

Synthesis of amphiphilic diblock copolymer brushes by successive RAFT polymerization of lauryl methacrylate and PEO-containing macromonomer

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Reversible addition-fragmentation chain transfer (RAFT) polymerization of lauryl methacrylate (LMA) in the presence of *S*-methoxycarbonyl phenylmethyl dithiobenzoate (MCPDB) as a RAFT chain transfer agent (CTA) and subsequent RAFT polymerization of poly(ethylene oxide) monomethyl ether methacrylate (PEO₅MEMA or PEO₄₅MEMA) was done with the aim to prepare amphiphilic diblock copolymer brushes of controlled structure. The molecular weight of PLMA and PLMA-*b*-PPEO₅MEMA copolymers was evaluated by several methods including SEC calibrated using polystyrene standards, and end-group analysis by ¹H NMR and UV-Vis. The kinetics of LMA polymerization was followed by ¹H NMR spectroscopy by comparing the signals attributed to the monomer and corresponding monomeric units in PLMA. RAFT polymerization of LMA at the ratio [MCPDB] : [AIBN] = 4 demonstrated the “living” character enabling to synthesize PLMA with a low polydispersity ($M_w/M_n = 1.08\text{--}1.19$) and a relatively high molecular weight (M_n up to 60 000, degree of polymerization DP up to 260). Several diblock copolymers PLMA-*b*-PPEO₅MEMA with various lengths of the blocks and a high molecular weight (M_n up to 300 000) were prepared and characterized. RAFT polymerization of PEO₄₅MEMA from PLMA as a macro-CTA failed.

Key words: RAFT, macromonomer, PEO, diblock copolymer, amphiphilic copolymer

INTRODUCTION

The polymers of higher (alkyl)methacrylates are of significant importance in material science due to their low glass transition temperature [1]. Lauryl methacrylate (LMA), an industrially important monomer, is soluble in polar and non-polar solvents at >45 °C. Hence, it is difficult to polymerize it by the living anionic polymerization technique which generally works well at <–60 °C. Nevertheless, attempts were made to polymerize LMA using anionic polymerization at a low temperature [2–4]. Anderson and co-workers attempted to synthesize the block copolymer of methyl methacrylate (MMA) and LMA using anionic polymerization at –78 °C [2]. However, they obtained polymers with a broad molecular weight distribution ($M_w/M_n = 1.72$). Group transfer polymerization (GTP) been employed for the polymerization of

LMA at room temperature, and low molecular weight polymers with moderate control were obtained [5, 6]. The synthesis of diblock copolymers PMMA-*b*-PLMA by GTP was reported [7], where the products had molecular weights of about 6 500 and a narrow MWD (<1.14). Later, employing GTP, Sannigrahi and coworkers [8] were able to prepare diblock copolymers of MMA and LMA with a relatively high molecular weight (about 40 000) and a narrow MWD (<1.15). Nevertheless, although GTP provided controlled polymerization of alkyl (meth)acrylates at ambient temperature, molecular weight control was lost when higher molecular weights ($M_n = 50\ 000$) were targeted.

Atom transfer radical polymerization (ATRP) is one of the methods of controlled / “living” radical polymerization suitable for the synthesis of acrylic and methacrylic homo- and block copolymers [9–14]. Haddleton and co-workers [15] have examined the ATRP of *n*-butyl, *n*-hexyl and *n*-octyl methacrylates, using ethyl-2-bromoisobutyrate as an initiator, CuBr

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as a catalyst, and *N*-(*n*-butyl)-2-pyridylmethanimine as a ligand. Later, ATRP of LMA, using the initiating systems ethyl-2-bromobutyrate / CuCl / different ligands, was reported [16–18]. It was shown that bipyridine type ligands did not ensure an adequate control over polymerization. PLMA with moderately narrow MWD ($M_w / M_n = 1.29$) was obtained in the presence of triamine and methanimine type ligands. The synthesis of block copolymers of PLMA and PMMA was accomplished by the sequential monomer addition method [19].

Reversible addition-fragmentation chain transfer polymerization (RAFT) is the process which indeed allows the polymerization of lauryl (meth)acrylate in a controlled way. Several bi- and multifunctional chain transfer agents (CTA) have already been used for the polymerization of LMA by RAFT [20, 21]. The ability to polymerize LMA in a controlled manner could offer a new possibility for the synthesis of well-defined homo- and block copolymers. The hydrophobic nature of PLMA can also be used in constructing various amphiphilic block copolymers [22].

Challenging monomers for construction of hydrophilic blocks are poly(ethylene oxide) monomethyl ether methacrylates (PEO_xMEMA). The subscript *x* refers to the number of ethylene oxide units in the macromonomer; two macromonomers with *x* = 5 and *x* = 45 were used in the present study. PEO is one of the structurally simplest polymers (oligomers), which exhibits complex solution properties. It is unique among the polymers in being soluble in many organic solvents and water. PEO₄₅MEMA was used as a macromonomer in the synthesis of cationic bottle brush polymers [23–25] suitable for the conditioning of various surfaces, and amphiphilic graft copolymers [26, 27] capable of forming stable aggregates in solution. Microspheres of amphiphilic polymers have been applied in many fields, such as solid-phase organic synthesis, polymeric catalysis and biomedicine [28, 29].

