

THE INFLUENCE OF THE REACTION PARAMETERS FOR THE SYNTHESIS OF THE POLYMER SUITABLE FOR THE CONSTRUCTION OF THE MEMBRANES WITH VARIABLE SIZE OF PORES

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ABSTRACT

In the recent years, the significance of the membranes with variable sizes of pores has rapidly increased. Membranes that include material that instantly changes the solubility at the certain temperature have application in controlled drug delivery as well as the protein separation. Suitable material for the construction of that type of membrane should be the diblock-copolymer that consists of one active block, and hydrophobic matrix block. The active component should change its solubility at the temperature that is between the room temperature and human body temperature. The main challenges for the synthesis of the diblock-copolymer are high molar mass for the sufficient mechanical stability and low polydispersity index in order to obtain microphase separation. The mechanically stable components of the diblock copolymer were, polystyrene (PS), while as an active component, poly-(2-(2ethoxy)-ethoxy)methoxy methacrylate (PDMEEMA) was used. The synthesizes were done by the sequential anionic polymerization mechanism. The possibilities of prevention of unwanted side reactions on the carbonyl group of the methacrylate by the presence of the different cations in the reaction systems as well as the possible sterical hindering was tested. It is concluded that the presence of the larger cation as an additive in the reaction system decreases the polydispersity index, while the size of the counter ion of the initiator does not influence the final polydispersity index. It is also observed, contrary to the expectations that use of sterically unhindered chain ends does not necessarily lead to the unwanted side reaction on the methacrylate side chain.

Keywords: anionic polymerization, diblock-copolymer, polymer membranes

1. INTRODUCTION

Polymer materials that change their solubility with the change of temperature are of the great significance for the construction of the membranes that changes their permeability with the temperature. This type of membranes could be applied as the temperature switch, as well as for the protein separation and/or controlled drug delivery [1,2]. Therefore, the main goal of this work is to synthesize a temperature-sensitive polymer which is suitable for the construction of the mentioned membrane. As the main application of the membrane should be within or at least in close relation to human body, polymer for this purpose must be chemically stable, non toxic, with a switching

temperature below 40°C in order to prevent protein degradation. Suitable material for this purpose should be diblock-copolymer that contains one block that shows lower temperature solution temperature (LCST) behaviour while the other block would be mechanical carrier [3,4]. The blocks of the synthesized diblock-copolymer will be poly(2-(methoxyethoxy)ethyl methacrylate) (PDMEEMA) (as the active component), and polystyrene (PS) (as the mechanically stable component). DMEEMA shows LCST point at 26°C [5,6,7,8].

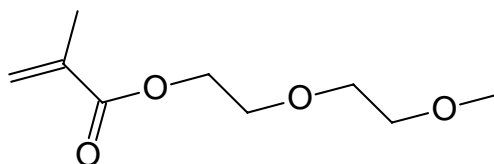


Figure 1: Structure formula of 2-(methoxyethoxy)ethyl methacrylate (DMEEMA)

Essential issue for the construction of the membrane is to get the structure of PDMEEMA cylinders packed in the PS matrix as this structure would provide opened pores through the whole active layer of the membrane [9]. This structure is obtained if the molar amount of minor component (in this case PDEEMA) is between 0.2 and 0.4 [10,11,12]. Polydispersity index must be as low as possible in order to preserve microphase separation. Finally, the diblock-copolymer should have high molar mass (at least 100000 g/mol) for the enough mechanical stability. All those challenges could be fulfilled if the sequential anionic polymerization is employed for the synthesis [13]. As it has been reported that the ratio charge/size of the cation (often called “hardness” of the cation) strongly influences the kinetics of the polymerization of the methacrylates with long side chains [14], the possible differences in reaction yield during the initiation with lithium and potassium was tested. The formation of electrostatic bonds between the oxygen atoms (via their free electron pairs) and counter ion has also been observed. If the larger cation (e.g. potassium or caesium) is present in the system, it is possible that bonds between all of the side chain oxygen atoms and cation. Therefore, it is even possible that recombination of the living chain end occurs. In that case, the negative charge is transferred to the carbonyl oxygen, and double bond between the last two carbon atoms in the chain is formed, terminating the reaction [15]. To prevent this unwanted reaction, another cation that could prevent formation of electrostatic bonds and unwanted termination could be added [16,17]. In this paper Zn²⁺ ion was added in the form of diethyl zinc. Addition of the cations and destruction of the stable potassium – oxygen complex should slow down the reaction rate, but at the same time should slow down the side reaction and prevent formation of unwanted products.

