).

Membranes can be neutral or charged, with a homogenous or heterogenous structure, and the transport of the substances can be active or passive. According to the material that is used for the construction, membranes can be divided into the following groups:³

- inorganic membranes
- polymeric membranes
- biological membranes

The first two categories are quoted as artificial membranes, and have a great significance for various industrial processes. A biological membrane is the barrier within or around a cell. It consists of a lipid bilayer, composed of a double layer of lipid molecules and proteins.⁴ The main task of the cell membrane is to control the movement of substances in and out of cells

1.1.2. APPLICATIONS

Driving forces for the operation of membranes are usually pressure and/or concentration gradients, and the process is known as a filtration. The most common membranes separation processes are water purification, reverse osmosis, dehydration of natural gases, removal of microorganisms from dairy products, dialysis and microfiltration.⁴

The role of the membranes in separation processes in industry has rapidly increased in the past decades. Application of the porous membranes in industrial processes mainly depends on their pore dimensions. In most of the cases, membrane processes includes no phase transitions, and the process is pressure driven. Application of the membranes also includes protein separation, and originally this work was intended to focus on membranes for that purpose.

As the possibility of membrane applications is determined by the dimension of the pores, membranes with various pore dimensions are especially interesting for industrial applications. The original motivation of this work was to construct membranes whose pore dimensions could be altered by an external stimulus. This external stimulus might be achieved by changing the temperature or the pH value of the environment. The variation of the temperature or pH would trigger a change in the pore dimensions resulting in a membrane serving as an on/off switch at the “switching” temperature or pH.

1.1.3. PREREQUISITES FOR THE CONSTRUCTION OF A MEMBRANE

The main goal of this work is to synthesize a temperature-sensitive polymer which is suitable for the construction of the membrane. As the main application of the membrane should be protein separation, polymer for this purpose must be chemically stable, non toxic, with a switching temperature below 40°C in order to prevent protein degradation (see page 18). Materials for this membrane should also have sufficient mechanical stability to make the construction of the membrane possible. A potential approach to this type of membrane is described on page 17.

1.2. PHASE BEHAVIOR OF POLYMERS

In order to make a membrane, the phase behavior of polymers should be considered. The mechanical properties of polymer materials for membrane applications are strongly determined by the compatibility and the miscibility of the copolymer components. Therefore, special attention is paid to the mixing properties of the polymer and the presence of the phase separation.

1.2.1. PHASE SEPARATION PROCESSES

1.2.1.1. IN BULK

Two polymers are miscible if the free enthalpy of their mixing is below 0. The free enthalpy of mixing is defined as:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

ΔG_m – free energy of mixing

ΔH_m – enthalpy of mixing

T – temperature

ΔS_m – entropy of mixing

The enthalpy of mixing can be expressed according to Flory and Huggins⁶⁻⁸ as:

$$\Delta H_m = RT\chi\phi_A\phi_B \quad (2)$$

R – universal gas constant (8.315 J/Kmol)

χ – Flory - Huggins interaction parameter

ϕ_i – volume fraction of the component i

The Flory-Huggins parameter χ can be presented as:

$$\chi = \frac{Z}{k_b T} \left[\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right] \quad (3)$$

Z – number of nearest segments

k_b – Boltzman constant

ϵ_{AB} – interaction energy between segments A and B

The interaction parameter determines the surface tension between segments A and B. In other words, this parameter determines the preference of the segment to be surrounded by segments of the same or the other kind.

The entropy of mixing is given as:

$$\Delta S_m = -R \left(\frac{\varphi_A}{N_A} \ln \varphi_A + \frac{\varphi_B}{N_B} \ln \varphi_B \right) \quad (4)$$

N_i – degree of polymerization of component i

The entropy and the enthalpy of the mixing process are in direct confrontation. The enthalpy tends to be minimized, and the equations 2 and 3 clearly indicate that the decrease of the enthalpy can be gained by the decrease of the number of the nearest segments (parameter Z in the equation 3). This possibility can be fulfilled if the area between the two phases is minimal. On the contrary, the system prefers a conformation with the highest entropy, and consequently, to increase the area between the two phases (eq. 4). The balance of those two effects determines the microstructure of the polymer (see pages 19-22).

The entropy of mixing is in most cases positive ($\phi_i < 1$, and hence, $\ln \phi_i < 0$), but for higher degrees of polymerization (high N_i), the change in entropy is small. Then the slight repulsive interactions between segments ($\Delta H_m > 0$) can no longer be compensated by the entropy contributions leading to positive value for ΔG_m , and macrophase separation occurs.

As macrophase separation tends to hamper the mechanical properties, it should be circumvented whenever it is possible. This is especially important in polymer blends. A polymer blend is a class of materials, in which two or more polymers are mixed together to create a new material with different physical properties.⁹ Here, macrophase separation can be avoided by using compatibilizers. Those compatibilizers self-assemble at the interface between blend components, and dispersed phase separated blends are achieved. Block copolymers that consist of at least two different blocks might be suitable as compatibilizers. If one block is compatible to the one component of the blend, and the other block is compatible with the second component of the blend, macrophase separation will not occur as the block copolymer will be located at the interface of the component resulting in a one-phase system.¹⁰⁻¹²

1.2.1.2. IN SOLUTION

According to equation 1, mixing needs a negative free energy of mixing, ΔG_m which can be realized by a negative enthalpy (ΔH_m) or a positive entropy of mixing (ΔS_m). In most cases, the entropy of mixing is positive, and increases with the temperature resulting in a decrease of the order in the system. Then, the entropy term $T\Delta S_m$ increases, the free energy becomes negative and the mixing is spontaneous.

1.2.1.3. UPPER CRITICAL SOLUTION TEMPERATURE (UCST)

For many polymer-solvent combinations, both the entropy and the enthalpy of the mixing are positive. At low temperatures the unfavorable enthalpy effect could predominate over the entropy and the free enthalpy for the process of mixing (ΔG_m) becomes positive resulting in a phase separation. Equations 1-4 give the dependency of the thermodynamical parameters (ΔG_m , ΔH_m , ΔS_m) of the mixing process on the composition of the polymer. Therefore, those equations can predict whether the polymer is soluble in certain solvent (if $\Delta G_m < 0$) or not (if $\Delta G_m > 0$).

Those equations quantify the Flory Huggins theory which takes account of the great dissimilarity in molecular sizes expression for the free energy of mixing.⁶⁻⁸ According to Flory and Huggins, the polymer is not considered to be a chain of monomers, but rather, a chain of polymer segments. Huggins and Flory introduced the lattice model for description of the thermodynamics parameter when the polymer is dissolved by a solvent. This lattice model creates a lattice of "points". Each point can be occupied by a solvent molecule or a polymer segment. The polymer chain is divided up into polymer segments, such that each polymer segment has the same volume as a solvent molecule.⁶⁻⁸ The temperature above which a single phase exists for all compositions is called upper critical solution temperature (UCST).¹³ Example for a system exhibiting a UCST behavior is poly(N,N dimethylacrylamid) in a water-dioxane mixture.¹⁴

An idealized phase diagram of a system exhibiting an UCST behavior is presented in Figure 1a. The UCST defines the maximum temperature where the change from one phase system to the two phase system occurs. After passing the UCST, the system will be in one phase, no matter of its composition. On the other hand, Figure 1b shows a behavior where the system changes from a two phase to an one phase system.

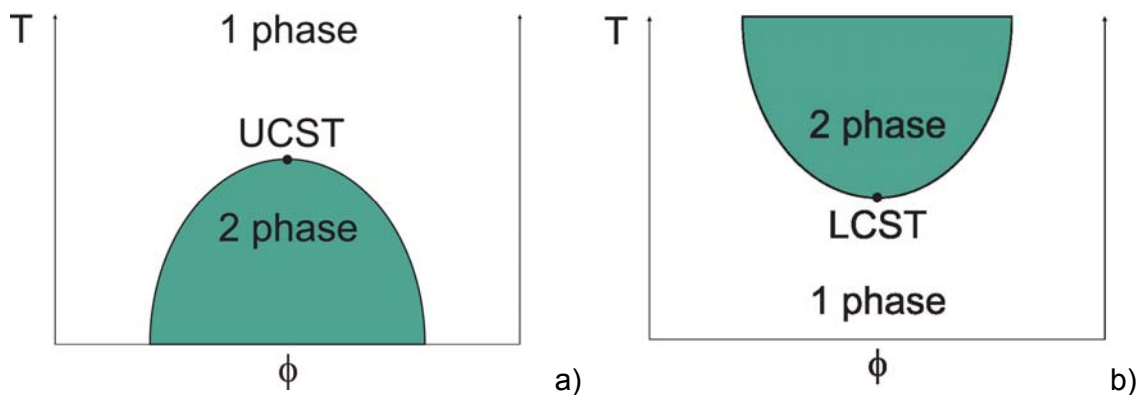


Figure 1: Idealized phase diagram of the system that shows
a) UCST behavior; b) LCST behavior

1.2.1.4. LOWER CRITICAL SOLUTION TEMPERATURE (LCST)

Although a dissolving process is usually associated with the increase of disorder (and thus, an increase in entropy), in some cases it is possible that the system becomes more ordered when solvation occurs. This may happen when hydrogen bonds between the molecules of the solvent and the polymer's repeating units are formed. As ΔS_m in this case is negative, the product $-T\Delta S_m$ in the equation 1 is positive, and ΔG_m can become positive even if the mixing is an exothermic process. As a consequence the polymer is insoluble resulting in a two phase system.

Hence, in analogy to the UCST, the corresponding lower critical solution temperature (LCST) can be defined as the temperature below which a single phase exists for all compositions. If the temperature is below the LCST, the system is in one phase. When temperature is increased, the polymer solubility rapidly decreases, the polymer precipitates, and two separate phases in the system are observed.

The thermodynamical background of a LCST behavior can be explained by large differences of the thermal expansion coefficients of the polymer and of the solvent. The solvent expands much faster than the polymer if the mixture is heated. The addition of the polymer to the solvent results in a decrease of the density of the solvent and a decrease of the translation entropy of the solvent molecules. This effect might be so strong that the solvent molecules can lose their ability to group around the polymer molecule, and the polymer precipitates.

The LCST for certain polymer/solvent systems strongly depends on the polarities of both the polymer and the solvent. If both are polar, the LCST is usually well below the boiling temperature of the solvent. On the contrary, if both components are non-polar, the LCST is usually close to the boiling point of the pure solvent.

The easiest and the most obvious sign of presence of two phases in system is an rapid increase in the turbidity of the solution at a certain temperature, hence the phase transition in solution can be determined by the measurement of the turbidity (see Figure 2).

1.2.1.5. TURBIDITY

Turbidity is the cloudiness of a fluid caused by suspended particles that are generally invisible to the naked eye. According to the Lambert's law, the relation between the intensities of incident light (I_0), and the intensity of primary beam (I) that passes through the solution at an angle 0° , for a path d and the turbidity (τ) is:

$$\tau = -\frac{1}{d} \ln\left(\frac{I}{I_0}\right) \quad (5)$$

The turbidity of polymer solution is determined by a comparison with the turbidity of a standard solution. By that way, turbidity is measured in internal relative units. The cloud point of a fluid is the temperature at which the dissolved matter is no longer completely soluble. It precipitates as a second phase and gives the fluid a cloudy appearance.

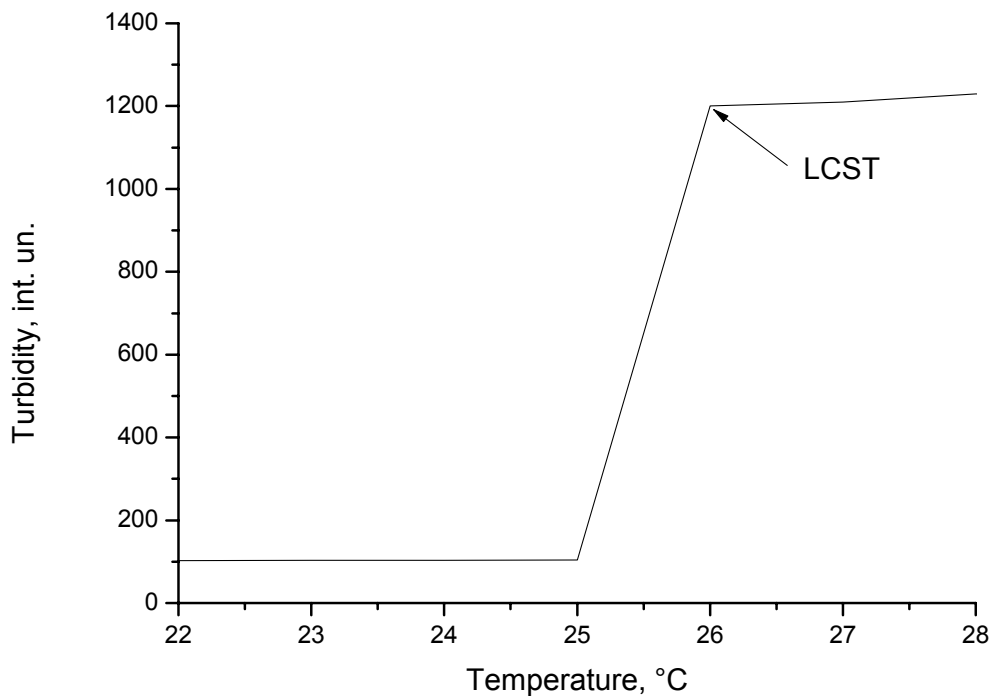


Figure 2: Idealized dependence of solubility of a polymer with a LCST behavior on a temperature with marked LCST point

On Figure 2 dependence of the turbidity behavior on the temperature of a polymer in solution is presented. The turbidity of the solution of a polymer with LCST behavior is negligible for temperatures lower than the LCST. When LCST is reached, the turbidity rapidly increases, and remains constant during further heating. The LCST of the polymer in Figure 2 would be 26°C.

1.2.1.6. LCST POLYMERS

In order to make materials for the membranes that can change the pore diameter under a temperature stimulus (see page 9 for the prerequisites), a lower critical solution temperature (LCST) behavior of certain polymer materials can be used (for example: poly(*N*-isopropylacrylamide) – PNIPAM or poly(2-(methoxyethoxy)ethyl methacrylate) – PDEGMA with LCST +33°C for PNIPAM and +26°C for PDEGMA).¹⁵ Such behavior is typical for the polymers that form hydrogen bonds to water.^{16,17}

Various polymethacrylates have been synthesized by introducing polar and hydrophilic functionalities on the ester moieties to provide water solubility. Oligo(ethylene glycol) methyl ether methacrylates (OEGMA) with different numbers of ethylene glycol groups in the side chain show a lower critical solution behavior in water. Their LCST strongly depends on the length of the methacrylates' ester group. The most interesting polymers are poly(2-(methoxyethoxy)ethyl methacrylate) (PDEGMA) and poly(2-(2-(methoxyethoxy)ethoxy) ethyl methacrylate) (PTEGMA) as they have a LCST close to room temperature (26°C and 52°C respectively).¹⁹⁻²³ The structures of those OEGMA monomers are:

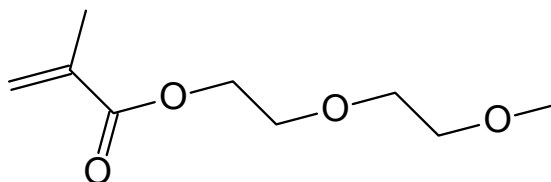


Figure 3: Structure formula of 2-(methoxyethoxy)ethyl methacrylate (DEGMA)

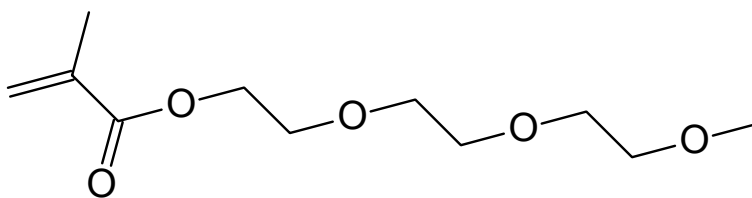


Figure 4: Structure formula of 2-(2-(methoxyethoxy)ethoxy) ethyl methacrylate (TEGMA)

As the LCST increases with an increasing of number of ethoxy groups, methacrylates with more than three ethoxy groups are not of interest.²⁴ Poly(oligo(ethylene glycol)methyl ether methacrylates) with an OH group at the side-chain end are soluble in water and show no LCST in water.²⁵ This indicates the significant effect of the ω -functionality of the side chain on the behavior in water. The more hydrophobic methyl group decreases the water solubility and induces the phase separation at higher temperatures. The balance between hydrophilicity and hydrophobicity in the structure is of most importance in order to attain the LCST behavior and thermosensitivity of these water-soluble polymethacrylates.^{26,27}

The LCST also decreases with a change of the end group at the side chain, so poly(2-(ethoxyethoxy)ethyl methacrylate) (the ethoxy counterparts of DEGMA) has a LCST at 4°C, while poly(2-(2-(ethoxyethoxy)ethoxy) ethyl methacrylate) (the ethoxy counterpart of TEGMA) has a LCST at 27°C. This clearly indicates the effect of the side chain not only on the water solubility but also on the cloud point behavior in water.²⁴

1.2.1.7. LCST AND MEMBRANE POLYMERS

The basic concept to use LCST polymers for making-up temperature sensitive membranes is to synthesize a binary block copolymer. One block is a mechanical carrier of the other, and gives mechanical stability to the membrane. The other block has a LCST, and serves as an active component of the membrane.

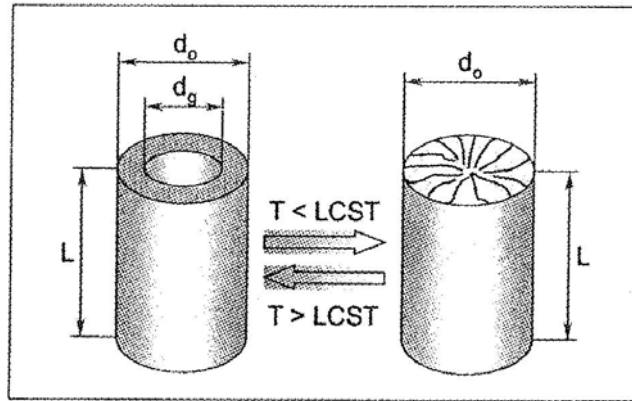


Figure 5: Behavior of cylinder-shaped polymer with LCST with the change of temperature²⁸

A basic requirement to use LCST polymers for making membranes is that the active component has a cylindrical shape embedded in the matrix of the mechanical carrier component. The length of those cylinders should be equal to the thickness of the active layer (marked as L on the Figure 5). In other words, the active component cylinders should be spread through the whole thickness of the membrane. The cylinders have a diameter d_o . If the temperature is below LCST, the active component of the diblock copolymer is soluble in the solvent, the chains are in random-coil shape, and the membrane pores are closed. By closing the pore, the transition of any substances through it is impossible. If the temperature is increased, the active component of the diblock copolymer is not soluble, it collapses, and the pore is open with the diameter d_g . That means that any substance that has a maximal dimension smaller than d_g can pass through the pore. By this simple mechanism the pore becomes transitive for any substance of appropriate size.

Although UCST polymers can be used for the same purpose, they are not of interest in this research. The main reason is that UCST polymers based membranes require lower temperatures in order to open the pores. As the main task of this membrane would be in protein separation processes, the open/close temperature should be as close to the temperature of the human body as possible. For UCST based membrane that would mean that the starting temperature should be above the human body temperature, and that pore opening should be obtained by cooling. On the other hand, application of the LCST polymers allows a start at room temperature, and an opening of the pores by simple heating.

1.2.2. MICROPHASE SEPARATION

Microphase separation is segregation of block copolymers which occurs on smaller dimensions than macrophase separation. In principle, microphase separation is also governed by equations (2)-(4). The main difference between macro and micro phase separation is that microphase separated phases are chemically linked. Therefore, the number of nearest segments (parameter Z in equation 3) is increased compared to the non-bonded phases which strongly influences the Flory-Huggins interaction parameter (χ in equations 2 and 3).

Two opposite factors are involved in microphase separation processes. The interface between the blocks tends to be minimized, due to enthalpic reasons. The entropic contribution, on contrary, leads to a random-coil conformation of the polymer chains, as these results in the maximum entropy. The later effect weakens the segregation between the blocks, and a morphology with a larger interface between the blocks than the minimal one is formed. The morphology of the diblock copolymer is determined by both opposing effects mentioned which are directing the system into the opposite directions.

When microphase separation occurs, diblock copolymers are assembled into regular patterns presented in Figure 6 with increasing the content of block A. For a nearly identical composition, the two blocks assemble in a lamellar structure (Figure 6d). If the composition changes in favor of block A, the structures shown in Figure 6 will be obtained. With increasing amount of block type B, the block A will assemble in a gyroids (Figure 6c), hexagonally packed cylinders (Figure 6b) and spheres packed on a body centered cubic (bcc) lattice (Figure 6a). If the composition is reversed, inverse patterns will result, which are not shown in Figure 6. Therefore, symmetrical sequence is obtained, starting from the lamellar structure.

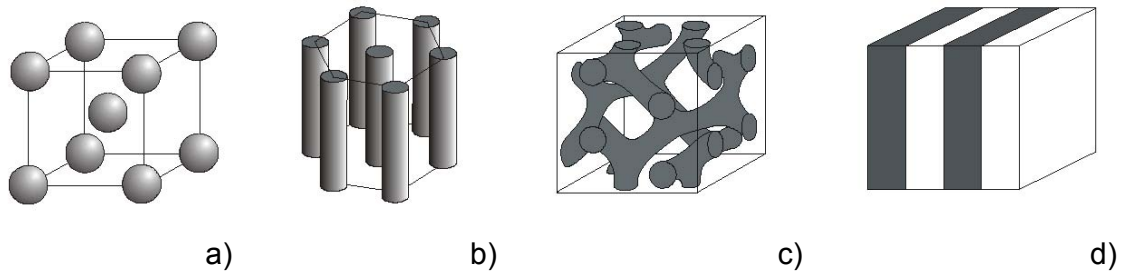


Figure 6: Schemes of different structures of two-component polymers

a) spheres arranged on a body-centered cubic lattice;

b) hexagonally packed cylinders;

c) gyroid;

d) lamellae

For low values of χN entropic reasons dominate over the enthalpic ones and the diblock copolymer is in a disordered isotropic phase. Microphase separation starts theoretically if the condition that $\chi N > 10.5$ is fulfilled.²⁹ Two areas of this phase diagram with the smooth border at $\chi N > 15$ can be described by two different approaches: the weak segregation limit (WSL) and the strong segregation limit (SSL).

In the WSL approach the boundaries between different microphases are not sharp, and there is a smooth transition of the composition at the interface of the different phases.^{29,37,38}

Diblock copolymers whose behavior is explained by the SSL show a high incompatibility of both blocks, which is a consequence of a high χ value. Because of that, even at a low degree of polymerization, a phase transformation is observed.³¹⁻³⁵ This theory does not extend directly into the WSL regime, and calculations based on the SSL region are restricted to $\chi N > 100$. The distinction between WSL and SSL does not necessarily depend solely on the type of the two blocks, as it is also influenced by N . Hence, for a given combination of N and χ , the phase behavior of block copolymer can be described by both theoretical approaches, i.e. for low N with the WSL and for high N with the SSL.

Self-consistent field theory (SCFT) is a “bridge” that allows calculations of the phase diagram of diblock copolymer that start from disordered structure, passes through the WSL, and ends in the SSL area.³⁶ This calculation includes the double gyroid morphology (Figure 6c) which is stable for $\chi N < 60$.

In general, a theoretically based phase diagram for a diblock copolymer system is shown in Figure 7.

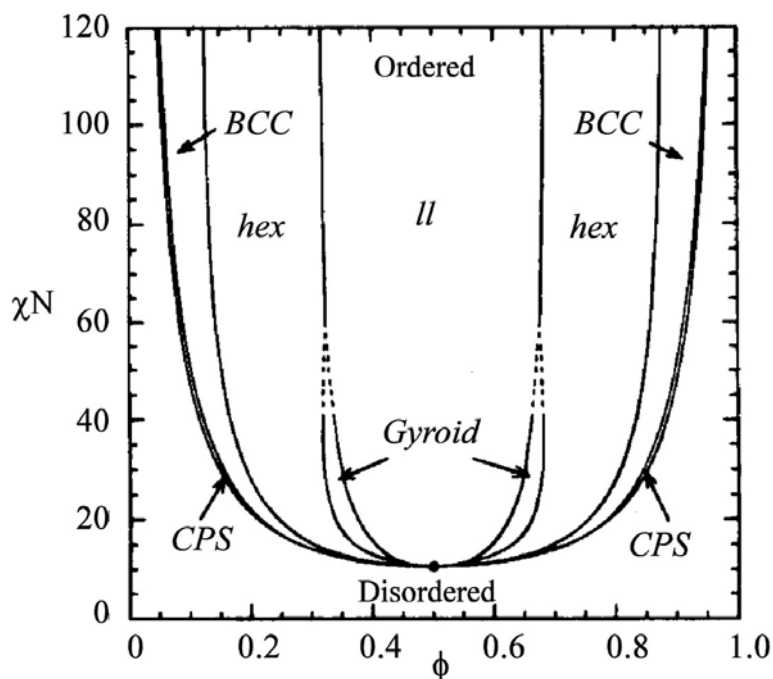


Figure 7: Theoretical phase diagram of a two-component polymer

(*ll* = lamellae; *hex* = hexagonally packed cylinders;

BCC = spheres arranged on a body-centered cubic lattice;

CPS = spheres arranged on a face-centered cubic lattice)⁸⁴

On this graph, the composition of the diblock copolymer is plotted in dependence of the product of interaction parameter and number of overall repeating units (χN). As every chain contributes to the enthalpy of mixing, the incompatibility of the two blocks is not solely determined by interaction parameter (χ , equation 3), but also influenced by the number of segments (N), and therefore product χN is presented at this Figure.

Calculation of this phase diagram included different approaches for different areas of the graph. Leibler²⁹, with corrections made by Fredrickson and Helfand³⁰ described this system for $\chi N < 15$. A second-order transition between the lamellar and the disordered phase was predicted for symmetric diblock copolymers. Matsen and Bates⁸⁴ made a calculation of this phase diagram without any approximation. They extended the phase boundaries unifying the WSL and SSL theories. Their calculation predicted the narrow areas of spheres arranged on a face-centered cubic lattice in the order-disorder transition. Another important prediction is the presence of a stable hexagonally packed cylinders structure, stable for the strong segregation regime.

The area of the graph for values of $\chi N > 100$, and has been first investigated theoretically by Meier³¹, Helfand and coworkers³²⁻³⁴, and Semenov³⁵. As this theory does not directly extend to the area $\chi N < 15$, calculation of Matsen and Bates covered $15 < \chi N < 100$ ³⁶.

A lamellar structure that is observed in block copolymers with approximately the same amount of both of blocks for a wide range of interaction parameters is not appropriate for a membrane as the blocks can “slide” one on another. On the other hand, a cubic structure (either body- or face- centered) cannot provide pores that are open through the whole layer of the membrane. The best copolymer structure for membranes is hexagonally packed cylinders, as it allows the active block to open or close the pore through the whole membrane. A gyroid structure might be applied as well, but this pattern is stable only in the narrow range of χN and Φ . From the phase diagram, it can be seen that hexagonally packed cylinders are obtained if the ratio of minority phase is in the range of 0.2-0.3. Beside microphase separation, polymers synthesized for the purpose of making membranes should have sufficient molar mass (>150 kg/mol) in order to obtain mechanical stability.

In order to prepare a membrane that alters the pore dimensions in dependence on the temperature, it is necessary to introduce a block with good mechanical stability. As polymerization behavior of styrene is well known and polystyrene has sufficient mechanical stability, it was decided to take polystyrene as the block in diblock copolymer with PDEGMA with a molar amount of DEGMA $x(\text{DEGMA})=0.3$.

1.2.2.1. FOX-FLORRY EQUATION

The glass transition is a property of amorphous polymers where their mechanical behavior changes from a brittle behavior to a viscous rubbery flow. The glass transition is a function of chain flexibility and occurs when there is enough vibrational (thermal) energy in the system to create a sufficient high free-volume to permit sequences of 6-10 main-chain carbons to move together as a unit. In its glassy state (at low temperatures) the mechanical behavior of the polymer is relatively constant. The material is very hard and brittle, and the properties do not change significantly with the temperature – the elasticity modulus remains high. However, as the temperature rises, there will be a point where the behavior of the polymer will rapidly change from a glassy to a very tough and leathery behavior. This change in behavior is evidenced by a sharp decline in the modulus (stiffness), or an increase in the impact strength as the temperature is increased. This region is termed the glass transition region. The temperature at the middle point of the transition from glassy to rubbery, the glass transition region, is defined as the glass transition temperature, T_g .

In phase separated polymers, every phase will undergo its own glass transition, and therefore, multiple glass transition temperatures will be observed. If the phase separation is not present in the copolymer, the temperature of a mixed glass transition of the copolymer will be in between the glass transitions of both homopolymer components.

The glass transition temperature of copolymer or miscible blend of two polymers might be described by the Fox equation as:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (6)$$

T_g – glass transition temperature of the copolymer or the blend

w_i – weight fraction of component i in copolymer

T_{gi} – glass transition temperature of component i

This equation gives lower values for the T_g than expected from a linear mixing rule as it reflects the effective higher free volume or randomness due to the presence of two components in a mixture. Systems which obey the Fox equation are considered to display intimate and uniform mixing while those which deviate from it, especially those that display two glass transition temperatures are considered to be poorly mixed or even phase separated.

1.3. CONTROLLED LIVING POLYMERIZATION

1.3.1. DEFINITION

Living polymerization is a type of polymerization where the reactions of termination and transfer do not occur, while the rate of initiation is much larger than the rate of propagation. Lengths of the different chains remain similar, and the polydispersity index remains low. Additional advantages are predetermined molar masses and control over the end-group chemistry. By the current nomenclature, “living” and “controlled” polymerization are observed as a synonyms. Usual criteria for recognizing a polymerization mechanism as controlled are:³⁹

1. The conversion of the monomer depends on time in a 1st order fashion
2. The dependence of the degree of polymerization on the monomer conversion is linear.

If those two conditions are fulfilled, polymerization reaction is classified as “controlled”.

The degree of polymerization (P_n) and the number average molar mass (M_n) in controlled polymerization can easily be determined as the degree of polymerization is linear function of conversion. This is a consequence of the absence of transfer and termination. In other words, all polymer chains synthesized via controlled mechanisms consist ideally of the same number of monomer units, and thus, they have a low polydispersity index according to the Poisson distribution (see equation 11 on the page 29).

Controlled polymerizations have a great significance in polymer synthesis as they provide the opportunity to control properties of a material via introducing variations in composition and functionality at a molecular level. Through appropriate selection of a functional (macro)initiator, copolymers formed in a "living"/controlled polymerization process can have any desired structure. It is possible to obtain gradient, block and graft copolymers, as well as polymers with complex architectures, including comb shaped polymer brushes, stars, and hyperbranched copolymers.⁴⁰⁻⁴⁵

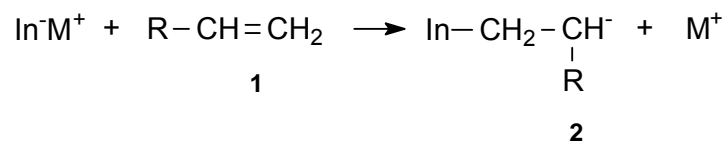
1.3.2. ANIONIC POLYMERIZATION

Anionic polymerization is a addition polymerization between carbanions as an active species (accompanied by counter-ions) and the monomer. The active centers are nucleophilic, and monomers taking part in anionic polymerizations should contain electron accepting substituents which are able to stabilize the carbanion. Stabilization occurs through a delocalization of the negative charge. Therefore, any nucleophiles must be protected or removed. Typical monomers for anionic polymerization include styrene, dienes, methacrylates, acrylates, vinyl-piridines and epoxides. Beside those types of monomers, it is also possible to polymerize cyclic compounds with a polarized carbon – heteroatom bond. In the presence of a nucleophilic initiator, this bond can be cleaved, and a stable and reactive carbanion is formed. Examples of these types of monomers are cyclic ethers, sulphides, lactones and siloxanes.

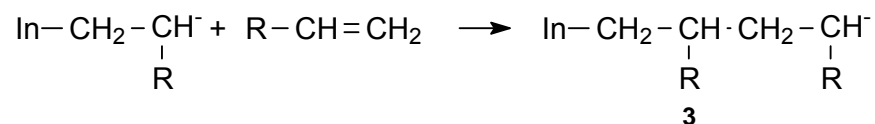
Anionic polymerization, like all addition polymerizations proceeds in three steps: initiation, propagation and termination.⁴⁶ (see Figure 8). During initiation, the initiator anion (In^-) attacks the monomer (1), and a carbanion (2) is formed. In the propagation step, this carbanion reacts with another monomer molecule, and new monomer units are added to the end of the chain (3). Finally, termination occurs when an electrophilic species is added to the reaction and reacts with the carbanion, leading to a stable macromolecule (4). If no self-termination occurs, this type of polymerization is called a living polymerization. During living polymerizations, the chain grows as long as monomer is present in system. Once all monomer has polymerized, the reaction will stop, but all chain ends will remain living. If a new batch of monomer is added, the reaction continues, and the chain propagates.

Schematically, the three steps of anionic polymerization are summarized Figure 8:

Initiation:



Propagation:



Termination:

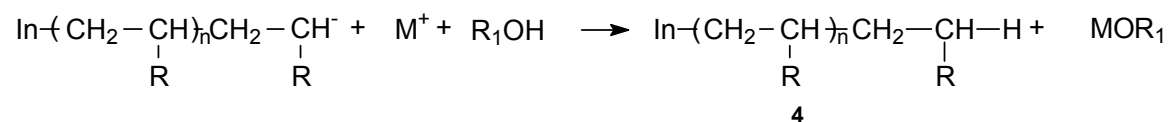


Figure 8: Initiation, propagation and termination of the anionic polymerization

A suitable initiator should initiate the polymerization rapidly and quantitatively, without any side reactions. The reactivity of the initiators used in anionic polymerization should be similar to those of the propagating species, so the most nucleophilic initiator is not always the best choice. As initiators for anionic polymerization, Brønsted-Lowry's or Lewis's bases can be used. Organic-metal compounds are often used, as they spontaneously release carbanions that can initiate the polymerization. The activation energy for initiation of the monomer is low for these compounds, so their reaction rate is fast enough even at -70°C .

