Synthesis and Characterization of Pentablock Copolymers Based on Pluronic® L64 and Poly(methyl methacrylate)[1]

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Abstract—The synthesis and characterization of amphiphilic pentablock copolymers based on Pluronic® L64 (PEO_{13}-PPO_{30}-PEO_{13}) and poly(methyl methacrylate) (PMMA), synthesized via atom transfer radical polymerization (ATRP) is reported. The L64 is first transformed into a bifunctional ATRP macroinitiator which was subsequently chain extended with MMA by ATRP to afford PMMA-*b*-L64-*b*-PMMA pentablock copolymers. The chemical structure of the synthesized amphiphilic block copolymers is characterized by FTIR, ^1H NMR spectroscopy, and gel permeation chromatography (GPC). The GPC profiles of the block copolymers clearly show an increase in molar mass after the ATRP of MMA and monomodal molecular weight distributions for all the samples. Finally, preliminary studies on their aggregation behavior in aqueous solution have also been investigated by measuring the scattering light intensity as function of block copolymer concentration to estimate the critical aggregation concentration (CAC). The CAC decreases with increasing of hydrophobic content in copolymer, i.e., ~25 and ~15 mg/mL, respectively, is estimated for the pure L64 and $PMMA_{13}$-*b*-L64-*b*-$PMMA_{13}$. Further, with increase in temperature, the CAC is found to decrease that is attributed to the dehydration of the PEO segments at higher temperatures.

INTRODUCTION

Pluronic® block copolymers are commercially available nonionic amphiphilic triblock copolymers consisting of hydrophobic poly(propylene oxide) (PPO) in the middle and hydrophilic poly(ethylene oxide) (PEO) as the terminal blocks. Because of their high biocompatibility and nontoxicity, pluronics block copolymers have been widely studied for biomedical applications, such as drug delivery [1], gene therapy and vaccination [2–13] to name a few. The weak hydrophobicity of PPO block is responsible for high CMC values which circumscribes their applications. So when introduced into blood these micelles are easily smashed. Thus, to tune the self-assembly behavior and enhance their properties and applications, pluronic block copolymers have been modified with various polymers, including star-like PMMA [14], poly(*N*-isopropylacrylamide) [15, 16], poly(acrylic acid) [2, 16, 17], poly(lactic acid) [18–

21], poly[(diethylamino)ethyl methacrylate] [22, 23], poly(ε-caprolactone) [24–26], poly (vinyl pyrrolidone) [27] and poly(octafluoropentyl methacrylate) [28].

In the current study, the Pluronic® L64 (PEO_{13}-PPO_{30}-PEO_{13}) has been transformed into pentablock copolymers of various compositions by chain extension with methyl methacrylate (MMA) through atom transfer radical polymerizations (ATRP). ATRP, the so-called "controlled" radical polymerization, is based on the dynamic equilibrium between the active species (growing chains) and the dormant species (inactive adducts) catalyzed by transition metal complexes, such as CuCl/bipyridine and etc. [29]. ATRP was selected due to its wide applicability to a wide array of vinyl type monomers, requirement of less vigorous experimental conditions and its effectiveness in controlling molecular weights [30–37]. To achieve the desired block copolymers by ATRP, L64 was first converted into a bifunctional ATRP macroinitiator which subsequently yielded PMMA-*b*-L64-*b*-PMMA pentablock copolymers by ATRP of MMA. The reason for the selection of MMA is that it is bio-

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compatible and hydrophobic in nature, which will influence the aggregation behavior of the block copolymer in solution. Finally, the solution properties of the synthesized block copolymers in aqueous solution were investigated by measuring the light scattering intensity as function of block copolymer concentration.

EXPERIMENTAL

Reagents

Pluronic® block copolymer (L64), α-bromoisobutyryl bromide (98%) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Methyl methacrylate (99%) was obtained from Merck and before use, the inhibitor was removed through alumina column. Cuprous chloride (98%, International Laboratory, USA) and 2,2-bipyridine (98%, Riedel-De-Haen) were used as received. Triethylamine (90%, Daejung Germany) was dried by refluxing over potassium hydroxide for 3 hours and distillation (65−67°C) and stored over molecular sieves. L64 was dried before use in vacuum oven at 50°C overnight, while the THF was dried by refluxing with benzophenone and sodium metal until purple color persisted followed by distillation (65−67°C).

Conversion of L64 into ATRP Macroinitiator

L64 was transformed into ATRP macroinitiator (Scheme) by reacting L64 (4 mmol with respect to hydroxyl functionality) with α-bromoisobutyryl bromide (24.8 mmol) in the presence of triethylamine (16.6 mmol) as a catalyst in THF (50 mL). Initially, L64 was dissolved in THF followed by the addition of triethylamine. The solution was cooled using ice/sodium chloride mixture. Subsequently, α-bromoisobutyryl bromide was added dropwise under argon atmosphere and the temperature was allowed to rise to room temperature. The reaction was carried out at room temperature for 12 hours with continuous stirring. The reaction solution was filtered and washed with THF to remove triethylammonium bromide precipitate. Further purification was carried out as: 3 g charcoal was added to the filtrate and stirred it for 2 h, dried over magnesium sulfate [38]. The solution was filtered and THF was evaporated. The product was recovered after washing three times with n-hexane and drying under vacuum overnight at 50°C.