The aim of the present study was the synthesis of amphiphilic diblock copolymers PLMA-*b*-PPEO_xMEMA of controlled structure by RAFT polymerization, using *S*-methoxycarbonyl-phenylmethyl dithiobenzoate (MCPDB) as a RAFT CTA. During RAFT polymerization of LMA, the effects of the monomer concentration and the [LMA] : [AIBN] : [MCPDB] ratio on the “livingness” of the system were attempted to ascertain. RAFT polymerization of PEO macromonomers with different length of the PEO chain from PLMA as a macro-CTA was foreseen as a method for the synthesis of amphiphilic diblock copolymers of bottle-brush structure.

EXPERIMENTAL

Materials

Poly(ethylene oxide) monomethyl ether methacrylate (M_n 300) (PEO₅MEMA) and lauryl methacrylate (LMA) were from “Aldrich”. Poly(ethylene oxide) monomethyl ether methacrylate (M_n 2080) (PEO₄₅MEMA) was purchased from “Aldrich” as a 50% aqueous solution and freeze-dried to recover the anhydrous monomer. 2,2'-Azobis(isobutyronitrile)

(AIBN) was purified by recrystallization from methanol. 1,4-Dioxane (DO) was distilled from metallic Na. Toluene and THF were dried over CaH₂ and distilled. *S*-Methoxycarbonyl-phenylmethyl dithiobenzoate (MCPDB) was synthesized by the method described elsewhere [30].

RAFT polymerization of lauryl methacrylate

LMA (25 g, 98.5 mmol), MCPDB (0.125 g, 0.40 mmol), AIBN (0.027 g, 0.16 mmol) and DO (58.33 g) were placed in a flask. The system was deoxygenated by N₂ bubbling for 30 min, and polymerization was carried out under vigorous stirring at 80 °C. To terminate the reaction, the mixture was cooled, and the polymerization mixture was poured onto methanol for precipitation. The solution was decanted and the precipitate washed three times with methanol, dried in a vacuum oven at ambient temperature for 48 h to give 20.7 g of the product (yield 83%). PLMA with the degree of polymerization DP = 60, thereafter called also as the macro-CTA (PLMA)₆₀, was obtained as a bright pink viscous paste.

Block copolymerization using PLMA as a macro-CTA

In a typical procedure (Table 2, entry 2), PEO₅MEMA (0.907 g, 3.02 mmol), PLMA₆₀ (0.5 g, 0.032 mmol), AIBN (0.0016 g, 0.0097 mmol) and toluene (4.13 g) were placed in a flask. The reaction mixture was deoxygenated by N₂ bubbling for 30 min and polymerized under vigorous stirring at 80 °C for 6 h. Finally, the copolymer was precipitated by pouring the solution to methanol, dispersed in water and dialyzed against water / THF (70/30 v/v) (MWCO 12 000–14 000) for a week, and dried at 30 °C to give 1.04 g of the product (yield 74%). The diblock copolymer (PLMA)₆₀-*b*-(PPEO₅MEMA)₆₇ was obtained as a pink viscous paste.

Characterization

Size exclusion chromatography (SEC)

The molecular weight of the polymers was estimated using SEC instruments: Deltachrom pump (Watrex Comp.), autosampler Midas (Spark Instruments, The Netherlands), two columns with PL gel MIXED-B LS (10 μm), separating in the range of molecular weights approximately 400–1 × 10⁷ g · mol⁻¹, and a refractive index detector Shodex RI 71 or the evaporative light scattering detector PL-ELS-1000 (Polymer Laboratories). THF was the mobile phase; its flow-rate was 0.5 ml/min. The injection-loop volume was 0.1 ml. Polystyrene reference standards in the range 4 000–1.6 × 10⁶ were used for the calibration of the system.

NMR spectroscopy

¹H NMR spectra were recorded on a “Unity Inova Varian” spectrometer using CDCl₃ as a solvent for PLMA and block copolymers PLMA-*b*-PPEO₅MEMA.

The composition of the block copolymers PLMA-*b*-PPEO₅MEMA (molar fraction of PEO₅MEMA block $m_{\text{PEO}_5\text{MEMA}}$) was calculated according to the intensity (integral) of the signals at 4.1 ppm ($I_{4.1}$) and 3.9 ppm ($I_{3.9}$), correspond-

ing to protons in oxymethylene groups in PEO₅MEMA and LMA, respectively:

$$m_{\text{PEOMEMA}} = \frac{I_{4.1}}{I_{4.1} + I_{3.9}} \cdot 100\% \quad (1)$$

The calculation of the number-average molecular weight of PLMA (M_n^{PLMA}) from ¹H NMR spectra was based on the ratio between the intensity (integrals) of the signals of the protons from the oxymethylene group of LMA at 3.9 ppm ($I_{3.9}$) and *ortho*-aromatic protons of dithiobenzoate at 7.9 ppm ($I_{7.9}$). M_n was calculated according to the equation:

$$M_n^{\text{PLMA}} = \frac{I_{3.9}}{I_{7.9}} M^{\text{LMA}} + M^{\text{MCPDB}}, \quad (2)$$

where M^{LMA} and M^{MCPDB} are the molecular weights of LMA and MCPDB, respectively.

The number-average molecular weight of the block copolymers $M_n^{\text{PLMA-b-PPEOMEMA}}$ was calculated according to the equation:

$$M_n^{\text{PLMA-b-PPEOMEMA}} = M_n^{\text{PLMA}} + \frac{m^{\text{PEOMEMA}} \cdot M^{\text{PEOMEMA}}}{m^{\text{LMA}} \cdot M^{\text{LMA}}} \cdot M_n^{\text{PLMA}}, \quad (3)$$

where M^{LMA} and M^{PEOMEMA} are the molecular weights of LMA and PEO₅MEMA, respectively; m^{LMA} and m^{PEOMEMA} are molar fractions of PLMA and PPEO₅MEMA blocks, respectively, obtained from ¹H NMR spectra.