Initiators in anionic polymerization also include solutions of alkali metals and naphthalenes in polar solvents.^{42,43} Electrons from the outer shell of the alkali metal are transferred to the aromatic rings of naphthalene, and a soluble colored radical anion is formed⁴⁴ (5). This naphthalenid anion has a strong affinity to transfer its radical character to the monomer. The monomer (e.g. styrene) has a higher affinity to unpaired electrons compared to the naphthalenide, and the radical anion of styrene (6) is formed. The anion radicals have a strong affinity to recombine, and a single bond

(7) is created between the two styryl units.⁵⁰ The resulting dianion serves as a bifunctional initiator.

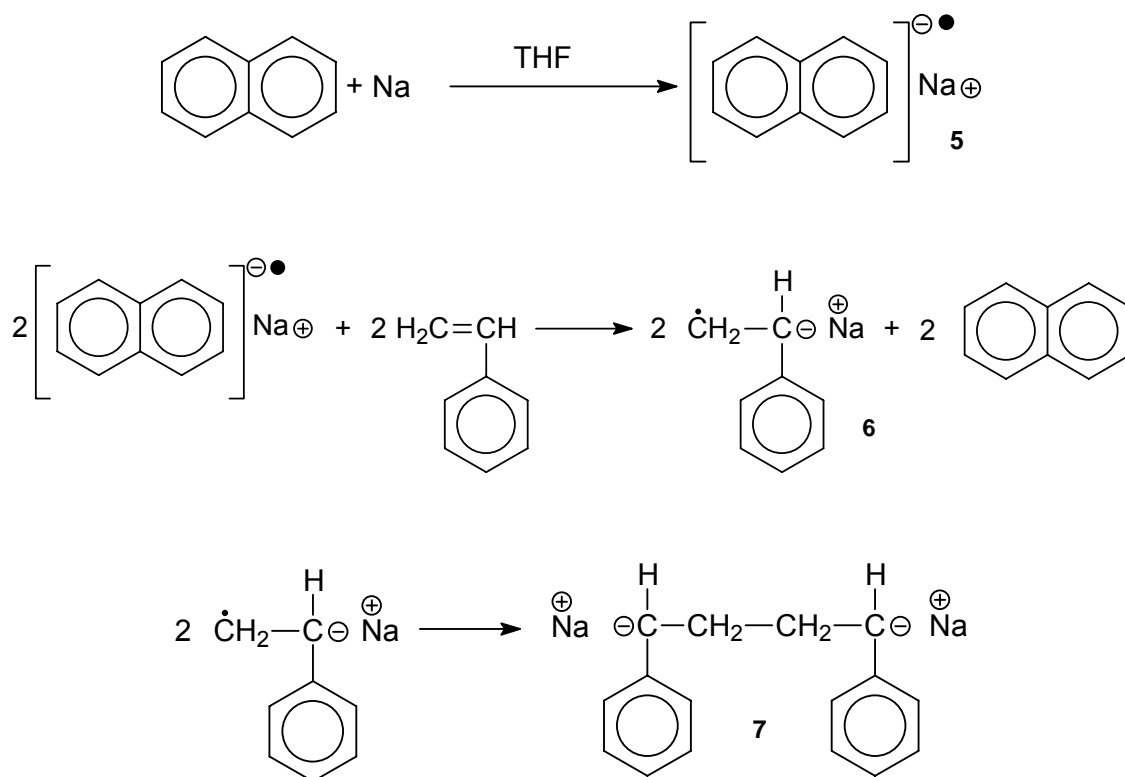


Figure 9: Reaction scheme for the synthesis of the bifunctional initiator

If an ideal mixing takes place during the initiation process, all of the initiator anions react simultaneously with the monomer, and the growth of all chains also begins at the same instance. In that ideal case, all polymer chains had the same length and the degree of polymerization can be expressed as the ratio between the number of polymerized monomers and the number of polymer chains:

$$P_n = \frac{[M_0]x_p}{[P]} \quad (7)$$

P_n – degree of polymerization

$[M_0]$ – starting concentration of the monomer

x_p – degree of monomer conversion

$[P]$ – number of polymer chains

The number of polymer chains is equal to the amount of initiator, so equation 7 can be written as:

$$P_n = \frac{[M_0]x_p}{[In]} \quad (8)$$

Equation 8 shows the linear dependence of the degree of polymerization on the monomer conversion, which is one condition to classify a polymerization as controlled.

However, the monomer addition is an equilibrium reaction, resulting in fluctuations of the number of monomers in a polymer chain. Therefore, different molar mass averages might be defined. The number average molar mass is arithmetic mean or average of the molar masses of individual macromolecules.

$$M_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{\sum c_i}{\sum \left(\frac{c_i}{M_i} \right)} \quad (9)$$

M_n – number average molar mass

M_i – molar mass of the i^{th} polymer chain

N_i – number of polymer chains with molar mass M_i

The weight average molar mass represents the average over the molar masses of the chains rather than their number. It is defined as:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum c_i M_i}{\sum c_i} \quad (10)$$

The ratio $\frac{M_w}{M_n}$ is called polydispersity index, and it gives a measure of the width of the molar mass distribution of the polymer.

As already indicated on page 24, in living polymerizations all chains should approximately have the same length. In an ideal case, they should be Poisson distributed and their polydispersity index is expressed by:

$$\frac{M_w}{M_n} = 1 + \frac{P_n}{(P_n + 1)^2} \quad (11)$$

Assuming $P_n \gg 1$, the equation becomes simpler:

$$\frac{M_w}{M_n} = 1 + \frac{1}{P_n} \quad (12)$$

It is obvious that the polydispersity index $\left(\frac{M_w}{M_n}\right)$ depends on the degree of polymerization (P_n), and that it decreases if the degree of polymerization is increasing. Usually, a minimum polydispersity of 1.03 can be obtained experimentally. If the initiation is slow, the molar mass distribution becomes broader as it is consequence that not all chains start to grow simultaneously. The number of monomer units incorporated into various chains alters with their time of initiation, leading to a broader distribution of chain lengths and consequently, to a higher polydispersity index.

Termination normally should not occur in living anionic polymerization as no protons or electrophilic species are present in the system. However, termination can occur through unintentional quenching due to trace impurities. This includes trace amounts of oxygen, water or alcohols. Therefore working with pure and dry chemicals is of the highest priority for anionic polymerization. Intentional termination can occur through the addition of water or alcohol to end the polymerization process.

1.3.2.1. KINETICS OF ANIONIC POLYMERIZATION

To gain a better understanding of the principles and mechanisms of anionic polymerization, the following chapter describes the basic kinetic principles of this technique.

The rate equation of the initiation process can be expressed as:

$$v_i = -\frac{d[In^-]}{dt} = k_i [In^-][M] \quad (13)$$

In this equation $[In^-]$ represents the initiator concentration; k_i the rate constant of the initiation reaction, and $[M]$ the monomer concentration.

The rate of monomer consumption (rate of propagation) is described by:

$$v_p = -\frac{d[M]}{dt} = k_p [M] \sum_{i=1}^{\infty} [M_i^-] = k_p [M][M^-] \quad (14)$$

$[M^-]$ represents the concentration of all the living chain ends in the reaction system, independent of their degree of polymerization and k_p represents the apparent rate constant which is composed of the individual rate constant of all active centers. As the initiation is much faster than the propagation ($k_i \gg k_p$ see page 25), the number of living chain ends equals the number of initiator molecules ($[M^-] = [In^-]$). The solution of equation 14 gives the dependence of the monomer conversion on time

$$\ln \frac{[M]_0}{[M]} = k_p [In^-] t \quad (15)$$

Equation 15 indicates a 1st order dependence of the monomer conversion on the time, which is the condition to classify this type of polymerization as controlled.

For an anionic polymerization, the degree of polymerization equals the ratio between the initial concentrations of initiator and monomer, as it was described by the equation 8 at page 28.

The choice of the solvent has a great influence on the anionic polymerization. In non-polar solvents, polymer chains and counter-ions are organized in clusters, and only a small number of free chain ends are available. If the solvent polarity increases, carbanions and counter-ions are no longer organized in that manner, and they exist either as single ion pairs or as solvated ions. If the chain end is associated with the counter ion too closely, a new monomer unit cannot be added and therefore, the propagating chain is in the dormant state. On the other hand, when the counter ion is separated from the propagating chain end the carbanion can add a monomer unit, and the chain propagates. In anionic polymerizations, the dynamic equilibrium between active and dormant species is strongly shifted to the dormant species. Although anionic polymerizations are faster if the solvent is more polar because then the equilibrium is shifted more into the direction of the more loose ion pairs, the rate of propagation does not directly depend on the solvent's dielectric constant. The dependence of the nature of the ion pairs on the polarity of the solvent is presented in Figure 10.

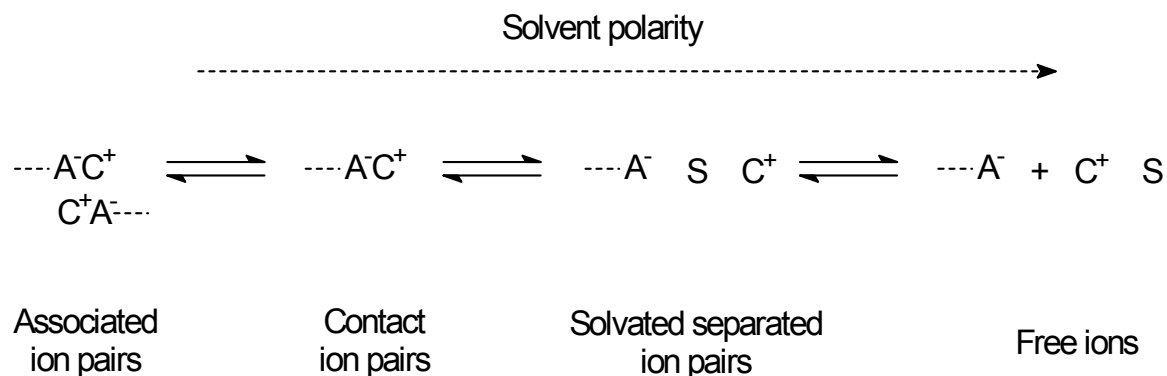


Figure 10: Dependence of the structure of ion pairs on the polarity of the solvent (A⁻ living anion, C⁺ counter ion, S solvent molecule)

The propagation reaction will proceed with both free ions and with ion pairs. If the contribution of both types of ion pairs (contact ion pairs and solvent separated ion pairs) is combined into one expression, the rate of propagation can be written as:

$$v_p = -\frac{d[M]}{dt} = k_{p-}[A] \cdot [M] + k_{p+-}[A^-C^+] \cdot [M] \quad (17)$$

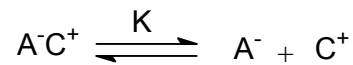
k_{p-} - propagation rate of the free ions

$[A^-]$ – concentration of the free ions

k_{p+-} - propagation rate of the ion pairs

$[A^-C^+]$ – concentration of the ion pairs

The equilibrium between the ion pairs and free ions is



with the dissociation constant:

$$K = \frac{[A^-] \cdot [C^+]}{[A^-C^+]} \quad (18)$$

Because of $[A^-] = [C^+]$

$$[A^-] = \sqrt{K[A^-C^+]} \quad (19)$$

As the degree of dissociation is small, the concentration of ion pairs is close to the concentration of all types of propagating centers; $[A^-C^+] \approx [M^-]$, and the concentration of the ions is:

$$[A^-] = \sqrt{K[M^-]} \quad (20)$$

Hence

$$[A^-C^+] = [M^-] - \sqrt{K[M^-]} \quad (21)$$

Combination of equations 16 and 17 gives the equation for the apparent rate of the reaction:

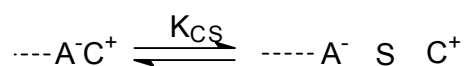
$$k_p = \frac{k_{p-}[A^-] + k_{p+-}[A^-C^+]}{[M^-]} \quad (22)$$

Combination of equations 20, 21 and 22 gives:

$$k_p = \left(\frac{K}{[M^-]} \right)^{1/2} (k_{p-} - k_{p+-}) + k_{p+-} \quad (23)$$

If k_p is plotted in dependency of $(K/[M^-])^{1/2}$, a linear extrapolation results in k_{p+-} as ordinate segment, and $(k_{p-} - k_{p+-})$ as a slope.

However, the situation is even more complex, as the two different types of ion pairs have to be considered in polar solvents. Each of them contributes to the overall reaction rate with their individual reaction rates (k_c for contact ion pairs and k_s for solvent separated ion pairs; $k_s > k_c$). Those two types of ion pairs are in equilibrium with the equilibrium constant K_{CS} :



Accordingly, k_{p+-} is also an apparent rate constant which can be defined in analogy to equations 17-23:

$$k_{p+-} = x \cdot k_s + (1-x) \cdot k_c \quad (24)$$

with x being the fraction of solvent separated ion pairs.

$$x = \frac{(k_c + k_s K_{CS})}{1 + K_{CS}} \quad (25)$$

Note that the propagation rate of free anions is independent of the solvent, but still is influenced by the temperature. The ions pairs however are present in the system in two forms, either as contact ionic pairs, or as solvent separated ones. As

solvation is an exothermic process, on lower temperatures, the equilibrium is shifted towards the solvent separated ions, while on higher temperatures, ion pairs are more predominant. As associate ion pairs are less reactive than solvent separated ones, the reaction rate decreases with increasing the temperature. In an Arrhenius plot, where the logarithm of apparent rate constant ($\log k_{p+}$) is plotted as a function of the reciprocal temperature (T^{-1}), even the upward curvatures were reported, which can be interpreted as “negative” activation energy.

If the polymerization is performed in a non-polar solvent, the initiator (i.e. *n*-BuLi) is aggregated (e.g. benzene and toluene solution *n*-BuLi is aggregated in hexamers). Assuming the aggregation is an equilibrium process with K_e the equilibrium constant is defined as

$$K_e = \frac{[BuLi]^6}{[(BuLi)_6]} \quad (26)$$

The concentration of “monomeric” BuLi reads:

$$[BuLi] = [K_e (BuLi)_6]^{1/6} \quad (27)$$

As only a monomeric initiator is able to initiate the polymerization, the rate equation for the initiation reaction in non-polar solvents is:

$$v_i = -\frac{d[M]}{dt} = k_i K_e^{1/6} [M][BuLi]^{1/6} \quad (28)$$

The reaction rate in non-polar solvents depends on the sixth root of the concentration of the initiator. Therefore, the reaction rate in non-polar solvents is lower compared to polar ones. In non-polar solvents also the living chain ends are aggregated in clusters (e.g. polystyrene is organized in dimers and polybutadiene in tetramers). Therefore, the concentration of living chain ends available for new monomer units is low, and the reaction is slower compared to the case of non-polar solvents.

1.3.2.2. ADDITIVES IN ANIONIC POLYMERIZATION

As it was presented in Figure 10, the propagating chain ends can be present in different states. Each of those propagate at their own rate, hence, the overall reaction rate is heavily influenced by the position of the equilibrium. If most of the living chain ends are present as a free ions, the overall reaction can become too fast, which would lead to the unwanted side-products. The number of free ions can be reduced, and thus the reaction rate can be decreased if the equilibrium is shifted towards the more associated species. This can be accomplished by adding e.g. inorganic salts that contain a common cation (e.g. if the reaction is initiated with BuLi, LiCl might be added as an additive).²⁶

On the other hand, if chain ends are present in solution as associated chain ends, and therefore cannot take part in the propagation, it is possible to shift equilibrium towards the free ions. This can be done by additives that react with cations. In order to keep the concentration of anions and cations in the system constant, dissociation of associated ion pairs is favored leading to an increase in anion concentration. Example of those type of additives are lithium alkoxyde (in the case of initiation with BuLi), which can be added to the reaction, or be formed in situ.

1.3.3. GROUP TRANSFER POLYMERIZATION (GTP)

1.3.3.1. BASIC PRINCIPLES

In group transfer polymerization (GTP) a compound containing a silyl-ketene-acetal moiety initiates the polymerization of acrylates or methacrylates in the presence of a catalyst.^{51,52} The catalyst used in group transfer polymerizations is usually a nucleophilic compound, but it must neither be too nucleophilic as it might initiate anionic polymerization (e.g. cyanide anion is not suitable) nor contain any crystallized water as it would terminate the reaction (e.g. tetrabutylammonium fluoride crystallizes with three molecules of water).

In general, GTP can be explained by two different theoretical approaches. The main difference between two approaches is whether the organosilicon-group remains attached to the polymer chain (associative mechanism), or it behaves like a cation, leaving carbanion at the chain end (dissociative mechanism).

1.3.3.2. ASSOCIATIVE MECHANISM

In the associative mechanism, the chain propagation starts with an approach of the catalyst to the silicon atom of the living chain end (9). The activated chain end reacts with the monomer and forms a hexacoordinated intermediate (10). A new single C-C bond between the ketene-silyl-acetal moiety and the monomer is established; at the same time, the trialkyl-silyl group is transferred to the carbonyl atom of the newly attached monomer leading to an establishment of a new Si-C bond (10). Simultaneously, the oxygen-silicon bond is cleaved and as a result the activated silyl-ketene acetal group is transferred to the end of polymer chain (11).⁵³ The nucleophilic catalysts may detach from the silicon atom and the chain end goes into the dormant state (12).

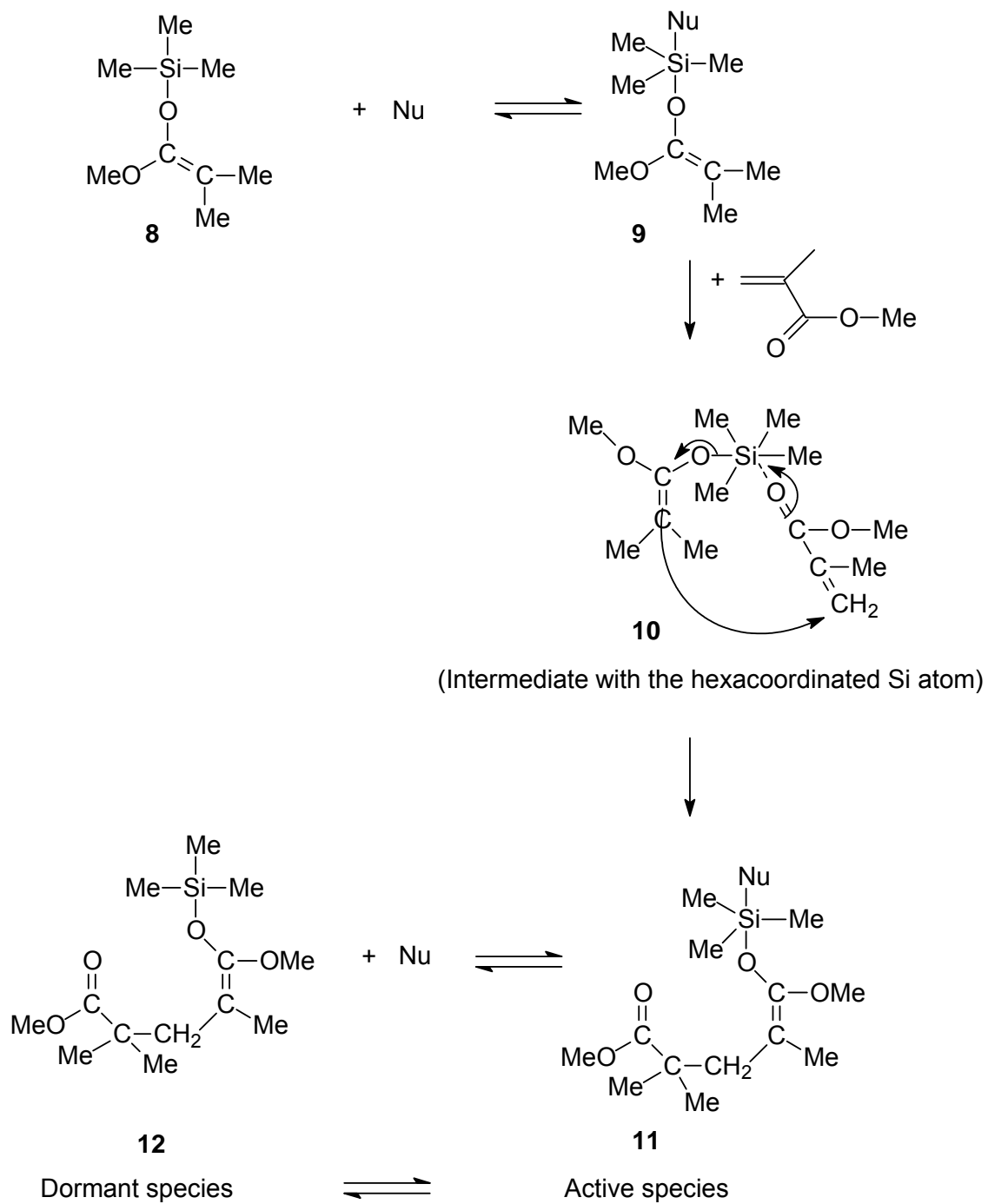


Figure 11: General reaction scheme of the GTP of MMA (associative mechanism)

1.3.3.3. DISSOCIATIVE MECHANISM

In the other limiting case, GTP might be interpreted as an anionic polymerization in the presence of a bulky trialkylsilyl counterion. The negative charge is delocalized over the oxygen atom and carbon atom (13) where the new carbon-carbon bond is established (14). After a new monomer unit is added, the living chain end reacts with the trialkylsilyl group, and the system goes into the dormant state (15). The polymer chain grows in an analogous manner to classical anionic polymerization, and termination occurs when an electrophilic species is added.

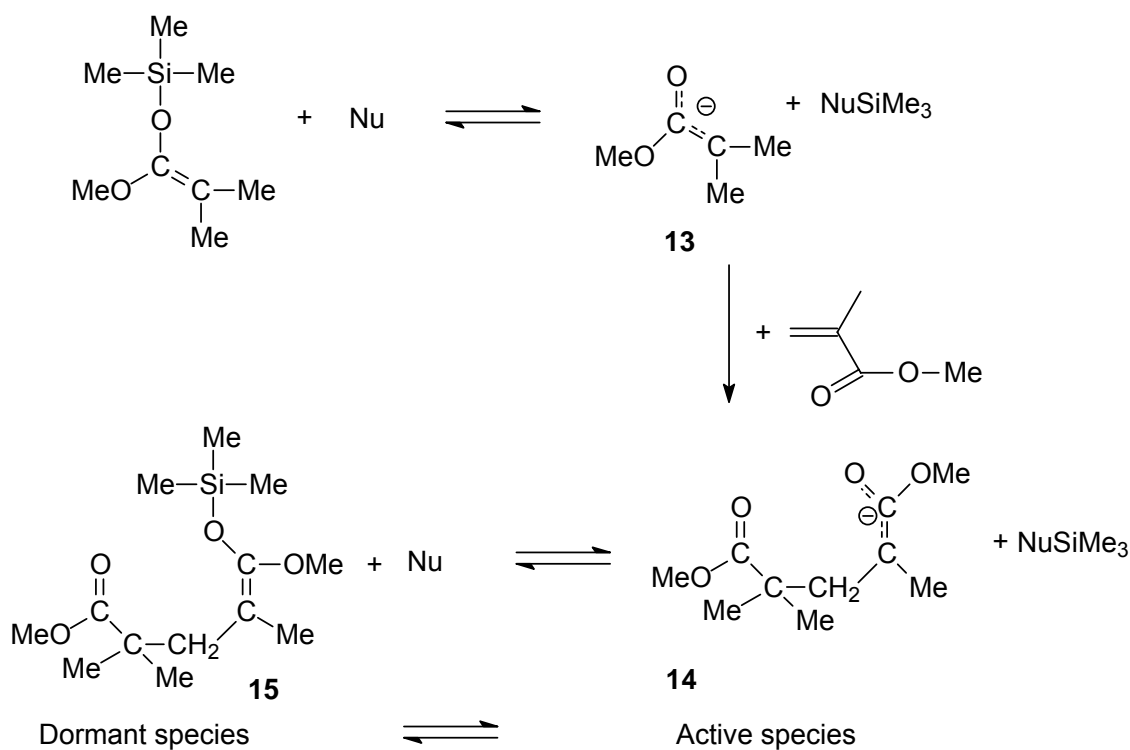


Figure 12: General reaction scheme of the GTP of MMA (dissociative mechanism)

In both cases, the equilibrium is strongly shifted towards dormant species, which results in the higher polydispersity index compared to the anionic polymerization.⁹⁵ As no transfer and termination reactions are observed, and the reaction is of first order with respect to the monomer concentration, GTP is considered as a living polymerization process.

1.3.4. ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

1.3.4.1. BASIC PRINCIPLES

Atom transfer radical polymerization is a controlled/"living" polymerization based on a radical pathway. It is one of the most versatile systems, because of the easy availability of many kinds of initiators, catalysts, and monomers. It represents an alternative to other types of living polymerization techniques which are usually limited to certain groups of monomers and which are highly sensitive to impurities. Radical polymerization, in contrast, can (co)polymerize numerous monomers, can even be performed in water while using emulsions or suspensions, and is readily applicable to industrial processes.

The general scheme for ATRP reaction is:

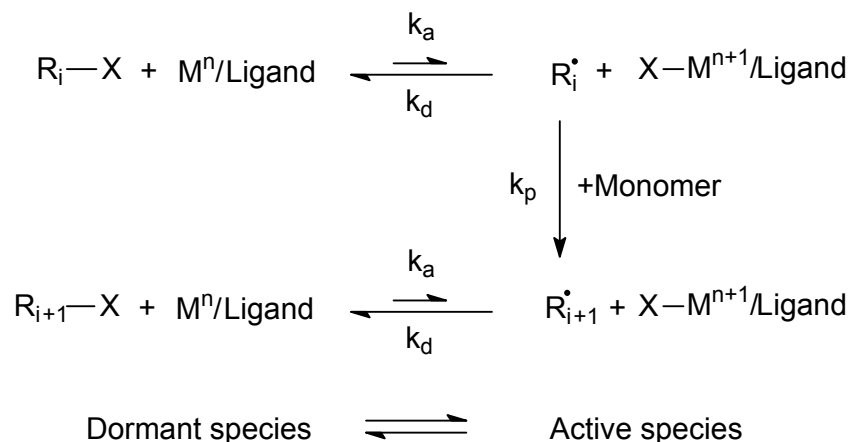


Figure 13: General reaction scheme of the ATRP

Here, R_i represents a polymer chain with the degree of polymerization i , X stands for a halogen atom at the chain end (bromine or chlorine). M^n is a transition metal in oxidation state $+n$ which is complexed by the ligand forming agent.

The ATRP is based on an electron transfer process, which includes a reversible halogen transfer between the initiator or the dormant propagating chain end ($R-X$) and a transition metal complex in a lower oxidation state (M^n/Ligand). As a result, propagating radicals are formed at the chain end (R^\bullet) and metal complexes in a

higher oxidation state with a coordinated halide ligand (e.g. $X-Mt^{n+1}/\text{Ligand}$) are created.⁵⁴⁻⁵⁷ The propagating radical at the end of the chain reacts with a monomer unit, leading to an increase of the degree of polymerization by one (R_{i+1}^*). Still, a radical moiety is located at the chain end, it reacts with the halogen atom, and goes back to the dormant state ($R_{i+1}-X$), while the transition metal is reduced to its lower oxidation state (M^n). Rarely, the radical R_{i+1}^* can react with a second monomer unit again.⁵⁴⁻⁵⁷

The radicals are formed at a rate, which is expressed by the constant of activation (k_a), they propagate with a constant of propagation (k_p) and they are reversibly deactivated with the constant of deactivation (k_d). The reversible dynamic equilibrium between the dormant species (alkyl halide) and active species (radicals) is strongly shifted towards the dormant species ($k_a \ll k_d$).⁵⁵⁻⁵⁷ That means that most of the time the polymer chains are in a state in which they cannot propagate.

The reaction is initiated when an initiator that contains a suitable halogen atom is added to the reaction system. The ATRP initiator is either a small molecule or macromolecule with one or more cleavable atoms or groups, containing a halogen atom. Organic halides that are similar in the molecular structure as the propagating radical are often chosen as initiators. Bromo- substituted acid derivatives are in general more reactive than their chloro- substituted counterparts and both lead to good molar mass control. The added initiator $R-X$ can be a monofunctional initiator, it can be used to introduce an additional functionality to the α -chain end, or it can even be a macroinitiator (a polymer containing initiator site(s))⁵⁷⁻⁶²

To fulfill the prerequisites for the controlled polymerization (see page 24), the initiation of the ATRP should be fast and complete resulting in a control over the molar mass and to keep the molar mass distribution narrow.

Initiators are generally simple, commercially available, α -bromo or α -chloro acid derivatives. The catalyst is a transition metal that is complexed by one or more ligands. The metal/ligand complex does not need to be used in a one-to-one ratio with the initiator but can be used in much smaller amounts. Beside the initiator, a deactivator can be added. The role of the deactivator is to enable the deactivation process to occur immediately. This results in a higher initiator efficiency as the

equilibrium is reached more rapidly, and the control over initiation process is better.⁵⁶ Usually, as a deactivator a salt of the transition metal in a higher oxidation state, e.g. CuBr_2 is used. The deactivator can be formed in situ, or, for better control, a small amount of it (relative to the metal/ligand complex) can be added.

Polymers with an appropriate end group prepared by other polymerization techniques might be used as macroinitiators or macromonomers. By this technique it is possible to obtain well defined block or graft copolymers.

However, the synthesis of block copolymers is not as simple as it is in case of anionic polymerization. As ATRP is in principle a radical mechanism, the reaction should be terminated after one block is synthesized, and the polymer should be purified from the residual monomer. As the halogen atom is positioned at the end of the chain, each chain can act as an initiator for a further polymerization. In the next step, this macroinitiator acts as an initiator for the polymerization of the second block.

Monomers that are typically used in ATRP usually contain substituents that stabilize the propagating radicals (e.g. styrenes, (meth)acrylates, acrylonitrile). ATRP is successful at leading to high molar masses (over 50000 g/mol) and narrow molar mass distributions (less than 1.4). The propagating rate (k_a) is unique to each monomer, and it is important that the other components of the polymerization (initiator, catalysts, ligands and solvents) are optimized in order to keep the concentration of the dormant species higher than the concentration of the propagating radicals. On the other hand, concentration of free radicals must not be too low in order to avoid slow reaction rates, or even to stop the reaction.

Termination in ATRP occurs when transition metal has no capability of being oxidized. This might be fulfilled by simple exposure of the reaction mixture to air when the metal is oxidized by oxygen. Then it cannot accept halogen atoms any more, and reaction is terminated.

Hence, oxygen should be removed as much as possible, although it is possible to run ATRP polymerization with a small amount of oxygen in the system, if a reducing agent is present.⁵⁷ The transition metal in lower oxidation state can serve as a reducing agent as well. (This is just a possibility as it is impossible to determine

amount of oxygen in the reaction mixture, and to calculate required amount of the salt of lower oxidation state). Then, a fraction of the metal in the lower oxidation state is “sacrificed” as it reacts with oxygen, and it cannot take part in the reaction of polymerization. Additionally, the metal complex is tolerant of protic media, so that ATRP can be performed in solvents like water or alcohols.^{57,61,62}

1.3.4.2. EFFECTS OF CATALYST SYSTEMS TO THE ATRP

The most important component of ATRP polymerization is the catalyst because it determines the equilibrium between the active and dormant species and, consequently, the reaction rate and the molar mass distribution. The main requirements for the metal catalyst is that it must be stable in two oxidation states, that it has an affinity to halogens, and that its coordination sphere is expandable, so it can adopt the halogen atom in the oxidized state. The transition metal complex should be soluble in the reaction medium as this provides control over concentration.

The role of the ligand in ATRP is to solubilize the transition metal salts. The choice of ligand greatly influences the effectiveness of the catalyst in a specific polymerization reaction. Amine-based ligands are widely used for Cu-mediated ATRP.⁶⁰⁻⁶⁶

1.3.5. COPOLYMERS

1.3.5.1. DEFINITION AND TYPES

In general, copolymers are any macromolecules that contain units of two or more different monomer species. Copolymers might be divided in several groups, according to the order of the monomer units in the polymer chain:

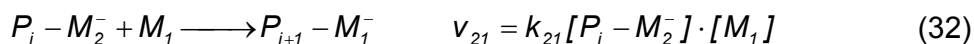
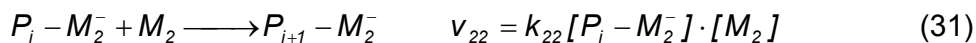
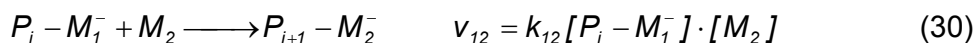
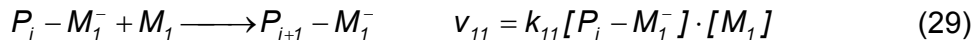
- Statistical (random) copolymers – the monomer units are distributed randomly in the copolymer
(M₁-M₁-M₂-M₁-M₁-M₂-M₂-M₂-M₁)

- Alternating copolymers – the monomer units of different type are alternating in the polymer chain
(M₁-M₂-M₁-M₂-M₁-M₂-M₁-M₂)
- Block copolymers – one block consists only of one type of monomer, and the second block consists only of the other monomer species
(M₁-M₁-M₁-M₁-M₂-M₂-M₂-M₂)
- Gradient copolymers – the composition of the consecutive monomer units gradually changes
(M₁-M₂-M₁-M₁-M₁-M₂-M₂-M₁-M₁-M₂-M₂-M₂-M₁-M₂)
- Graft copolymers – shorter polymer chains serve as side chains linked to the main chain.

