CHAPTER III

Synthesis and Characterization of Tri- and PentaBlock Copolymers via Atom Transfer Radical Polymerization

3.1 Introduction

Polymers synthesized by controlled/living radical polymerization (CRP) techniques [1-3] such as nitroxide mediated polymerization (NMP)[4], atom transfer radical polymerization (ATRP)[5], reversible addition-fragmentation transfer polymerization (RAFT)[9,10] and organo-tellurium mediated living radical polymerization (TERP)[11-14] are powerful techniques for macromolecular engineering and have dominated literature since their discoveries. CRP is a free radical polymerization that has been adapted to control the undesirable reactions that would normally lead to uncontrolled, unpredictable growth and termination; and would result in higher molecular weight and broad molecular weight distribution which dramatically affect the key properties of the final polymer. CRP, and specifically ATRP, is rapidly becoming the preferred synthetic method for producing novel materials; as it allows the mass control of fine structure.[15-18] Well-defined polymers with precisely controlled structural parameters are accessible through living ionic polymerization processes however; ionic living polymerization requires stringent process conditions and the procedures are limited to a relatively small number of monomers.[19-24] The discovery of ATRP in 1995 and its development since then has offered a new tool and a new ability to control the course of polymerization. It has proved to be one of the most efficient and widely used systems for the formation of homo and block copolymers.[25-31]

Block copolymers of styrene and methacrylates are not only challenging synthetically but also interesting because of the morphological, phase, and mechanical properties of such polymers. Herein, we have attempted to demonstrate the versatility of ATRP to enable preparation of different tri- and pentablock copolymers of styrene, n-butyl methacrylate and methyl methacrylate. There are only few literature reports about the ATRP of the above mentioned monomers. Cheng et al.[32] reported the emulsion ATRP of poly (n-butyl methacrylate-*b*-styrene-*b*-n-butyl methacrylate) (PBMA-*b*-PS-*b*-PBMA) triblock copolymer but the control over the number average molecular weight (M_n) and molecular weight distribution (MWD) was not good enough, and Weidisch et al.[33] did the triblock copolymer synthesis via living anionic polymerization. To the best of our knowledge this is the first ever successful attempt to synthesize, poly (n-butyl methacrylate-*b*-styrene-*b*-n-butyl methacrylate) (PBMA-*b*-PS-*b*-PBMA) and poly(methyl methacrylate-*b*-n-butyl methacrylate-*b*-styrene-*b*-n-butyl methacrylate-*b*-methyl methacrylate) (PMMA-*b*-PBMA-*b*-PS-*b*-PBMA-*b*-PMMA) linear tri- and pentablock copolymers via solution ATRP. MWD for all the samples ranged between 1.06-1.31, which is well below the theoretical lower limit of 1.50 for a conventional free radical polymerization. PBMA-*b*-PS-*b*-PBMA, triblock copolymer shows synergistic effects on the tensile properties and also shows a higher tensile strength and stiffness compared to that of the PS-*b*-PBMA diblock copolymers.[33,34]

3.2 Experimental

3.2.1. Materials

The monomers styrene (Aldrich, 99%), *n*-butyl methacrylate (Aldrich, 99%), methyl methacrylate (Aldrich, 99%) were passed through activated alumina and then washed with aqueous sodium hydroxide solution followed by distilled water to remove inhibitors. Subsequently, they were dried for 24h over calcium hydride and finally distilled under reduced pressure. CuBr (Aldrich, 99.995%) and CuCl (Aldrich, 99.995%) were purified by washing with glacial acetic acid, followed by absolute ethanol and ethyl ether, and then dried under vacuum. *N,N,N,N',N'*-pentamethyldiethylenetriamine (PMDETA, 99%), di-methyl-2,6-dibromoheptanedioate (DMDBHD, 97%) were obtained from Aldrich and used without further purification. Toluene (Aldrich, 99%) was dried over calcium hydride and was distilled under reduced pressure and used. Calcium hydride (Junsei, 97%) and DOWEX MSC-1 macroporous ion-exchange resin (Aldrich, 20-50 mesh) were used as received.