2 EXPERIMENTAL

As the requirements concerning the purity of the chemicals are extreme, the special attention was paid to the preparation and purification of the chemicals. Styrene and DMEEMA monomers were treated with the aluminum oxide in order to remove stabilizer, stirred over calcium hydride and distilled. All of the organometallic compounds were used as received. Tetrahydrofuran (THF) was refluxed over sodium – potassium alloy for thirty minutes and then transferred to the reactor. All of the reactions were done in 2 dm³ reactor cooled to -63°C by the silicon liquid. The reactor was cleaned by flushing with THF and after that the high vacuum was applied. All chemicals were transferred into the reactor through the vacuum line by applying under- or overpressure created by the dry nitrogen. By this method of transfer, entering of moisture and oxygen was prevented as much as possible. Polymerization reactions were done in the sequential manner. Styrene was synthesized as the first block. THF, styrene and appropriate amount of the organometallic initiator was introduced to the reactor, and the reaction lasted for two hours. After that, the appropriate amount of the DMEEMA monomer was introduced and the reaction lasted for another two hours. During the polymerization of the sample 3 diethyl zinc was added as an additive simultaneously with the DMEEMA monomer. The reaction was terminated with methanol and yielded polymer was precipitated in water – methanol mixture (30/70 vol %). The average molar masses were determined by the Gel Permeation Chromatography (GPC with cross linked polystyrene as a stationary phase and the THF as a solvent). The molar compositions of the

polymers were determined by the ^1H NMR (deuterated chloroform as the solvent and tetramethylsilane as a reference). The molar composition of the diblock-copolymer was determined from the chemical shifts of the hydrogen atoms from the different respective functional groups (phenyl group from the polystyrene units), and side chain of the PDEEMA units. Chemical shifts of the five hydrogen atoms in the phenyl ring are in area between 6,0 and 7,5 ppm, and the shifts of the protons of the DMEEMA side chain are in area between 3,4 and 4,1 ppm. The counter ions, additive, calculation of the molar masses for both the PS precursor and diblock-copolymers and calculated molar ratio of PDMEEMA block are presented in table 1.

Table 1: Initiators taken for the polymerizations and theoretical calculation of molar masses and molar amounts of the diblock-copolymers

Entry	Counter ion	$M_n^{\text{BI,theo}} 10^{-3}$ g/mol	$M_n^{\text{DB,theo}} 10^{-3}$ g/mol	$x(M_2)^{\text{theo}}$
1	Li^+	25.9	34.4	0.153
2	K^+	22.7	43.1	0.333
3	K^+ (Zn^{2+} as an additive)	45.3	96.3	0.383

3. RESULTS AND DISCUSSION

Data for polymers yielded in those reactions are compiled in table 2. All of the presented molar masses are apparent versus polystyrene calibration. The sample number 1 is synthesized with the lithium as the counter ion (reaction was initiated with the *sec*-butyl lithium). Samples number 2 and 3 were both synthesized with potassium as the counter ion. In both of cases reaction was initiated with the 1,1 diphenyl hexyl potassium. In the sace of the sample number 3, zinc cations were added in the form of diethyl zinc simultaneously with the DMEEMA monomer. The aim of the addition of Zn^{2+} ions is to prevent the interaction between the living chain ends and the potassium cations. Comparing the obtained results with the theoretical calculation, it is obvious that obtained molar masses and molar amount of second block for the sample number 1 are in good accordance with the calculated ones. The difference in masses could be attributed to the polystyrene calibration. The polydispersity index remained low, so it is reasonably to conclude that the microphase separation occurred. In the sample number 2, molar mass of the diblock-copolymer is again in a good accordance with the calculated value, but the polydispersity index is too high for the microphase separation. Possible reason for such a high value is bimodal distribution of the molar masses that is a consequence of the partial termination of the polystyrene precursor during the introduction of the DMEEMA monomer in the reaction. This presumption was corroborated by the NMR analysis, as the amount of PDMEEMA is significantly lower than the calculated one. Concerning sample number 3, it is obvious that the polymerization of polystyrene has been done according the calculation, and the value of the obtained molar mass is very close to the calculated one and the polydispersity index remained low (1,07). However, the molar mass of presumed diblock-copolymer is very close to the molar mass of the polystyrene precursor (the difference between the masses is inside the error margin of the detector), so it is obvious that DMEEMA did not polymerize. As the termination due to the impurities in the DMEEMA can be overruled as the conditions and procedures for chemicals' preparation was the same for all of the samples, it might be concluded that addition of Zn^{2+} ion slowed reaction down to the such a low speed that the polymerization practically stops.

Table 2: Obtained molar masses and molar amounts of each block with different reaction systems.

Entry	$M_n^{\text{BI}} 10^{-3}$ g/mol	$M_n^{\text{DB}} 10^{-3}$ g/mol	M_w/M_n	$x(M_2)$
1	-	22.1	1.05	0.132
2	-	44.0	1.60	0.18
3	47.8	49.9	1.07	0

4. CONCLUSION

In this work, the influence of the counter ion to the polymerization of PS-PDMEEMA diblock-copolymer was tested. Polymerization reactions were done in presence of lithium, potassium and

simultaneous presence of potassium and zinc cations. The best results were obtained employing the lithium as the cation. The molar mass was in good accordance with the calculation, the polydispersity index was low, and the molar amount of PDMEEMA was acceptable. In the case of potassium as a counter ion, partial termination during the addition of the second monomer occurred, bimodal distribution of molar mass was observed and, as a consequence, the polydispersity index was higher and at such a value microphase separation is not expected. Simultaneous presence of both potassium and zinc cations rapidly decreases the polymerization rate of DMEEMA, and reduces the speed of reaction to the point that it can be neglected. Therefore, having all mentioned in mind, the polymerization of PS-PDMEEMA block-copolymer in the presence of the lithium cation could be recommended.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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