1.3.5.2. COPOLYMERIZATION PARAMETERS

If two different monomers (M₁ and M₂) are present in a batch polymerization process, and their polymerization is initiated, initiation and propagation for both monomers will start in parallel. The composition of a copolymer is usually not the same as the composition of the monomers in the starting reaction mixture. This is a consequence of the different rates of addition of the two different types of monomers to the macroradicals, carbocations or carbanions that are present in the polymerization.

As a consequence, at the active chain end, either M₁ or M₂ can be present. Assuming that the rate of monomer addition to the active chain end does not depend on a length of the chain, four propagation reactions are possible:



As the rate of disappearance of both monomers from the reaction mixture is the same as the rate of incorporating monomer units into the polymer chain, the change of monomer concentration on time may be expressed as:

$$-\frac{d[M_1]}{t} = k_{11}[P-M_1^-] \cdot [M_1] + k_{21}[P-M_2^-] \cdot [M_1] \quad (33)$$

$$-\frac{d[M_2]}{t} = k_{22}[P-M_2^-] \cdot [M_2] + k_{12}[P-M_1^-] \cdot [M_2] \quad (34)$$

By the combination of equations 33 and 34, the rate of incorporation of the two types of monomers into the polymer chain (composition of the macromolecular chain) can be calculated:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{k_{11}[P-M_1^-] + k_{21}[P-M_2^-]}{k_{22}[P-M_2^-] + k_{12}[P-M_1^-]} \right) \quad (35)$$

In order to eliminate the concentration of the living chain ends from this equation, it is assumed that an equilibrium is achieved, and that the concentration of living chain ends is constant. This is the case if their rates of interconversion are equal:

$$\frac{d[P-M_1^-]}{dt} = k_{21}[P-M_2^-] \cdot [M_1] - k_{12}[P-M_1^-] \cdot [M_2] = 0 \quad (36)$$

which leads to:

$$\frac{[P-M_1^-]}{[P-M_2^-]} = \frac{k_{21} \cdot [M_1]}{k_{12} \cdot [M_2]} \quad (37)$$

Introducing r_1 and r_2 as k_{11}/k_{12} and k_{22}/k_{21} respectively, equation 37 can be rearranged to the so-called Mayo-Lewis equation:⁸⁵

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{(r_1[M_1] + [M_2])}{(r_2[M_2] + [M_1])} \quad (38)$$

The values of r_1 and r_2 quantify the relative reactivity of the monomer and the living chain-end. They represent the ratio of rates of homopolymerization and heteropolymerization, and they are called copolymerization parameters.

Equation 38 is only valid if the rate of monomer addition to the living chain ends is determined solely by the last unit in the monomer chain. Furthermore, it is assumed that depolymerization, dissociation, or formation of monomers complexes with the components of reaction system are absent.

In order to determine the copolymerization parameters, from the equation 38, the method proposed by Fineman and Ross⁶³ introduces two additional parameters, G and F .⁶⁴

$$F = \frac{x^2}{y} \quad (39)$$

$$G = \frac{x(y-1)}{y} \quad (40)$$

with

$$x = \frac{[M_1]}{[M_2]} \quad (41)$$

$$y = \frac{d[M_1]}{d[M_2]} \quad (42)$$

Equation 41 gives the monomer ratio in the reaction mixture, while equation 42 calculates the ratio of monomer units incorporated in polymer chain.

With parameters F and G , equation 38 can be rearranged.⁶⁴

$$G = r_1 F - r_2 \quad (43)$$

As the constants r_1 and r_2 may vary, depending on number assignments given to the monomers, Kelen and Tudos⁶⁵ introduced an arbitrary positive constant α . They defined another two parameters, η and ξ , as:

$$\eta = \frac{G}{\alpha + F} \quad (44)$$

$$\xi = \frac{F}{\alpha + F} \quad (45)$$

The value of α distributes the experimental data symmetrically on the plot and it is determined from the parameter F .

$$\alpha = \sqrt{F_M F_m} \quad (46)$$

F_M – highest experimental value of F

F_m – lowest experimental value of F

The relation between the parameters η and ξ is expressed as:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (47)$$

A plot of η versus ξ , should result in a straight line with $-r_2/\alpha$ and r_1 as the intercepts for the extrapolation to $\xi=0$ and $\xi=1$ respectively. This method can only be employed if the conversion is lower than 40%.

Depending on the values of r_1 and r_2 , the structure of the polymer may vary. Special cases of copolymerization are:

- $r_1=r_2=0$; The rate of homopolymerization is negligible ($k_{11}=k_{22}=0$) for both components. Monomer M_1 is added only to the living chain ends of P- M_2 and the monomer M_2 is added only to the living chain ends of P- M_1 type. As a result an ideal alternating polymer is obtained.
- $r_1=r_2=1$; Homopolymerization and heteropolymerization rates are equal ($k_{11}=k_{12}$ and $k_{22}=k_{21}$). As the monomer M_1 can either add to P- M_2 or P- M_1 a random copolymer is yielded.

- $r_1 > 1$ and $r_2 > 1$; In this case, the rate of heteropolymerization is negligible ($k_{12} = k_{21} = 0$). Monomer M_1 only attaches to the living chain end of P- M_1 type and the monomer M_2 behaves analogously. This type of behavior is rather rare and leads to a block copolymer or a blend of two homopolymers.

1.3.5.3. BLOCK COPOLYMERS AND END FUNCTIONALIZATION

By controlled polymerization techniques, block copolymers can be synthesized as the reaction proceeds stepwise. In the first stage, one monomer is polymerized, and when its conversion is complete, the second monomer is added, and the chain growth continues. In this sequential way monomers with different electrophilicity can be polymerized. The first synthesized block is made of monomers with lower electrophilicity, and the second block is made of monomers with higher electrophilicity. During the reaction, the nucleophilicity of the active species should be high enough to initiate the polymerization of the second monomer quickly and quantitatively.

On the other hand, the nucleophilicity of the living chain end must not be too high in order to prevent unwanted side reactions. For example, if a methacrylate is added to a living polystyrene, beside the expected polymerization at the vinyl group of the methacrylate, a reaction can also occur at the carbonyl group. Therefore, the nucleophilicity of living polystyrene must be decreased. This is done by adding 1,1-diphenylethene (DPE) to the living polystyrene chain end. When the carbanionic functionality is located at the DPE unit, the attack of the carbonyl group is impossible due to sterical reasons. As DPE does not homopolymerize, it can be added in excess.

As in anionic polymerization the active chain end shows a high reactivity to electrophilic molecules, polymers can be end functionalized. By adding an appropriate substance at full monomer conversion, e.g. carboxylic groups (if CO_2 is added) or hydroxyl groups (if an epoxy compound is added and product is later hydrolyzed) can be obtained. Hence, macroinitiators for other types of mechanisms can be synthesized employing this approach.

2. CHALLENGE

The challenge of this work is the preparation of a polymer, which is suitable for making up a membrane with variable pore size for protein separation. The polymer should be a block copolymer having one active component and one matrix block and should fulfill the following requirements:

- The switching temperature of the active component should be close to the human body temperature. For this purpose, PDEGMA will be used as it shows a lower critical solution temperature at 26°C.
- The polydispersity index should be low in order to obtain microphase separation which is necessary an arrangement of the PDEGMA block in a columnar manner. This will be obtained by controlled polymerization techniques.
- The molar amount of the active component should be in the range of $x(\text{PDEGMA})=0.2-0.4$ to obtain a diblock copolymer with hexagonally packed cylinders.
- The polymer should exhibit a sufficient mechanical stability to allow the construction of the membrane. Mechanical stability will be achieved if the polymer's molar mass exceeds 150000 g/mol.

3. EXPERIMENTAL

3.1. PREPARATION OF THE EQUIPMENT FOR POLYMERIZATION

As anionic polymerization is very sensitive to any kind of oxidative or protonating species, all chemicals and equipment that were used must be kept under absolutely water and oxygen free conditions.

3.1.1. PREPARATION OF THE POLYMERIZATION REACTOR

The polymerization reactor was made of glass (double wall), and the volume was 2 dm³. The reactor was cooled via a silicon based cooling liquid which was circulated between the two walls. The vacuum line, as well as several joints for introduction of the reactants into the reactor were connected to the reactor. The reactor was equipped with a temperature and pressure measuring device, as well as stirrer. It was cleaned by washing with methanol and THF. Then it was emptied, flushed with nitrogen and exposed to high vacuum. This step was repeated twice in order to remove any residual methanol.

Gaseous contaminants (oxygen, carbon dioxide) were removed from the reactor and the lines using high vacuum. The main part of high vacuum line was a Duran glass tube connected to a turbo molecular pump with two joint sites for flasks. Between the glass tube and the pump, two cooling traps operated with liquid nitrogen were positioned. The role of those traps is to prevent any chemicals to reach the pump.

Solvent and monomers were transferred into the reactor through the vacuum line by applying under- or overpressure. Overpressure was created by pure and dry nitrogen. Initiators and additives were transferred into the reactor using conventional syringe techniques under a nitrogen counter stream. All syringes and needles were flushed with argon or nitrogen prior to use. If reactions were done in a flask, all reactants and solvents were transferred using syringe techniques with a nitrogen

counterstream applied. By this method of transfer, entering of moisture and oxygen was prevented as much as possible.

3.1.2. PREPARATION OF THE GLASWARE

Before starting polymerization or distillation, all glassware was dried at 70°C and then heated under vacuum up to 650°C to remove any kind of moisture. The glassware was connected to the vacuum line using high vacuum grease, but with special attention on preventing the vacuum grease of entering the reaction flask.

3.1.3. GLOVE BOX

The glove box was filled with argon and equipped with two rubber gloves that allowed to work inside it. The introduction of the chemicals and equipment into the glove box was done through a vacuum chamber. The glove box was operated with a slight overpressure (up to 5 mbar), while a slight underpressure (up to 5 mbar) was allowed during the manipulation with the gloves. During all the time, the level of oxygen and water was monitored. The level of oxygen was kept under 1 ppm, and the level of water under 0.1 ppm.

3.2. PREPARATION OF CHEMICALS FOR POLYMERIZATION

3.2.1. SOLVENTS

Tetrahydrofuran (THF) and toluene were refluxed over potassium, distilled in a two-step distillation still and directly transferred into the reactor. If reactions were done in ampoules or flasks, THF or toluene was transferred in a round bottom flask over sodium-potassium alloy. A blue color in THF proves that the solvent is free of protic impurities. Prior to reaction, an appropriate amount of THF or toluene was distilled from sodium potassium alloy.

Commercial anisole was flushed with nitrogen or argon and degassed by three freeze-pump-thaw cycles.

3.2.2. MONOMERS

Commercial 2-(methoxyethoxy)ethyl methacrylate (DEGMA) contained stabilizers which needed to be removed prior to polymerization. Removal of the stabilizers was done by passing DEGMA through an aluminum oxide column. After that, DEGMA was flushed with argon and degassed by three freeze-pump-thaw cycles and distilled under high vacuum. This procedure was repeated for every polymerization, as distilled DEGMA tends to polymerize when stored longer than a few hours – even at -18 C.

Commercial styrene contains stabilizers, and it was activated by passing through an aluminum oxide column and stored over Bu_2Mg under an argon atmosphere. Prior to polymerization, styrene was degassed by three freeze-pump-thaw cycles, and an appropriate amount of styrene was distilled under vacuum.

tert-Butylmethacrylate (*t*BMA) was activated by passing through an aluminum oxide column, distilled under reduced pressure, and stored over CaH_2 . It was degassed by three freeze-pump-thaw cycles and distilled prior reaction.

3.2.3. INITIATORS

All commercially available organometallic compounds (*n*-buthyllithium; *sec*-buthyllithium, diethylzinc, triethylaluminum) were used as received.

α -phenylisopropyl potassium was synthesized in a two step procedure with methyl-(α -phenyl-isopropyl) ether as an intermediate.

Methyl-(α -phenyl-isopropyl) ether (cumyl-methoxy ether, CME) was obtained by addition of methanol to α -methyl-styrene in the presence of perchloric acid as a catalyst. All chemicals for this synthesis were used as received. α -methyl-styrene (58,8 ml, 0,46 mol) and methanol (37,1 ml, 0,91 mol) were mixed in the presence of 0,25 ml of 70 wt.% HClO₄. The mixture was refluxed for 48 hours and then hydrolyzed with water and NaOH. The organic phase was distilled at reduced pressure (30 mbar) and CME was collected at 85°C. The theoretical yield of this reaction is 42 g of CME.⁶⁷

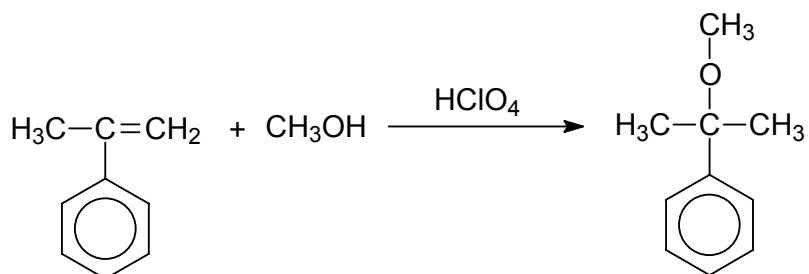


Figure 14: Reaction scheme for the synthesis of the methyl-(α -phenyl-isopropyl) ether (CME)

Subsequently, methyl-(α -phenyl-isopropyl) ether was directly reacted with potassium.⁶⁸ 0.2 mol (30 g) of methyl-(α -phenyl-isopropyl) ether were mixed with 0.4 mol (15.6 g) of potassium in dry toluene in an argon atmosphere. The reaction mixture was stirred at room temperature overnight. It became dark red from the α -phenylisopropyl potassium formed.

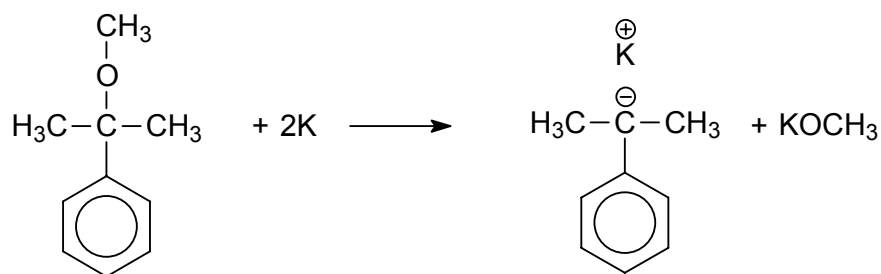


Figure 15: Reaction scheme for the synthesis of the α -phenylisopropyl potassium

Potassium methoxid (side product of this reaction) shows a low solubility in toluene (approx. 10^{-5} mol/l), so the liquid phase was transferred to a round bottom flask. The methoxid residual in the initiator solution, does not interfere with the use as initiator.⁷⁰

Diphenyl-methyl potassium was synthesized from commercially available diphenylmethane, naphthalene and THF. 40 mmol (1.6 g) of potassium and 40 mmol (5.1 g) of naphthalene were dissolved in dry THF and stirred overnight at room temperature. Then, 40 mmol (6.7 g) of diphenylmethane was dissolved, and the reaction mixture was stirred for additional 48 hours at room temperature. The resulting dark red solution was transferred into a sealed bottle filled with argon, sealed, and kept at $+4^\circ\text{C}$.^{50,69,70} The reaction pathway for the synthesis of the diphenyl methyl potassium is:

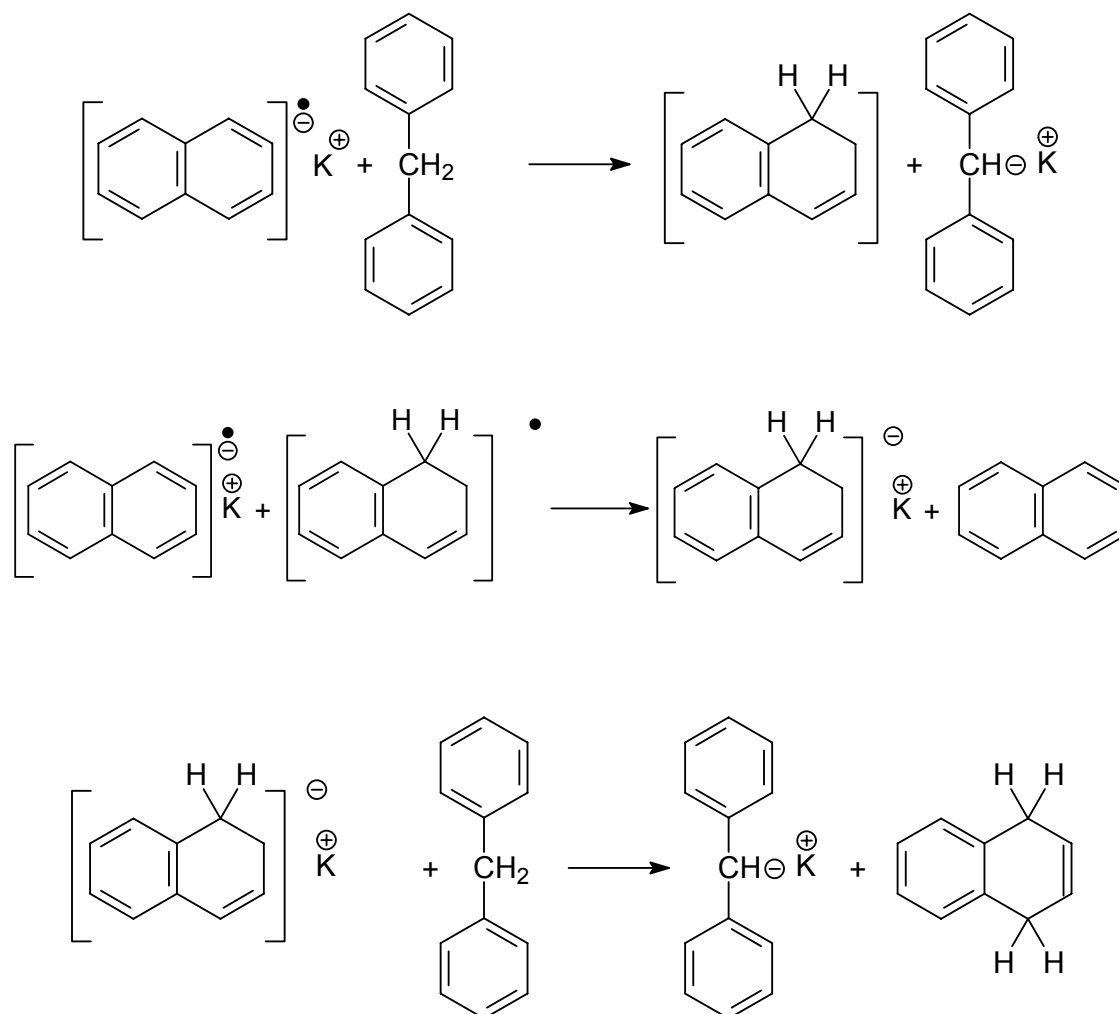


Figure 16: Reaction scheme for the synthesis of the diphenylmethyl potassium

Commercial methyl trimethylsilyl dimethylketene acetal (MTS) and ethyl α -bromoisobutyrate (aBriBu) were degassed by three freeze-pump-thaw cycles prior to use.

3.2.4. CHAIN-END MODIFIATORS

Commercial 1,1-diphenylethene (DPE) was titrated with BuLi solution in hexane under an inert atmosphere until a red color was persistent, and distilled under high vacuum conditions.

Styrene oxide was distilled under reduced pressure and stored over calcium hydride. Prior to reaction an appropriate amount of styrene oxide (usually around 0,5 ml) was distilled under reduced pressure.

α -bromoisobutyrylbromide (α -EiBuBr) was stirred over CaH₂, degassed and distilled at reduced pressure prior to the reaction.

3.2.5. CATALYSTS

Tetrabutylammoniumbibenzoate (TBABB) was synthesized according to the literature.⁸¹ All chemicals for the TBABB synthesis were used as received. 5 g of benzoic acid (41 mmol) were dissolved in 40 ml of 40 mass % of aqueous tetrabutylammonium hydroxide (TBAOH) (61 mmol of TBAOH). After a homogenous solution was obtained, the mixture was extracted with dichloromethane. Additional 5 g (41 mmol) of benzoic acid were added to the solution. The solution was dried with MgSO₄, filtered and evaporated. The residual solid was dissolved in 125 ml of warm THF. Subsequently, the volume was reduced to 60 ml. 125 ml of diethyl ether were added in small amounts and the solution was allowed to stand overnight. The solvent was removed, and the final product was dried *in vacuo*. The reaction scheme for the synthesis of TBABB is:

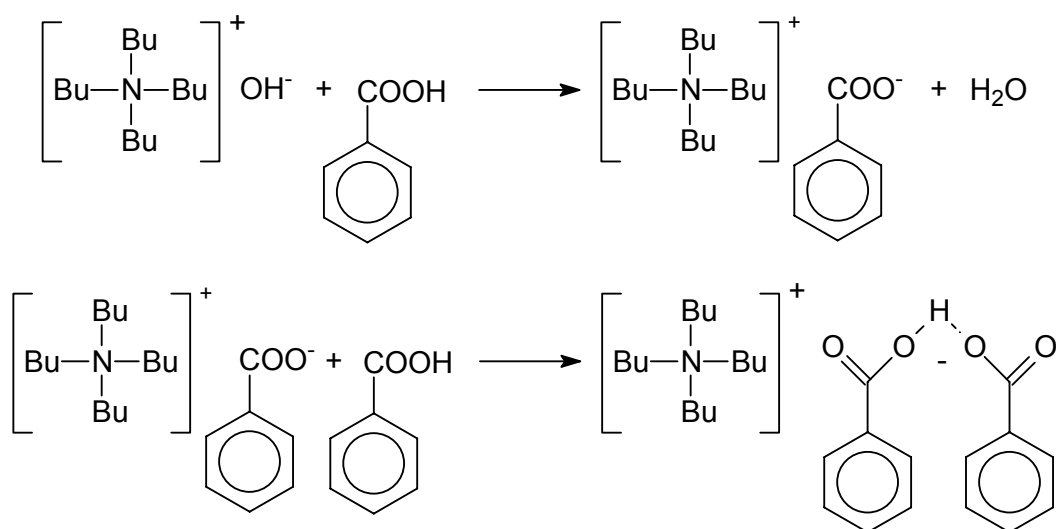


Figure 17: Reaction scheme for the synthesis of TBABB

Tris(dimethylamino)sulfoniumbifluoride (TASHF₂) was prepared according to the literature.⁸¹ 0,89 g of tris(dimethylamino)sulfoniumbifluorotrimethylsilicate (TASSiF₂) were dissolved in 1 ml of acetonitrile (19 mmol, 0,78 g) which was not dried, so that the water contaminants were used for the hydrolysis and stirred at room temperature overnight. The acetonitrile was removed in vacuum. The resulting white powder of TASHF₂ was weighted, dissolved in 5 ml of THF (4,45 g; 61,8 mmol) and stirred overnight in order to get a saturated solution of TASHF₂ in THF. The solution was decanted, and the remaining TASHF₂ was dried and weighted again. From the difference in the masses of TASHF₂ and the known volume of THF, the concentration of decanted solution was determined.⁷²

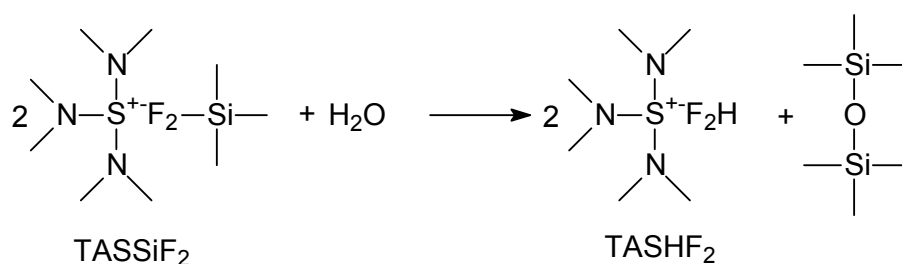


Figure 18: Reaction scheme for the synthesis of TASHF₂

Commercial copper (I) bromide was used as received.

3.2.6. LYGAND FORMING AGENTS

Commercial N,N,N',N'',N''' pentamethyldiethylenetriamine – PMDTA was flushed with nitrogen or argon prior to use.

Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was synthesized according to the literature.⁸²⁻⁸⁴ Tris-(2-aminoethyl) amine (TREN) was titrated with hydrochloric acid until a pH of approximately 4 was reached. The tris-(2-aminoethyl) amine trichloride (TRENCl₃) was precipitated, separated and washed with water. Then, a mixture of 6,2 g of (TRENCl₃), 3 ml of water, 20 ml of 85% formic acid and 17 ml of 37% formaldehyde were heated to 120°C for eight hours (as long as the evolution of carbon dioxide was observed). All of the volatile fractions were removed by application of vacuum. The solid residue was treated with 40 ml of 10% sodium

hydroxide in water and extracted with diethyl ether. After removal of the ether, Me₆TREN was distilled at reduced pressure (70-71°C at 67 Pa) as a colorless oil.

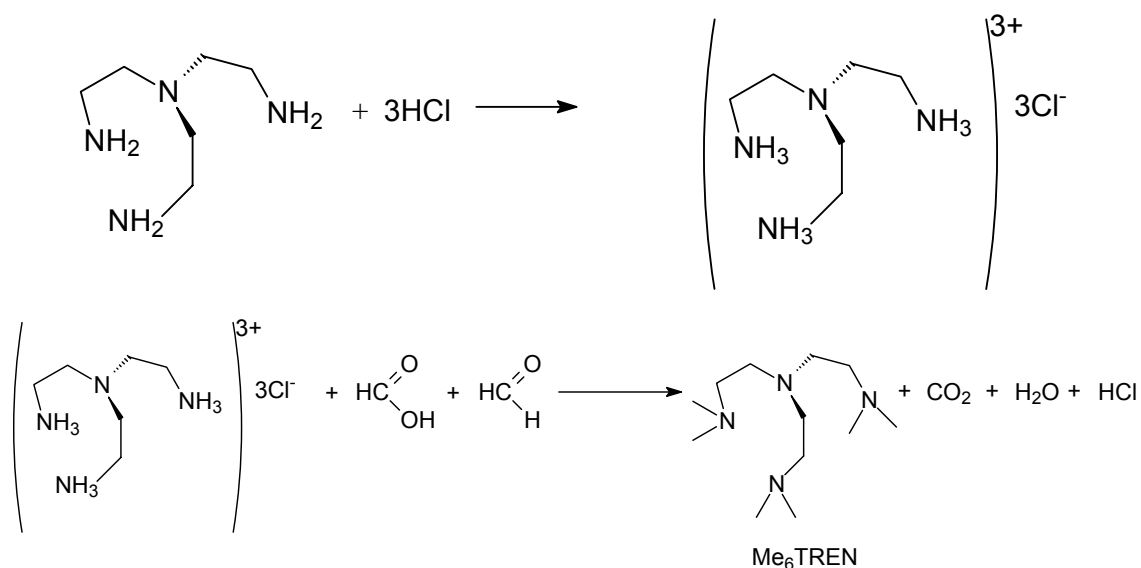


Figure 19: Reaction scheme for the synthesis of Me₆TREN

3.2.7. OTHER CHEMICALS

2,6-di-tert-butyl-4-methylphenol (BHT) was used as received as an anti-oxidant for the synthesized polymer.

3.3. CHARACTERIZATION TECHNIQUES

3.3.1. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance spectroscopy (NMR) is one of the most used techniques for the characterization of polymers. In this work, ¹H NMR was used. The chemical shift of the spectra is referenced versus tetramethyl silane (TMS). For this work, all NMR spectra were done in CDCl₃. The resonance signal of the solvent (δ=7.26 ppm) was used for reference.

The NMR spectra were performed on a Bruker AV300 NMR spectrometer operating at a field of 7 T (300.13MHz) using a 5 mm ^1H / TXI probe and a sample temperature of 298K. ^1H spectra were recorded by applying a 10 μs 90° pulse. The relaxation delay was chosen in a way that the sample was fully relaxed.

3.3.2. GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography – GPC (also known as Size Exclusion Chromatography – SEC) is a technique for determination of the molar mass distribution of polymers. As a stationary phase, cross-linked polystyrene, porous glass or silica gel are used. The pore size of the stationary phase is too small to accommodate larger polymer molecules, and they pass relatively quickly through the column. The analyzed polymer is fractionated according to its hydrodynamic volume. When size of the molecules decreases, the probability of diffusion into the small pores of the stationary phase increases, the path that molecules must pass becomes longer. Therefore, larger molecules elute first, and the elution volume (V_e) increases with the decrease of molar mass.⁷⁶

The elution volume of a polymer of a given molar mass can be described as:

$$V_e = V_0 + K_d V_i \quad (48)$$

V_e – elution volume

V_0 – volume between the gel particles

V_i – the overall sum of all pore volumes

K_d – partition coefficient between the mobile and the stationary phase

The most commonly used stationary phase is cross-linked polystyrene gel, as it can be used for a wide range of polymers and solvents. As GPC separates polymer molecules according to their molecular sizes, it is necessary to establish a calibration curve to obtain a molar mass distribution. The calibration curve is constructed by determining the elution volumes of polymer standards with narrow molar mass distribution. The calibration curve is commonly presented in a $\log M=f(V_e)$ diagram.

The relation between molar mass and the polymer size is different for each type of polymer. Therefore, a calibration curve for polystyrene will give absolute values of molar masses for polystyrene only. Other polymers have a different dependence of the molar mass on the elution volume, so their calculated molar masses obtained by polystyrene calibration will be apparent ones. As the goal of GPC is to obtain the molar mass distribution, the concentration of each fraction of the polymer is determined by the use of on-line detectors. The complete elugram is equidistantly divided, and the concentration of polymer in each slice (c_i) is measured. Each slice corresponds to a certain molar mass (M_i) which is determined from the calibration curve. The average molar masses are calculated using equations 9 and 10:

Two different detectors were used to determine the concentration, c_i : an UV and a RI detectors.

UV detector is a highly selective detector that only detects at a certain wavelength (e.g. the phenyl ring at 254 nm). The solvent that is used must not adsorb at this wavelength. The advantage of this detector is that it is not sensitive to changes in temperature and pressure.

A differential refractometer (RI detector) compares the refractive index of both the sample and the pure solvent. The main advantage of this detector is that all units in the polymer can be measured, and the main disadvantage is that it is sensitive to changes of temperature and pressure.

All GPC measurements were conducted at room temperature with THF as a solvent and 2,6-di-tert-butyl-4-methylphenol as internal standard. Flow rate was 1.0 ml/min, provided by a VWR-Hitachi 2130 pump. The RI detector was a Waters 2410 ($\lambda=930$ nm), the UV detector was a Waters, operated at 254 nm, or 300 nm, as stated in the experimental part. Samples were injected using Waters 717 autosampler, with injection volumes of 20 μ l. Raw data were flow rate corrected and processed using PSS WinGPC Unity software.

3.3.3. DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is a method of thermoanalytical analysis in which the difference of the required energy that is needed to keep a sample and a reference material at the same temperature is measured as a function of the temperature. Both the reference and the sample undergo the same temperature change during the experiment and usually the temperature is increased linearly with time. The reference should have a well-defined heat capacity over the range of the measured temperature range. The main application of DSC lies in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC.⁷⁷ The result of a DSC experiment is a curve of heat flux versus temperature or versus time, and glass transition is observed as a “step” on the graph.

DSC measurement in this work has been done between -100°C and +160°C, with a heating/cooling rate of 10 K/min. The glass transition temperature (T_g) was taken from the DSC curve as the center of the step transition in the second heating. The calorimeter used for measurements in this work was a Netzch 204 Phoenix.

3.3.4. CLOUD POINT MEASUREMENTS

Cloud point measurements were performed with a turbidity meter Aqalytic PC Compact. Polymer samples were dissolved in water ($w(\text{polymer})=0.1$ mass%) overnight. The solution of the sample was tempered, and the measurements of the transitivity of a standard solution and subsequently the sample were done. The measurement of the transitivity of the standard solution was used to set the device to the standard value in internal units (usually 100 or 1000 units). Then, the transitivity of the sample solution was compared to the transitivity of standard solution. The temperature was varied 15 and 30°C, with an temperature increment of 1°C.

3.4. GENERAL POLYMERIZATION PROCEDURE

Anionic polymerizations were done in two different modes. For more diluted system (monomer concentration less than 1 wt%) the reactions were performed in a reactor, and in for more concentrated systems (monomer concentration around 10 wt%) reactions in flasks were done.

3.4.1. REACTIONS BY ANIONIC MECHANISM IN REACTOR

Reactions were performed at -70°C with changing to room temperature in the later stages of some of the reactions. This approach was used in the polymerization of styrene and styrene containing diblock copolymers. An appropriate amount of THF was treated with 5-10 ml of *sec*-BuLi solution in cyclohexane (1.4 M) and stirred overnight at room temperature. The monomer for the first block was introduced to the reactor through the line. After initiation the reactions ran for a selected period of time (1 to 3 hours). If a homopolymer was synthesized, the reaction was terminated with a mixture of degassed methanol and hydrochloric acid. If a diblock copolymer was synthesized, a precursor of the first block was taken (usually 10 -20 ml solution) using nitrogen overpressure in the reactor. The precursor sample was terminated outside the reactor with 2-3 ml of degassed methanol with few drops of HCl.

Prior to the synthesis of the second methacrylate block, 1,1-diphenylethene (DPE) was added at -70°C . The reaction of the living chains with DPE was running for 30 minutes. After that, the second monomer was added and the temperature was raised (-40°C or room temperature, depending on the reaction) and the reaction proceeded for an appropriate period of time (2 to 4 hours, depending on the reaction). The reaction was terminated with a mixture of 10 ml degassed methanol and a few drops of HCl. If a precipitation was not done immediately, the polymer solution was kept at 4°C . In order to prevent oxidative decomposition, 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added. Precipitation was done in hot water, methanol or *n*-heptane (depending on the polymer). The polymer was dried *in vacuo* at 40°C overnight.