3.2.2. Methods

To determine molecular weight (M_n) and molecular weight distribution, M_w/M_n (MWD), GPC was done using Waters M 77251, M 510 with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series). The pore size of the columns was 50, 100, 10^3, and 10^4 Å, respectively, with a refractive index detector at a flow rate of 1 mL/min. Tetrahydrofuran (THF) containing triethylamine (2%, $(C_2H_5)_3N$) was used as the elution solvent at 40 °C, and the instrument was calibrated with polystyrene standards, 0.889k, 4k, 10.4k, 30k, 44k and 104k (American Polymer Standards Corp.). The glass transition temperatures (T_g) of the polymers were measured in the range of 0-200 °C at a heating rate of 10 °C/min and was determined from the middle of the change in heat capacity using differential scanning calorimeter (DSC, TA Instrument 2100 Series) measurement. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from room temperature to 800°C at a heating rate of 10 °C/min using TA-2050 (TA instruments).

^{1}H NMR spectra were run on a JEOL JNM-LA300WB. All spectra were measured in $CDCl_3$ and the chemical shifts were referenced to tetramethysilane (TMS) at 0 ppm. To study the morphology, an energy-filtering transmission electron microscopy (TEM) [EF-TEM, EM 912 OMEGA (ZEISS, S-4700), 120 kV] was used. For TEM observation, the block copolymer solutions 3 mg/ml in toluene was drop casted on 400 mesh carbon-coated copper grids, annealed at 100 °C for 12 hours and finally stained with I_2 vapours for 5 hours. TEM image processing for inverse fast Fourier transformation (IFFT) image analysis was carried out by Digital Micrograph Software (version 3.0 manufactured by Galtan Inc.).[35]

3.3. Polymerization procedures

3.3.1. Preparation of α,ω-difunctional bromo-terminated polystyrene (macroinitiator) and its purification.

A dry 50 mL two necked round bottom flask (rbf) equipped with a magnetic stirrer bar was charged with CuBr (0.14 g, 0.96 mmol) under a flowing stream of nitrogen. It was then sealed with rubber septum and following this, deoxygenated PMDETA (0.17g, 0.96 mmol) and styrene (9.42 g, 96.00 mmol) were added via argon-washed syringes. The mixture was stirred until the formation of a homogeneous solution. After this, DMDBHD (1.70 g, 4.80 mmol) was added via a gas tight syringe and the polymerization was carried out at 100 °C in an oil bath maintained at this temperature. After 100 min, the reaction was terminated by exposure to air and contents were dissolved in around 150 mL of THF, washed with DOWEX MSC macroporous ion-exchange resin for about 1 hour, and filtered through a column of alumina.

The THF was removed by evaporation, and the polymer was precipitated in large excess of methanol. The polymer was redissolved in THF and precipitated again. It was then dried overnight under vacuum at 40 °C. GPC analysis showed M_n = 1434, with a MWD = 1.06, maximum yield: 69 % determined gravimetrically. ^{1}H NMR ($CDCl_3$): δ=7.1, 6.9 ppm (aromatic protons), δ=4.5 (CHBr), δ=3.3 (methoxy protons from the initiator), δ=1.0-2.8 ppm (backbone protons).