Synthesis of PMMA-b-PEO-b-PPO-b-PEO-b-PMMA Pentablock Copolymers

The synthesis of the intended block copolymers was carried out by ATRP of MMA using the synthesized L64 based bifunctional macroinitiator, employing CuCl/2,2-bipyridine as catalyst system at 60°C in THF as illustrated in Scheme. In a typical experiment, macroinitiator (0.2 mmol), MMA (7.5 mmol) and 4 mL THF were taken in a Schlenk tube. The air was removed from the reaction mixture and replaced with an inter environment by bubbling argon through it for at least 30 min, followed by the addition of 2,2-bipyridine and then CuCl (molar ratio 3 : 1). The reaction was carried out at 60°C for a specified time. The reaction was stopped by exposing the reaction mixture to air and stirring at room temperature, followed by filtration to remove the copper catalyst. Before further purification, after passing through the alumina column, all the solvent and the unreacted monomers were evaporated by rotary evaporator for gravimetric analysis to estimate composition of the synthesized block copolymers. Purification was carried out by passing the THF solution of the product through alumina column to remove the remaining copper catalyst and the blue color. The solution was concentrated by evaporating most of the THF using rotary evaporator and the product was recovered by precipitation in n-hexane and drying under vacuum at 50°C overnight. To achieve block copolymers of various compositions, the ATRP was carried out by keeping the amount of macroinitiator fixed and varying the amount of MMA in the feed.

Preparation of Aqueous Solutions

L64 is soluble in water while the respective pentablock copolymers, because of the increased hydrophobicity, could not be dissolved directly in water. The solubility depends on length of the hydrophobic chain, smaller the chain length of the hydrophobic block, easier will be the solubility in water, and vice versa. Therefore, aqueous solutions of the pentablock copolymers were prepared as: the block copolymer was dissolved in small amount of THF, followed by drop wise addition of water. THF was allowed to evaporate at room temperature from the stirring solution that gave stock cloudy aqueous solution (with some sedimentation) of the block copolymer, which was diluted to a series of various concentrations and filtered before analysis.

PMMA-*b*-L64-*b*-PMMA
Scheme 1.
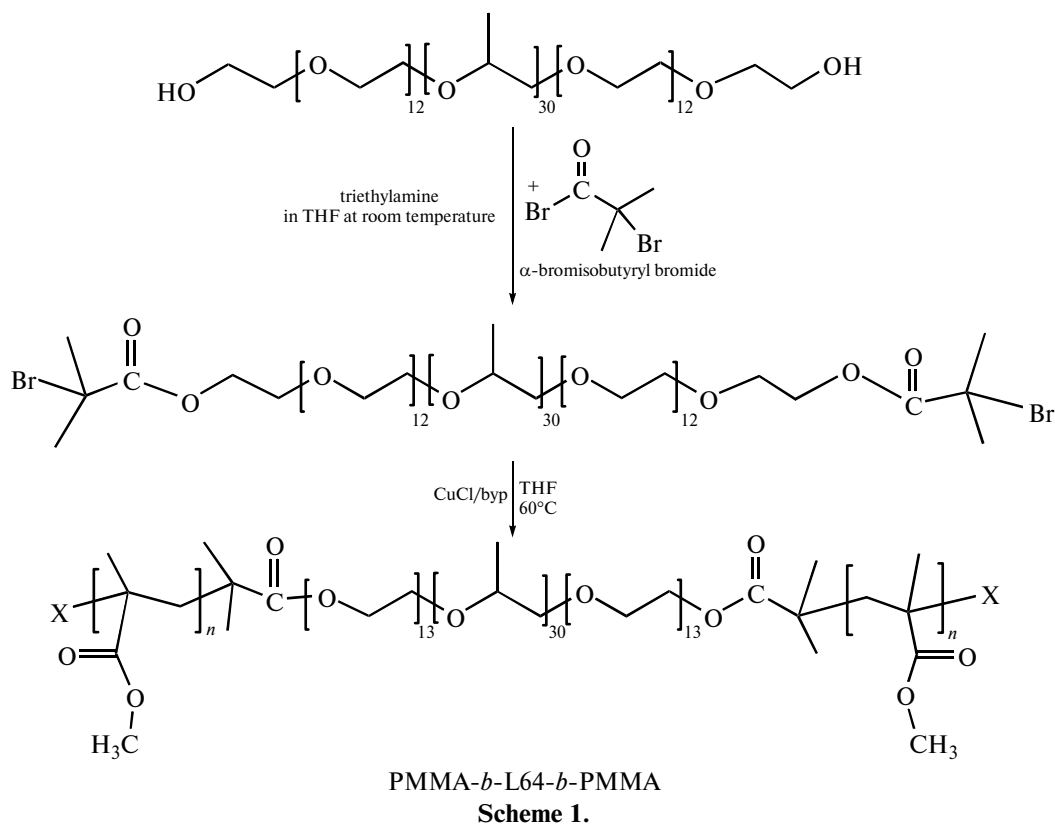
Characterization Techniques

^{1}H NMR spectra were acquired in *d*-chloroform on a Bruker Advance Digital 300 MHz spectrophotometer. FTIR spectrometer Nicolet[TM] 6700, Thermo Scientific U.S. was used for the analysis of the functional groups of the synthesized materials. The molar mass and molar mass distribution (polydispersity index, M_w/M_n, where the M_w and M_n is the weight average and number average molar mass, respectively) of the block copolymer was determined by gel permeation chromatography (GPC) on a Viscotek GPCmax VE2001 module system coupled with a Viscotek TDA302 (triple detector array) system using the polystyrene standards for conventional calibration in HPLC grade THF at 35°C. The flow rate was 1 mL/min and injection volume was 100 μL. A Brookhaven TMC350 laser scattering system, equipped with a power adjustable vertically polarized 350 mW argon ion laser of wavelength 637 nm, was used for measuring the scattering intensity of the block copolymer solutions as function of block copolymer concentrations.