To follow the kinetics of LMA polymerization, ¹H NMR spectra of the reaction mixture before and during polymerization were recorded. The calculation of the consumption of the monomer ($\ln \frac{[M]_0}{[M]_t}$) and monomer conversion q (%) was based on the peak areas of the signals assigned to protons in the oxymethylene group of LMA at 4.1 ppm (monomer) and 3.9 ppm (polymer):

$$\ln \frac{[M]_0}{[M]_t} = \ln \left(\frac{I_{3.9} + I_{4.1}}{I_{4.1}} \right), \quad q = \frac{I_{3.9}}{I_{3.9} + I_{4.1}} \cdot 100. \quad (4)$$

UV-Vis spectroscopy

UV-Vis spectra of PLMA in butyl acetate were recorded with a Cintra 101 spectrophotometer.

The calculation of M_n^{PLMA} from UV-Vis spectra was based on the absorption of dithioester end groups at a wavelength of $\lambda = 520$ nm. It was assumed that no dithioester groups were lost and that the end groups of polymers were 100% terminated by dithioester groups.

$$M_n^{\text{PLMA}} = \frac{c^{\text{LMA}}}{c^{\text{MCPDB}}} \cdot M^{\text{LMA}} + M^{\text{MCPDB}}, \quad (5)$$

where M^{LMA} and M^{MCPDB} are the molecular weights of LMA and MCPDB, respectively; c^{LMA} is the concentration of PLMA, expressed as the concentration of monomeric units LMA (mol/l), and c^{MCPDB} is the concentration of MCPDB (mol/l) determined from the calibration curve.

RESULTS AND DISCUSSION

RAFT polymerization of lauryl methacrylate

To ensure control of the polymerization and to obtain PLMA with a desirable chain length, RAFT polymerization of LMA was done at different ratios of the monomer, initiator AIBN and MCPDB as a RAFT CTA. According to the mechanism of RAFT polymerization [3], termination reactions become negligible at a very low concentration of the initiator and a large excess of CTA over the initiator. A reasonable ratio of a monomer, initiator and CTA should be used; however, since at a very low concentration of the initiator the polymerization may not proceed at all because of the inhibiting effect of residual oxygen or other impurities, and at a large excess of CTA the molecular weight of the synthesized polymer is low. In the present study, the ratio [CTA] / [AIBN] was kept equal to 2.5 or 4.

Figure 1 represents the ¹H-NMR spectrum of PLMA, obtained by RAFT polymerization of LMA in the presence of MCPDB. The signals of aromatic protons of MCPDB at 7.2–7.9 ppm unambiguously evidence the process to proceed through the RAFT mechanism. The signals at 0.85–2.1 ppm attributed to the protons of methyl- and methylene groups in the polymer main chain and the aliphatic residue of LMA are consistent with the structure of PLMA. A distinct signal at 3.9 ppm belongs to protons in the oxymethylene group of LMA and can serve as analytical for calculating the molecular weight of PLMA.

RAFT polymerization of LMA was rather fast, giving over an 60% monomer conversion within 1 h for [CTA] / [AIBN] = 2.5 and within 4 h for [CTA] / [AIBN] = 4 (Fig. 2, b). Of course, a larger excess of CTA ensures a better control of the process, but at the same time lowers the rate of propagation. It should be noted that after 6 h of polymerization, the conversion of the monomer is nearly the same whatever the CTA : IBN ratio.