3.4. Block copolymerizations

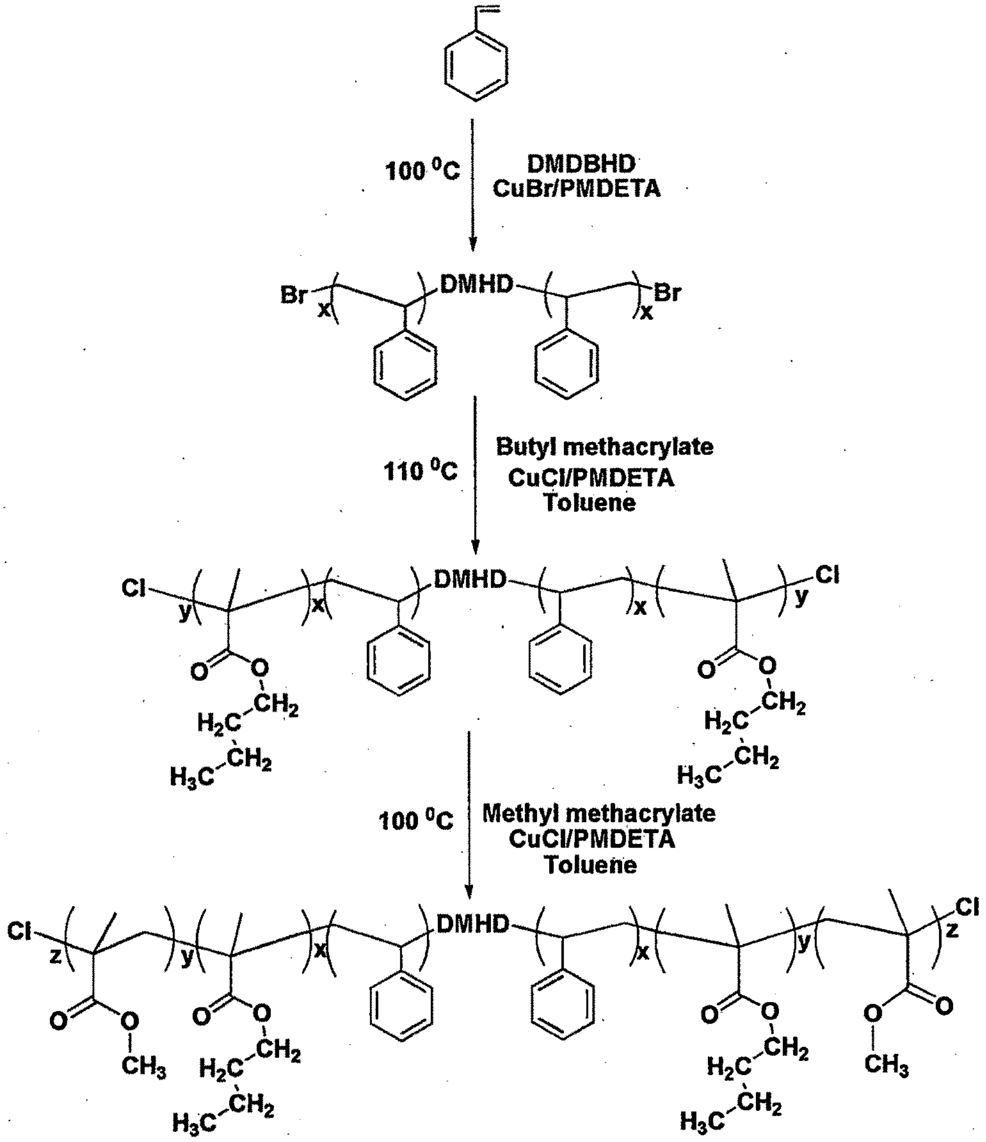
3.4.1. Preparation of poly (*n*-butyl methacrylate-*b*-styrene-*b*-*n*-butyl methacrylate), triblcok copolymers, BAB1 and BAB2.

A dry 100 mL two necked rbf equipped with a magnetic stirrer bar was charged with toluene (7.25 g), CuCl (0.052 g, 0.527 mmol) and α,ω-difunctional bromo-terminated polystyrene (0.75 g, 0.527 mmol) under a flowing stream of nitrogen. It was then sealed with rubber septum and following this, *n*-BMA (14.96 g, 105.40 mmol) was added via argon-washed syringe. Deoxygenated PMDETA (0.11 mL, 0.527 mmol) was then introduced via a gas tight syringe under a stream of nitrogen. The mixture was stirred until the formation of a homogeneous solution. Finally block copolymerization was carried out at 110°C in an oil bath maintained at this temperature. The polymerization was carried out for 130 min. GPC analysis showed M_n = 17379, with a MWD = 1.29, maximum yield: 60 % determined gravimetrically.