RESULTS AND DISCUSSION

The amphiphilic block copolymers PMMA-*b*-L64-*b*-PMMA of various compositions were synthesized via atom transfer radical polymerization (ATRP) by using Pluronic® L64 as bifunctional macroinitiator, CuCl/2,2-bipyridine as the catalyst system as described in detail in the Experimental section above. The structure of the synthesized block copolymers and molecular weights were characterized by ^{1}H NMR, FTIR spectroscopy, and gel permeation chromatography (GPC).

Figure 1 depicts the ^{1}H NMR spectrum of L64 based bifunctional macroinitiator in *d*-chloroform. Characteristic signals due to PPO and PEO could be seen at $\delta_H \sim 1.07$ ppm *a* (CH$_3$ of PPO) and 3.3–3.7 ppm *c* (combined signals due to −OCH$_2$−CH$_2$− and −OCH−CH$_2$ of PEO and PPO, respectively). The peak at $\delta \sim 1.9$ *b* and 4.3 ppm *d* are attributed to the terminal methyl protons of Br−C−(CH$_3$)$_2$, and methylene protons attached next to the ester linkage, respectively. The presence of *b* and *d* signals clearly confirms the successful conversion of L64 into macroinitiator. Further verification of the successful transformation of L64 into macroinitiator was achieved by FTIR spectroscopy.

Figure 2a shows the FTIR spectrum of pure L64, where characteristic broad signal at ~3476 cm^{-1}, due to the terminal hydroxyl (O−H) stretching, peaks in the range ~2700 to 3000 cm^{-1}, due to methylene stretching, and an intense peak centered at 1088 cm^{-1}, due to C−O−C ether stretching, could be seen. On treating with α-bromoisobutyryl bromide, as shown in
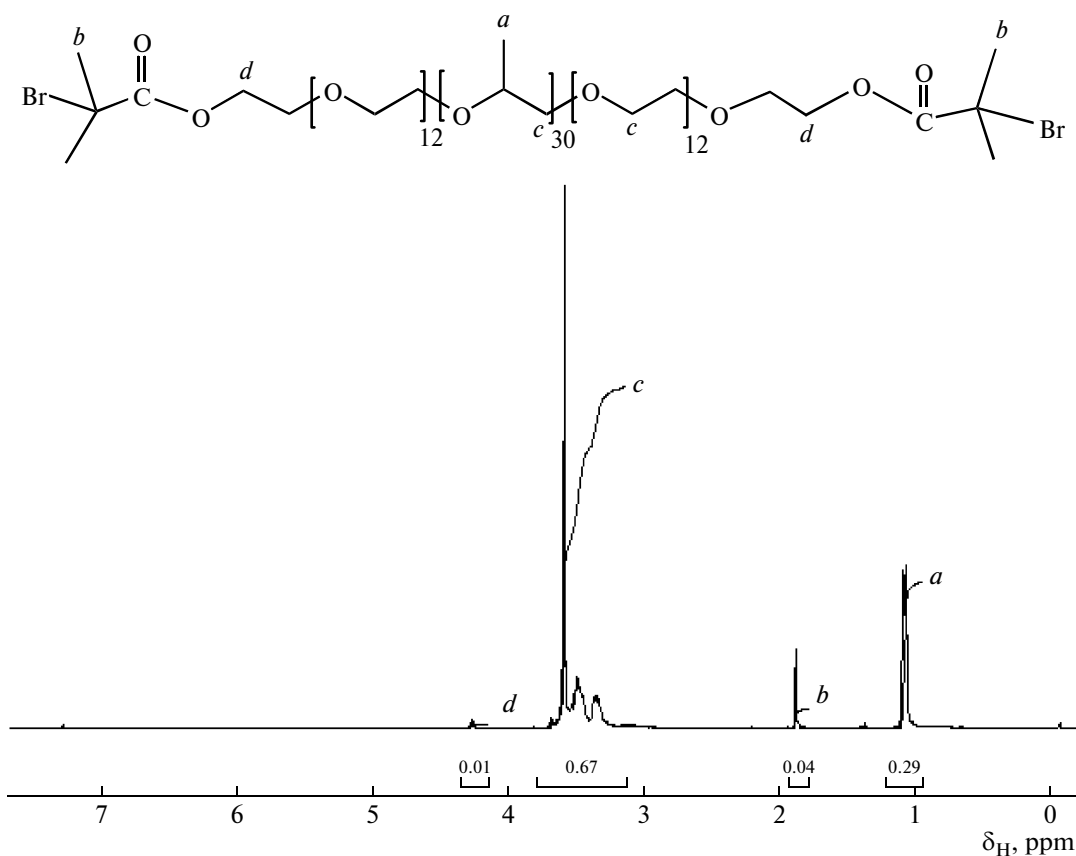
Fig. 1. ^{1}H NMR spectrum of L64 based bifunctional macroinitiator. The chemical structure and assignment of the respective ^{1}H NMR peaks of the L64 based bifunctional ATRP macroinitiator are shown at the top.