3.4.2. REACTIONS BY ANIONIC MECHANISM IN FLASKS AND GTP POLYMERIZATIONS

Reactions performed in flasks were done in the glove box at room temperature. Therefore, only reactions which do not require external temperature control were carried out this way. All reactants and glassware were introduced into the glove box. The reactions were initiated with *sec*-BuLi solution in cyclohexane (1.4 M) and ran for a selected period of time (30 minutes to 3 hours, depending on the reaction).

In the case of GTP the components, THF, the monomers, and the initiator (MTS) were added. The polymerization was started by addition of the catalyst (TASHF₂ or TBABB) and ran for an appropriate period of time (usually 1 to 3 hours).

The termination and the work up procedure were performed in both cases in an analogous manner as described in the previous chapter.

3.4.3. ATRP POLYMERIZATION

All polymerizations via ATRP mechanism were done in the glove box. Homopolymerization of both polystyrene and PDEGMA were tried. The polymerization of diblock copolymers (PS-PDEGMA and PDEGMA-PS) was performed in a sequential manner: Ethyl α -bromoisobutyrate (EiBuBr) was used as an initiator and N,N,N',N'',N''' pentamethyldiethylenetriamine (PMDTA) as a ligand forming agent. An appropriate amount of copper salt was dissolved in anisole and subsequently PMDTA and the monomer were added. The reaction ran usually for four hours and was terminated by exposing the reaction mixture to the air. The copper complexes were removed using an aluminum oxide column, and the polymer was precipitated in methanol or *n*-heptane (depending on the type of polymer synthesized) and dried. The homopolymer obtained via this procedure contains a bromine group at the end, and can serve as a macroinitiator for polymerization of the second block. To do so, an appropriate amount of the macroinitiator was introduced into the glove box, dissolved in anisole and the ligand forming agent as well as the copper salt were added in an analogous manner like in the polymerization of the first block. The reaction was terminated by exposing the mixture to the air, and the copper compounds

were removed from the reaction mixture by filtering through an aluminum oxide column. Precipitation of the diblock copolymers was done in *n*-heptane or methanol (depending on the polymer synthesized). The polymer was dried *in vacuo* at 40°C overnight.

3.4.4. SEQUENTIAL ANIONIC – ATRP POLYMERIZATION

In this procedure a polystyrene macroinitiator was prepared by anionic polymerization of styrene with subsequent end-functionalization with α -bromo-isobutyric acid bromide. Instead of a direct linkage of the α -bromo-isobutyric group to the living chain end of polystyrene, an interstep with an addition of styrene oxide was introduced. By this way, the degree of end functionalization should be higher, as the esterification of the α -bromo-isobutyric group with hydroxyl-anion stemming from styrene oxide is easier to obtain than a direct reaction with the styryl anion.⁷⁸⁻⁸⁰

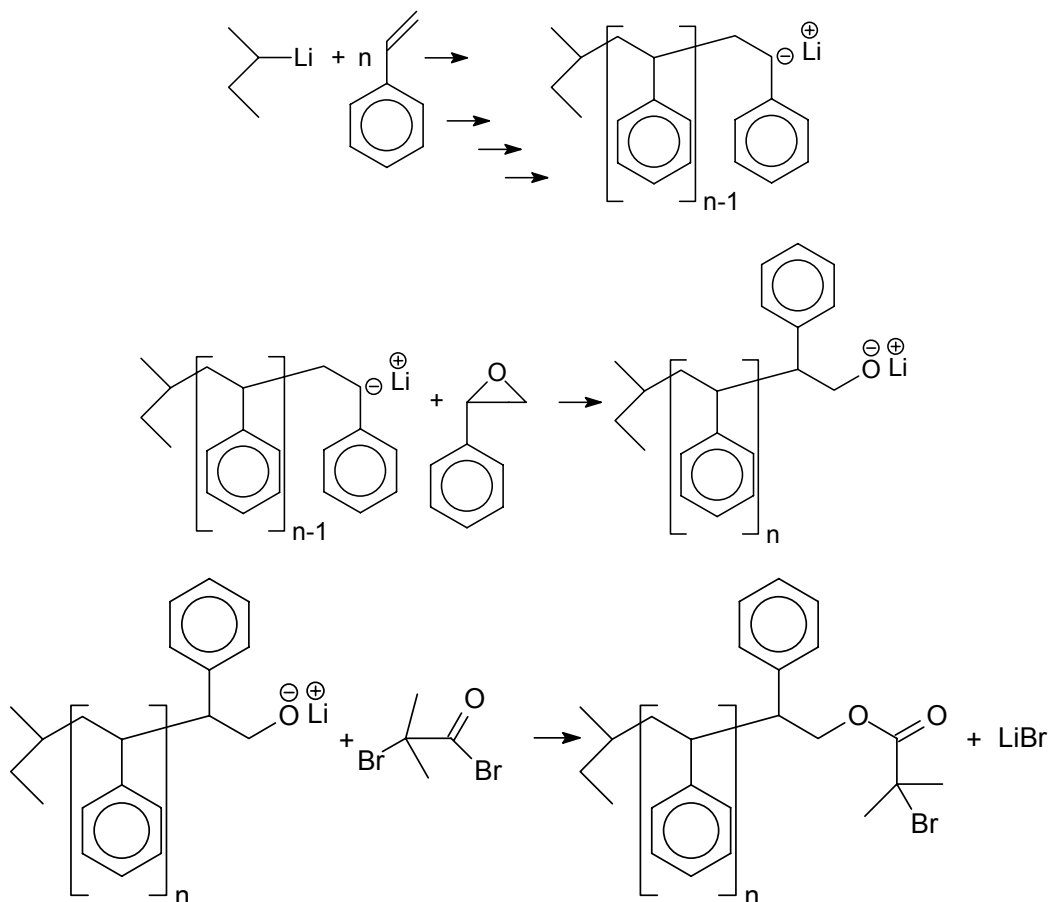


Figure 20: Reaction scheme for the synthesis of the polystyrene macroinitiator

The stereochemistry of this reaction is strongly influenced by the polarity of the solvent. If the reaction is done in non polar solvents (e.g. toluene), chains are organized in clusters, and therefore steric reasons are dominant in the determination of the structure of the polystyrene-styrene oxide anion. Therefore, the phenyl ring of styrene oxide tends to take a position as far as possible from the neighboring phenyl ring in the polystyryl anion, and styrene oxide's phenyl ring is in α position to the oxygen atom. On the other hand, if the solvent is polar (e.g. THF), the chain ends are evenly distributed in the solution, and electronic reasons are predominant. Therefore, phenyl ring from the styrene oxide is in the β position to the oxygen atom. As the macroinitiator in this work was synthesized in the THF, this product is presented in the reaction scheme.

The polystyrene macroinitiator was synthesized in the reactor at -70°C . Typically, 500 ml of THF were titrated with 5-10 ml of *sec*-BuLi solution in cyclohexane (1.4 M) and stirred overnight at -30°C . Styrene was introduced and the polymerization was initiated by addition of a *sec*-BuLi solution in cyclohexane. After 2 hours the precursor was taken and styrene oxide was introduced at -70°C . After additional two hours α -bromoisobutyrylbromide (α -EiBuBr) was added and the reaction mixture was heated up to room temperature overnight. 10 ml of a degassed methanol HCl were introduced; the polymer was precipitated in methanol and dried *in vacuo* at 40°C overnight. Prior to polymerization of the second PDEGMA block it was further dried under high vacuum conditions to remove any traces of moisture.

The ATRP polymerizations of the second PDEGMA block were conducted in a manner analogous as described in the chapter 3.4.3.

4. RESULTS AND DISCUSSION

4.1. HOMOPOLYMERIZATION OF DEGMA

4.1.1. ANIONIC POLYMERIZATION

As a first step, the homopolymerization of DEGMA was done via an anionic polymerization mechanism to explore properties of PDEGMA and to compare the course of the reaction to literature results.²³⁻²⁷ DEGMA can be can be polymerized in the presence of different additives (e. g. diethylzinc) which affect the tacticity and the molar mass distribution of the final product.

First experiments (sample HA1) were done in the presence of lithium alkoxides, prepared in situ, by addition of *n*-BuLi to THF.⁹⁴

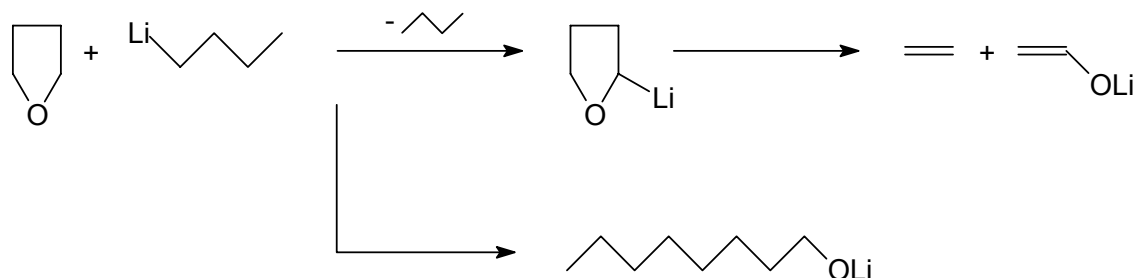


Figure 21: Reaction scheme for the formation of the lithium alkoxides

The polymerization of DEGMA was initiated by 1,1-diphenyl-3-methyl pentyl lithium which was prepared in situ by adding DPE to a *sec*-BuLi solution. This initiator was used as it possesses two phenyl groups to prevent the attack on the carbonyl group of methacrylate due to sterical reasons.

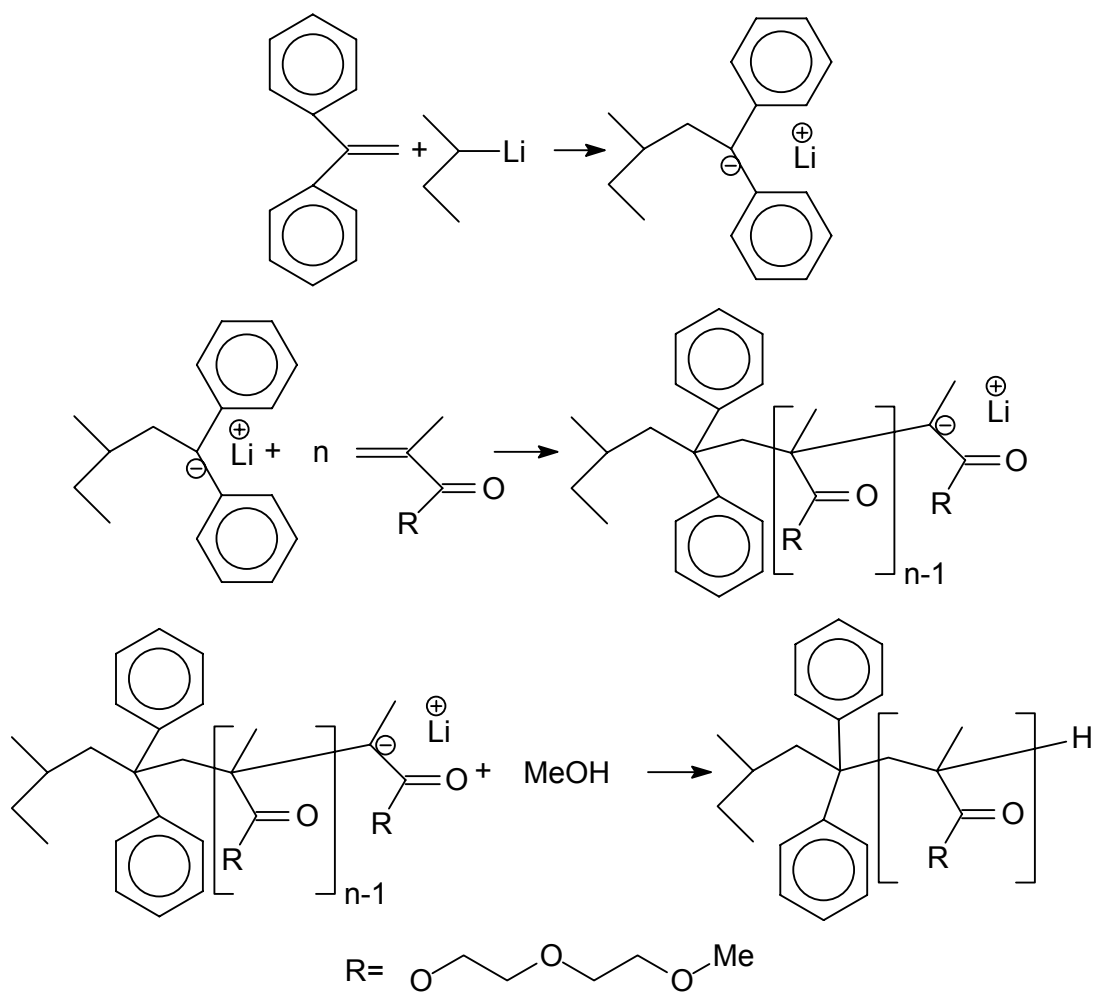


Figure 22: Reaction scheme for the synthesis of the PDEGMA homopolymer via the anionic polymerization

Precipitation was tried in methanol, water and mixtures of both (75 wt% and 50 wt% methanol), but in all cases only milky, turbid solutions were gained. As all attempts to recover the polymer were unsuccessful the solution was evaporated. The result was a very viscous liquid containing inorganic salts. This liquid was redissolved in a small amount of THF and solution was filtered. After evaporation of the filtrate a transparent, viscous liquid was recovered that was analyzed by GPC measurements.

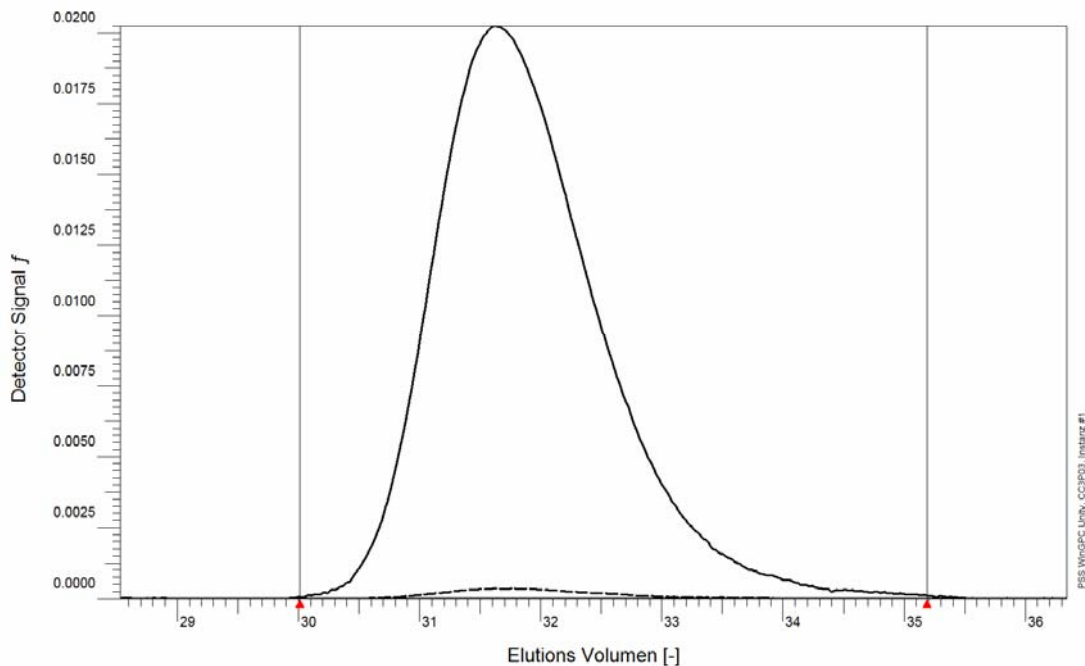


Figure 23 : GPC elugram of sample HA1 solid line – RI signal; dashed line – UV signal

From Figure 23 it can be seen that the sample is monomodal. The apparent number average molar mass of this polymer is $M_n = 7990 \text{ g/mol}$ versus polystyrene calibration, with a polydispersity index of 1,08. The lower molecular mass compared to the calculated one might be explained by the polystyrene calibration. The ratio between the apparent molar mass and the calculated one is:

$$\frac{M_n^{GPC}}{M_n^{calc}} = \frac{7990 \text{ g/mol}}{20400 \text{ g/mol}} = 0.40$$

The UV signal that can be observed in Figure 23 comes from the two phenyl rings of the DPE unit.

4.1.2. GROUP TRANSFER POLYMERIZATION

As the main goal of this work was to synthesize a diblock copolymer, alternative pathways for polymerization of DEGMA were tested. As a group transfer

polymerization of methacrylates up to molar masses of 60000 g/mol has already been reported¹, it was supposed that PDEGMA with a sufficient molar mass (up to 50K) might also be synthesized by a GTP mechanism.

For the polymerization of the sample HG1, general procedure for the GTP was followed. Precipitation was unsuccessfully tried in both polar (methanol/water mixture) and nonpolar solvents (hexane), so the solvent was removed under reduced pressure. The residual transparent, viscous liquid was used for GPC measurements. Theoretical molar mass was $M_n^{theo}=2800$ g/mol. This relatively low molar mass was chosen for the first experiment in order to clarify the behaviour of the system, and to examine the suitability of GTP for this type of monomer.

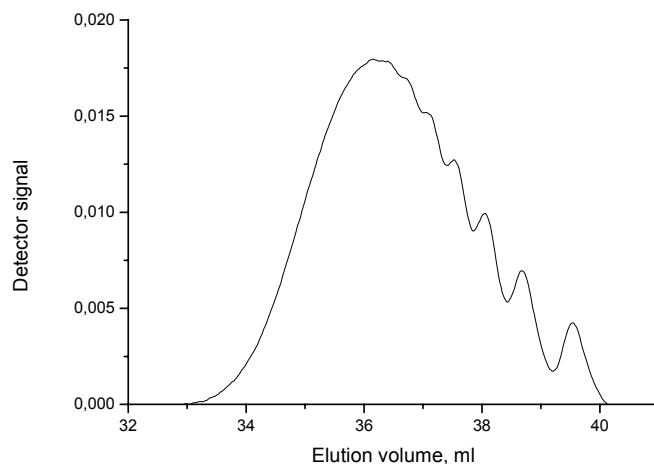


Figure 24 : Elugram of sample HG1 (RI detector)

Figure 24 show the elugram from that the apparent number average molar mass was determined as $M_n=1190$ g/mol (versus polystyrene calibration) with a polydispersity index of 1.33. The peaks at higher elution volumes stem from the oligomeric parts of the sample. The lower apparent molar mass compared to the calculated one could be the result of the PS calibration used. The ratio between the calculated molar mass, and the apparent one measured by GPC is 0.42.

This ratio is in agreement with the result gained by the anionic polymerization of DEGMA (sample HA1).

In a follow up experiment (sample HG2), tetrabutylammonium bibenzoate (TBABB) was used as a catalyst. 50 ml THF, 0,42 mmol of MTS (0,1 ml) and 27.1 mmol (5 ml) of DEGMA were mixed. Then, 0,05 mmol of TBABB solution in THF was added dropwise. The reason for dropwise addition is described in the previous reaction. After two hours, the reaction was terminated with 10 ml of MeOH. A polymer could not be precipitated, so the solvent was removed under reduced pressure. The theoretical molar mass of this polymer was 12100 g/mol. A viscous, transparent liquid came as a result, its elugram is given in Figure 25.

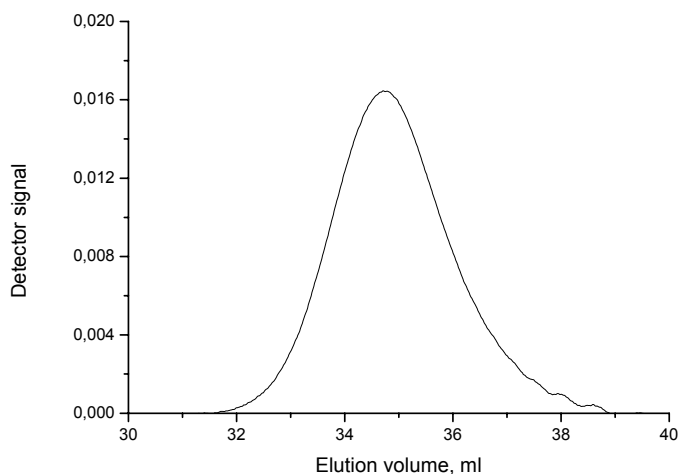


Figure 25: Elugram (RI detector) of sample HG2

The apparent number average molar mass was $M_n=3000$ g/mol (calibration versus polystyrene) and the polydispersity index was 1.17. The ratio between the calculated molar mass, and the apparent one measured by GPC is:

$$\frac{3000 \text{ g / mol}}{12100 \text{ g / mol}} = 0.25$$

Comparing this value with the values obtained in the other experiments, it is obvious that this value is lower. The reason for that might be that polymerization of DEGMA did not run here until a full monomer conversion was obtained. Therefore, it is concluded that TBABB is not an optimal catalyst for the polymerization of DEGMA by a GTP mechanism.

4.1.3. ATOMIC TRANSFER RADICAL POLYMERIZATION

As another backup solution for the polymerization of DEGMA, the mechanism of ATRP was explored. The first polymerization via an ATRP mechanism was performed in order to obtain a PDEGMA homopolymer.

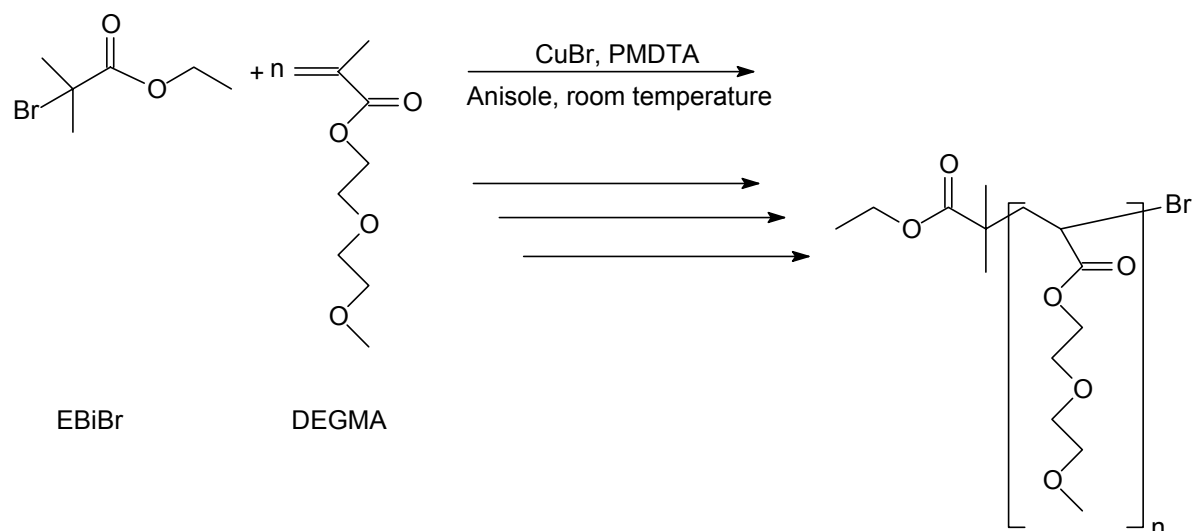


Figure 26: Reaction scheme for the synthesis of the PDEGMA homopolymer via the ATRP

For the polymerization of sample HR1 27, 1 mmol of DEGMA, 0.128 mmol of CuBr, 0.128 mmol of PMDTA and 1 ml of anisole were mixed and the reaction was initiated by adding of 0.256 mmol of EBiBr. The solution became dark green. The reaction ran for four hours at room temperature. Theoretical molar mass was 20000 g/mol. The GPC trace of the polymer obtained is shown in Figure 27.

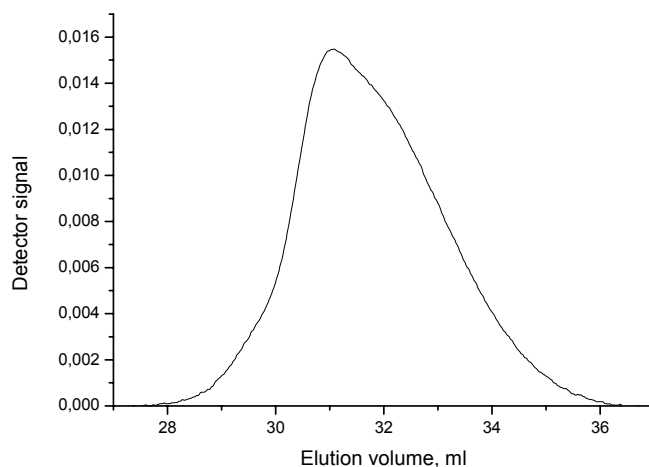


Figure 27: Elugram (RI detector) of sample HR1

The apparent number average molar mass is $M_n=7200$ g/mol (versus polystyrene calibration) and the polydispersity index is 1.28. The ratio between the calculated and measured molar mass is:

$$\frac{7200 \text{ g / mol}}{20000 \text{ g / mol}} = 0.36$$

Although this value is lower than the one obtained by anionic polymerization and TASHF₂ catalyzed GTP, but this sample proved that PDEGMA polymer can be obtained by the ATRP mechanism.

It is obvious from this GPC elugram that a multimodal distribution is present in this polymer. It is supposed that impurities in the monomer caused some unwanted side reactions. Obviously, a straightforward procedure (passing DEGMA solely through an Al₂O₃ column) was not sufficient, hence in further experiments DEGMA was additionally distilled from CaH₂ prior to polymerization via ATRP.

4.1.4. COMPARISON OF THE RESULTS

The homopolymerization of the PDEGMA was performed via three different reaction mechanisms (anionic, GTP and ATRP). A comparison of those results is presented in table 1.

Table 1: Theoretical and apparent molar masses of PDEGMA synthesized via different polymerization mechanisms

Sample	Mechanism	$M_n^{theo.}$, g/mol	$M_n^{app.}$, g/mol	M_w/M_n	M_n^{app}/M_n^{theo}
HA1	Anionic	20400	7990	1.08	0.40
HG1	GTP (TASHF ₂)	2800	1190	1.33	0.42
HG2	GTP (TBABB)	12000	3000	1.17	0.25
HR1	ATRP	20000	7160	1.28	0.36

Comparing the ratio between the calculated and apparent number average molar masses, it is obvious that samples HA1, HG1 and HR1 show a ratio of approximately 0.4. It can be assumed, that this ratio represents the deviation between the absolute molar mass of PDEGMA and the apparent one obtained by PS calibration. Following that hypothesis the comparison shows, that all three mechanisms are able to polymerize DEGMA in a controlled manner. However, in case of ATRP the polydispersity index is significantly higher than in all other mechanisms, whereas in GTP was only explored for lower molar masses. Hence, table 1 indicates, that anionic polymerization should be the primary choice, followed by GTP.

In the case of GTP, sample HG2 exhibits a lower ratio, which might lead to the conclusion that the conversion of DEGMA was not complete or that the use of TBABB as catalyst may cause some difficulties in the GTP similar to the GTP of tert-butylmethacrylate. As the use of TASHF₂ as catalyst resulted in a better agreement of M_n^{app}/M_n^{theo} and lower polydispersity index that catalyst shows a greater potential to be used in copolymerization with tBMA, it was preferred for the upcoming experiments.

4.2. POLYMERIZATION OF POLYSTYRENE-POLYTERT-BUTYLMETHACRYLATE COPOLYMERS

As it was shown in the previous chapter, PDEGMA can be polymerized in a controlled manner. However, there is almost no information available if and how the polymerization of DEGMA proceeds if this process is initiated by a polystyrene anion. In order to improve our understanding of sequence exchange from polystyrene to PDEGMA in the block copolymer synthesis, we decide to “simulate” the behavior of DEGMA, by using tert-butylmethacrylate as a model substance as a first step – especially as the polymerization of *t*BMA has already been studied in detail.⁸⁹ *Tert*-butyl methacrylate (*t*BMA) contains a bulky ester group which might result in similar effects compared to the long ester group of DEGMA. However, in two important aspects *t*BMA and DEGMA may behave differently. The ester group of DEGMA is linear, while the ester group of *t*BMA is branched. On the other hand, DEGMA contain ether groups, and the free electron pairs of the oxygen atom as well as the polarization of the C-O bond will have a strong influence on the formation and stability of the carbanion.

The polymerization of PS-*Pt*BMA block copolymer was performed in a sequential manner. The reasons for the order of sequences and addition of DPE were already described in the chapter 3.4.1.

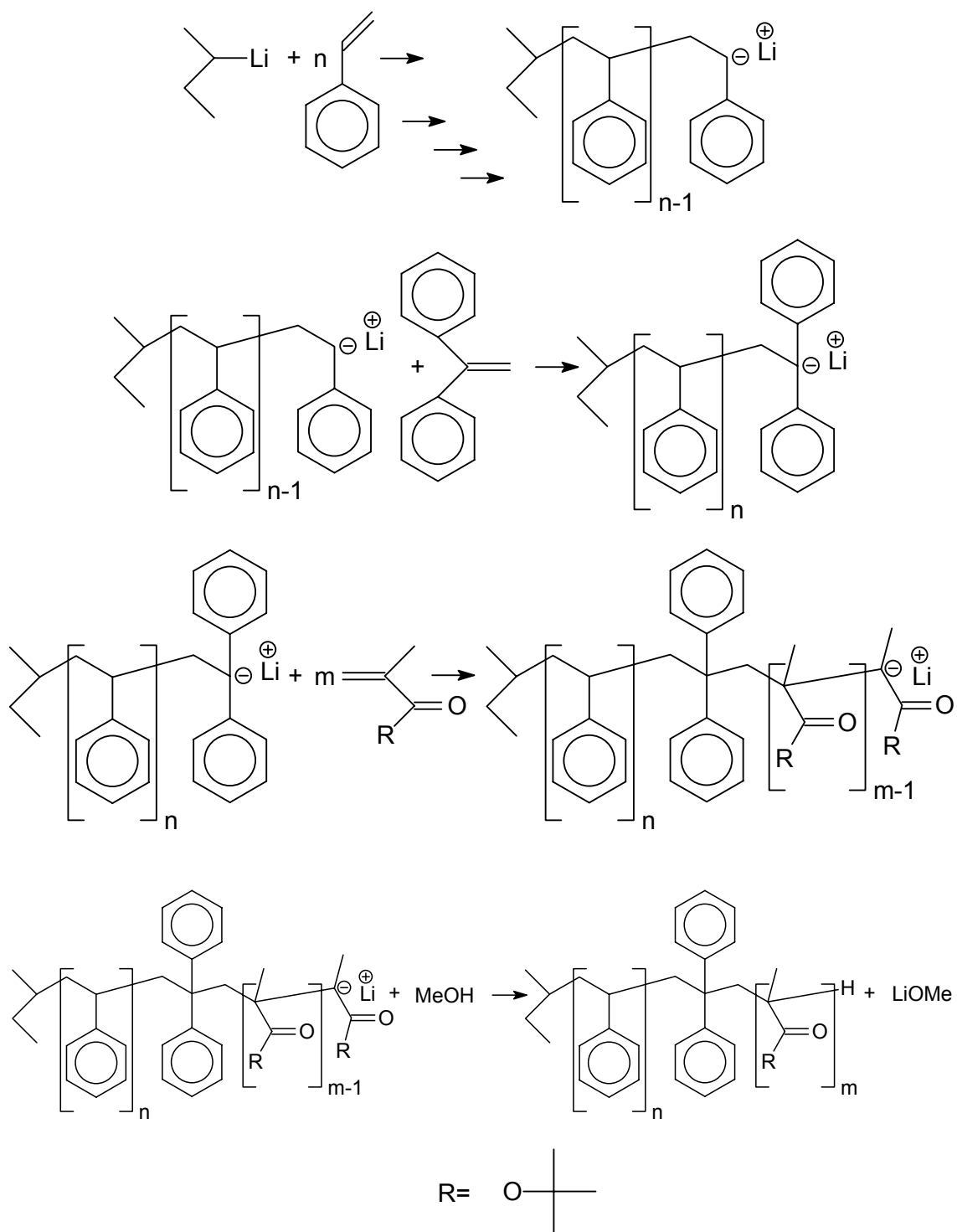
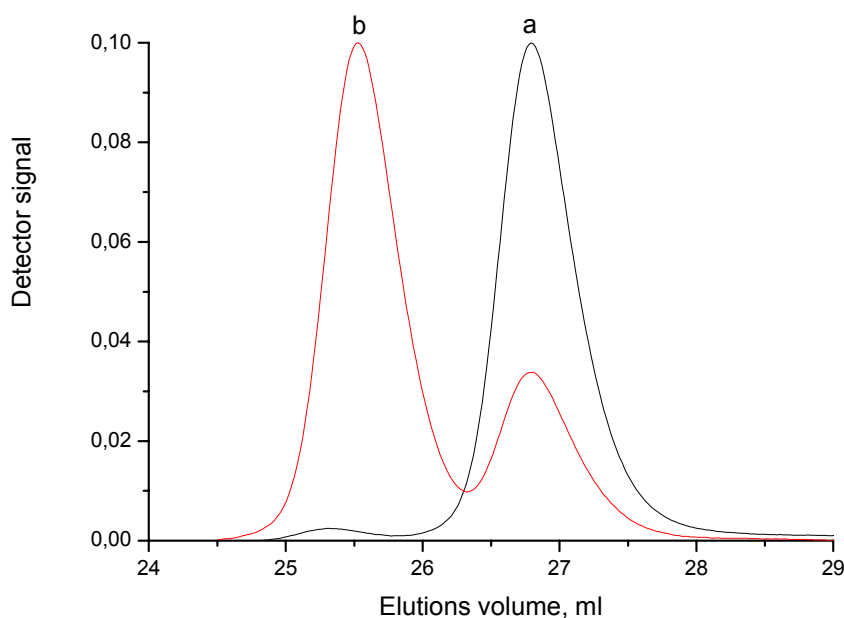


Figure 28: Reaction scheme for the synthesis of the PS-PtBMA block copolymer via the sequential anionic polymerization

The polymerization (sample ST1) was performed following the general procedure for diblock copolymers in the reactor. 87 mmol of styrene (10 ml) were dissolved in 500 ml of THF at -63°C , and the reaction was initiated by 0.0588 mmol

of *sec*-BuLi (solution in cyclohexane $c=0.14$ mol/l, 0.42 ml of solution). The reaction ran for two hours, and the colour of the reaction mixture was yellow. A precursor was taken, and 2.83 mmol of DPE (0.5 ml) were added, which resulted in a colour change to dark red. One hour later, 17.4 mmol of *t*BMA (2.8 ml) were added. The reaction mixture became colourless, and the reaction was terminated with MeOH after two hours. The theoretical overall molar mass of this diblock copolymer was $M_n^{theo}=209600$ g/mol, with the PS precursor $M_n=154000$ g/mol and P*t*BMA block $M_n=55600$ g/mol. The apparent average molar masses of block copolymer and the precursor were determined by GPC. The elugrams are presented on the Figure 29.