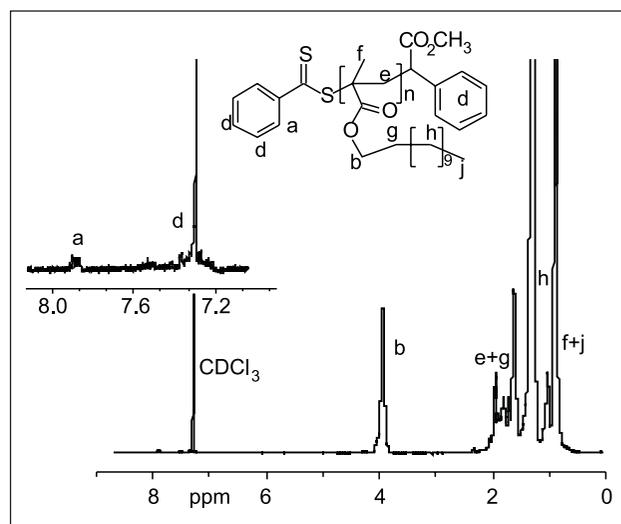


Fig. 1. ¹H NMR spectrum of PLMA ($M_n = 25\,500$, PDI = 1.19) in CDCl_3

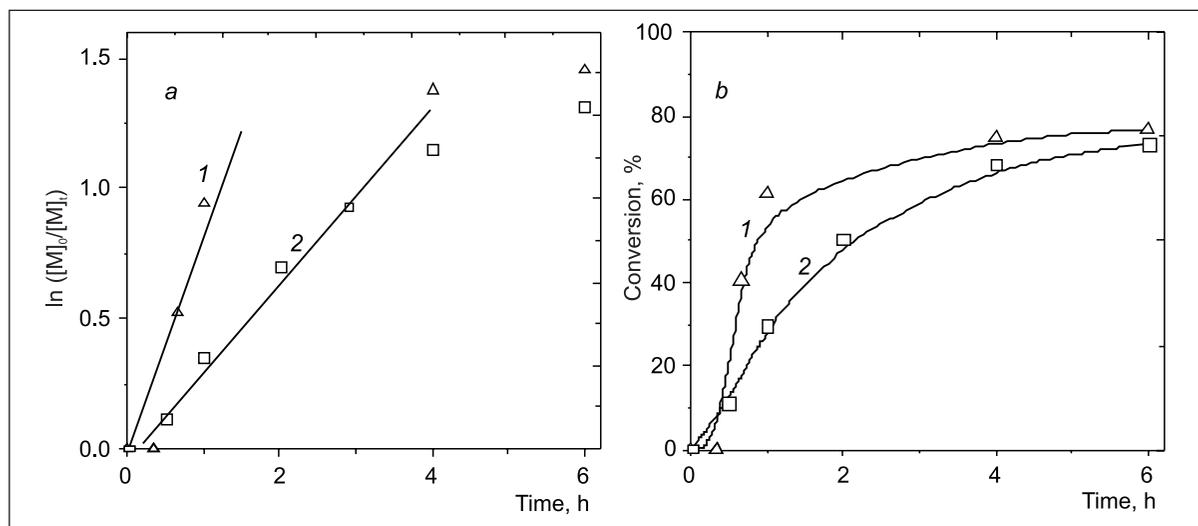


Fig. 2. Semilogarithmic kinetic plots (a) and conversion curves (b) for polymerization of LMA in D0 at 80 °C in the presence of MCPDB. $[LMA] = 1.7 \text{ mol/l}$, $[LMA]_0 / [AIBN]_0 = 300$, $[CTA] / [AIBN] = 2.5$ (1) and 4 (2)

At a 4-fold excess of MCPDB over AIBN, the kinetic plot in semilogarithmic coordinates was linear (Fig. 2, a), demonstrating that steady-state radical concentration under RAFT polymerization of LMA was constant. $[M]_0$ and $[M]_t$ in the logarithmic ordinate denote the initial and the current concentration of the monomer in the feed, respectively. The same dependence was observed for the RAFT polymerization of MMA mediated by MCPDB [30, 31]; further, PMMA obtained by the RAFT polymerization has been used as a macro-RAFT agent to carry out polymerization of *N*-isopropylacrylamide [32]. The relationship between $\ln([M]_0 / [M]_t)$ and the reaction time for LMA polymerization at a 2.5-fold excess of MCPDB seems to be linear during the first hour of the polymerization only (Fig. 2). A significantly higher rate of polymerization at a 2.5-fold excess of MCPDB versus a 4-fold excess may suggest that conventional free-radical polymerization operates in parallel with the RAFT process in this case. Nevertheless, even a 2.5-fold excess of MCPDB could be sufficient to control polymerization. It was found in an earlier study [20] that polymerization of LMA in the presence of the difunctional CTAs 1,4-bis(2-(thiobenzoylthio)prop-2-yl)benzene or 1,4-bis(thiobenzoylthiomethyl)benzene at a low ratio of CTA to AIBN (1.6) showed characteristics of a controlled radical polymerization with a linear increase in M_n with conversion.

Figure 3 presents SEC traces of PLMA synthesized at different MCPDB : AIBN ratios. PLMA synthesized at $[CTA] / [AIBN] = 4$ is characterized by a unimodal and sharp elution curve which is consistent with the excellent control of the process. In contrast, the elution curve of PLMA synthesized at $[CTA] / [AIBN] = 2.5$ is bimodal with the second peak at a low elution volume. The presence of a high molecular fraction in the last-mentioned polymer evidences that two parallel processes – RAFT and conventional free-radical polymerization – took part in parallel. Of course, the radi-

cal polymerization of LMA is well controlled by the RAFT chain transfer agent MCPDB if the ratio of CTA to AIBN approaches 4.

Semilogarithmic kinetic plots and conversion curves for the RAFT polymerization of LMA at a very low concentration of the initiator ($[LMA] / [AIBN] = 600$) are presented in Fig. 4. The linear relationship between $\ln([M]_0 / [M]_t)$ and the reaction time for LMA polymerization at a 2.5-fold excess of MCPDB indicate that these conditions are sufficient to maintain the constancy of the propagating species, i. e. good control over the process of polymerization. Surprisingly, at $[CTA] / [AIBN] = 4$ polymerization is very slow, and the conversion hardly exceeds 5%. Thus, the optimal $[MCPDB] / [AIBN]$ ratio depends on the $[LMA] / [AIBN]$ ratio being lower at a lower concentration of the initiator.

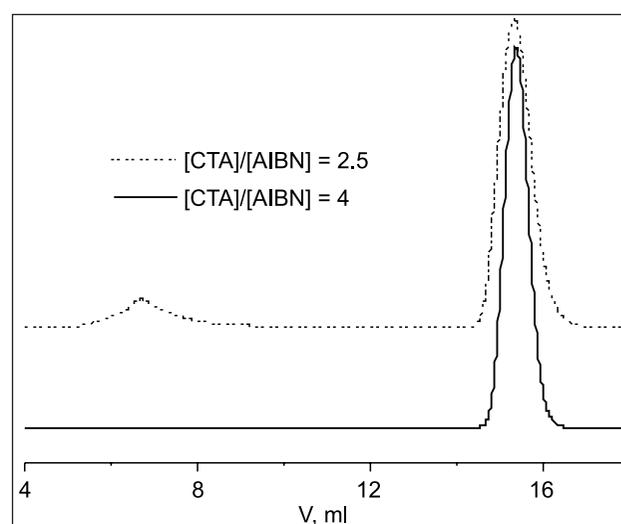


Fig. 3. SEC traces of PLMA samples synthesized at $[CTA] / [AIBN] = 2.5$ and 4 (reaction time 3 and 7 h, respectively). $[LMA] / [AIBN] = 300$