Fig. 2b, the OH stretching peak disappeared, while new signals appeared at 1731 and 628 cm^{-1}, respectively, due to the carbonyl group of the terminal ester linkages, and C−Br of the resultant macroinitiator, indicating successful formation of the macroinitiator.

Figure 3 is the representative ^{1}H NMR spectrum of PMMA-*b*-L64-*b*-PMMA, synthesized via ATRP of MMA, employing the synthesized L64-based bifunc-

tional macroinitiator. The ^{1}H NMR spectrum shows characteristic signals from all blocks in the synthesized block copolymer. The signals *a* and *c*, as discussed earlier, correspond, respectively, to (−CH$_3$ of PPO) and −OCH$_2$−CH$_2$−/−OCH−CH$_2$ of PEO/PPO segments. The signals *b*, *d*, and *e* are, respectively, from methyl (−CH$_3$), methylene (−CH$_2$−), and methoxy (−OCH$_3$) protons of the PMMA segments in the syn-

Synthesis parameters and characteristic data of the block copolymers

| Sample	[M] : [I] : CuCl : byp^a	Reaction duration, hours	Conversion^b, %	M_n^c, g/mol	M_n^d, g/mol	M_w/M_n^e
Macroinitiator	−	12	−		1800	1.3
PMMA$_9$-*b*-L64-*b*-PMMA$_9$	50 : 1 : 1 : 3	6	36	8000	3000	1.4
PMMA$_{13}$-*b*-L64-*b*-PMMA$_{13}$	60 : 1 : 1 : 3	6	43	17000	3800	1.4
PMMA$_{24}$-*b*-L64-*b*-PMMA$_{24}$	70 : 1 : 1 : 3	6	69	26000	4200	1.6

Where the subscript to PMMA represents the degree of polymerization of PMMA as calculated from conversion (%) of MMA into PMMA estimated by gravimetric analysis, ^{a}feed molar ratio of monomer [M], initiator [I], CuCl, and 2,2 bipyridine, ^{b}calculated from gravimetric analysis, ^{c}determined by ^{1}H NMR, ^{d}number average molar mass, and ^{e}polydispersity index obtained from GPC.

(a)

(b)
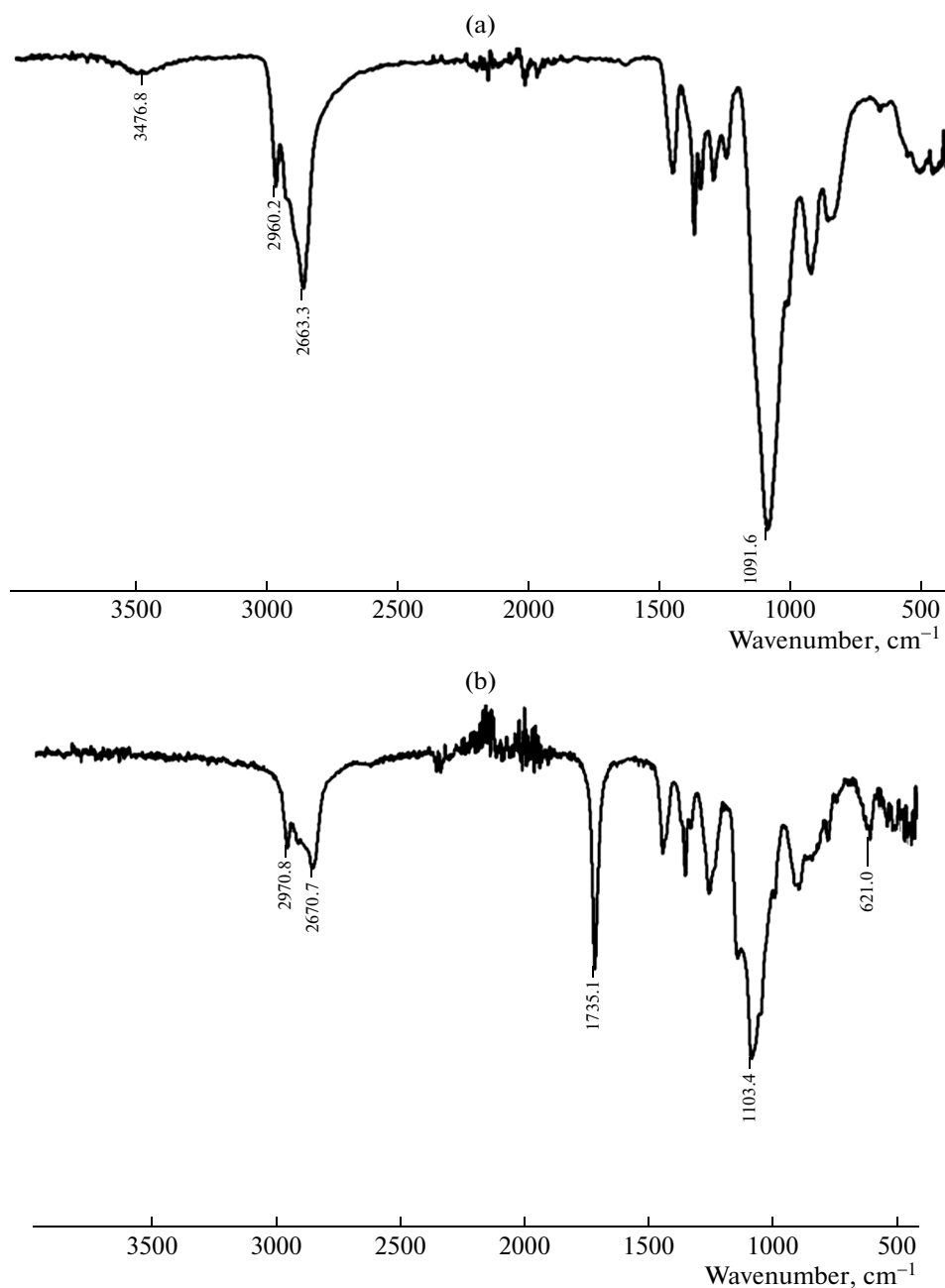
Fig. 2. FTIR spectra of (a) L64 and (b) L64 based bifunctional macroinitiator.