*Figure 29: Elugram (RI detector) of sample ST1 a) PS precursor;
b) PS-PtBMA block copolymer*

Number average molar mass of the polystyrene precursor was 55200 g/mol (polydispersity 1.10) while apparent number average molar mass of the diblock was 97900 g/mol (polydispersity 1.20). The small peak that at lower elution volume on the precursor elugram comes from a coupling of the polystyrene chains. The elugram of the diblock shows a bimodal distribution. The position of the peak at higher elution volumes indicates that residual polystyrene homopolymer is present; hence termination occurred during the addition of the *t*BMA monomer. Comparing the areas of both of peaks at the GPC curve of diblock copolymer, it is obvious that approximately 25 % of polystyrene

chains were terminated during the addition of the *t*BMA monomer. The average molar mass of the polystyrene precursor was lower than calculated, which might indicate that the full monomer conversion has not been reached, or impurities were present in the monomer or the initiator.

This experiment proved that the coupling of a methacrylate chain to a PS precursor is possible by sequential anionic polymerization. Based on the chemical similarities of *t*BMA and DEGMA, it was supposed that the later can be coupled to the living PS chain in an analogous manner. However, due to the presence of the termination during the addition of the *t*BMA, it was decided to synthesize PDEGMA containing block copolymers solely with an methacrylate based second block.

4.3. POLYMERIZATION OF P*t*BMA-PDEGMA COPOLYMERS

4.3.1. ANIONIC POLYMERIZATION

In a second approach to gain some information on the synthesis of PDEGMA containing block copolymers, the preparation of P*t*BMA-PDEGMA macromolecules was investigated. The particular system was chosen for two reasons. First, it was supposed that the coupling of DEGMA to a methacrylate anion would be easier to establish compared to a polystyryl one as in the former case both types of living centres are very similar. Second, in a P*t*BMA-PDEGMA block copolymer, the P*t*BMA block can be hydrolyzed leading to polymethacrylic acid – poly (methoxyethoxy)ethyl methacrylate block copolymer.⁹³ The resulting PMAA-PDEGMA macromolecule are amphoteric in nature and might be used for *pH* sensitive membranes.

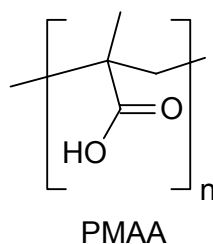


Figure 30: Structure of the polymethacrylic acid (PMAA)

As the reactivity of the tert-butylmethacrylate anion is probably higher than the one of DEGMA, P*t*BMA was synthesized as the precursor, and PDEGMA as a second block. In the case of P*t*BMA-PDEGMA block copolymers, *n*-BuLi was taken as an initiator, unless the use of different initiator was specified.

From the experiments done on the PS-P*t*BMA systems, it was found that the use of sterically unhindered carbanionic species does not lead to side reactions in the polymerization of P*t*BMA. Possible reasons for this behaviour are size and shape of the tert-butyl group which prevents the carbonyl group to be attacked. The reaction scheme for P*t*BMA-PDEGMA synthesis via sequential anionic polymerization mechanism is:

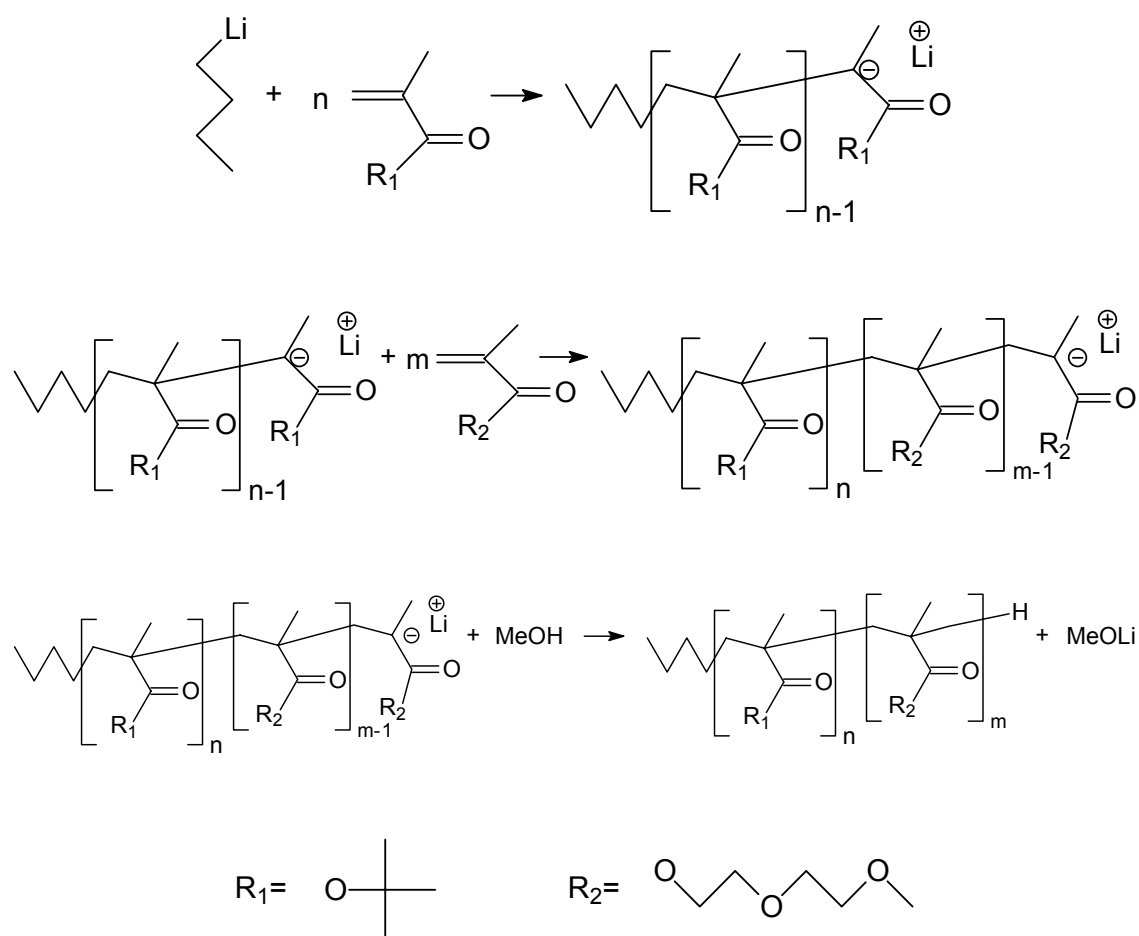


Figure 31: Reaction scheme for the synthesis of the P*t*BMA-PDEGMA block copolymer via the sequential anionic polymerization

For synthesis of the PtBMA-PDEGMA block copolymers (samples A9-A12) the general polymerization procedure for anionic polymerization was followed. Amounts of chemicals used in the synthesis are compiled in table 2.

Table 2: Amounts of chemicals taken for the synthesis of PtBMA-PDEGMA block copolymers

Entry	n(<i>t</i> BMA), mmol	n(DEGMA), mmol	n(In), mmol	x(PDEGMA) (theo.)	M _n ^{PtBMA} /10 ³ g/mol (theo.)	M _n ^{PDEGMA} /10 ³ g/mol (theo.)	M _n ^{PtBMA} /10 ³ g/mol	M _n ^{DB} /10 ³ g/mol	M _w /M _n	x(PDEGMA)
A9	18.4	27.1	0.8	0.57	2.4	7.2	-	5.5	1.40	0.39
A11 ^{e)}	37.1	32.4	0.11	0.46	48.1	55.4	23	24	2.77	<0.01
A12 ^{f)}	63.8	15.9	0.16	0.20	56.9	18.7	509	509	1.04	Not detected

^{e)}Initiated with 1,1-diphenyl-hexyl lithium prepared in situ

^{f)}Reaction in the presence of 2 mmol of Et₂Zn

n(*t*BMA) – amount of monomer taken for the synthesis of the first block (*t*BMA)

n(DEGMA) – amount of monomer taken for the synthesis of the second block (DEGMA)

n(In) – amount of the initiator (*n*-BuLi unless otherwise specified)

x(DEGMA) (theo) – calculated molar ratio of PDEGMA in the diblock copolymer

M_n^{PtBMA} (theo.) – calculated molar mass of the PtBMA block

M_n^{PDEGMA} (theo.) – calculated molar mass of the PDEGMA block

M_n^{PtBMA} – apparent number average molar mass of PtBMA precursor versus polystyrene calibration (GPC)

M_n^{DB} – apparent number average molar mass of the diblock copolymer versus polystyrene calibration (GPC)

M_w/M_n – polydispersity index of the diblock copolymer

x(DEGMA) – molar ratio of PDEGMA in the diblock copolymer as determined from ¹H NMR

Representative results of a PtBMA-PDEGMA block copolymer obtained by sequential anionic polymerization are shown in Figure 32 and 33.

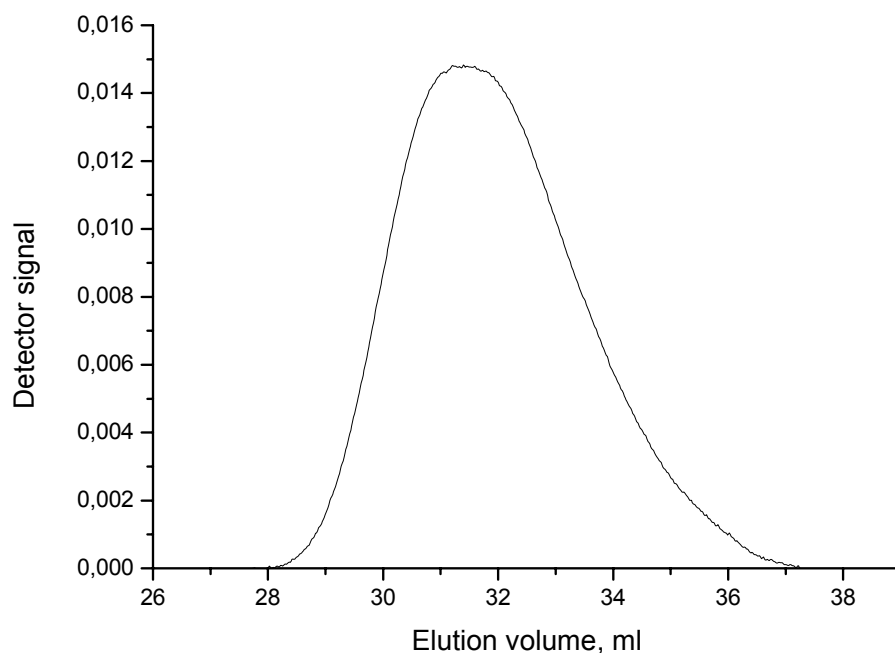


Figure 32: GPC elugram (RI detector) of PtBMA-PDEGMA block copolymer (sample A9)

The apparent number average molar mass versus polystyrene calibration was $M_n = 5500$ g/mol (polydispersity index 1,40). Although the polydispersity index is relatively high, the results look promising as a basis for the future polymerizations of diblock copolymers of high molar masses. To check the composition of this diblock copolymer, a NMR measurement was done.

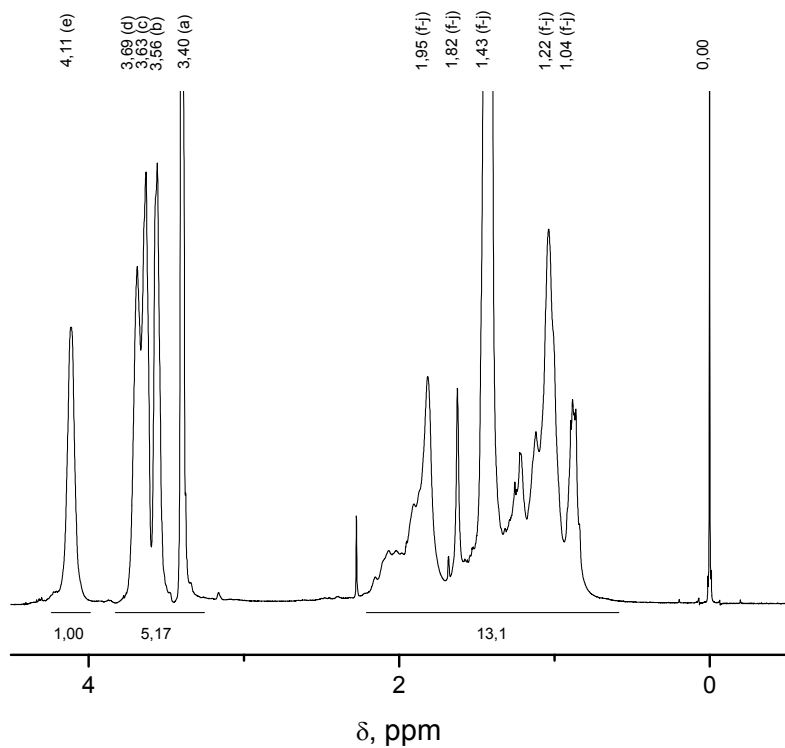
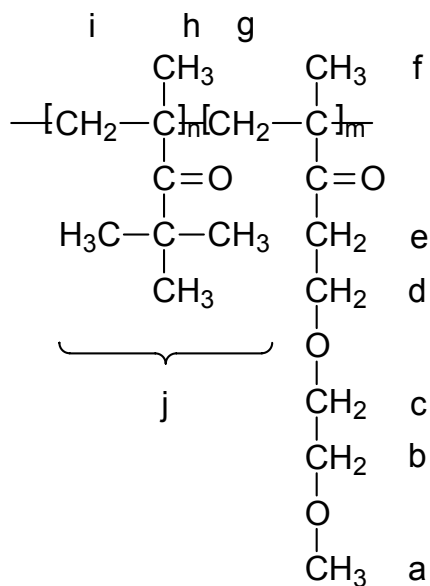


Figure 33: ^1H NMR spectra of sample A9 in CDCl_3

Table 3: Assignments of protons chemical shifts in
PtBMA-PDEGMA copolymers

δ , ppm	Ass.	No. of protons
1.0-2.1	f, g, h, i	10
1.2	j	9
3.40	a	3
3.56	b	2
3.63	c	2
3.68	d	2
4.11	e	2



The part of the spectra between 1.0 and 2.1 ppm represents all protons in PtBMA (14 atoms) and the protons of the main polymer chain of PDEGMA (5 atoms). The number ratio of PtBMA in the diblock copolymer can therefore be calculated as:

$$x(\text{PtBMA}) = \frac{\frac{I(1,0-2,2) - 5 \cdot \frac{I(3-4,5)}{11}}{14}}{\frac{I(1,0-2,2) - 5 \cdot \frac{I(3-4,5)}{11}}{14} + \frac{I(3-4,5)}{11}} \quad (49)$$

where $I(x-y)$ is value of the integral in the chemical shift range $x-y$.

Using this formula, the relative molar amounts of PtBMA and PDEGMA were calculated as $x(\text{PtBMA})=0,61$ and $x(\text{PDEGMA})=0,39$. It is obvious that this copolymer contains less PDEGMA than it was expected from the monomer ratio. However, this amount of DEGMA should be sufficient to perform LCST behaviour and to obtain hexagonally packed cylinders as a structure of diblock copolymer, (assumption based on the theoretical phase diagram of a two component polymer, see page 21).

For the next experiment (sample A11), 1,1-diphenyl hexyl lithium was used as an initiator. This compound contains two sterically demanding phenyl rings at carbanion moiety which prevent the attack of the tBMA monomers' carbonyl group.

The results, however, were disappointing. The apparent molecular masses versus polystyrene calibration were $M_n(\text{P}t\text{BMA})= 23000 \text{ g/mol}$ ($M_w/M_n= 2,67$) and $M_n(\text{P}t\text{BMA-PDEGMA})= 24000 \text{ g/mol}$ ($M_w/M_n=2,77$). As those results might induce the conclusion that some of DEGMA units are present in the polymer, a ^1H NMR measurement was done.

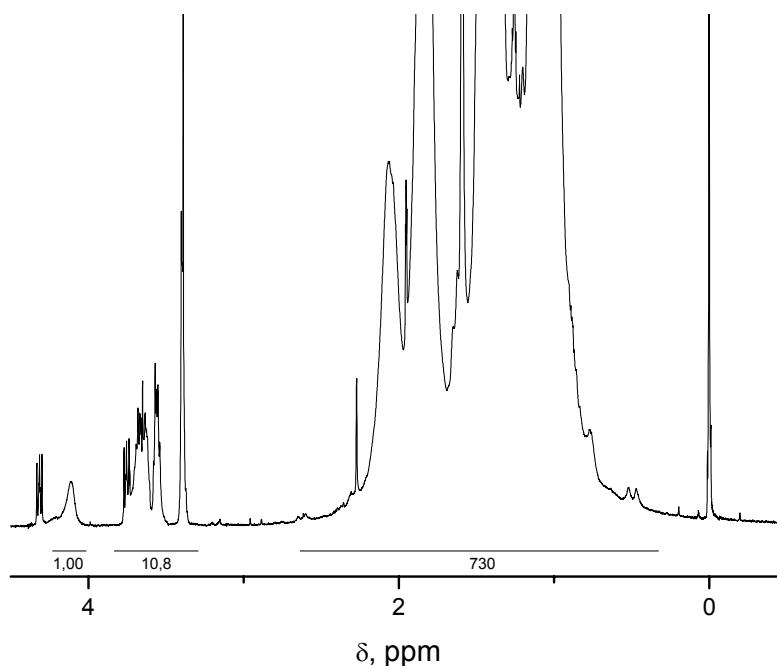


Figure 34: ^1H NMR spectra of sample A11 in CDCl_3

However, comparing the integral values of P*t*BMA and PDEGMA units, and employing equation 51, it is obvious that the molar ratio of PDEGMA is as low as 1 % in this polymer. On the other hand, the molar mass distribution of the P*t*BMA precursor has already been rather broad, so it might be concluded that the polymerization of P*t*BMA with this initiation system did not work properly; hence the problem was in the system before DEGMA was added.

According to the literature²³, the polymerization of methacrylates with longer ester groups containing ether moieties (e.g. TEGMA) can be suppressed in the presence of larger alkali metal cations, as the ether group complexes the anion and stabilizes the dormant enolate.

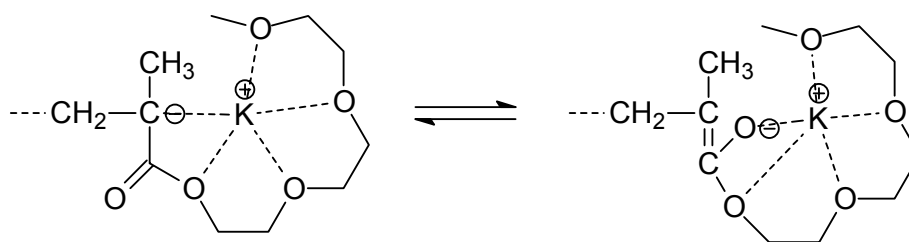


Figure 35 : Stabilizing the enolate anion at the living chain end by alkali metal cation²³

The stability of this complex varies depending on the length of the side chain, and “hardness” of the counter ion (ratio charge/size). In the case of TEGMA,²³ the potassium cation fits into this ether “pocket”, and the complex formed is too stable to allow a polymerization. As DEGMA has a shorter side chain, it was supposed that use of a potassium based initiator would still result in a successful polymerization. Hence, potassium was chosen as a soft counterion and an alternative to lithium.

To circumvent the complexation of the potassium ion, diethyl zinc was used as an additive in the polymerization of sample A12.^{25,26} Et₂Zn interacts with the enolate anion in a manner that both the polymerization rate and the nucleophilicity are reduced. Furthermore, it reduces the possibility of potential side reactions, and leads to a narrower mass distribution. For the polymerization of diblock copolymer A12, Et₂Zn was introduced as a 1M solution in heptanes, after a full conversion of tBMA was reached. Ten minutes later, the DEGMA monomer was added.

The apparent number molar masses for the P_tBMA precursor (versus polystyrene calibration) were $M_n = 430000$ g/mol (polydispersity index 1.17), however, the P_tBMA-PDEGMA copolymer exhibited $M_n = 509000$ g/mol (polydispersity index 1.04). The two GPC traces were nearly identical and ¹H NMR measurement confirmed that no diblock was obtained.

Previous experiments (A9, A11) indicated that the amount of DEGMA which was incorporated in P_tBMA-PDEGMA copolymer strongly depends on the length of P_tBMA precursor. To investigate the dependence of the PDEGMA amount in block copolymer on the length of the P_tBMA precursor, a series of P_tBMA-PDEGMA samples were synthesized under the analogous conditions, but with different molar

masses. The concentration of both comonomers was kept constant and their ratio was chosen in a manner that the diblock copolymer contains 35 mol % of PDEGMA.

Table 4: Concentration of reactants and results of synthesis of sample A13 (apparent M_n versus polystyrene calibration)

Sample nr.	c <i>t</i> BMA, mol/l	c DEGMA, mol/l	$c \cdot 10^3$ <i>n</i> -BuLi, mol/l	M_n , (calc.), g/mol	M_n (appar.), g/mol	M_w/M_n	X_{DEGMA} , 1H NMR
A13a	0.614	0.326	7.4	20200	36300	1,12	0,208
A13b	0.614	0.326	4.8	31100	104000	1,11	0,049
A13c	0.614	0.326	1.4	103600	178000	1,16	0,042

It is obvious from table 4 that the apparent molar masses are much higher than the calculated ones. Possibly, some of the initiator was deactivated before it initiated the polymerization. 1H NMR measurements of the A13 samples were done to check the composition of the diblock copolymer, and special attention was paid to the part which represents the PDEGMA block.

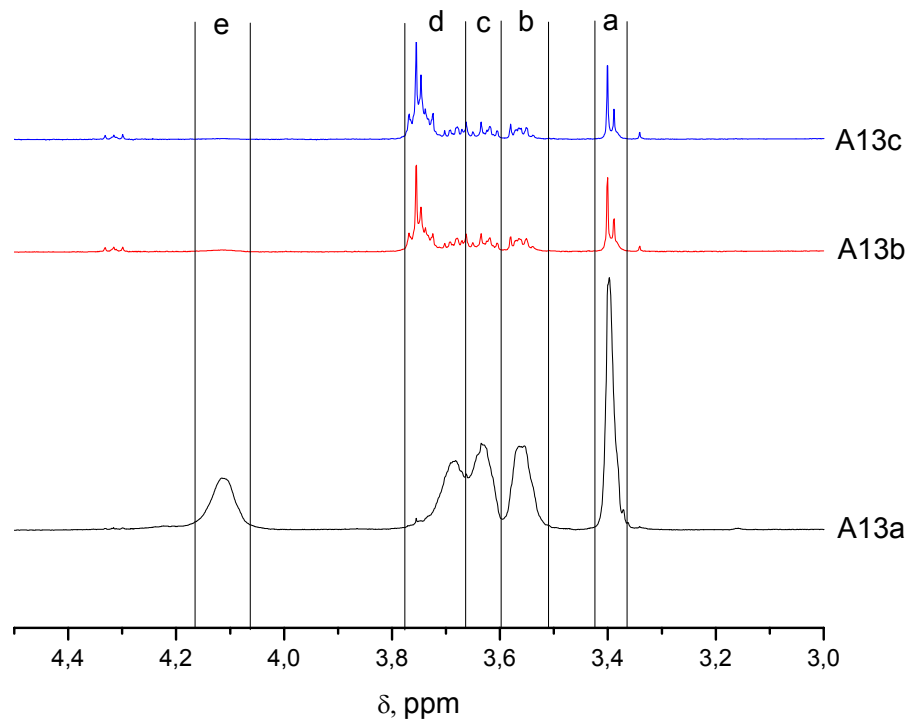


Figure 36: 1H NMR spectra of sample A13 a) A13a; b) A13b; c) A13c

Assignments of the resonance signals of protons in the DEGMA side chain are given on page 82. From the Figure 36, it is obvious that polymerizations of the samples A13b and A13c failed, as the intensity of the resonance signals of protons marked as b, c and d (table 3) should be approximately the same. It is supposed that the three small peaks at chemical shifts 4,3 ppm in spectra b and c represent products of an unwanted side reactions.

A possible side reaction that might terminate the polymerization is an intermolecular attack of one of the carbon atoms adjacent to ether oxygen on the carbanion. The ether is cleaved and the formation of the resulting alcoholate will lead to a termination. Due to the polarization of C-O bond, the partly positive carbon atom can react with the living anion. Best to our knowledge, this reaction is not described in the literature. However, the synthesis of DEGMA containing polymers with molar mass exceeding 50000 g/mol has not been reported.

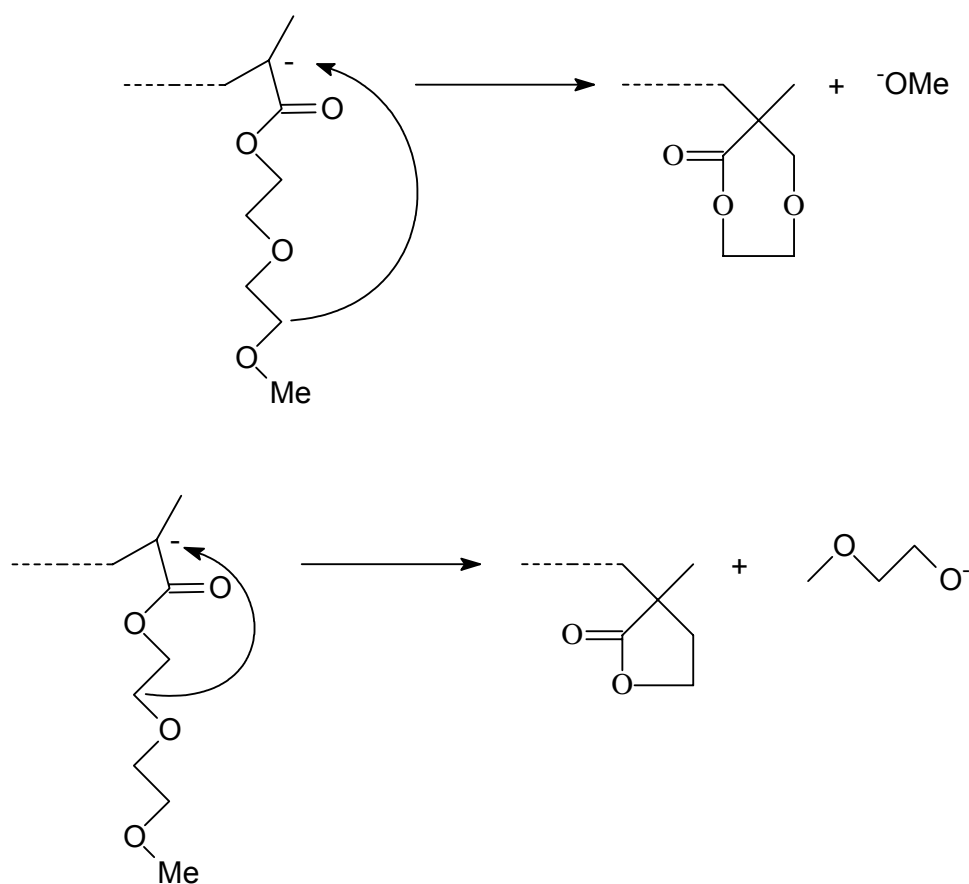


Figure 37: Possible reactions of termination of the DEGMA polymerization by the reaction of a living chain end with its own side chain

Those two cyclic esters can be detected by ^1H NMR. Chemical shifts of hydrogen atoms can be estimated by simulation using the MesteRec software package.

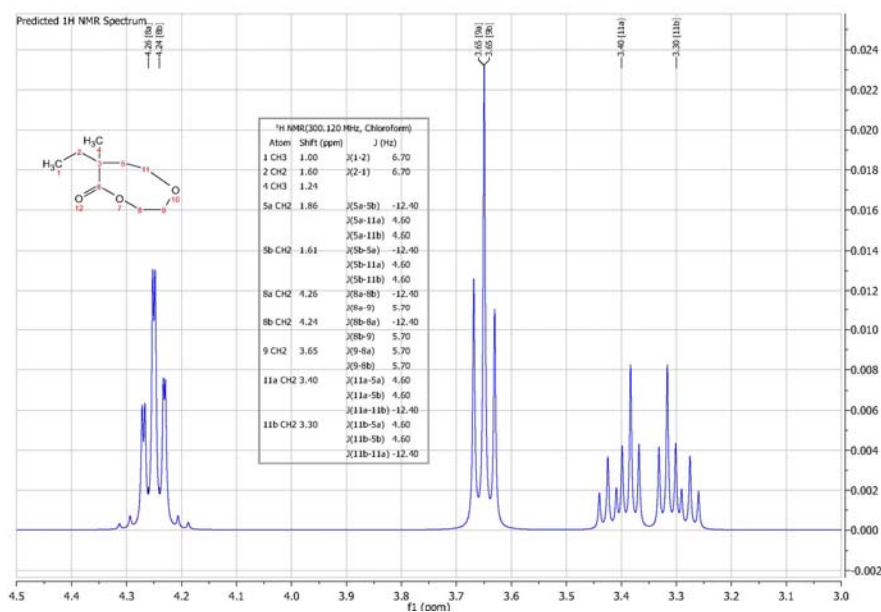


Figure 38: Predicted ^1H NMR spectre of the possible side product with the 7-member ring during the polymerization of DEGMA

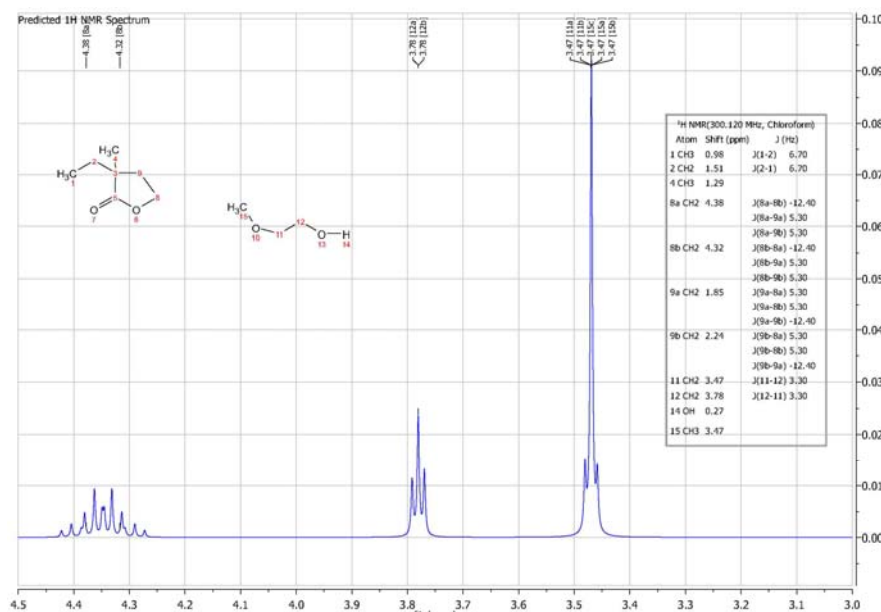


Figure 39: Predicted ^1H NMR spectre of the possible side product with the 5-member ring during the polymerization of DEGMA

Taking into account the signals that appear at the chemical shifts of 4.3-4.4 ppm in the samples A13b and A13c (Figure 36), it is reasonable to conclude that the termination of the polymerization reaction occurred via those pathways. However, it is very hard to judge which one of two presented reaction occurred.

Comparing NMR spectra presented in Figure 36 and taking into account molar masses of samples A13a-A13c, it may be hypothesized that molar mass of the P β BMA precursor has a significant effect on the success of the DEGMA polymerization: The polymerization of DEGMA cannot be initiated after certain length of P β BMA chain is reached. However, also the concentration of living chain ends might also cause such behaviour, i.e. if the concentration of living chain ends does not exceed a limiting value, the DEGMA polymerization fails.

On the basis of the experiments A9 – A13, it was concluded that it was not possible to obtain a P β BMA-PDEGMA with a molar mass exceeding 150000 g/mol and an amount of PDEGMA of 30 mas %. Therefore, it was decided to employ another mechanism.

4.3.2. GROUP TRANSFER POLYMERIZATION

The technique of group transfer polymerization was chosen as methacrylates can be polymerized with that technique up to molar masses of 80000 g/mol.⁷³ As group transfer polymerization can only be applied for acrylates and methacrylates in THF at room temperature, attempts to synthesize P β BMA-PDEGMA were made.

The concentration of the educts of the P β BMA-PDEGMA synthesis and the results achieved are presented in table 5.