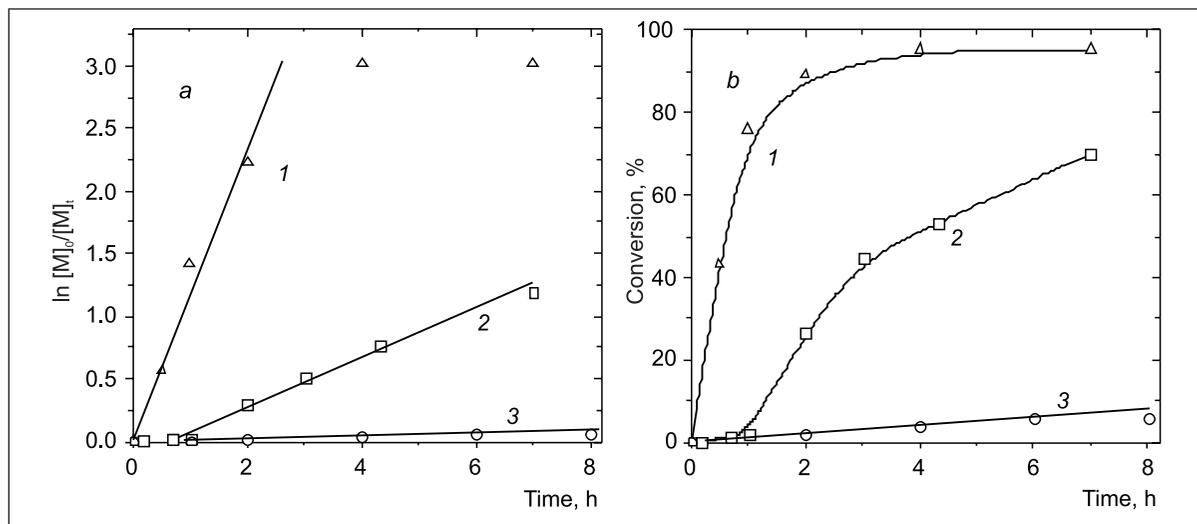


Fig. 4. Semilogarithmic kinetic plots (a) and conversion curves (b) for polymerization of LMA in bulk (1) and in DO (2, 3) at 80 °C in the presence of MCPDB. [LMA] = 1.7 mol/l, [LMA] / [AIBN] = 600, [CTA] / [AIBN] = 2.5 (1, 2) and 4 (3)

Although a decrease in initiator concentration impedes termination reactions, a large excess of CTA over AIBN favours the loss of dithioester molecules due to side reactions [34]. The origin of the retardation of RAFT polymerization at a very low concentration of the initiator is indeed the subject of a scientific debate where two main explanations are put forward. One explanation assumes that the intermediate radicals undergo slow fragmentation [35–38]. The other is based on termination reactions of intermediate radicals, which reduce the total number of radicals in the polymerization medium [39–41]. According to the second assumption, such termination reactions would give rise to the formation of three-armed star macromolecules with a large molecular weight.

Generally, RAFT proceeds at a lower rate compared with conventional free-radical polymerization, and consequently experiments are carried out at a high monomer concentration or even in a bulk. However, high concentrations lead to an increase in viscosity, especially at a high conversion. Moreover, considering the synthesis of block copolymers with a bottle-brush structure via a “grafting through” RAFT, the viscosity related to the use of a macro-RAFT agent is known to be very problematic. In order to study the effect of the con-

centration of the monomer, RAFT polymerization of LMA in the bulk and in DO was done in the same conditions (Fig. 4). The rate of polymerization in the bulk was rather high, giving an over 75% conversion of the monomer within 1 h. Control of the process was sufficient up to the monomer conversion of ca 90% (during 2 h) which was evidenced by linearity in the semilogarithmic coordinates. The rate of RAFT polymerization in DO was apparently lower, and the linearity in semilogarithmic coordinates showed good control over the process up to a 70% monomer conversion (during 7 h). SEC measurements confirmed the effectiveness of the RAFT polymerization of LMA both in bulk and DO (Table 1).

Generally, dilution favours intramolecular reactions (like fragmentation) against intermolecular reactions (like termination) [40] which could explain better control of the process [41]. This observation also reflects a more homogeneous growth of the polymer chains related to the decrease in viscosity. However, if the medium is too diluted, a loss of molecular weight control is observed at high conversions [41].

The molecular weight (MW) of PLMA was estimated by several methods including SEC calibrated using polystyrene standards, and end-group analysis by ¹H NMR and UV-Vis.