thesized block copolymer. The presence of ^{1}H NMR signals from both the L64 and PMMA segments in the spectrum verifies the successful synthesis of the PMMA-*b*-L64-*b*-PMMA pentablock copolymers. By comparing the integration values of signals *a* from L64 and *b* from PMMA segments, the number average molecular weights were calculated and tabulated in table. The values quite differ from the values determined by GPC and the reason could be the different hydrodynamic volumes of the block copolymers in THF solvent as compared with the PS standards used

in GPC calibration. Also, the presence of unreacted L64 in the macroinitiator would contribute to the very high values of the M_n (than the predicted values) estimated by the ^{1}H NMR spectroscopy and higher polydispersity values. The % conversion of monomer (MMA) into polymer was calculated after passing the solution through alumina column and the lower values of gravimetric conversion could be due to the loss of significant amount of sample in the purification column, therefore, the calculated DP values from gravimetric conversion values are underestimated.
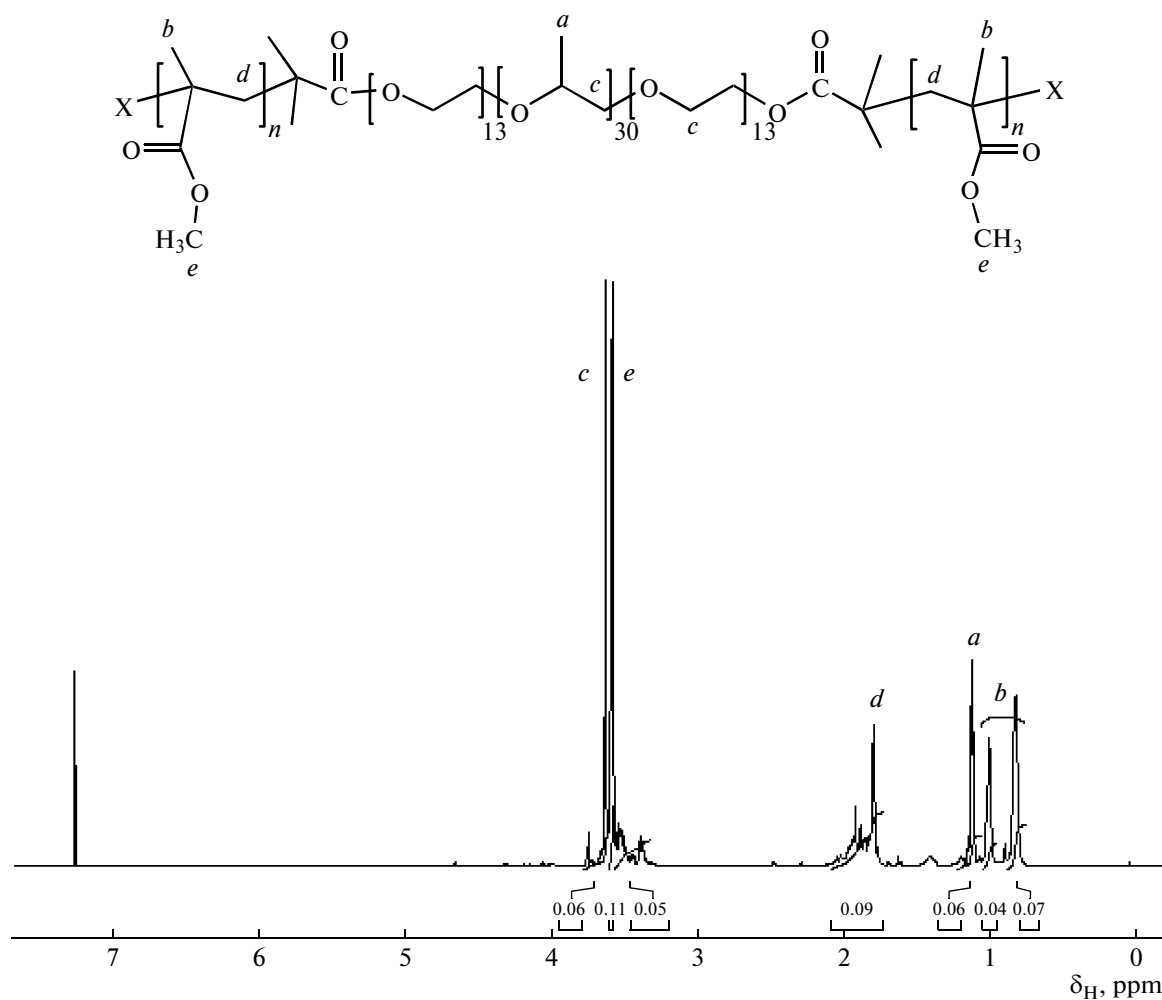
Fig. 3. ^{1}H NMR spectrum of PMMA-*b*-L64-*b*-PMMA pentablock copolymer, measured in *d*-chloroform. The chemical structure and assignment of the respective ^{1}H NMR peaks of the PMMA-*b*-L64-*b*-PMMA block copolymer are shown at the top.