Table 5: Amounts of chemicals taken for the synthesizes of P*t*BMA-PDEGMA block copolymers via GTP

Entry	n(<i>t</i> BMA), mmol	n(DEGMA), mmol	n(MTS), mmol	n(Cat), mmol	x(PDEGMA) (theo)	M_n^{PtBMA} /10 ³ g/mol (theo.)	M_n^{PDEGMA} /10 ³ g/mol (theo.)	M_n^{PtBMA} /10 ³ g/mol	M_n^{DB} /10 ³ g/mol	M_w/M_n	x(PDEGMA)
G1	61.4	27.1	0.46	0.04 ^{a)}	0.306	19.0	11.1	-	22.0	1.26	0.55
G2 ^{b)}	61.4	27.1	0.46	0.04 ^{c)}	0.594	19.0	11.1	-	16.9	1.07	0.10

^{a)}TBABB was used as a catalyst

^{b)}PDEGMA was synthesized as a first block and P*t*BMA as a second

^{c)}TASHF₂ was used as a catalyst

n(*t*BMA) – amount of *t*BMA taken for the first block (P*t*BMA)

n(DEGMA) – amount of DEGMA taken for the second block (PDEGMA)

n(MTS) – amount of the initiator (MTS)

n(Cat) – amount of the catalyst

x(PDEGMA) (theo) – calculated molar ratio of PDEGMA in the diblock copolymer

$M_n^{P*t*BMA}$ (theo.) – calculated molar mass of the P*t*BMA block

M_n^{PDEGMA} (theo.) – calculated molar mass of the PDEGMA block

$M_n^{P*t*BMA}$ – apparent number average molar mass of P*t*BMA precursor versus polystyrene calibration (GPC)

M_n^{DB} – apparent number average molar mass of the copolymer versus polystyrene calibration (GPC)

M_w/M_n – polydispersity index of the entire polymer

x(DEGMA) – molar ratio of PDEGMA in the block copolymer as determined by ¹H NMR

For the first polymerization (sample G1) a 70:30 monomer ratio was used, with a theoretical molar mass of the P*t*BMA block of $M_n^{theo}=19000$ g/mol, and for the diblock copolymer $M_n^{theo}=30100$ g/mol respectively. The polymerization was started by adding 0.02 ml of a TBABB solution in THF ($c=2$ mol/l; 0.04 mmol). After two hours, a sample was taken, and 5 ml (5,1 g, 27,1 mmol) of DEGMA were added. The reaction continued for additional two hours, it was terminated with 10 ml of methanol and precipitated in hexane. However, it was impossible to obtain any traces of P*t*BMA precursor polymer.

As TBABB was accidentally used, which is known not to catalyze the GTP of P*t*BMA at all, it was surprising that some polymer was obtained at the end.⁸⁶

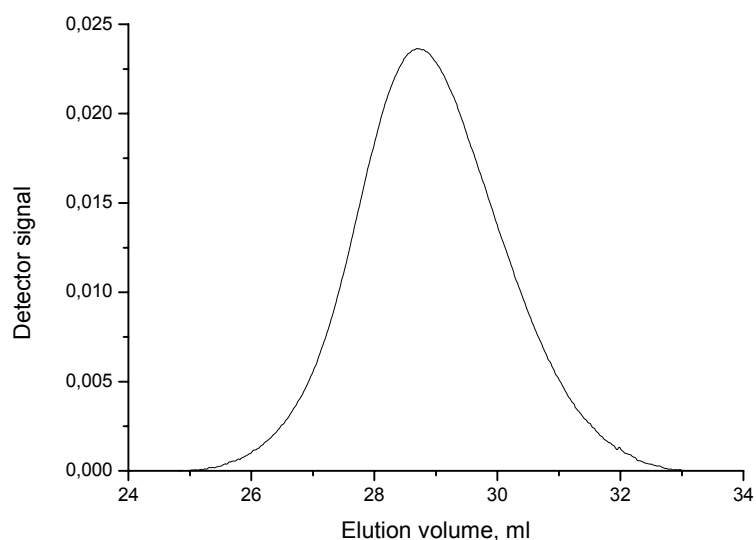


Figure 40: GPC traces of sample G1 (RI detector)

The GPC analysis of this polymer reveals a considerable narrow ($M_w/M_n=1.26$) monomodal peak at $M_n^{app}=22000$ g/mol.

The most likely explanation for the unexpected results is that the polymer is solely composed of PDEGMA and that the *t*BMA units are not incorporated at all. However, the theoretical molar mass of a MTS initiated PDEGMA homopolymer would be lower ($M_n=19000$ g/mol), even taking into account potential deviations due to different calibration curves. Hence, it may be speculated, that *t*BMA units were incorporated into the polymer.

The corresponding, ^1H NMR is shown in Figure 41.

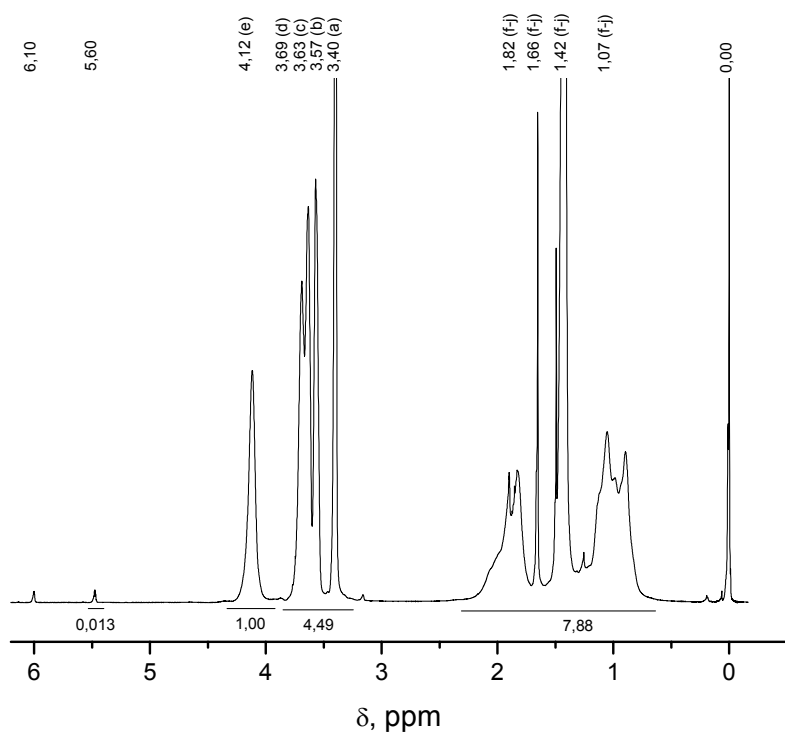


Figure 41: ^1H NMR spectra of sample G1

Assignments of proton chemical shifts were presented on page 82. Comparing the integral values of the resonance signals assigned to the PDEGMA ester group ($\delta = 3.0 - 4.5$ ppm), and the resonance signals of *t*BMA ($\delta = 0.8 - 2.2$ ppm), it is possible to check if *t*BMA units are present in this polymer.

The resonance signals at chemical shifts of 5.6 and 6.1 ppm indicate the presence of vinyl protons, there is still residual of DEGMA monomer left in this diblock copolymer, and the amounts of *t*BMA and DEGMA units cannot be calculated according to the equation 49. The resonance signals of vinyl protons do not come from the *t*BMA residual monomer, as in that case, calculation would reveal the negative value for the amount of PDEGMA in copolymer. As resonance signal at chemical shift at 5.6 nm comes from one vinyl proton, and one DEGMA unit contains nine ester group protons, the contribution of PDEGMA to the integral value $I(3-4.5)$ must be adjusted as:

$$I(\text{PDEGMA}) = I(3 - 4,5) - 9 \cdot I(5,6) \quad (50)$$

With this adjustment, the composition of this diblock copolymer can be recalculated in the analogous manner to equation 49:

$$x(\text{PtBMA}) = \frac{\frac{I(1-2,2) - 5 \cdot \frac{I(\text{PDEGMA})}{11}}{14}}{\frac{I(1-2,2) - 5 \cdot \frac{I(\text{PDEGMA})}{11}}{14} + \frac{I(\text{PDEGMA})}{11}} \quad (51)$$

After this correction, the relative molar ratios were calculated as 0,56 for PDEGMA and 0,44 for PtBMA (mass ratios $w(\text{PtBMA})=0.38$ and $w(\text{PDEGMA})=0.62$).

This calculation proves the presence of the tBMA units in the G1 copolymer, but it is still unclear if the G1 copolymer has a block, random or alternating structure.

In order to check the presence of the phase separation, a DSC measurement was done.

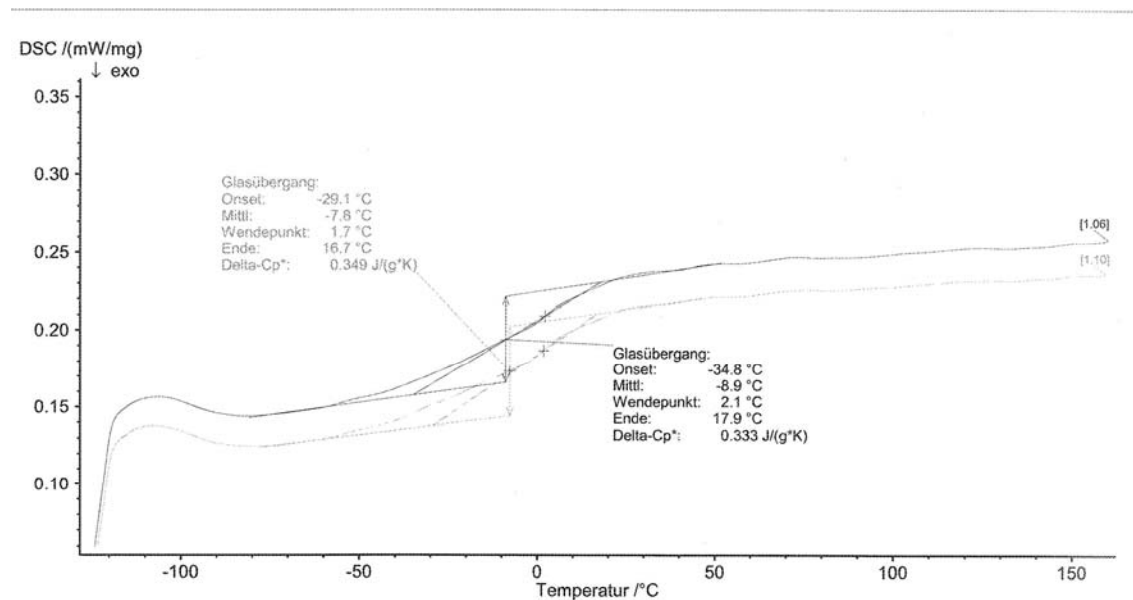


Figure 42: DSC thermogram of sample G1

From Figure 42 it is obvious that only one glass transition is present. The glass transition temperature found in the second heating cycle ($-7,8^{\circ}\text{C}$) is between the glass transition temperatures of P*t*BMA (122°C) and PDEGMA (-42°C). That rules out the existence of two separated blocks. Therefore, it is very likely that a random or alternating copolymer is present. The expected mixed glass transition temperature was calculated from the Fox equation (equation 6). The weight fractions of $w(\text{P*t*BMA})=0.38$, leads to a $T_{g_{\text{mix}}}^{\text{calc}}=1.3^{\circ}\text{C}$, which is in reasonable agreement with the glass transition temperature determined by DSC ($T_{g_{\text{mix}}}^{\text{DSC}}= -7.8^{\circ}\text{C}$).

Table 6: Parameters to calculate the glass transition temperature ($T_{g_{\text{mix}}}$) of sample G1

Sample G1	W(P <i>t</i> BMA)	w(PDEGMA)	$T_{g_{\text{mix}}}/^{\circ}\text{C}$ (calc.)	$T_g^{\text{DSC}}/^{\circ}\text{C}$
	0.38	0.62	1.3	-7.8

The reasons for the absence of a phase separation might be that blocks of the polymer are too short, or no blocks were present in polymer at all. As the presence of both *t*BMA and DEGMA units in this polymer was proven by ^1H NMR, and the course of the reaction indicates that no blocks are present, it is reasonable to conclude that this P*t*BMA-PDEGMA copolymer is of a random structure.

As polymerization of P*t*BMA-PDEGMA did not result in a block copolymer, it was supposed that a change in the block sequence polymerization may give better results. In experiments conducted so far it was shown that the possibility of the attachment of PDEGMA as a second block strongly depends on the length of the polymer chain of the P*t*BMA precursor. Therefore, it was decided to synthesize the DEGMA block first, as it is shorter, and P*t*BMA as a second block. Both monomers are taken in amounts that will lead to a molar ratio $x(\text{PDEGMA})=0.31$ which should result in a hexagonally packed cylinders structure of the final diblock copolymer.

As at it was observed in the previous experiment, the P*t*BMA block cannot be obtained using TBABB as a catalyst. Therefore, TASHF₂ was taken.

General reaction procedure for group transfer polymerization was followed, and the amounts of educts are given in Table 5 (sample G2). The theoretical molar

mass was $M_n^{theo}=30000$ g/mol, and theoretical molar ratio of DEGMA was 0.31. A very viscous, sticky liquid was yielded.

The apparent molar masses were $M_n=16900$ g/mol and $M_w=18000$ g/mol (versus polystyrene calibration). The peak at lower elution volume in the elugram (Figure 20) gives an apparent molar mass of approximately 31000 g/mol, and the peak at higher elution volume gives an apparent molar mass of approximately 16300 g/mol. The amounts of the PDEGMA homopolymer, and the PDEGMA-*t*BMA copolymer were determined by the deconvolution of the elugram, and by comparison of the integral peak areas (Figure 43). The elugram indicates that the addition of *t*BMA to the reaction mixture caused most of the active PDEGMA chains to be terminated; hence only very small amount (7%) of the block copolymer was detected at lower elution volumes.

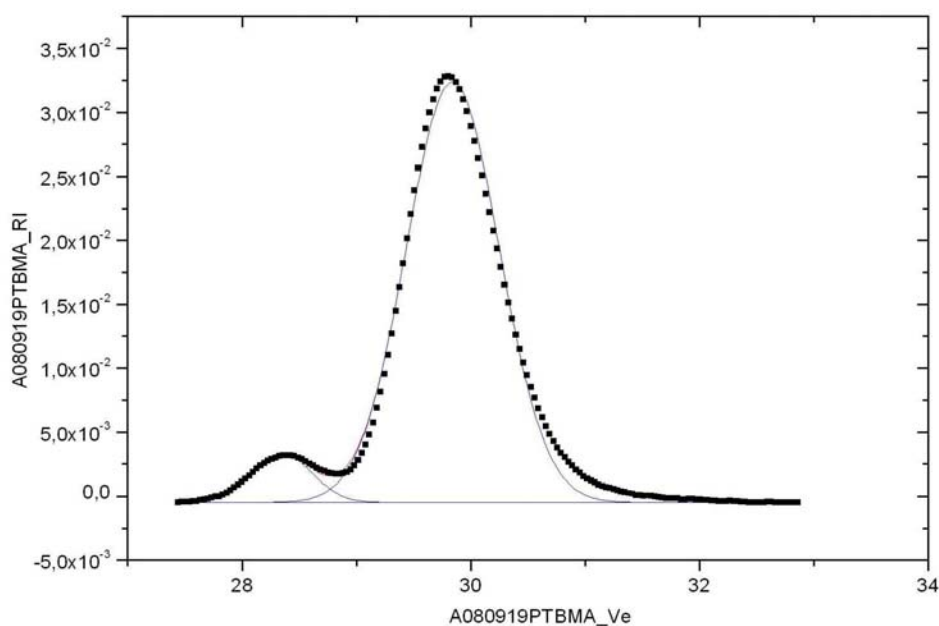


Figure 43: Deconvolution of the elugram (RI detector) of sample G2

To explore the overall composition of this polymer, ^1H NMR measurement was done.

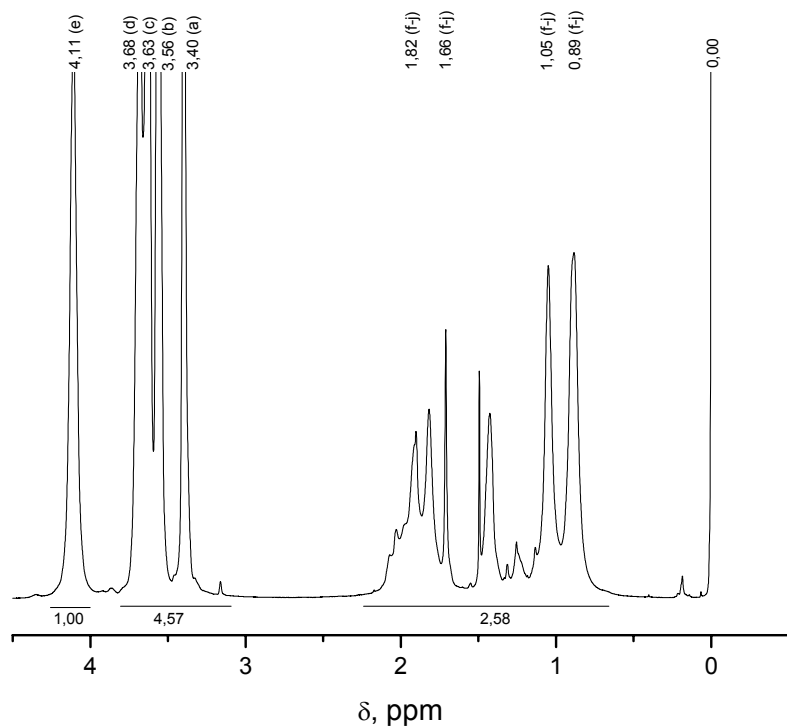


Figure 44: ^1H NMR spectra of sample G2 in CDCl_3

The composition was calculated revealed a P*t*BMA content of only $x(\text{P*t*BMA})=0,086$ ($w(\text{tBMA})=0,067$). It is obvious that only a small amount of *t*BMA was incorporated into this polymer. As the amount of P*t*BMA is low, no phase separation is expected in this copolymer.

Sample G2 consists of two components where one component is a PDEGMA homopolymer, and the second is either a random PDEGMA-P*t*BMA copolymer or a block copolymer where phases are not separated. In both cases, it is unlikely that the polymer exhibits a LCST behavior.

To support this hypothesis, a cloud point measurement was done.

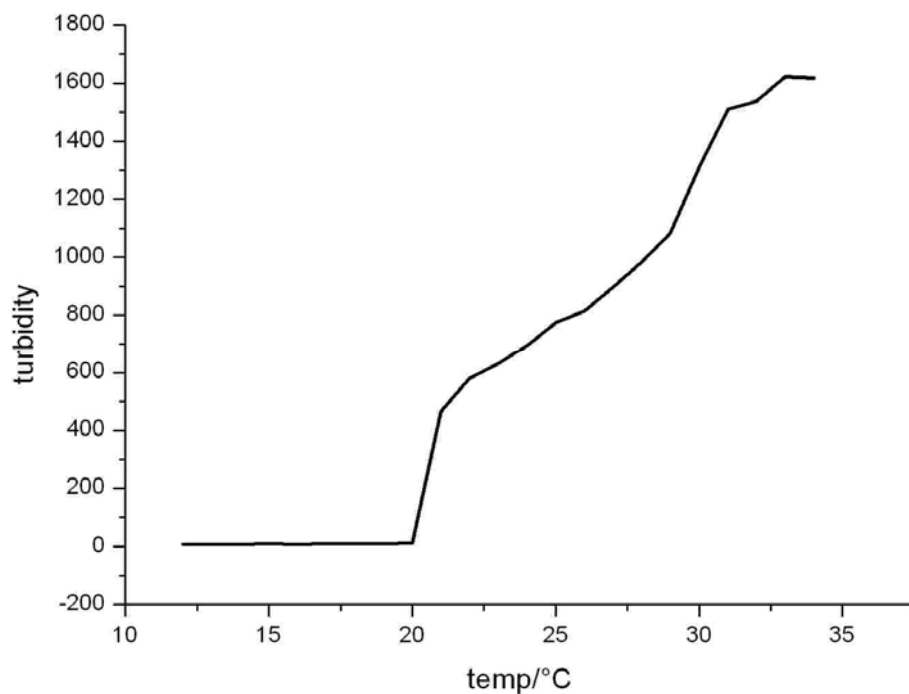


Figure 45: Dependence of the turbidity of a 0,1 wt. % water solution of the sample G2 on a temperature

From Figure 45 it can be observed that turbidity increases discontinuously at 20°C, and then gradually increases with the temperature. That leads to the hypothesis is that even an amount as low as $w(\text{PtBMA})=10$ mass. % significantly changes the cloud point behavior by interacting with PDEGMA. Therefore, turbidity increases, but not in the distinct manner which is characteristic for a LCST behavior (see Figure 1). Therefore, it might be concluded that microphase separation in this polymer did not occur. The most likely structure of this sample is therefore a blend of two components. One component is the PDEGMA homopolymer, and the other one is the PDEGMA-PtBMA copolymer.

On the basis of the turbidity measurement, it might be concluded that macrophase separation between the components of the blend had occurred, but microphase separation between the blocks of diblock copolymer did not occur. Possible reasons for the absence of microphase separation would that the interaction parameters of the PtBMA-PDEGMA system are too low, and/or that the PtBMA chains are too short. If the PtBMA chains are too short, a possible solution to obtain phase

separation might be to synthesize a copolymer with higher molar masses, keeping the molar amount of PDEGMA between 0.2 and 0.4. However all attempts to obtain such a polymer were unsuccessful. Hence, interaction parameter must be increased by changing the system to a PS-PDEGMA block copolymer. It is supposed that the interaction parameter of polystyrene-polymethacrylate system would be higher compared to the polymethacrylate-polymethacrylate one, as the differences in the structure between the PS and PDEGMA are much larger.

4.3.2.1. COPOLYMERIZATION PARAMETERS

As a P*t*BMA-PDEGMA copolymer was unexpectedly yielded in a TBABB catalyzed group transfer polymerization, it was decided to pay attention to this system and to determine the copolymerization parameter. The values of copolymerization parameters can also give a clue about the structure of a P*t*BMA-PDEGMA copolymer polymerized in batch.

The copolymerization parameters from the P*t*BMA-PDEGMA system were determined by performing four batch polymerizations with the different starting compositions. In all cases, the general procedure for group transfer polymerization was followed. Both *t*BMA and DEGMA monomers and MTS were dissolved in THF. Tetramethylsilicon was added to the reaction mixture as an internal standard, and the reactions were initiated by adding the TBABB catalyst. Samples of the reaction mixture were taken 1, 2, 4, 8 and 16 minutes after the initiation, and the reaction was terminated by adding MeOH/HCl mixture. The ratio of the residual monomer concentration of DEGMA ($[DEGMA]$) and *t*BMA ($[tBMA]$) (x in the equation 41) in the reaction mixture were determined from 1H NMR. The vinyl protons of *t*BMA have resonance signal at 6.0 and 5.5 ppm, while the vinyl protons of DEGMA have resonance signals at 6.1 and 5.6 ppm, hence they can clearly be distinguished. The composition of the polymer ($d[PDEGMA]/d[tBMA]$), y in equation 42) was determined from the resonance signals of the ester groups of P*t*BMA and PDEGMA. Assignments of the resonance signals of the protons in the ester groups are presented in table 3, and corrections for the residual monomer are calculated according to equations 52 and 53.

Table 7: Compositions of reaction mixture for the determination of copolymerization parameters in PtBMA-PDEGMA system with parameters necessary for the determination of copolymerization parameters by the method of Kelen and Tudos⁶⁵ (see pages 45-46)

Compos. (start)	[tBMA]	[DEGMA]	d[PtBMA]	d[PDEGMA]	x	Y	F	G	ξ	η
05:95	0,0430	0,957	0,870	0,130	0,0449	6,69	0,000300	0,0382	0,00750	0,948
	0,0460	0,954	0,317	0,683	0,0482	0,464	0,00500	-0,0557	0,111	-1,24
	0,0550	0,945	0,118	0,882	0,0582	0,134	0,0253	-0,377	0,388	-5,77
	0,0580	0,942	0,445	0,555	0,0616	0,802	0,0047	-0,0152	0,106	-0,340
10:90	0,0950	0,905	0,596	0,404	0,105	1,48	0,00750	0,0338	0,157	0,712
	0,099	0,901	0,230	0,770	0,110	0,299	0,0404	-0,258	0,502	-3,20
	0,119	0,881	0,121	0,879	0,135	0,138	0,132	-0,846	0,768	-4,90
50:50	0,483	0,517	0,955	0,045	0,934	21,2	0,0411	0,890	0,483	0,517
	0,485	0,515	0,858	0,142	0,942	6,04	0,147	0,786	0,485	0,515
	0,494	0,506	0,701	0,298	0,976	2,35	0,405	0,561	0,494	0,506
	0,517	0,483	0,382	0,617	1,07	0,619	1,85	-0,658	0,517	0,483
	0,564	0,435	0,448	0,552	1,30	0,812	2,07	-0,301	0,564	0,435
70:30	0,665	0,335	0,928	0,072	1,99	12,9	0,306	1,83	0,884	5,30
	0,671	0,329	0,880	0,120	2,04	7,33	0,567	1,76	0,934	2,90
	0,686	0,313	0,721	0,279	2,19	2,58	1,86	1,34	0,979	0,708
	0,712	0,288	0,560	0,440	2,47	1,27	4,80	0,530	0,992	0,109
	0,734	0,266	0,576	0,424	2,76	1,36	5,60	0,728	0,993	0,129

The copolymerization parameters were determined by the Kelen-Tudos^{64,65} method. A graph of η versus ξ was plotted, and interpolated linearly. The parameters η and ξ were calculated as it was described by equations 39-47. The arbitrary constant α was calculated according to equation 46 as 0.04.

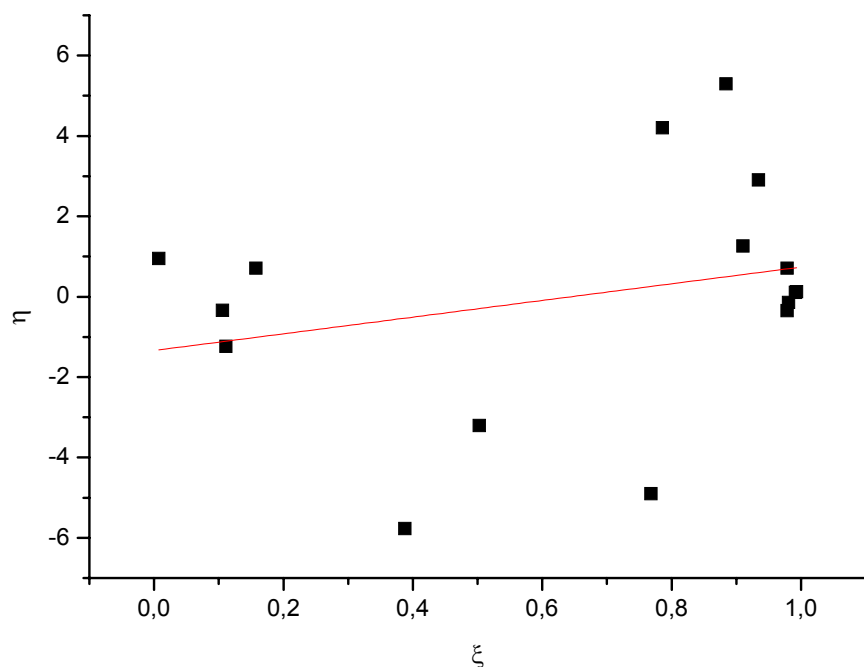


Figure 46: Diagram of the dependence of η on ξ for the copolymerization of tBMA and DEGMA

The values of the intercepts at $\xi=0$ and $\xi=1$ are $-r_{tBMA}/\alpha=-1.34$ and $r_{DEGMA}=0.73$ respectively, which reveals the copolymerization parameters as $r_{tBMA}=0.054$ and $r_{DEGMA}=0.73$. The physical meanings of those parameters are the preferences of the living chain end to the next approaching monomer unit. If the last unit of the living chain is of tBMA type, it will have an approximately 20 times stronger affinity to react with the DEGMA monomer than with the tBMA monomer (see the equation 38); another manifestation that the tBMA homopolymerization is not catalyzed by TBABB. On the other hand, a living chain end containing a DEGMA unit at the end will have only a 1.5 times stronger affinity to a heteropolymerization compared to a homopolymerization. Hence, those values of copolymerization parameters clearly indicate the higher reactivity of DEGMA compared to the tBMA in the GTP.

Therefore, presence of two consecutive *t*BMA units is not very likely and the copolymer should rather be a random one. The values of the copolymerization parameters of P*t*BMA-PDEGMA system are compared with similar systems in Table 8:

Table 8: Comparison of the copolymerization parameters of different acrylate and methacrylate systems

Entry no.	Polymerization mechanism	Monomer 1	Monomer 2	r_1	r_2	Ref.
1	Radical	MMA	Acrylic acid	0.13	0.29	46
2	Radical	MMA	Methacrylic acid	0.34	0.96	46
3	Radical	MMA	Methyl acrylate	0.47	2.3	46
4	GTP (TBABB)	MMA	Methyl acrylate	0.04	8.3	66
5	GTP (TBABB)	MMA	Butyl acrylate	0.4	6.7	66
6	GTP (TASFH ₂)	MMA	<i>t</i> BMA	4.6	0.16	90
7	Anionic	<i>t</i> BMA	(dimethylamino) ethyl methacrylate	0.04	1.3	91
8	GTP (TBABB)	<i>t</i> BMA	DEGMA	0.054	0.73	

Comparing the determined copolymerization parameters r_{tBMA} with the values for the same monomer with different comonomers and polymerization systems (entries 6 and 7), it can be seen that r_{tBMA} is generally low (max. 0.16, entry 6). This clearly indicates that the polymerization of P*t*BMA is a challenging task. However, the situation is even more dramatic if the r_{MMA} (entry 6) is compared to a copolymerization of MMA with acrylic comonomers (entries 4 and 5). The copolymerization parameters of MMA with methyl acrylate (MA) and butyl acrylate (BA) are 17 and 200 times higher than the r_{tBMA} of the aforementioned pair. Entries 1-3 are presented to exhibit the strong influence of the polymerization mechanism on the values of copolymerization parameters.

The values for the r_{tBMA} and r_{DEGMA} also indicate that the copolymerization diagram of the P*t*BMA-PDEGMA pair should exhibit an azeotropic point where the compositions of the reaction mixture and the polymer are the same. The composition of azeotropic mixture can be determined from equation 38, under the condition:

$$\frac{d[M_{DEGMA}]}{d[M_{tBMA}]} = \frac{[M_{DEGMA}]}{[M_{tBMA}]} \quad (52)$$

In that case, the equation 38 becomes:

$$\frac{[M_{DEGMA}]}{[M_{tBMA}]} = \frac{(r_{tBMA} - 1)}{(r_{DEGMA} - 1)} \quad (53)$$

According to this equation, the composition of the azeotropic mixture is calculated as $x(tBMA)=0.22$ and $x(DEGMA)=0.78$.

4.3.3. COMPARISON OF THE RESULTS

The polymerization of P*t*BMA-PDEGMA copolymers was done by anionic as well as group transfer polymerization. In both cases, polymers (samples A13a and G2) with comparable apparent number average molar masses (36300 and 31000 g/mol, respectively, versus polystyrene calibration) were obtained. Those values are too low for a sufficient mechanical stability to construct a membrane. However, in the case of anionic polymerization, the amount of PDEGMA in block copolymer was $x(PDEGMA)=0.21$. On the other hand, in the case of GTP, the sequence of monomer addition was reversed, and the polymerization of PDEGMA as a precursor was tried. Addition of *t*BMA resulted in the termination of 93% of the living PDEGMA chains, which lead to a yield of only 7%. Therefore, it was concluded that TBABB is not suitable catalyst for the polymerization of P*t*BMA-PDEGMA copolymer as it yielded only the random copolymer and the deviation of M_n^{GPC} and M_n^{theo} is much higher than for the other experiments.

As the best results for the PDEGMA homopolymerization were gained by the anionic polymerization, this mechanism will be used for the first attempts to polymerize a PS-PDEGMA block copolymer, and the atomic transfer radical polymerization will be used as a backup solution.

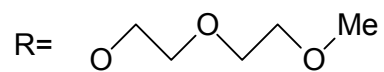
4.4. POLYMERIZATION OF POLYSTYRENE-POLYDEGMA COPOLYMERS

4.4.1. ANIONIC POLYMERIZATION

As the syntheses of both polystyrene and PDEGMA homopolymers by anionic polymerization were reported,²¹⁻²³ and the final polymer for the membrane application should consist of a PS-PDEGMA block copolymer, the synthesis of PS-PDEGMA by sequential anionic polymerization was tried. On the basis of the successful polymerization of a PS-P t BMA copolymer, it is likely that the PS-PDEGMA system behaves in an analogous manner. This presumption is based on the fact that both DEGMA and t BMA are methacrylates, and that they both contain bulky ester groups.

A polystyryl anion can initiate the polymerization of DEGMA, but the living carbanion of PDEGMA cannot initiate the polymerization of styrene due to differences in the nucleophilicity. Therefore, styrene is polymerized first, then, the living chain end of the polystyrene block serves as an in-situ macroinitiator for the polymerization of DEGMA. If DEGMA is added directly to the reaction mixture that contains polystyryl anions, unwanted side reactions might occur. Beside a polymerization of the vinyl bond, the carbonyl group of the methacrylate may be attacked by the polystyryl anion, resulting in a termination of the polymerization reaction. Therefore, it is necessary to reduce the reactivity of the living polystyrene chain end by adding an excess of 1,1-diphenylethene (DPE). Due to the sterical reasons, DPE does not homopolymerize, so each of the living chain ends contains one single DPE unit at the end. For the same sterical reasons a living chain end that contains a diphenylethenyl anion cannot attack the carbonyl group of a methacrylate. On the other hand, once a DEGMA unit is attached to the chain end, it cannot react with a DPE unit as the reactivity of the methacrylate anion is not sufficient. Therefore, by adding DPE in excess, and by a thirty minutes reaction time between the polystyryl anion and DPE before adding DEGMA, possible side reactions should be prevented.