Table 1. RAFT polymerization of LMA at different ratios of the monomer, initiator and MCPDB. [M] = 1.7 mol/l, T = 80 °C, t = 7 h

| No. | [LMA] / [AIBN] | [CTA] / [AIBN] | Conv. % | $M_n \cdot 10^{-3}$ (SEC) | $M_n \cdot 10^{-3}$ (UV) | $M_n \cdot 10^{-3}$ (NMR) | $M_n \cdot 10^{-3}$ (Calc)* | M_w / M_n | DP (NMR) |
|-----|----------------|----------------|---------|---------------------------|--------------------------|---------------------------|-----------------------------|-------------|----------|
| 1 | 300 | 4 | 78 | 15.0 | 9.3 | 15.2 | 10.2 | 1.08 | 60 |
| 2 | 600 | 2.5 | 55 | 25.5 | 28.2 | 31.1 | 34.0 | 1.19 | 122 |
| 3** | 600 | 2.5 | 95 | 49.2 | 62.6 | 66.0 | 58.0 | 1.08 | 260 |

* Theoretical number – the average molecular weight, $M_n(\text{Calc}) = \frac{[\text{LMA}]}{[\text{MCPDB}]} \cdot q \cdot M_{\text{LMA}} + M_{\text{MCPDB}}$;

[LMA] and [MCPDB] are initial molar concentrations of LMA and MCPDB, respectively;

M_{LMA} (254) and M_{MCPDB} (330) are molecular weights of LMA and MCPDB, respectively;

q is conversion of the monomer, mol. p.;

** in bulk.

The presence of dithiobenzoate end groups introduced by the RAFT process from MCPDB allowed determination of the degree of polymerization of PLMA using UV-Vis and ^1H NMR spectroscopy. Generally, dithiobenzoate compounds of the $\text{ArC}(=\text{S})\text{S}-$ structure show a distinct absorption at $\lambda = 520$ nm. The absorption of PLMA solution at that wavelength was used to calculate M_n . Despite weak signals of the *ortho*-aromatic protons of dithiobenzoate at 7.9 ppm, calculation of number-average molecular weight M_n of PLMA was possible by comparing the intensity of this signal with the intensity of the signal at 3.9 ppm, which belongs to protons from the oxymethylene groups of LMA. However, this method for estimating the molecular weight of PLMA is not very accurate, and a certain error is incurred due to the large difference in integrated areas of *ortho*-aromatic protons of dithiobenzoate and protons from the oxymethylene groups of LMA.

It is obvious that MW determined by SEC yields only apparent values because of a significant difference in hydrodynamic volume between linear polystyrene standards and a compact PLMA brush. Nevertheless, the agreement among MW values estimated by various methods is rather good. The entries for M_w / M_n given in Table 1 are estimated from the SEC analysis and show a very low polydispersity of the polymers.

Three PLMA samples, with the characteristics listed in Table 1 are used as macro-CTA in the synthesis of PLMA-*b*-PPEO₅MEMA diblock copolymers.

RAFT polymerization of PEO_xMEMA using PLMA as a macro-CTA

In the next stage, an attempt was made to prepare diblock copolymers by the RAFT polymerization of PEO₅MEMA or PEO₄₅MEMA from PLMA as a macro-CTA. There are very few papers focused on the synthesis of amphiphilic diblock copolymers containing PEO side chains by the RAFT method. Using polystyrene as a macro-CTA, amphiphilic copolymers containing poly(ethylene oxide) methyl ether acrylate block (PPEO₁₂MEA or PPEO₄₅MEA) have been successfully synthesized [42]. In the presence of poly(butyl acrylate) (PBA) as a macro-CTA, amphiphilic diblock copolymers with shorter PEO side chains (PBA)₈₁-*b*-(PPEO₉MEA)₉₅ and

(PBA)₉₅-*b*-(PPEO₉MEA)₄₂ were prepared [43]. The synthesis of (PPEO₉MEMA)₁₆₀-*b*-(PBA)₆₂ was successful under heterogeneous conditions in water [44].

Several well-defined PLMA-*b*-PPEO₅MEMA diblock copolymers were successfully prepared and characterized in the present study (Table 2). RAFT polymerization of PEO₅MEMA in the presence of PLMA as a macro-CTA was very sensitive to the reaction conditions, and insoluble cross-linked gels were easily formed. This may be related to the high tendency of chain transfer to $-\text{CH}_2-\text{CH}_2\text{O}-$, which leads to the formation of cross-linked gels at relatively low conversions [45]. Conventional free-radical polymerization of PEO₅MEMA macromonomers is known to yield similar gels unless chain-transfer agents are used [46]. The use of an effective chain transfer agent was found to be one of the ways to control gelation [46, 47]. In the RAFT polymerization, the role of such chain transfer agent could be played by derivatives containing dithiobenzoate. Unfortunately, the use of RAFT CTA was not sufficient to avoid gelation. Dilution of the reaction mixture by toluene (runs 2–4) helped to decrease the viscosity of the reaction mixture and to obtain soluble diblock copolymers PLMA-*b*-PPEO₅MEMA. The length of the second block was well predetermined by the ratio of the macromonomer to macro-CTA, if the first block was short ((PLMA)₆₀, Table 2, run 2). The use of a longer block of PLMA ((PLMA)₁₂₂, Table 2, runs 3, 4) resulted in a block of PPEO₅MEMA 1.5–2 times longer than expected. The longer chains formed during controlled radical polymerization, as compared with the calculated values, give a message that the ratio of the macromonomer to macro-CTA is changed, i. e. PLMA as a macro-CTA is partly inactivated. The longest PLMA used as a macro-CTA ((PLMA)₂₆₀) showed a good livingness, and the length of the block of PPEO₅MEMA was close to the expected value (at a low ratio of the macromonomer to macro-CTA, Table 2, run 5) or shorter (at a high ratio of the macromonomer to macro-CTA, Table 2, run 6).