BAB2 block was prepared using the same procedure described above except, to a dry 100 ml two necked rbf, 4.94 g toluene, CuCl (0.09 g, 0.902 mmol), α,ω-difunctional bromo-terminated polystyrene (1.29 g, 0.902 mmol), *n*-BMA, (8.96 g, 63.20 mmol) and deoxygenated PMDETA (0.19 mL, 0.902 mmol) was used. The polymerization was carried out for 190 min. For the calculation of monomer conversion during the polymerization, samples were withdrawn at regular time intervals under nitrogen atmosphere, diluted with THF and analyzed by GPC. BAB2 block copolymer was synthesized in order to show the living character of the triblock copolymerization.

3.4.2. Preparation of poly(methyl methacrylate-*b*-*n*-butyl methacrylate-*b*-styrene-*b*-*n*-butyl methacrylate-*b*-methyl methacrylate), pentablock copolymer (CBABC).

In order to synthesize pentablock copolymer, a dry 50 mL rbf equipped with a magnetic stirrer bar was charged with toluene (4.59 g), CuCl (0.049 g, 0.499 mmol) and α,ω-chloro-terminated BAB1 triblock copolymer (8.67 g, 0.499 mmol) under a flowing stream of nitrogen. It was then sealed with rubber septum and following this, MMA (4.98 g, 49.90 mmol) was added via argon-washed syringe. Deoxygenated PMDETA (0.10 ml, 0.499 mmol) was then introduced via a gas tight syringe under a stream of nitrogen. The mixture was stirred until the formation of a homogeneous solution. Finally block copolymerization was carried out at 100 °C in an oil bath maintained at this temperature. The polymerization was carried out for 200 min. The GPC analysis showed M_n = 19000, with a MWD = 1.31, maximum yield: 47 % determined gravimetrically.



Scheme 3.1. Schematic representation of the Atom Transfer Radical Polymerization of the macroinitiator (Br-PS-Br), poly(n-butyl methacrylate-b-styrene-b-n-butyl methacrylate), triblcok copolymer (BAB), and Poly(methyl methacrylate-b-n-butyl methacrylate-b-styrene-b-n-butyl methacrylate-b-methyl methacrylate), pentablock copolymer (CBABC).

Table 3.1. Results for the synthesis of bifunctional macroinitiator, BAB1, BAB2 and CBABC Block Copolymers via ATRP.

Experiment	Initiator/Macroinitiator	Stoichiometry $[M]_0/[MI]_0/[CuX]/[PMDETA]$	time/temp (min/°C)	Yield (%)	M_n, theo[e] (g/mol)	M_n, expt (g/mol)	M_w/M_n
Br-PS-Br[a]	DMDBHD	20/1/0.2/0.2	100/100	69	1783	1434	1.06
BAB1[b]	Br-PS-Br[a]	200/1/1/1	130/110	60	18498	17379	1.29
CBABC[c]	BAB1	100/1/1/1	200/100	47	22085	19000	1.31
BAB2[d]	Br-PS-Br[a]	70/1/1/1	40/110	21	3524	3024	1.29
			80/110	42	5615	6123	1.27
			130/110	61	7506	7592	1.25
			190/110	93	10691	11000	1.28

[a] styrene:DMDBHD:CuBr:PMDETA = 20:1:0.2:0.2, bulk. [b] *n*-BMA:Br-PS-Br[a]:CuCl:PMDETA = 200:1:1:1, 50 vol % toluene vs [M]. [c] MMA:BAB1:CuCl:PMDETA = 100:1:1:1, 100 vol % toluene vs [M]. [d] *n*-BMA:Br-PS-Br[a]:CuCl:PMDETA = 70:1:1:1, 50 vol % toluene vs [M]. [e] $M_{n,theo}$ = $M_{n,\text{Initiator/Macroinitiator}}$ + $\{[M]_0/[MI]_0 \times$ Molar mass of the monomer $\times$ Yield$\}$.