The reaction scheme for synthesis of PS-PDEGMA via sequential anionic technique is presented on Figure 28 with



The amounts of chemicals taken for the synthesis of PS-PDEGMA and the results achieved are presented in Table 9:

Table 9: Amounts of chemicals taken for the syntheses of PS-PDEGMA block copolymers and results

Entry	n(S) mmol	n(DEGMA) mmol	n(In) mmol	n(DPE) mmol	T(DEGMA) °C	x ^{DEGMA} (theo)	M _n ^{PS} (theo)/ 10 ³ g/mol	M _n ^{PDEGMA} (theo)/ 10 ³ g/mol	M _n ^{PS} / 10 ³ g/mol	M _n ^{PS- PDEGMA} / 10 ³ g/mol	M _w / M _n	x ^{PDEGMA}
A1	104.4	18.9	0.42	2.22	-63	0.15	25.9	8.5	-	22.1	1.05	0.132
A2	87	10.2	0.033	0.89	-63	0.11	275	58	-	116	1.04	0.01
A3 ^{a)}	43.5	10.9	0.033	0.5	-63	0.20	137	62.3	45.7	46.8	1.07	0
A4a ^{a)}	78.3	21.8	0.057	2.22	-63	0.22	143	72	183	179.6	1.07	0
A4b ^{a)}					+20				183			
A5 ^{a)}	39.2	16.3	0.037	2.22	+20	0.30	110	83.6	48.3	49.1	1.07	0
A6 ^{b)}	43.5	21.7	0.2	2.83	-70	0.33	22.7	20.4	-	44.0	1.60	0.18
A7 ^{b)}	43.5	21.7	0.05	0.72	-70	0.33	90.7	81.7	819	903	1.12	0
A8 ^{c)}	87	54.2	0.2	-	-70	0.38	45.3	51	47.8	49.9	1.07	0.02
A15	87	37.8	0.066	0.83	-63	0.30	137	107	-	293	1.09	0.02
A16	51	15	0.4	2.83	-63	0.28	13.3	7.0	-	-	-	0.22
A17	43.5	10.9	0.21	2.83	-63	0.20	21.5	9.8	-	-	-	0.36

^{a)}DEGMA monomer was cleaned with 2 mmol of Et₃Al prior to distillation

^{b)}Initiator cumyl potassium

^{c)}Initiator diphenyl-methyl potassium

$n(S)$ – amount styrene
 $n(\text{DEGMA})$ – amount of DEGMA
 $n(\text{In})$ – amount of initiator *sec*-BuLi (unless otherwise specified)
 $n(\text{DPE})$ – amount of DPE taken for the modification of living chain end
 $T(\text{DEGMA})$ – temperature of the synthesis of the PDEGMA block
 $x(\text{PDEGMA})$ (theo) – calculated molar ratio of DEGMA in diblock copolymer
 M_n^{PS} (theo) – calculated molar mass of the polystyrene block
 M_n^{PDEGMA} (theo) – calculated molar mass of the PDEGMA block
 M_n^{PS} – number average molar mass of polystyrene precursor (GPC)
 $M_n^{\text{PS-PDEGMA}}$ – apparent number average molar mass of entire polymer versus polystyrene calibration (GPC)
 M_w/M_n – polydispersity index of entire polymer
 $x(\text{PDEGMA})$ – molar ratio of DEGMA in entire polymer (determined from $^1\text{H NMR}$, equation 56)

A possible side reaction during the polymerization of methacrylates is the formation of β -keto-esters at the end of the chain.⁸⁷ This side product results from the reaction of the living chain end with the penultimate ester group of the same chain resulting in a cyclic β -keto ester.

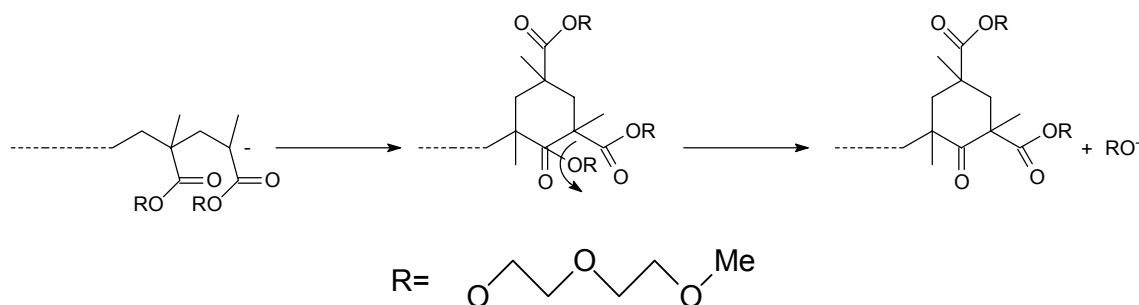


Figure 47: The reaction pathway for the formation of β -keto ester

The β -ketoester exhibits a prominent absorption at a wavelength of 300 nm. Consequently, GPC analysis of all of the PS-PDEGMA samples was performed using an UV detector operated at 300 nm to trace the potential products of the back biting reaction. However, in the synthesis of PS-PDEGMA block copolymers, the presence of a β -keto-ester was not detected.

Hence, UV measurements at GPC were generally performed at a wavelength of 254 nm which is the absorption maximum of the polystyrene's phenyl ring.

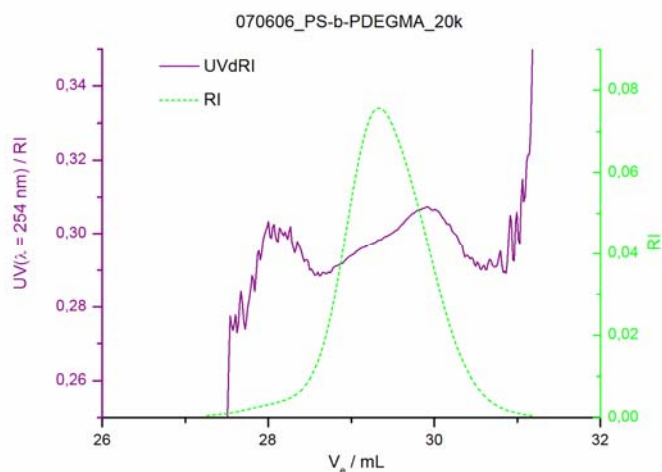


Figure 48: GPC elugram (RI and UV(254 nm)/RI) ratio) of sample A1

As it might be observed from the RI signal in Figure 48, the polymer exhibits a monomodal distribution. The number average molar mass of the polymer A1 was $M_n=22100$ g/mol (apparent value versus polystyrene calibration), and the polydispersity was 1,05. A polystyrene precursor of this polymer was not taken.

From the elution curve it can not be concluded if a polystyrene homopolymer or the desired diblock is present. Usually, some traces of remaining homopolymer can be detected in the final mixture due to termination when adding the second monomer.

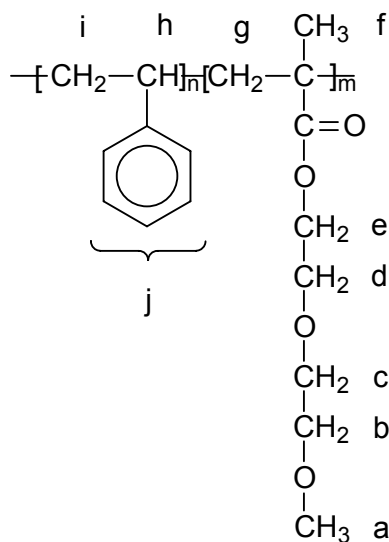
Another clue that can give the answer to the composition and possible presence of methacrylate blocks is the UV(254 nm)/RI ratio. As polystyrene shows both UV and RI signals and polymethacrylates do not show any UV absorption at the wavelength of 254 nm, it is possible to calculate UV(254 nm)/RI ratio and to check its dependence on the elution volume. In the case of a polystyrene homopolymer, the graph of UV(254 nm)/RI in dependence of the elution volume will be a constant. On the other hand, if both PS and PDEGMA are present in the diblock copolymer, the graph will show a slope due to the change in composition. For the PS homopolymer, the ratio UV(254

nm)/RI reaches approximately a value of 0.35. The presence of the methacrylates “dilutes” the UV(254 nm) signal, and therefore, UV(254 nm)/RI value decreases.

As the average value of the UV(254 nm)/RI in this graph is around 0.32 it is difficult to judge the composition of the polymer. Hence ^1H NMR was used to reveal the composition. Assignments of the protons are given in Table 10:²³

Table 10: Assignments of chemical shifts of the protons in PS-PDEGMA polymer

δ , ppm	Ass.	No. of prot.
0.8-2.1	f, g, h, i	8
3.40	a	3
3.56	b	2
3.63	c	2
3.68	d	2
4.11	e	2
6-7.5	j	5



Although one unit of DPE is present between the blocks of PS and PDEGMA, it is not depicted due to the high degree of polymerization of the PS block, as the contribution of the two phenyl rings of DPE can be neglected.

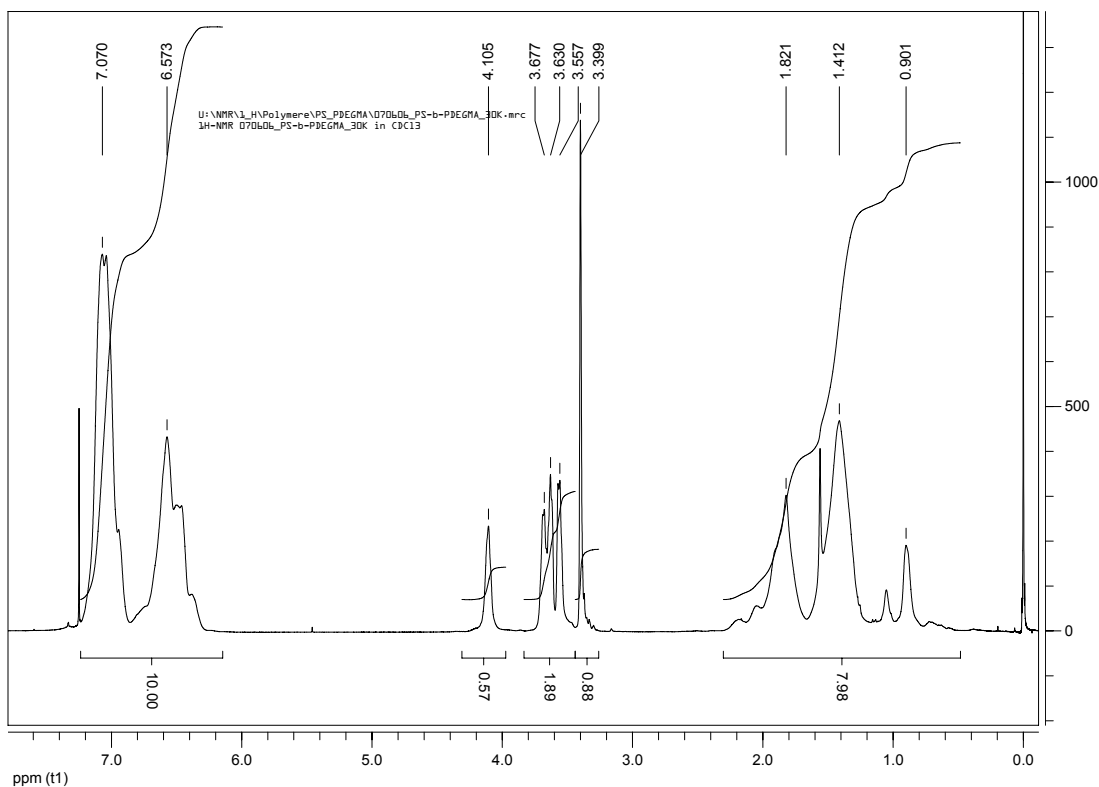


Figure 49: ^1H NMR of sample A1

The NMR spectrum shows the presence of both the phenyl ring (6-7.5 ppm) and the ester group (3.5-4.2) of the PS-PDEGMA polymer. The number ratio of PDEGMA in this diblock can be calculated as:

$$x(\text{PDEGMA}) = \frac{\frac{I(3-4,5)}{11}}{\frac{I(6-7,5)}{5} + \frac{I(3-4,5)}{11}} \quad (54)$$

where $I(x-y)$ is value of the integral in the range $x-y$. The number ratio of polystyrene is $x(\text{PS})=0,87$, and the mass fraction is $w(\text{PS})=0,78$. Those values are close to calculated ones ($x(\text{PS})=0.85$).

On the basis of the previous experiment it was decided to synthesize a new copolymer (sample A2) with an increased molar mass ($M_n^{\text{theo}}=275000$ g/mol) and the same molar ratio of PDEGMA.

The GPC elugrams of sample A2 show one major peak at an elution volume of 26 ml, and a very small one at an elution volume of 24 ml. As UV/RI ratio for former is 0.35 it is reasonable to conclude that this peak corresponds to PS. However, the precise composition of polymer that corresponds to lower elution volume peak is unclear. It is supposed that, although in a very low concentration, it consists of a PS-PDEGMA diblock copolymer.

The apparent average molar masses of entire polymer were 116000 (M_n) and 121000 (M_w) versus polystyrene calibration, and the polydispersity was 1,04.

The results of ^1H NMR reveal a $x(\text{PS})=0,99$ and $x(\text{PDEGMA})=0,01$. Calculation of the molar mass of PDEGMA block in this polymer reveals a value of 1160 g/mol. Comparing this value with the expected one ($M(\text{PDEGMA})=58000$ g/mol), it is obvious that measured value is 50 times lower, and that the reaction has failed.

A possible reason for the negligible amount of the PDEGMA block in this polymer might be the presence of impurities in the DEGMA monomer, leading to the termination of the living polystyrene chains. The living anion of polystyrene has a light yellow colour, while the living chain end modified with DPE has an intensive red colour. Therefore, it is possible to observe if the termination of all chain ends occurs in this phase of the reaction. On the other hand, the living chain ends of the methacrylates are colourless, hence, it is impossible to judge by the bare eye whether the reaction was terminated or not. Therefore despite the purification, DEGMA could have contained some impurities that led to the disappearance of the red colour and the termination of the reaction. Because of that, it was decided to introduce an additional DEGMA purification step. 2-3 ml of triethyl aluminium solution in hexane (2-3 mmol of Et_3Al) were added to the DEGMA monomer until a persistent yellow colour for ten minutes was obtained. The DEGMA monomer was distilled after that and introduced into the reaction mixture.

In the next experiment (sample A3), it should be determined whether the length of polystyrene chain has an influence on the polymerization of DEGMA. Hence, the theoretical molar mass of PS precursor was reduced to one half (137300 g/mol) and molar mass of DEGMA block was calculated as 62300 g/mol.

The elugram of the polystyrene precursor shows a monomodal peak at an elution volume of 27.5 ml and additionally slight traces of coupling (peak at 25 ml) can be detected. The corresponding number and weight average molar masses were 45700 and 47600 g/mol respectively (polydispersity 1.04). The elugram of the PS-PDEGMA copolymer, shows a slight decrease in elution volume (27.3 ml). Hence, there is an increase in the molar masses (apparent number and weight average molar masses were 46800 and 49900 g/mol, respectively, versus polystyrene calibration – polydispersity 1.07). Those values indicate a number average molar mass of the PDEGMA block of $M_n^{GPC}(\text{DEGMA})=1100$ g/mol. To check for the potential presence of DEGMA units in this polymer, ^1H NMR was done.

The ^1H NMR spectrum of sample A3, indicates a relative molar ratio of $x(\text{PDEGMA})=0.04$.

Knowing the absolute molar mass of the polystyrene precursor (measured by GPC), and the molar ratio of the polystyrene in diblock copolymer (calculated from the equation), it is possible to determine the degree of polymerization for the diblock copolymer as:

$$P_n(\text{PS} - \text{PDEGMA}) = \frac{P_n(\text{PS})}{x(\text{PS})} \quad (55)$$

The degree of polymerization of the PDEGMA block can be calculated as:

$$P_n(\text{PDEGMA}) = P_n(\text{PS}) - P_n(\text{PS} - \text{PDEGMA}) \quad (56)$$

This calculation using equations 55 and 56 reveals a degree of polymerization of PDEGMA of 18, and a number average molar mass of PDEGMA block of $M_n^{calc}(\text{DEGMA})=3400$ g/mol. Comparing this value with the apparent one, it is obvious that the apparent number average molar mass is lower. The ratio $M_n^{GPC}/M_n^{calc}=0.32$ is in the reasonable agreement with the data presented in table 1 (see page 72, homopolymerization of DEGMA).

As the previous reaction procedure (sample A2) did not result in the polymer of the calculated molar mass (333000 g/mol), and composition ($x(\text{DEGMA})=0.11$), it was supposed that a reaction temperature of -63°C for polymerization of the DEGMA block is too low to obtain a meaningful conversion of DEGMA. Consequently, it was decided to compare the number average molar masses that could be achieved at -63°C and at $+20^{\circ}\text{C}$. Therefore, the DEGMA monomer was added to the living polystyrene chain ends capped with DPE at -63°C . Two hours later, a sample was taken, and the temperature was raised to room temperature. The reaction continued for additional 50 minutes.

The resulting apparent molar masses and polydispersity indexes are presented in table 11:

*Tab.11 : Apparent molecular mass averages of sample A4
(calibration versus polystyrene)*

	M_n (g/mol)	M_w (g/mol)	D
PS	183000	193600	1,06
PS-DPE	182200	193800	1,06
PS-DPE-PDEGMA (-63°C)	179600	192100	1,07
PS-DPE-PDEGMA (20°C)	182400	193200	1,06

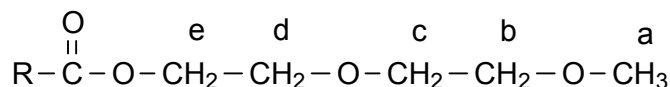
As it is obvious from those data, the apparent molar masses averages of all samples are the same within the error limit. It might be concluded that the polymerization of DEGMA was not initiated and that the synthesized polymer is a polystyrene homopolymer.

In the polymerization of sample A5, the second, PDEGMA block was polymerized at room temperature. The polystyrene block and DPE chain end modification were synthesized at -63°C , then the DEGMA was added, and a temperature ramp up to $+20^{\circ}\text{C}$ was started ($2,5^{\circ}\text{C}/\text{min}$). The polymerization of DEGMA continued for additional two hours under the isothermal conditions.

The average molar masses of the polystyrene precursor were $M_n=48300$ and $M_w=50500$. The average molar masses of the diblock were $M_n=49100$ and $M_w=52300$ versus polystyrene calibration. Comparing the molar masses of the polystyrene and the PS-PDEGMA diblock, it might be concluded that no DEGMA has reacted with the living polystyrene.

In order to check for side reactions, ^1H NMR was done.

To determine the possibility of side reactions on the side chain of DEGMA, special attention was paid to the analysis of the DEGMA ester group, which has the following structure:



, ppm	4.11	3.68	3.63	3.56	3.40
Number of protons	2	2	2	2	3

Comparing the chemical environments (and consequently chemical shifts) of the DEGMA side chain protons, it is obvious that the b, c and d protons (6 protons) have similar chemical environments, and therefore similar chemical shifts. Both the a and the e protons have significantly different chemical shifts, and therefore can easily be distinguished. If the PDEGMA block polymerized properly, the relative ratio between integrals of the resonance signals of protons a:(b+c+d):e should be 3:6:2. To check the ratio between these protons, special attention was paid to the part of the ^1H NMR that represents the side chain of DEGMA.

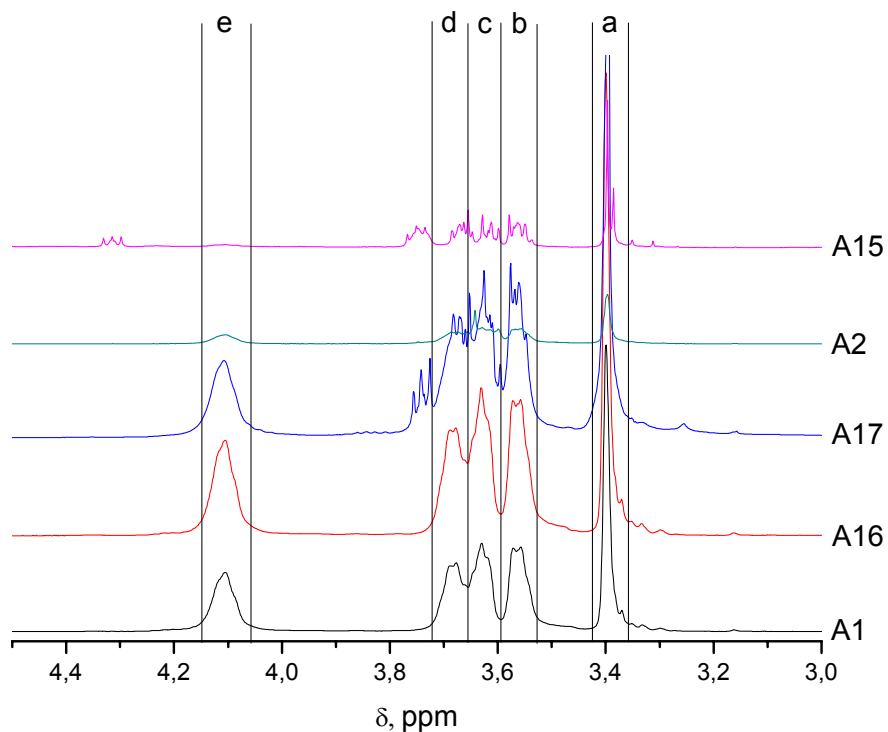


Figure 50: Comparison of ^1H NMR in CDCl_3 for PS-PDEGMA copolymers with different molar masses

Tab. 12: Relative integral values of different signals of PS-PDEGMA diblocks

Molar mass	Sample no	X_{PDEGMA} (NMR)	$I(a)$ (3,4 ppm)	$I(b,c,d)$ (3,5-3,8 ppm)	$I(e)$ (4,1 ppm)
200K	A15	0,02	3	8,39	0,49
	A2	0,01	3	8,42	1,60
30 K	A17	0,36	3	6,71	1,57
	A16	0,22	3	6,41	1,92
	A1	0,13	3	6,36	1,96
	PS-PDEGMA (theoretical)		3	6	2

$I(i)$ in this table represents the intensity of the resonance signal of the protons marked as i .

Comparing the theoretical ratio of the integrals to the measured ones, it can be observed that diblock copolymers with a molar mass of 30K (samples A1, A16 and A17), polymerized properly, as the number ratio of the integrals are in accordance with theoretical ones.

On the other hand, the measured integral ratio of the copolymers with a molar mass of 200000 g/mol (samples A15 and A2) expresses much higher deviation from the theoretical values. The intensities of the signals of the b, c and d protons are 25% higher than expected, while the intensity of the resonance signal of the e proton of the sample A15 is four times lower. Therefore, the most probable reason for the absence of the PDEGMA block is a reaction on the side chains of DEGMA units.

Beside the cleavage of the ester group which is presented on page 86, another possible side reaction might be a saponification of side chains of PDEGMA and the formation of diethylene glycol monomethyl ether (DGME). As the DGME anion is an alcoholate which terminates the polymerization process, the synthesized polymer does not contain any DEGMA units. The possible nucleophilic reactant that is present in the reaction system is a living DEGMA anion. This anion can react with the side chain of PDEGMA unit that has already been polymerized, resulting in the termination of the polymerization reaction. Possible reaction pathway is:

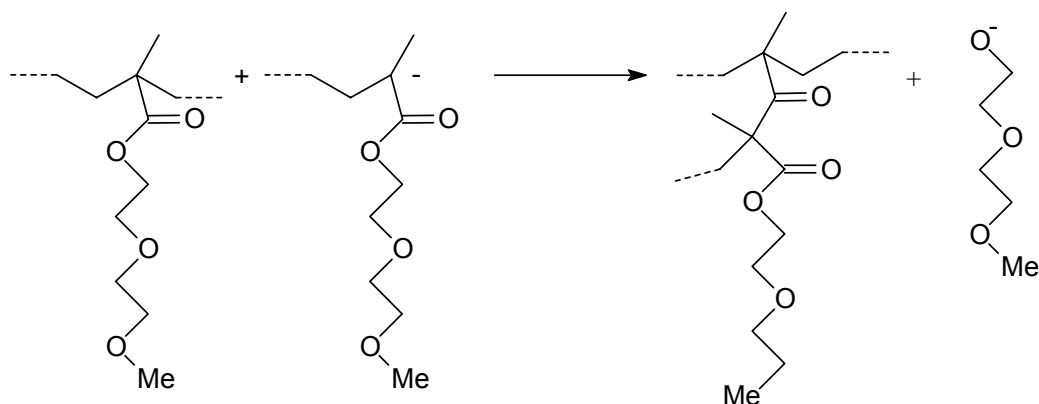
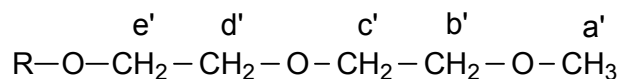


Figure 51: Possible reaction pathway for the reaction between the living DEGMA chain end and the side chain of another DEGMA unit



d, ppm	3.7	3.7	3.6	3.6	3.4
Number of protons	2	2	2	2	3

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In this case, the product would consist of two coupled PS chains with the minor amount of DEGMA between them, and the average molar mass of the product should be approximately doubled average molar mass of PS precursor. As the average degree of polymerization of polystyrene in the case of diblock-copolymers of high molar masses exceeds 1000, remain of DEGMA unit with the cleaved ester group (the unit at which two chains are bonded) could not be detected by the ^1H NMR spectra. However, the termination of the polymerization reaction is observed only in the cases of high molar mass diblock-copolymers ($M_n > 150\,000$ g/mol), while PDEGMA block can be detected in the case of the low molar mass copolymers ($M_n < 30\,000$ g/mol).

The most probable explanation for this behavior would be that two reactions occur simultaneously. One is the reaction of propagation of DEGMA, as presented on pages 66 and 103, with the rate constant k_p , and the other is the termination reaction as presented on page 114 with the rate constant k_t . Probably, k_p is slightly higher than k_t . It is supposed that in all of the cases, at least one DEGMA unit is polymerized with PS chain. In the next step, in the case of the low molar mass copolymers (and thus higher concentration of anionic chain ends) propagates, as the rate of the termination reaction is too low to stop the polymerization, resulting in the predicted PS-PDEGMA diblock-copolymer. On the other hand, if high molar mass copolymers are synthesized, the significance of the termination reaction increases, and its contribution to the overall reaction is higher. In that case, the result is chain that consists of two PS chains coupled with the very small amount of PDEGMA (if any) between them.

If termination by the mechanism presented on Figure 51 had occurred, and diethylene glycol monomethyl ether was formed, the resonance signals of the six protons (b', c' and d') in the ^1H NMR in should appear at similar chemical shifts like

the ones of PDEGMA (b, c and d), as their chemical environments are similar. On the contrary, if DEGMA polymerized without cleavage of the side chain, the resonance signal of the two protons in the α position to the carbonyl group (e) should be easily distinguishable from the analogous protons in diethylene glycol monomethyl ether (e'). The resonance signal of the methoxy groups (a and a') should appear at the same chemical shifts. Therefore, the relative ratio between the integral signals from protons a':(b'+c'+d'+e') should be 3:8. Comparing the intensities of the resonance signals from the table 12, page 113 (samples A2 and A15), it is obvious that ratio of their protons in the methylene groups are in accordance with this prediction. However, both samples A2 and A15 contain signals at a chemical shift of 4.1 ppm, which might imply that the DEGMA ester group is still present in the copolymer. The most probable explanation is that the polymer chains are attacked by the DEGMA anion and that the resulting PS-PDEGMA copolymer consists of two coupled PS chains with small amount of DEGMA between them.

The other possibilities for the reaction of the ester group of DEGMA living chain end with its own side chain, and subsequent termination of the DEGMA polymerization is presented on Figure 37. As sample A15 shows resonance signal at a chemical shift of 4.3 ppm, it might be concluded that those reactions had occurred and that the formation of the ester lead to the termination of the polymerization. Both of the side reaction results in products which have resonance signals at chemical shifts of 3.3 and 4.3 ppm (see page 86), coming from the protons in the α position to the carbonyl group. Therefore, it is very likely that those reactions occurred during the polymerization of PDEGMA block.

To check the hypothesis about a limiting value of the PDEGMA chain length, the homopolymerization results were re-evaluated. Assuming that the limiting molar mass for the synthesis of PDEGMA is approximately 8000 g/mol (number average molar mass of sample HA1, the highest achieved molar mass for DEGMA homopolymerization, $P_n(\text{DEGMA})=43$), the maximum ratio of PDEGMA in a high molar mass PS-PDEGMA block copolymer was estimated. For a PS precursor of 150000 g/mol ($P_n(\text{PS})=1440$), the calculation reveals:

$$x(\text{PDEGMA}) = \frac{P_n(\text{PDEGMA})}{P_n(\text{PS}) + P_n(\text{PDEGMA})} = 0.029$$

The limiting value of $x(\text{PDEGMA})=0.029$, corresponds to a mass ratio of $w(\text{PDEGMA})=0.05$. Comparing this value with results obtained from the experiments (Tab. 9), it is obvious, that for high molar mass polymers (>150000 g/mol) this limit has been reached.

Hence, it is questionable whether a polymer with the desired structure (hexagonally packed cylinders require minimum $x(\text{DEGMA})=0.20$) could be obtained using BuLi as an initiator. Therefore, it was decided to use potassium as a counter ion as it larger and “softer” (charge/size ratio) than lithium, but still easier to work with e.g. caesium.²²

For the first synthesis of a PS-PDEGMA block copolymer employing potassium as the counter ion (sample A6), cumyl potassium was used as an initiator.

The elugram of the sample A6 is presented on the Figure 52.

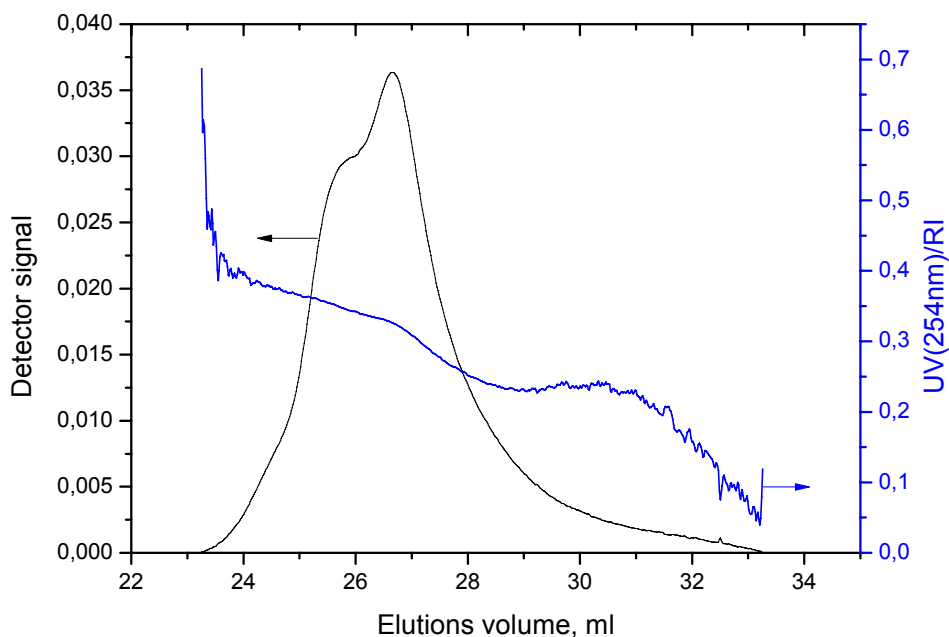


Figure 52: GPC traces (RI and UV/RI ratio) of sample A6

The GPC trace of the sample A6 reveals a bimodal distribution. The peak at the higher elution volume might come from the polystyrene precursor, and the peak at the lower elution volume might come from the diblock. The apparent number average molar mass of this copolymer was $M_n=44000$ g/mol, and the polydispersity index was 1.60. However, the molar mass distribution is too broad for a phase separation, and the PS-PDEGMA that might have been synthesized contains a significant amount of polystyrene precursor. To check the composition of this polymer and the possible presence of DEGMA units, ^1H NMR measurement was done.

From the ^1H NMR the molar ratio of blocks were calculated as $x(\text{PDEGMA})=0.18$ and $x(\text{PS})=0.82$. Using equations 55 and 56 the molar mass of the PDEGMA block can be calculated as 10000g/mol. Theoretical molar ratios were $x(\text{PDEGMA})^{\text{theo.}}=0.33$ and $x(\text{PS})^{\text{theo.}}=0.67$. Although it might appear that the PDEGMA block has reached its maximum length for the lithium as the counterion (see page 117), the behaviour of DEGMA in the presence of potassium counterions requires further investigations, as it is likely that the limiting length of the PDEGMA block might be higher or even does not exist at all in this system. It is obvious that a sufficient amount of PDEGMA for a LCST behaviour has been incorporated into the diblock, and it was decided to try the polymerization of a higher molar mass polymer (200000 g/mol) with the same initiating system and the same molar ratio of PDEGMA (sample A7).

The number average molar mass of the polystyrene precursor was 819000 g/mol, (polydispersity index 1.14), and number average molar mass for diblock was 903000 g/mol (polydispersity index 1.12). Comparing the obtained values and the shapes of the GPC elugrams, it is possible to conclude that no or only a negligible amount of DEGMA has been incorporated into the diblock copolymer. Possible reason for the very high molar mass of this polymer might be that some of the initiator was deactivated during the initiation process. That led to the very small number of activating carbanions and, consequently, to an increased molar mass.

Polymerization was also tried with diphenyl-methyl potassium (DMP) as initiator (sample A8). Polymerizations using this compound have been reported for low molar mass PS-PDEGMA block copolymers (up to 15000 g/mol),²¹ consequently,

the polymerization of higher molar mass polymer (100000 g/mol) and the same molar ratio of PDEGMA ($x(\text{PDEGMA})=0.383$) was tried.

The number average molar mass of polystyrene precursor was 47800 g/mol, (polydispersity index 1.07), and the apparent number average molar mass for entire polymer was 49900 g/mol (polydispersity index 1.07). A peak at lower elution volumes ($V_e=26$ ml) was detected due to the presence of coupled chains of polystyrene. Molar ratios, determined from ^1H NMR, were calculated as $x(\text{PDEGMA})=0.02$, and $x(\text{PS})=0.98$, the apparent number average molar mass of the PDEGMA block was 1800 g/mol and $P_n(\text{DEGMA})$ was approximately 10.