In order to follow the evolution of molecular weights (MW) under the growth of the second block, samples of diblock copolymers were analyzed by SEC in THF. We are aware that the results of analyses with RI detection or evaporative light scattering detection should be taken with caution be-

Table 2. Characteristics of diblock copolymers PLMA-*b*-PPEO_xMEMA synthesized from PLMA macroinitiators. [PEO_xMEMA] = 18% (in toluene), T = 80 °C, t = 6 h

| No. | [PEO _x MEMA] / [AIBN] | [PLMA] / [AIBN] | [AIBN] 10 ⁶ , mol | Conv., % | $M_n \cdot 10^{-3}$ (SEC) | $M_n \cdot 10^{-3}$ (NMR) | M_w / M_n | Block copolymer |
|-----|----------------------------------|-----------------|------------------------------|----------|---------------------------|---------------------------|-------------|---|
| 1* | 300 | 3 | 9.7 | gel | – | – | – | (PLMA) ₆₀ - <i>b</i> -(PPEO ₅ MEMA) _x |
| 2 | 300 | 3 | 9.7 | 82 | 31.1 | 36.3 | 1.10 | (PLMA) ₆₀ - <i>b</i> -(PPEO ₅ MEMA) ₆₇ |
| 3 | 1 800 | 2 | 45 | 53 | 308 | 324 | 1.20 | (PLMA) ₁₂₂ - <i>b</i> -(PPEO ₅ MEMA) ₉₇₀ |
| 4 | 2 500 | 4 | 1.4 | 74 | 245 | 263 | 1.19 | (PLMA) ₁₂₂ - <i>b</i> -(PPEO ₅ MEMA) ₇₇₆ |
| 5 | 200 | 2 | 9.5 | 88 | 88 | 89 | 1.29 | (PLMA) ₂₆₀ - <i>b</i> -(PPEO ₅ MEMA) ₇₇ |
| 6 | 2 000 | 2 | 9.5 | 95 | 144 | 142 | 1.28 | (PLMA) ₂₆₀ - <i>b</i> -(PPEO ₅ MEMA) ₂₅₄ |
| 7 | 300 | 4 | 1.6 | 0 | 62 | 68 | 1.14 | (PLMA) ₂₆₀ |

* [PEO_xMEMA] = 26%.

cause of linear polystyrene standards used for calibration of the equipment, which can give an inadequate estimation of the molecular parameters of comb-shaped copolymers. Consequently, the obtained values of MW are only apparent. Nevertheless, the good agreement between the values of MW of diblock copolymers, obtained by ^1H NMR and SEC (Table 2, runs 2, 3, 5, 6), indicates that the relative values of MW are not far from the absolute ones.

Finally, an attempt was made to synthesize well-defined diblock copolymers containing longer PEO side chains at the hydrophilic block. To this end, $\text{PEO}_{45}\text{MEMA}$ was used instead of PEO_5MEMA for the construction of the second block (Table 2, run 7). PEO_5MEMA and $\text{PEO}_{45}\text{MEMA}$ are the macromonomers differing in the length of the PEO chain only, but the activity of $\text{PEO}_{45}\text{MEMA}$ is usually lower, mainly due to steric effects [48, 49]. An attempt to prepare diblock copolymers $\text{PLMA-}b\text{-PPEO}_{45}\text{MEMA}$ was unsuccessful. SEC traces of the reaction mixture containing PLMA as a macro-CTA, $\text{PEO}_{45}\text{MEMA}$ and AIBN remained identical after 2 and 4 hours, showing the peaks attributed to PLMA and $\text{PEO}_{45}\text{MEMA}$ only, even at a relatively high AIBN concentration. This result could be related to the lower stabilization of the radical corresponding to LMA compared to that corresponding to $\text{PEO}_{45}\text{MEMA}$. As a consequence, fragmentation of the intermediate radical formed at the junction of the two blocks was slightly disfavoured towards the release of the PLMA macroradical and hence towards the formation of the block copolymer chains, whereas the growth of the parallel $\text{PPEO}_{45}\text{MEMA}$ homopolymer chains was favoured [50]. In our case, even homopolymerization of $\text{PEO}_{45}\text{MEMA}$ failed. This phenomenon is not yet clear and requires further analysis. One of the possible explanations is related to a different solubility of PLMA and $\text{PPEO}_{45}\text{MEMA}$ blocks in various solvents. Because of different solubility, the growth of the second block occurs under heterogeneous conditions in many solvents including toluene, THF, DO and even DO / water. After polymerization in toluene, the solution was homogeneous but cloudy; in all other cases the reaction medium before, during and after polymerization was heterogeneous. An alternative explanation of the failed reaction is related to an increase in the polarity of the medium. The dielectric constant of DO is 2.21 and of toluene 2.38, that of ethylene glycol being 34.5 and of water 78.3 [51]. The presence of PEO chains in the polymerization medium increases the dielectric permeability of the solution, which could have a direct effect on the solubility of PLMA.