3.5 Result and Discussion

Different polymerization conditions such as different reaction mediums and halogen exchange were utilized to achieve the desired well-defined block copolymers. As reported earlier,[36-38] there are two important factors in the synthesis of well-defined block copolymers; (a) the reactivity of the chain end-functionality and (b) the cross-propagation efficiency which can be achieved by a careful choice of suitable catalyst system and the order of block copolymer synthesis as well as by selecting different synthetic methodologies {i.e., halogen-exchange technique}.[37,39,40] The synthesis of poly (n-BMA-*b*-styrene-*b*-n-BMA) (BAB1) and poly(MMA-*b*-*n*-BMA-*b*-Styrene-*b*-*n*-BMA-*b*-MMA) (CBABC), linear tri- and pentablock copolymers were carried out by using copper halide as the transition-metal catalyst and PMDETA as the complexing ligand. The tri- and pentablock copolymers were synthesized by a three step procedure (Scheme 1). In the first step, a difunctional bromine-terminated polystyrene was synthesized[41,42] followed by the synthesis of BAB block copolymer macroinitiator in the second step. Finally the desired multiblock copolymer was obtained by further polymerizing MMA with the BAB block copolymer macroinitiator using ATRP technique. The GPC analysis of the homo- and block copolymers synthesized revealed the molecular weight characteristics and the blocking efficiency.

3.5.1. Synthesis of macroinitiators

α,ω-difunctional bromo-terminated polystyrene (Br-PS-Br) macroinitiator was synthesized by using commercially available difunctional initiator. DMDBHD and CuBr/PMDETA catalyst system in bulk was used for the subsequent block copolymerization with *n*-BMA, resulting in BAB1 triblock copolymer which was inturn used as the macroinitiator for the chain extension by MMA the results are summarized in Table 1. The polymerization was stopped at 69% monomer conversion in case of Br-PS-Br and 60% in case of BAB1 to ensure retention of alkyl halide chain end functionality. Table 1 summarizes the results of the synthesis. In both the cases the evaluation of GPC traces (Figure 1) suggests the complete disappearance of the macroinitiator as the polymerization time increases and confirms the formation of α,ω-difunctional bromo-terminated polystyrene and triblock copolymer macroinitiator respectively. The block nature of the polymer was further confirmed by ^{1}H NMR measurement. All the block copolymerizations were conducted using toluene as the solvent with CuCl/PMDETA as the catalyst at 110°C.