Figure 4 depicts the representative FTIR spectrum of PMMA-*b*-L64-*b*-PMMA, where the intensity of the C=O peak has significantly increased after ATRP of MMA, as compared with the same signal in FTIR spectrum of the initiator (Fig. 2b). The characteristic peaks due to C=C stretching and H−C= bending of MMA monomer at ~1638−1675 and ~805 cm^{-1} [39−41] are absent at the FTIR spectrum shown in Fig. 4, which is another strong indication of the successful synthesis of the desired pentablock copolymers.

To determine the molar mass and molar mass distributions, the synthesized block copolymers were characterized by gel permeation chromatography (GPC). Figure 5 shows the GPC traces of the synthesized block copolymers and the L64-based macroinitiator measured in THF, where the data clearly reveal a decrease in elution volume (corresponding to the increased molar mass) of the synthesized block copolymers as compared with the macroinitiator, which

confirms the successful synthesis of the pentablock copolymers. In addition, the data show a monomodal molar mass distribution for all the samples, however, the polydispersity is relatively higher.

The light scattering intensity is very sensitive to size and concentration of the scattering particles in solution, thus, to find out the behavior of the synthesized block copolymers in solution, scattering light intensity was measured as function of copolymer concentration. Figure 6a depicts the plot of scattering intensity as function of L64 block copolymer concentration, measured at room temperature. The data reveal an initial small increase in scattering intensity with concentration, followed by an inflection point above which a sharp increase in scattering intensity could be seen. The data suggest the formation of aggregates by the block copolymer above the inflection point that leads to enhanced scattering intensity. A similar behavior was also observed for the respective block copolymer as shown in Fig. 6b, however, the inflection point is at
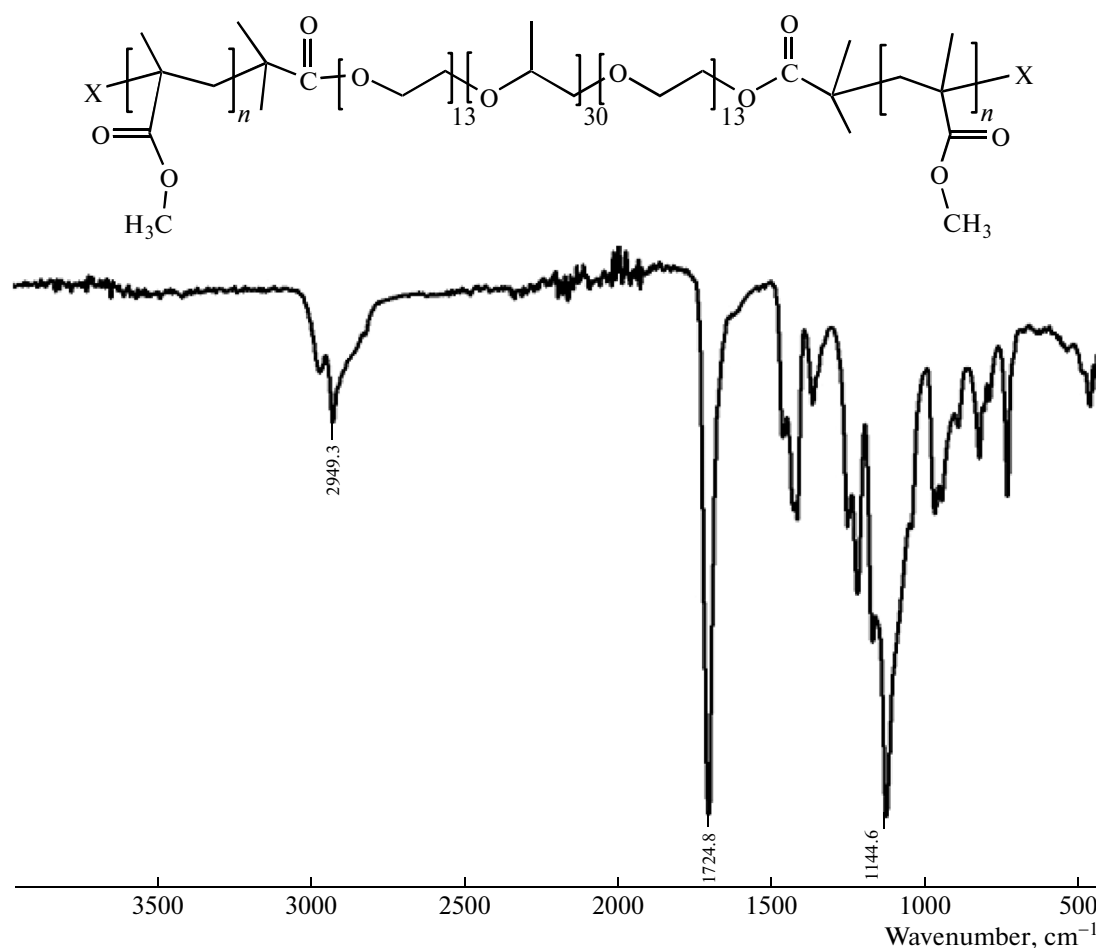
Fig. 4. FTIR spectrum of PMMA-*b*-L64-*b*-PMMA. Chemical structure of the PMMA-*b*-L64-*b*-PMMA is also given at the top.