The aggregation behaviour of the amphiphilic $\text{PLMA-}b\text{-PPEO}_5\text{MEMA}$ diblock copolymers in solutions of different polarity was evidenced by comparing their ^1H NMR spectra in CDCl_3 and D_2O (Fig. 5). The samples were allowed to equilibrate for 5 h at 40°C before measurements. The spectrum in CDCl_3 contains several sharp signals at 0.85–2.1 ppm, which belong to the protons of methyl- and methylene groups of the PLMA block; this block is well-solvated by CDCl_3 . These signals become remarkably weaker and broadened in D_2O

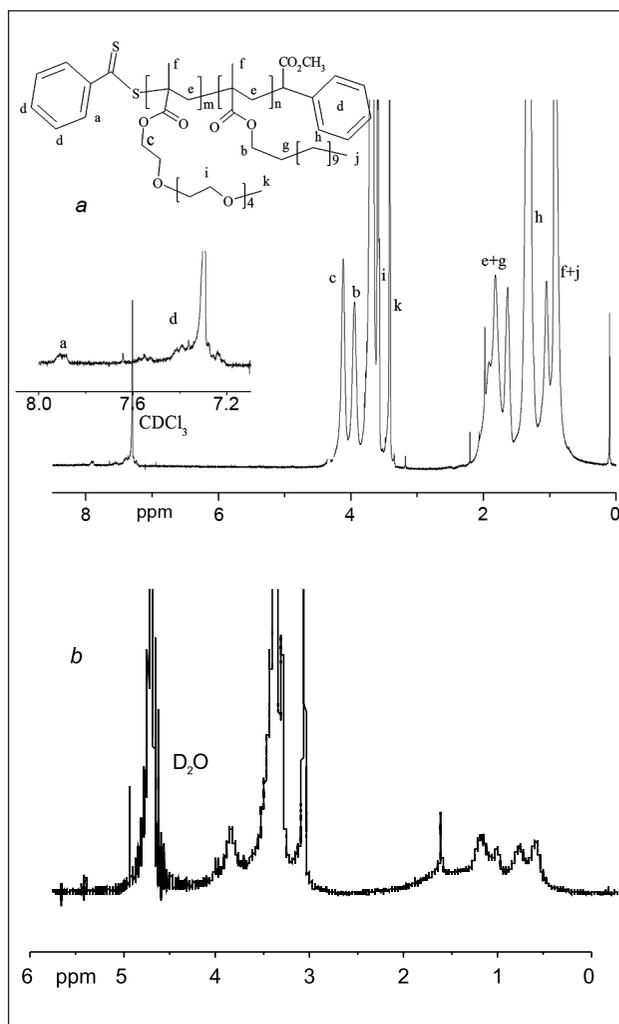


Fig. 5. ^1H NMR spectrum of $(\text{PLMA})_{60}\text{-}b\text{-(PPEO}_5\text{MEMA)}_{67}$ in CDCl_3 (a) in D_2O (b)

where the corresponding protons are poorly solvated and less mobile. The strongest signals in the spectrum in D_2O at 3.6 and 3.3 ppm belong to oxymethylene and oxymethyl groups of PEO, respectively, which are affinity to water. These data imply the formation of micelle-like aggregates in water, with PLMA presumably forming the hydrophobic core and PEO the hydrophilic corona.

CONCLUSIONS

Polymerization of lauryl methacrylate (LMA) in the presence of *S*-methoxycarbonyl phenylmethyl dithiobenzoate (MCPDB) as a RAFT CTA at the ratio $[\text{MCPDB}] : [\text{AIBN}] = 4$ showed characteristics of a controlled radical polymerization. The optimal ratio $[\text{MCPDB}] / [\text{AIBN}]$ depended on the ratio $[\text{LMA}] / [\text{AIBN}]$ being lower at a lower concentration of the initiator. PLMA with a low polydispersity ($M_w / M_n = 1.08\text{--}1.19$) and a relatively high molecular weight (M_n up to 60 000, degree of polymerization up to 260) was synthesized and used as a macro-CTA for the synthesis of amphiphilic diblock copolymers. Several diblock copolymers

(PLMA-*b*-PPEO₅MEMA) with various lengths of the blocks and a high molecular weight (M_n up to 300 000) were prepared and characterized. RAFT polymerization of PEO₄₅MEMA from PLMA as a macro-CTA failed.

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**AMFIFILINIŲ DIBLOKKOPOLIMERŲ ŠEPEČIŲ
SINTEZĖ VYKDANT NUOSEKLIĄ LAURILMETAKRI-
LATO IR PEO GRUPĘ TURINČIO MAKROMONOME-
RO RAFT POLIMERIZACIJĄ**

Santrauka

Siekiant gauti kontroliuojamos struktūros amfifilinius diblokko-polimerus, buvo vykdoma nuosekli laurilmetakrilato (LMA) ir poli(etilenoksido) metiletermetakrilato polimerizacija grįžtamojo jungimosi–fragmentacijos grandinės perdavos (RAFT) metodu, RAFT grandinės perdavos agentu naudojant S-metoksikarbonilfenilmetilditiobenzoatą (MCPDB). PLMA ir kopolimerų PLMA-*b*-PPEO₅MEMA

molekulinė masė buvo įvertinta keletu metodų, tarp jų molekulinų sietų chromatografija, kolonėlių kalibravimui naudojant polistireno standartus, ir atliekant galinių grupių analizę ¹H BMR ir UV-regimosios šviesos spektroskopija. Polimerizacijos kinetika buvo sekama ¹H BMR spektroskopijos metodu, lyginant signalus, priskirtus monomerui ir to paties monomero grandims PLMA. LMA polimerizacija, kai [MCPDP] : [AIBN] = 4, rodė kontroliuojamos radikalinės polimerizacijos požymius, ir susintetinto PLMA polidispersiškumas buvo mažas ($M_w / M_n = 1,08-1,19$), o molekulinė masė santykinai didelė (M_n iki 60 000, polimerizacijos laipsnis iki 260). Susintetinta ir apibūdinta keletas didelės molekulinės masės (M_n iki 300 000) diblokopolimerų PLMA-*b*-PPEO₅MEMA, besiskiriančių blokų ilgiu. PEO₄₅MEMA RAFT polimerizacija, PLMA naudojant kaip makroRAFT agentą, nevyko.