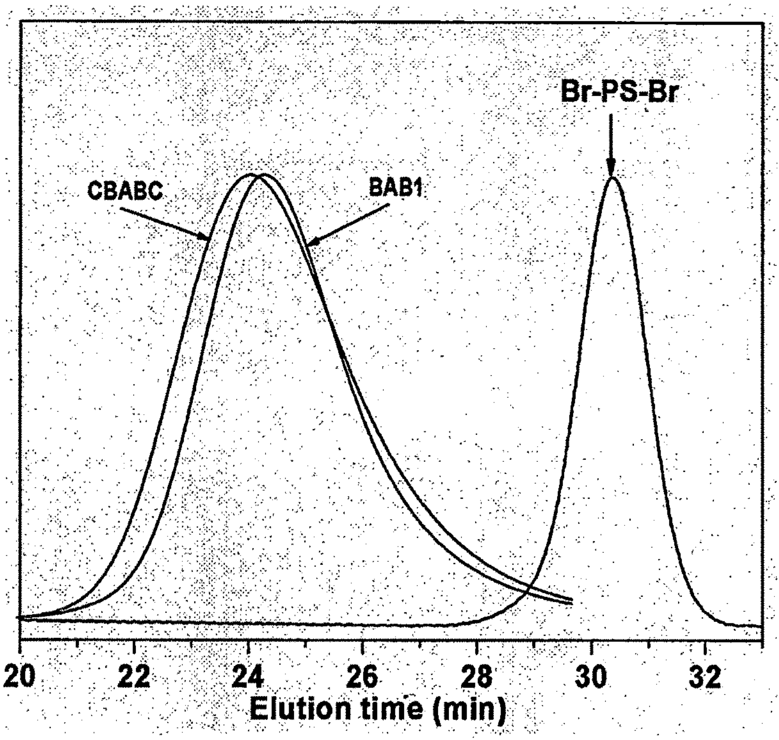


Figure 3.1. GPC chromatograms of (Br-PS-Br) macroinitiator, BAB1, and CBABC tri- and pentablock copolymers.

3.5.2. BAB1, BAB2 and CBABC Multiblock Copolymers

3.5.2.1. BAB1 Triblock Copolymer

α,ω-difunctional bromo-terminated polystyrene (Br-PS-Br), macroinitiator (M_n = 1434, MWD = 1.06, as shown in Table 1) was chain extended with n-butyl methacrylate using CuCl/PMDETA catalytic system with toluene as the solvent at 110°C to produce BAB1 triblock copolymer. The details of experimental conditions as well as the results of the molecular weight and molecular weight distribution are summarized in Table 1. The increase in molecular weight (M_n = 17379, MWD= 1.29) indicates the formation of BAB1 triblock copolymer. The ^{1}H NMR analysis (Figure 4a) of the BAB1 triblock copolymer in $CDCl_3$ showed a new signal at 3.9 ppm attributed to the methylene groups of $-COO\mathbf{CH_2}(CH_2)_2CH_3$, the signals at 6.4-7.5 ppm corresponding to the aromatic protons of polystyrene, and the signals at 0.8-1.25 ppm are attributing to the methyl protons of $-C(\mathbf{CH_3})(COOC_4H_9)$ and $-O(CH_2)_3\mathbf{CH_3}$. The signals at 1.39-2.0 ppm correspond to the methylene groups of $-CH_2-$, revealing that the polymer consisted of PS and PBMA.

An additional polymerization (BAB2) was carried out in order to show the living nature of the triblock copolymer (Figure 2). We found that the molecular weights increase almost linearly with conversion, indicating that the number of chains was constant and chain transfer reactions was negligible. Another important feature for the controlled radical polymerization observed was that the molecular weight distribution decreases with the progress of the polymerization, signifying that nearly all the chains started to grow simultaneously. This further indicated that a sufficiently fast deactivation process occurs in the mixed halogen system, though there was a slight increase in the case of BAB2[d] (Table 1) and at the end of the reaction. The loss of control at higher conversion was due to the lack of control/livingness caused by side reactions such as combination, termination and chain transfer to the polymer.

GPC traces for the progress of ATRP reaction of *n*-BMA are shown in Figure 3. The growing polymer peak continuously shifted to higher molecular weights with monomer conversion. These results supplement our earlier view that number of chains was constant. Thus, from Figure 2 and 3, one may conclude that the polymerization was controlled and had narrow molecular weight distribution (MWD < 1.29) with a good agreement between the theoretical and experimental molecular weights.