lower concentration (~15 mg/mL) as compared with the pure L64 (~25 mg/mL), which could be attributed to the enhanced hydrophobicity due to the PMMA segments in the block copolymer. It is worth mentioning, that the synthesized PMMA-*b*-L64-*b*-PMMA block copolymers could not be dissolved directly in water, thus, a calculated amount of the block copolymer was first dissolved in THF, followed by the addition of calculated amount of water dropwise; the THF was allowed to evaporate at room temperature for 24 hours. The obtained stock solution was further diluted into a series of solutions of various concentrations, which were filtered through 0.45 μm syringe filter directly into the measuring cell.

The particle size distribution was also analyzed by dynamic light scattering above the inflection point concentrations of L64 and the respective pentablock copolymer. The data are depicted in Fig. 7. The data reveal the formation micelles by the L64 of ~9 nm in size (diameter), however, the pentablock copolymer was found to form larger aggregates of ~65 nm in diameter. After inserting PMMA segments into the L64, the hydrophobicity increases which leads to lower critical

aggregation concentration and further, the formation of larger aggregates by the pentablock copolymer. That could be attributed to the formation of intermicellar network due to the presence of terminal hydrophobic PMMA segments in the block copolymer as has been observed for other amphiphilic block copolymers with terminal hydrophobic blocks [42, 43].

The effect of temperature on the solution behavior of $PMMA_{13}$-*b*-L64-*b*-$PMMA_{13}$ was also investigated, which, as shown in Fig. 8, reveals the shift of the inflection point towards lower concentration with increase in temperature. This effect could be attributed to the thermosensitivity of PEO segments in the block copolymers. With increase in temperature the dehydration of PEO leads to the decreased solubility of the block copolymer and hence aggregation takes place at lower concentration. The thermosensitive behavior of the block copolymer shows that their self-assembly in aqueous solutions could be tuned by temperature.

Increase in molar mass
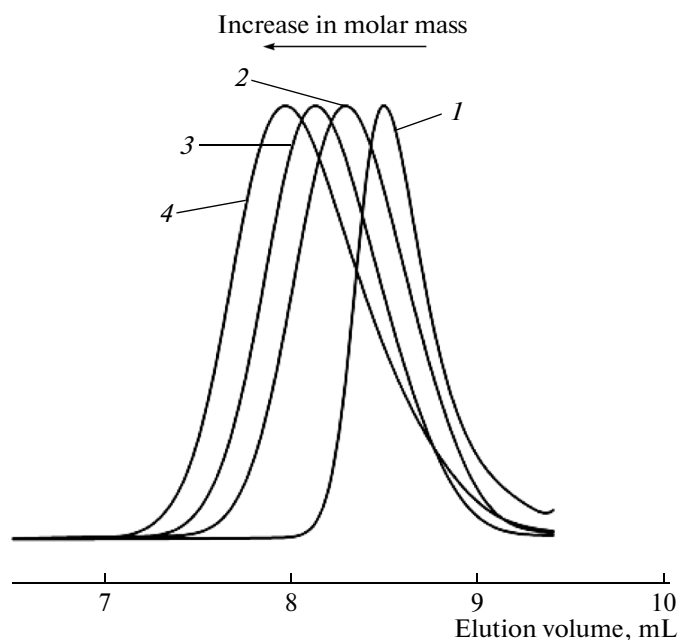
Fig. 5. Normalized GPC profiles of L64-based macroinitiator and the respective block copolymers with PMMA of various molar masses. (*1*) L64-based macroinitiator [M_n = 1800 g/mol, M_w/M_n = 1.3], (*2*) PMMA$_9$-*b*-L64-*b*-PMMA$_9$ [M_n = 3000 g/mol, M_w/M_n = 1.4], (*3*) PMMA$_{13}$-*b*-L64-*b*-PMMA$_{13}$ [M_n = 3800 g/mol, M_w/M_n = 1.4], (*4*) PMMA$_{24}$-*b*-L64-*b*-PMMA$_{24}$ [M_n = 4200 g/mol, M_w/M_n = 1.6].
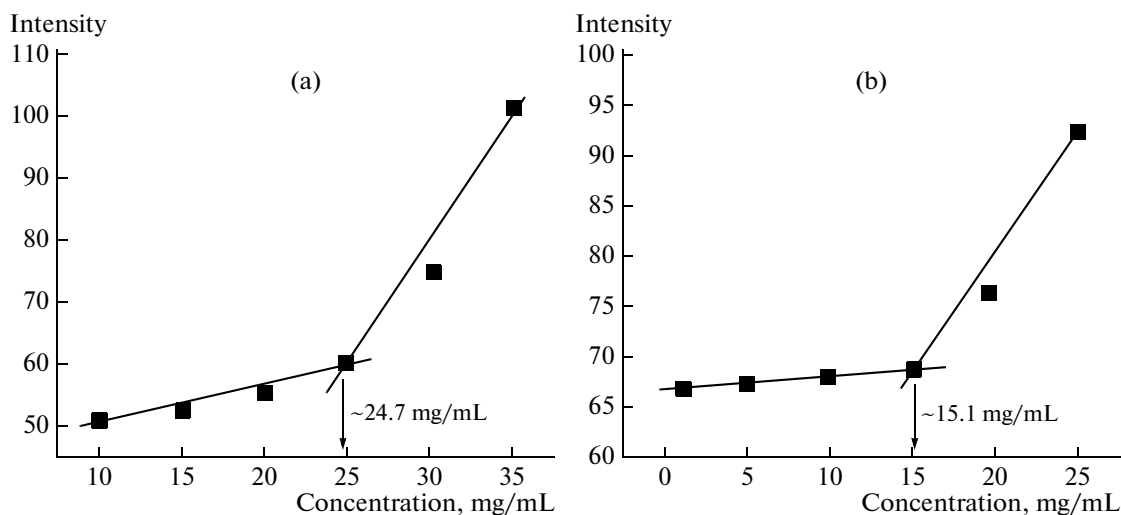