4.4.1.1. COMPARISON OF THE RESULTS

Comparing the polymers with a similar initiator/monomer ratio, but based on different initiators (samples A1 and A6), it is obvious that the molar mass of sample A6 is nearly doubled (22.1K – 44K), while the polydispersity index increased (1.05 – 1.60). The main reason for the increase in polydispersity index was that approximately 60% of the polystyrene precursor were not converted into a block copolymer in case of the sample A6. The polydispersity index and the high amount of PS homopolymer in this sample do not allow phase separation, but still this system looked promising for the synthesis of a high molar mass PS-PDEGMA block copolymer with an amount of PDEGMA exceeding 10 mol %.

Synthesis of lower molar mass PS-PDEGMA diblock copolymers (up to 30K) was successfully performed using the lithium based initiators. The resulting block copolymers were of low polydispersities (less than 1.15). However, the mechanical properties of these polymers were regarded to be too low for membrane making purposes, and needed to be increased up to at least 100000 g/mol.

The synthesis of diblock copolymers with higher molar masses (more than 100000 g/mol) was a challenging task. Different initiator systems, purification procedures and temperatures for the reaction were used. In nearly all cases, the polymerization of polystyrene block ran without any particular problems. However,

the polymerization of DEGMA could not be performed. During the polymerization of DEGMA aiming at molar mass of the desired diblock exceeding 100000 g/mol no significant increase in the molar masses were observed. As the formation of β -keto ester could be ruled out an unwanted reaction might have occurred on the side chain of DEGMA ester group, leading to a termination of the polymerization (see page 114). A further possible reason for the failure of the high molar mass copolymers might be that polymerization of DEGMA cannot propagate after certain number of DEGMA units were attached to the polystyrene. However, it is unclear if this limit is caused by polymerized DEGMA units or from the influence of the polystyrene block. If the later preposition was true, diblock copolymer containing DEGMA could be synthesized if polystyrene was not taken as the precursor. As this order of sequences is not dueable for anionic polymerization (see page 102), it was decided to use another system in order to get the appropriate diblock copolymer.

4.4.2. ATOMIC TRANSFER RADICAL POLYMERIZATION

As the polymerization of PS-PDEGMA block copolymers via an anionic polymerization did not result in a polymer with average molar mass of more than 100000 g/mol and a molar ratio of DEGMA $0.20 < x(\text{PDEGMA}) < 0.40$, the atomic transfer radical polymerization was chosen as an alternative procedure. The homopolymerization of PDEGMA by atomic transfer radical polymerization was successfully performed (sample HR1), so it was supposed that the polymerization of DEGMA can be initiated by the polystyrene synthesized as the first block. The polystyrene obtained by ATRP mechanism contains a bromine atom at the end, and, therefore it can serve as a macroinitiator for the polymerization of DEGMA.

The main advantage of the ATRP technique is that the order of sequences can be altered, while the main disadvantage is that the control over molar mass distribution is not as effective as in the case of the anionic polymerization.

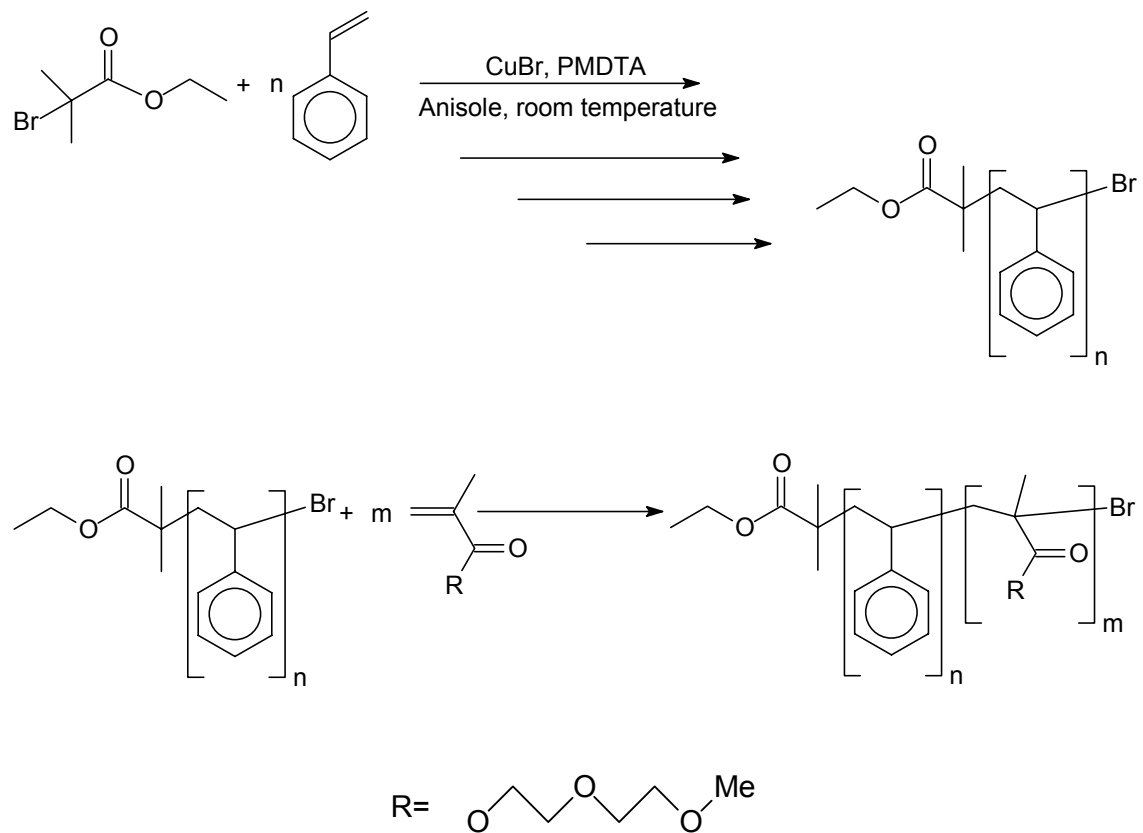


Figure 53: The reaction scheme for the synthesis of PS-PDEGMA block copolymer via an ATRP

Amounts of chemicals used for the synthesis of PS-PDEGMA and achieved results are presented in table 13.

Table 13: Amounts of chemicals taken for the synthesizes of PS-PDEGMA block copolymers via ATRP mechaism

Entry	n(S), mmol	n(DEGMA) mmol	n(In) mmol	n(CuBr) mmol	n(PMD TA), mmol	x(DEGM A) (theo)	$M_n^{PS}/10^3$ (theo) g/mol	M_n^{DEGMA} $/10^3$ (theo) g/mol	$M_n^{PS}/10^3$ g/mol	$M_n^{PS-PDEGMA}$ 10^{-3} g/mol	M_w/M_n	X_{PDEGMA}
R1S	43.5	-	0.168	0.168	0.168	-	27	-	11.5	-	1.02	-
R1D	-	0.8	0.02	0.02	0.02	0.33	-	7.5	-	15.9	1.21	0.231
R2S	97	-	0.101	0.101	0.101	-	135	-	153	-	1.06	-
R2D	-	8	0.05	0.05	0.05	0.129	-	30	-	154	1.06	0
R3D ^{a)}	54.2	-	0.167	0.167	0.167	-	61.1	-	10.5	-	1.02	1
R3S ^{a)}	-	10.0	0.095	0.095	0.095	0.20	-	21.5	-	11.6	1.15	1

^{a)}PDEGMA block was synthesized first

n(S) – amount of styrene

n(In) – amount of initiator (EBiBr or macroinitiator)

n(CuBr) – amount of CuBr;

$x(\text{DEGMA})^{\text{theo}}$ – calculated molar ratio of DEGMA in diblock copolymer

M_n^{PS} (theo) – calculated molar mass of the polystyrene block

M_n^{PDEGMA} (theo) – calculated molar mass of the PDEGMA block

M_n^{PS} – number average molar mass of the polystyrene block (GPC)

$M_n^{\text{PS-PDEGMA}}$ – apparent number average molar mass of entire polymer versus polystyrene calibration (GPC)

M_w/M_n – polydispersity index of entire polymer

X_{PDEGMA} – molar ratio of DEGMA in entire polymer

n(DEGMA) – amount of DEGMA

n(PMDTA) – amount of ligand forming agent (PMDTA)

In the first experiment the polystyrene precursor (sample R1S) was aimed at a theoretical molar mass of 27000 g/mol, the entire diblock should possess a theoretical molar mass of 34500 g/mol respectively, leading to a molar ratio of PDEGMA $x(\text{PDEGMA})=0.33$.

The number average molar mass of this polystyrene macroinitiator (sample R1S) was 11500 g/mol, and its polydispersity was 1.02. Before the polymerization of the second block, this polymer was exposed to high vacuum overnight in order to remove residual traces of MeOH.

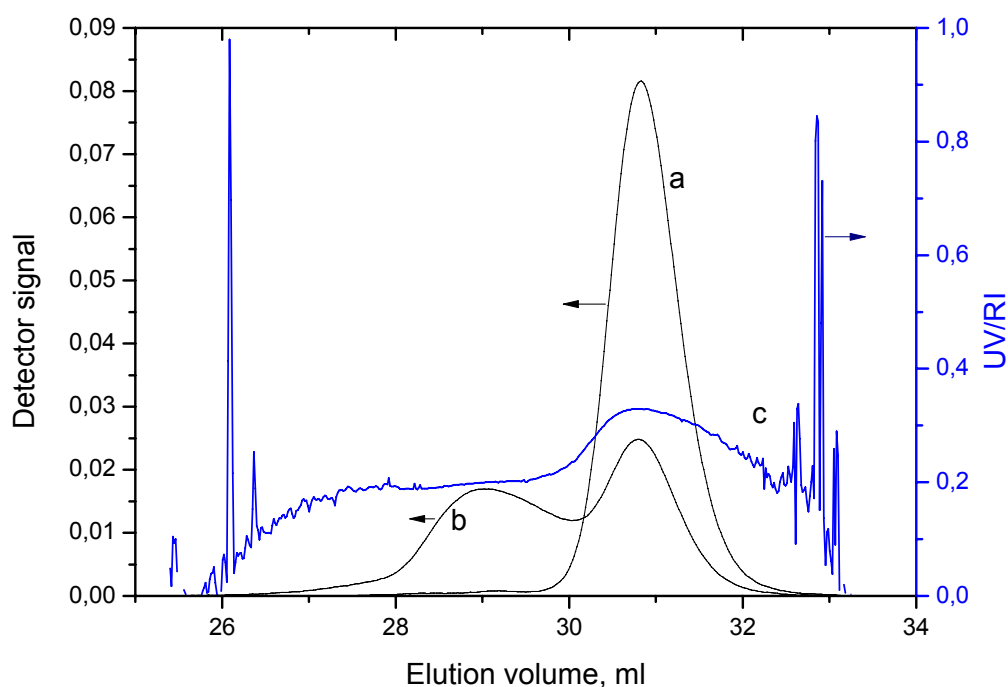


Figure 53. GPC elugram (RI detector) of sample R1: a) sample R1S; b) sample R1D; c) UV/RI ratio for sample R1D

The GPC analysis (Figure 53) of the diblock exhibited an apparent number average molar mass of 15900, and a polydispersity of 1.21. This molar mass is lower than the calculated one, which means that a significant amount of DEGMA was not initiated by the polystyrene macroinitiator. The peak at higher elution volumes on curve b Figure 53 ($V_e=31$ ml) corresponds to the residual polystyrene macroinitiator, while the peak having a maximum at $V_e=29$ ml corresponds to the diblock copolymer. From

the GPC it is obvious that still a significant amount of polystyrene precursor residual is present in this diblock. However, approximately 40% of polystyrene precursor served as an initiator for the polymerization of DEGMA, so it was decided to use the same system to get PS-PDEGMA block copolymers of higher molar masses.

As a next step, the synthesis of PS-PDEGMA with a molar mass of a more than 150000 g/mol was tried, following the same procedure. Theoretical molar mass of polystyrene precursor (sample R2S) was 135000 g/mol, and the theoretical molar mass of the PS-PDEGMA block copolymer (sample R2D) was 165000 g/mol.

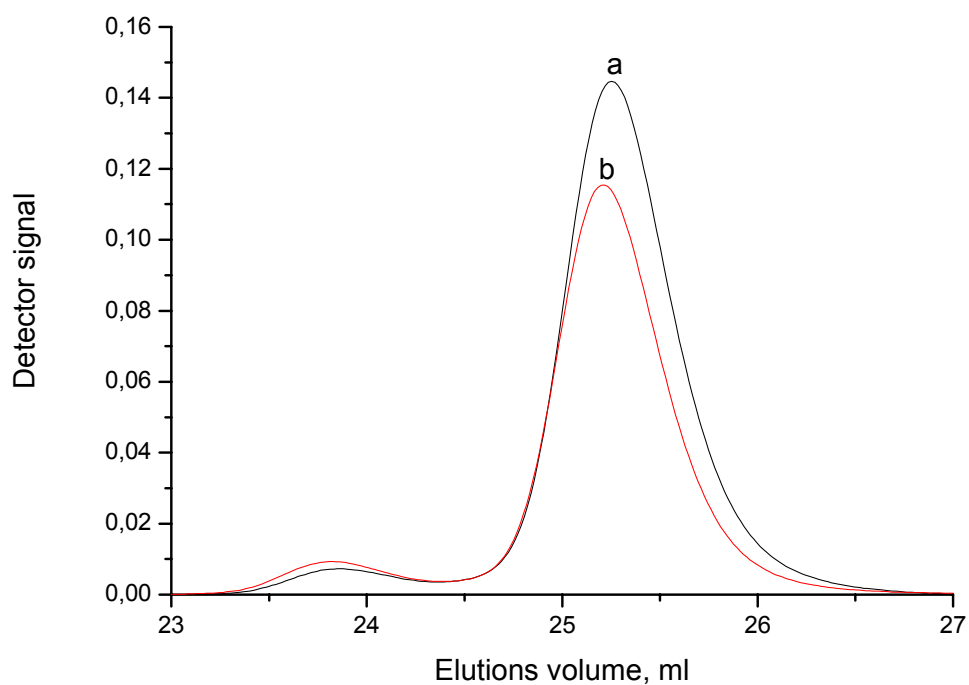


Figure 54: GPC traces (RI detector) a) sample R2S b) sample R2D

The number average molar mass of the polystyrene macroinitiator was 124000 g/mol, and its polydispersity was 1.05, while the apparent number average molar mass of entire polymer was 128500 g/mol, and the polydispersity was 1.06. Both the shape and the position of the GPC curve indicate that no DEGMA has polymerized which was proven by subsequent ^1H NMR analysis.

As the attempt to polymerize PS-PDEGMA block copolymer in a sequential ATRP fashion did not give the appropriate results, it was supposed that the length of the polystyrene chain has a strong influence on the ability of macroinitiator to initiate the polymerization of the second block. In other words, after a certain length of PS chain has been reached, the macroinitiator cannot initiate the polymerization of DEGMA. Consequently, the polymerization sequence should be reversed, as it was assumed, that under these conditions the formation of the block copolymer may be easier to accomplish.

Hence, in case of the experiment R3D a PDEGMA macroinitiator of a theoretical molar mass of 21500 g/mol was polymerized first, which served to initiate the polymerization of the subsequent PS block. The entire block copolymer was aimed at a molar mass of 82600 g/mol i.e. a molar ratio of $x(\text{PDEGMA})=0.20$.

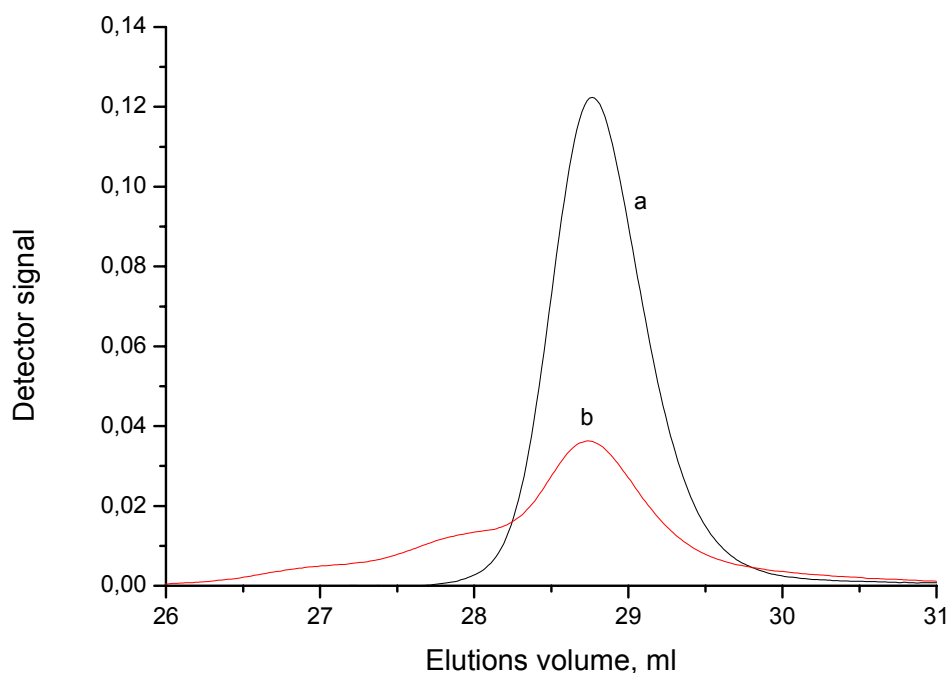


Figure 55: GPC traces (RI detector) a) sample R3D; b) sample R3S

The GPC analysis revealed an apparent number average molar mass of the PDEGMA precursor (sample R3D) of 26000 g/mol (versus polystyrene calibration), and a polydispersity of 1.02. The apparent number average molar mass of the entire polymer (sample R3S) was 27300 g/mol (versus polystyrene calibration), and the

polydispersity was 1.15. As it can be observed in Figure 55, only a small amount of styrene polymerized in a rather uncontrolled way. Although this procedure was chosen in order to increase the reactivity of macroinitiator, the reactivity of the PDEGMA-Br precursor was probably too low to initiate the polymerization of styrene.

Another possibility to link polystyrene to a PDEGMA chain would be the increase of the reaction temperature. On the other hand, an increase of the temperature might lead to unwanted cross-linking of the DEGMA units. During the previous experiments, DEGMA had shown a high affinity to cross-linking, resulting in an insoluble polymer network. As the polymerization of a PS-PDEGMA diblock copolymer of a molar mass of 200000 g/mol and a composition $0.20 < x(\text{PDEGMA}) < 0.40$ could not be performed in an ATRP manner, it was decided to combine two different mechanisms for the synthesis of the two different blocks.

4.4.3. SEQUENTIAL ANIONIC – ATRP POLYMERIZATION

In this sequential approach, anionic polymerization was employed to synthesize a block of polystyrene with a bromo-isobutyryl group at the end. This end-functionalized polystyrene would later be used as a macroinitiator for polymerization of PDEGMA block via ATRP. The pathway for this reaction is presented on page 63.

Three different PS macroinitiators were prepared. They were synthesized following the same procedures, but with different molar masses. Amounts of chemicals that were taken for those syntheses are presented in Table 14.

Table 14: Amounts of chemicals taken for the syntheses of polystyrene macroinitiators

	Styrene (mmol)	sec-BuLi (mmol)	Styrene oxid (mmol)	α iBuBr (mmol)	M_n^{calc} (g/mol)	M_n (g/mol)	M_w/M_n
C1S	61	3.08	4.41	3.24	2060	2500	1.06
C2S	87	0.49	0.92	0.81	18500	21400	1.02
C3S	52	0.026	0.05	0.045	208000	157000	1.06

As only polystyrene chains with a bromo-isobutyryl group at the end can serve as a macroinitiator for the polymerization of the PDEGMA block, it was necessary to determine degree of functionalization. The degree of functionalization was estimated from ^1H NMR spectra, by comparing the intensity of the resonance signal intensity of the *sec*-butyl group stemming from the initiator to that of the α -bromoisobutyryl group. This calculation can only be done for the first sample, as in the other two cases the intensity of the end-group protons in the spectra was too low. The degree of functionalization for the first polystyrene macroinitiator was calculated as 0.84.

The second PDEGMA block was synthesized by ATRP as already described, and the results are shown in Figure 56.

Table 15: Amounts of chemicals taken for the synthesis of PDEGMA block via ATRP polymerization mechanism and results (apparent number average molar mass versus polystyrene calibration)

	PS (mmol)	CuBr (mg)	PMDTA (μl)	DEGMA (mmol)	M_n^{calc} (g/mol)	M_n^{app} (g/mol)	D
C1	0.4	145	104	5.4	5040	8500*	3.76*
C2	0.05	14.5	10.4	5.4	41700	36000	1.61
C3	0.0067	3	2.5	5.4	309000	162000	1.06

*Values are given for entire polymer. Values of the apparent number average molar mass and polydispersity index for the peak at lower elutions volume are $M_n^{\text{app}}=23000$ g/mol (versus polystyrene calibration) and $D=1.46$, respectively.

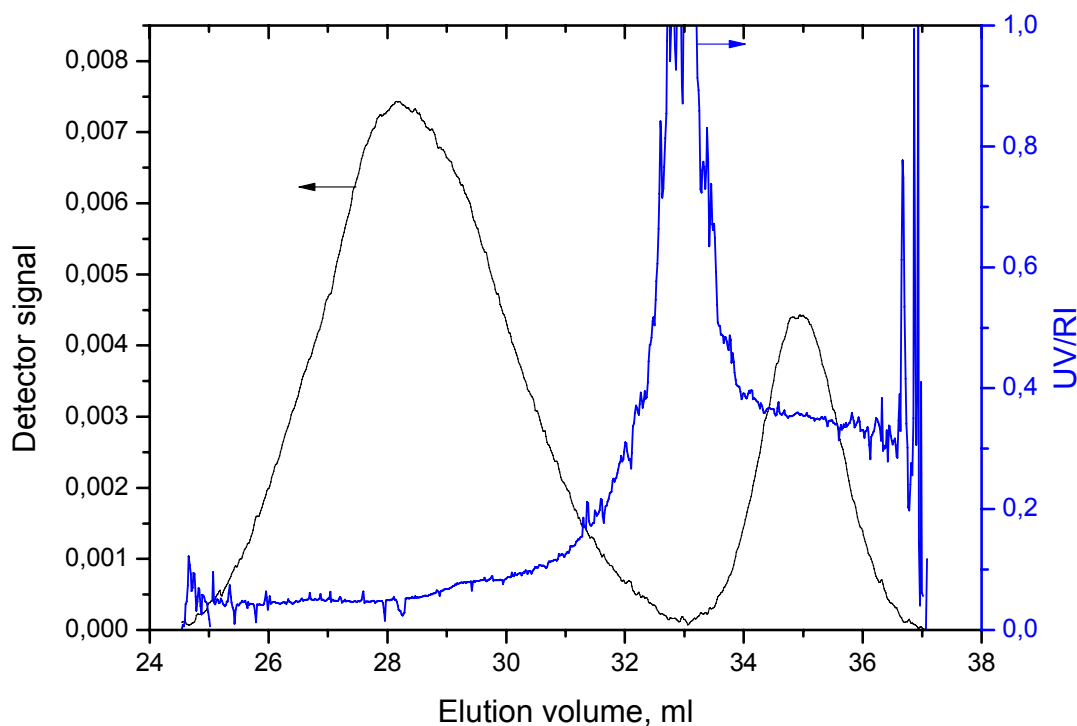


Figure 56: GPC traces (RI signal and UV/RI ratio) of sample C1

The peak at a higher elution volume ($V_e=35$ ml) represents the polystyrene precursor, which is proven by UV/RI ratio of 0.35. The peak at lower elution volume ($V_e=28$ ml) comes from the synthesized PS-*Pt*BMA block copolymer. The apparent number average molar mass of the synthesized block copolymer, excluding the precursor was 23000 g/mol. Comparing that value with the number average molar mass of the polystyrene macroinitiator (2500 g/mol), calculation reveals that apparent number average molar mass of PDEGMA block is 20500 g/mol ($P_n > 100$), which is significantly higher than in the case of anionic polymerization. Compared to sample A1 (which has approximately the same apparent number average molar mass), it is obvious that sample C1 contains more DEGMA units in the diblock copolymer. Therefore, sample C1 was taken as the basis for the further experiments with the increased molar mass.

Obviously a synthesis of a PS-PDEGMA block copolymer via a combined ATRP-anionic mechanism is possible, although approximately 20% of the

polystyrene did not initiate polymerization of DEGMA. To check the possibilities to increase the molar mass, the synthesis of diblock copolymers using the other two macroinitiators was attempted (samples C2 and C3).

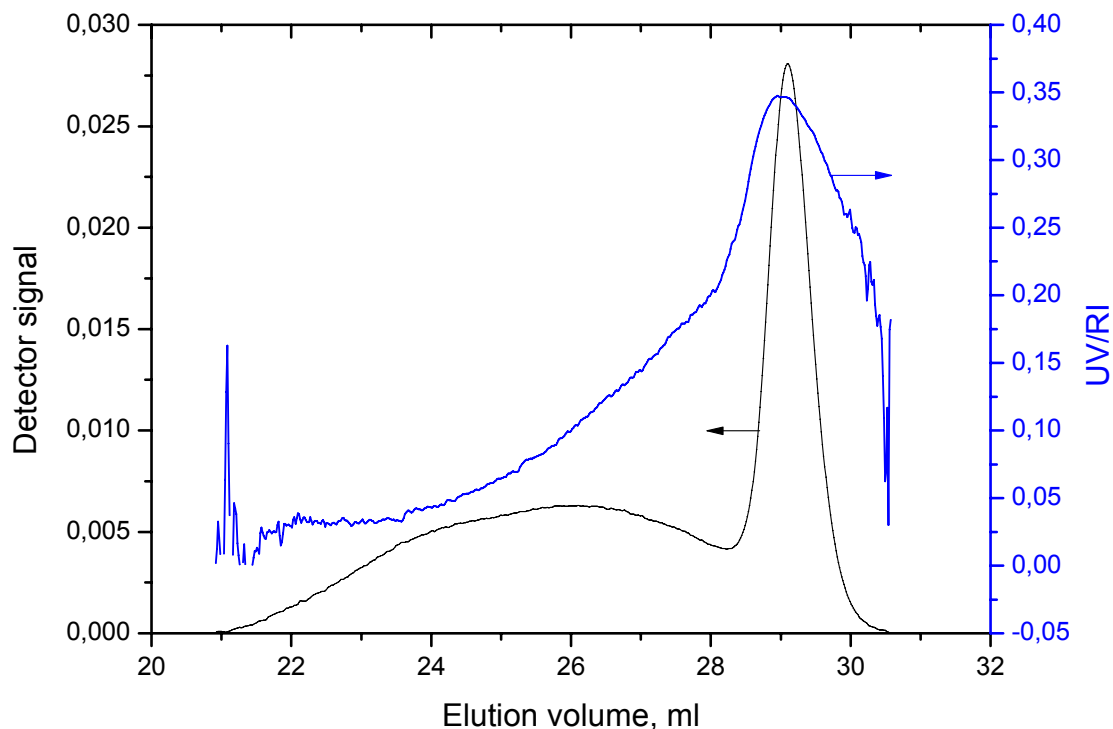


Figure 57: GPC traces (RI signal and UV/RI ratio) of sample C2

In case of sample C2 (Figure 57), it is obvious that the polymerization of PDEGMA block occurred in an uncontrolled manner, as the peak at lower elution volume is very broad, and that only a small amount of polystyrene served as a macroinitiator. However, from the shapes of UV and RI curves it is unclear if this polymer is really a diblock or just a blend of PS and PDEGMA.

For an even higher average molar mass of polystyrene macroinitiator, the GPC elugram is shown in Figure 58 (sample C3).

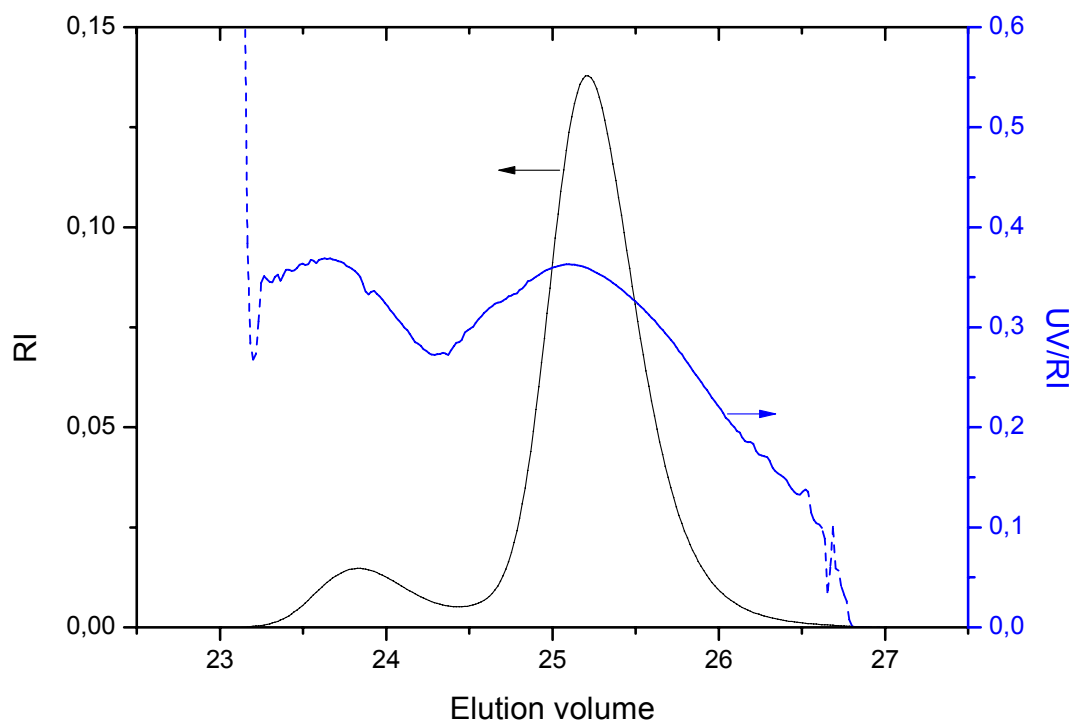


Figure 58: GPC traces (RI signal and UV/RI ratio) of sample C3

The GPC trace of this polymer shows a bimodal distribution. The peak at higher elution volumes ($V_e=25.5$ ml) comes from the polystyrene precursor. An UV/RI ratio of 0.35 reveals that this peak can be attributed to pure polystyrene, and that no DEGMA has polymerized. As the UV/RI ratio of the peak at the lower elution volume is also 0.35, it is reasonable to conclude that no DEGMA units are incorporated at all. It is reasonable to conclude that the peak at the lower elution volume comes from the PS chain coupling that occurred during the synthesis of the macroinitiator. Comparing the GPC results of samples C2 and C3 with the samples R2D and R3D (as they were aiming for the similar molar masses), it is obvious that results are comparable, and that no significant increases in the average molar mass of the PDEGMA block was obtained.

5. CONCLUSION AND OUTLOOK

Attempts to synthesize diblock copolymers containing a block which rapidly changes its solubility in water in dependency of the temperature whereas the other block is insoluble in water and gives mechanical stability were made. The mechanically stable components of the diblock copolymer were, polystyrene or poly(*tert*-butylmethacrylate), while as an active component, poly-(2-(2ethoxy)-ethoxy)methacrylate was used. The PS-PDEGMA diblock copolymers were synthesized up to molar masses of 44000 g/mol (sample A6; molar ratio of DEGMA 0.18). The highest achieved molar ratio of DEGMA in diblock copolymers was 0.36 (sample A17). Syntheses of P*t*BMA-PDEGMA block copolymers were also performed, but the number average molar masses of this type of polymer were lower compared to PS-PDEGMA (sample A9 – $M_n=5500$ g/mol; $x(\text{PDEGMA})=0.39$).

The syntheses were performed via following mechanisms:

- Sequential anionic polymerization (PS-PDEGMA and PS-P*t*BMA)
- Group transfer polymerization (PS-P*t*BMA)
- Atomic transfer radical polymerization (PS-PDEGMA)
- Combination of anionic and atomic transfer radical polymerization (PS block synthesized anionically and modified by the α -bromoisobutryl bromide; PDEGMA block synthesized via ATRP)

The highest molar masses (samples A1, A6, A16, A17 $M_n > 20000$ g/mol), lowest polydispersities (A1, A16 A17 $M_w/M_n < 1.1$), and molar amounts of DEGMA exceeding 10% (A1, A6, A16, A17) were gained by sequential anionic polymerization. The main disadvantage of sequential anionic polymerization is the tedious preparation procedure, as the chemicals must be very clean.

Group transfer polymerization was performed successfully for lower molar masses (up to 22000 g/mol), but the phase separation has not been achieved. On the other hand, a P*t*BMA-PDEGMA random copolymer was achieved employing TBABB as a catalyst, and copolymerization parameters were determined.

Atomic transfer radical polymerization has resulted in PS-PDEGMA polymers with molar masses up to 16000 g/mol (sample R1, molar ratio of PDEGMA 0.231), but the polydispersity index was higher compared to the analogous polymers synthesized via sequential anionic polymerization.

Using a combination of anionic and atomic transfer radical polymerization, PS-PDEGMA copolymers of molar masses up to 25000 were synthesized with significantly higher amounts of DEGMA (up to 80 mol%) compared to polymers prepared by anionic polymerization. However, the main problem in the synthesis diblock copolymers was the significant amount (over 20%) of the residual polystyrene macroinitiator.

The final goal of this work was to prepare the polymer which would be suitable for the construction of a membrane. A polymer required for this purpose should have molar mass of at least 150000 g/mol (in order to possess mechanical stability), and molar ratio of PDEGMA of 0.20-0.40. (in order to get desired structure of hexagonally packed cylinders of PDEGMA in the PS matrix) As the synthesis of this polymer could not be performed, the construction of a membrane was not attempted.

As the synthesis of block copolymer based on the PDEGMA as an active component did not result in appropriate polymer, further research in this field should be focused to the synthesis of block copolymer based on another LCST polymer. That might be poly(2-(2-(methoxyethoxy)ethoxy) ethyl methacrylate) (TEGMA) or poly(2-(ethoxyethoxy)ethyl methacrylate) (ethoxy counterparts of DEGMA). Alternatively, synthesis of block copolymer based on poly(*N*-isopropylacrylamide) – PNIPAM⁸³ can be performed.

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