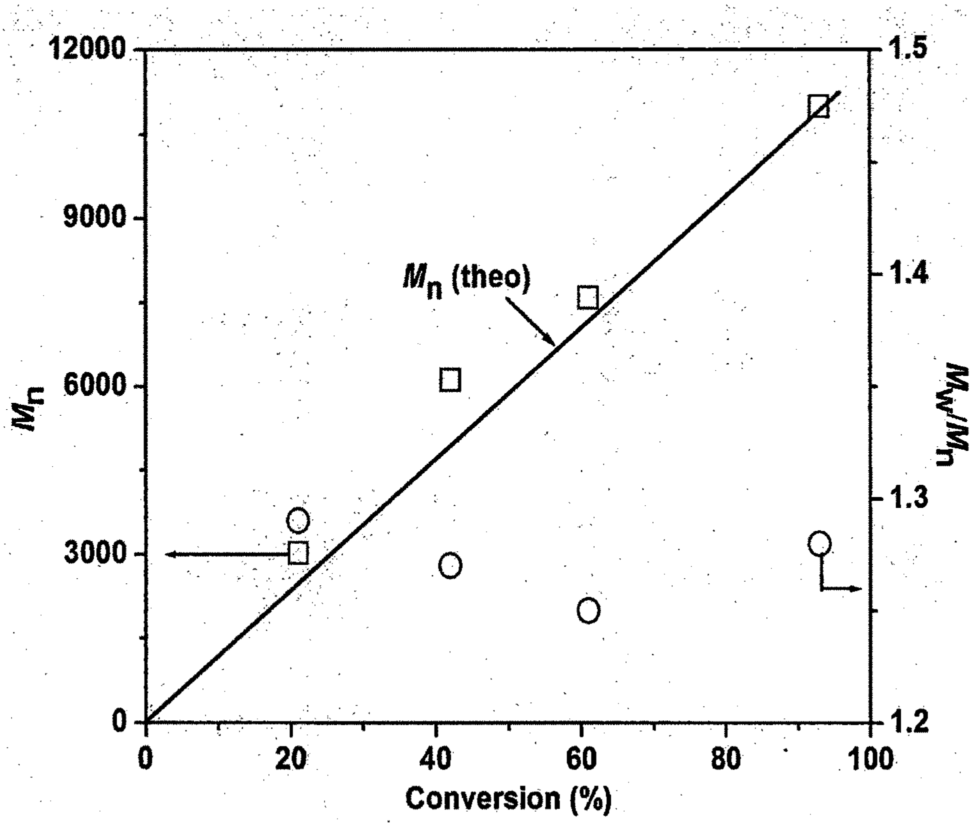


Figure 3.2. Evolution of molecular weight, (M_n) and molecular weight distribution, (M_w/M_n) with monomer conversion for the ATRP of n-butyl methacrylate (BAB2).

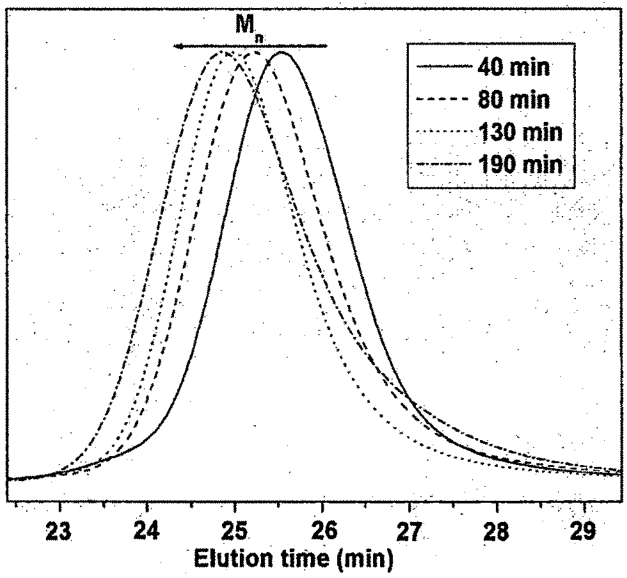


Figure 3.3. Evolution of the GPC chromatograms with conversion and time for the ATRP of n-butyl methacrylate (BAB2).