Fig. 6. Scattering light intensity as function of concentration of (a) L64 and (b) PMMA-*b*-L64-*b*-PMMA in aqueous solutions.

CONCLUSIONS

New pentablock copolymers of various compositions were successfully synthesized via atom transfer radical polymerization (ATRP) of methyl methacrylate while using the commercially available triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), PEO-*b*-PPO-*b*-

PPO)), namely L64 as the macroinitiator. The structure of the synthesized macroinitiator and the produced pentablock copolymers (PMMA-*b*-PEO-*b*-PPO-*b*-PEO-*b*-PMMA) was confirmed by ^{1}H NMR, and FTIR spectroscopy. The average molar masses and molar mass distribution were achieved by gel permeation chromatography, which revealed an increase
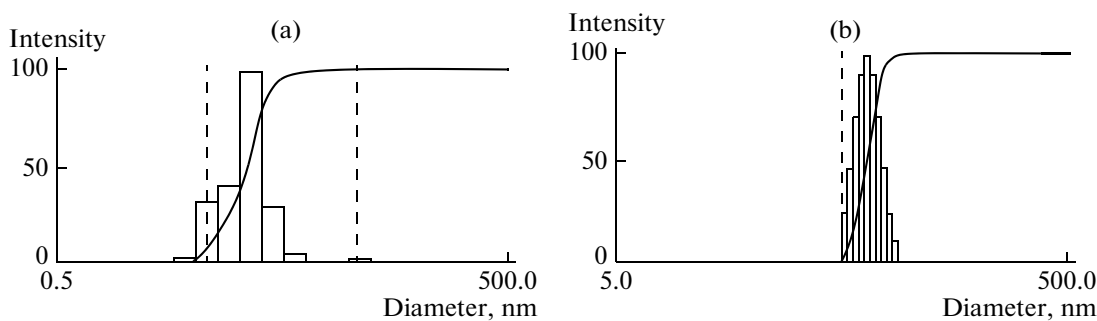
Fig. 7. Particle size distribution in aqueous solution for (a) L64 (mean diameter ~9 nm) and (b) the respective PMMA-*b*-L64-*b*-PMMA (mean diameter ~65 nm) at room temperature.
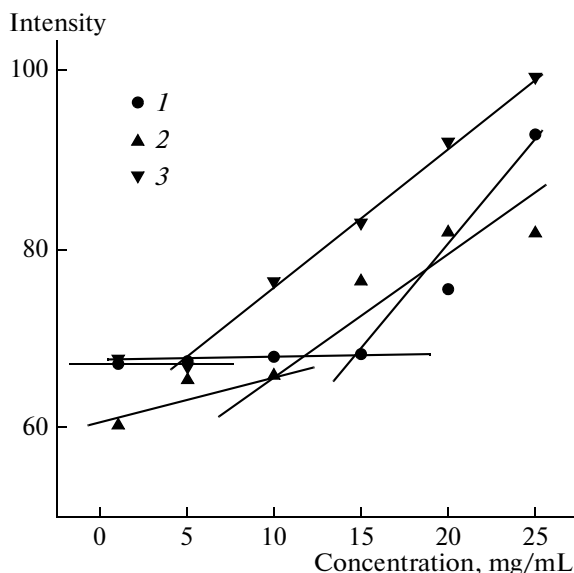
Fig. 8. Effect of temperature on the aggregation behavior of PMMA$_{13}$-*b*-L64-*b*-PMMA$_{13}$ in aqueous solution. $T = (1)$ 25, (2) 30, and (3) 35°C.

in molar mass after the ATRP of MMA that confirms the successful synthesis of the block copolymers. The initial investigations on their aggregation behavior in aqueous solution have also been carried out, which revealed an inflection point in the scattering intensity and block copolymer concentration plots, indicating aggregation in solution above the inflection concentration. Further, the effect of temperature revealed an increase in hydrophobicity of the block copolymer due to the dehydration of the PEO blocks at higher temperatures.

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