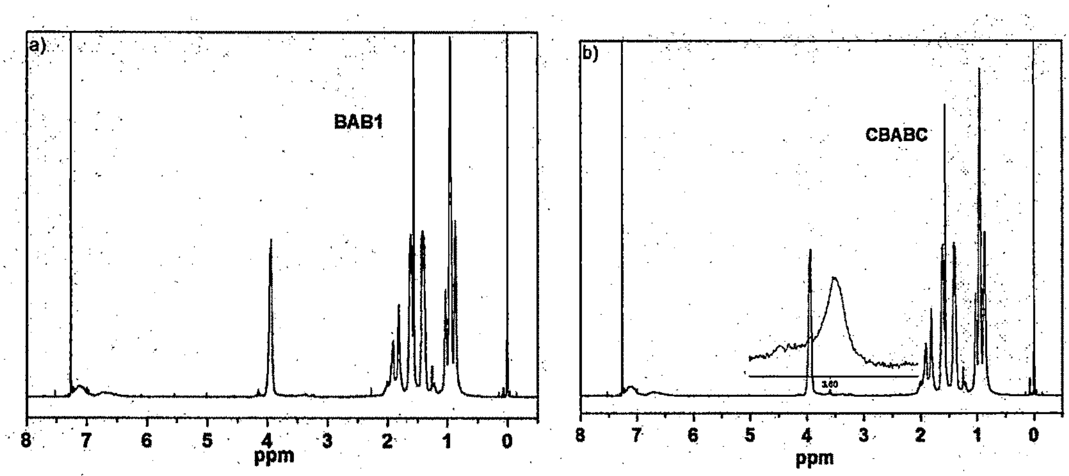


Figure 3.4. (a) ^1H NMR of BAB1, triblock and (b) CBABC pentablock copolymers.

3.5.2.2. CBABC Pentablock copolymer

In order to confirm the livingness of the triblock copolymer, CBABC pentablock copolymer was synthesized by using the BAB1 (as shown in Table 1) triblock copolymer (M_n= 17379, MWD = 1.29) as the macroinitiator and the polymeric chain was extended by MMA. The polymerization was carried out using CuCl/PMDETA catalytic system with toluene as the solvent at 100°C. The GPC traces of the block copolymer are shown in Figure 1. The gel permeation chromatogram of the CBABC block copolymer shows an increase in molecular weight, confirming the formation of the desired block copolymer. The ^{1}H NMR analysis (Figure 4b) of the pentablock copolymer in $CDCl_3$ showed a signal at 3.6 ppm attributed to $-OCH_3$ group of MMA along with the signal at 3.9 ppm which corresponds to methylene groups of $-COOC\mathbf{H}_2(CH_2)_2CH_3$ of the BAB1 triblock copolymer. The signals at 6.4-7.5 ppm corresponds to the aromatic protons of polystyrene, the signals at 0.8–1.25 ppm are attributed to the methyl protons of $-C(\mathbf{CH_3})OCH_3)$ and signals at 1.39–2.0 ppm correspond to the methylene groups of $-CH_2-$. The ^{1}H NMR analysis suggests that MMA has joined entirely with the polymer chain during the synthesis.

3.5.2.3. Thermal Analysis

Figure 5a and 5b shows the TGA and DSC thermograms of BAB1 and CBABC, tri- and pentablock copolymers, respectively. We clearly observe that the thermal degradation for BAB1 is around 270 °C and for CBABC around 290 °C in both cases the thermal degradation is flat initially and then steadily increasing. Good thermal stability of the block copolymers was confirmed by TGA. From Figure 5b, the two distinct glass transition temperatures (T_g's) of PnBMA at 35 °C and 96 °C are observed which correlates to PS in case of BAB1 triblock copolymer. For CBABC block copolymer, T_g of PnBMA and PS remains intact and a new T_g corresponding to PMMA at 106 °C was observed. This is due to the fact that for CBABC block copolymer, a relatively high concentration of PnBMA in the pentablock copolymer increased the mobility of the copolymer chains, and hence, it was possible to distinguish T_g's of PS and PMMA blocks. The values of T_g's are in good agreement with the literature cited, thereby suggesting that both block-copolymers are microphase separated. These results are also a direct evidence of the successful formation of the tri- and pentablock copolymer.

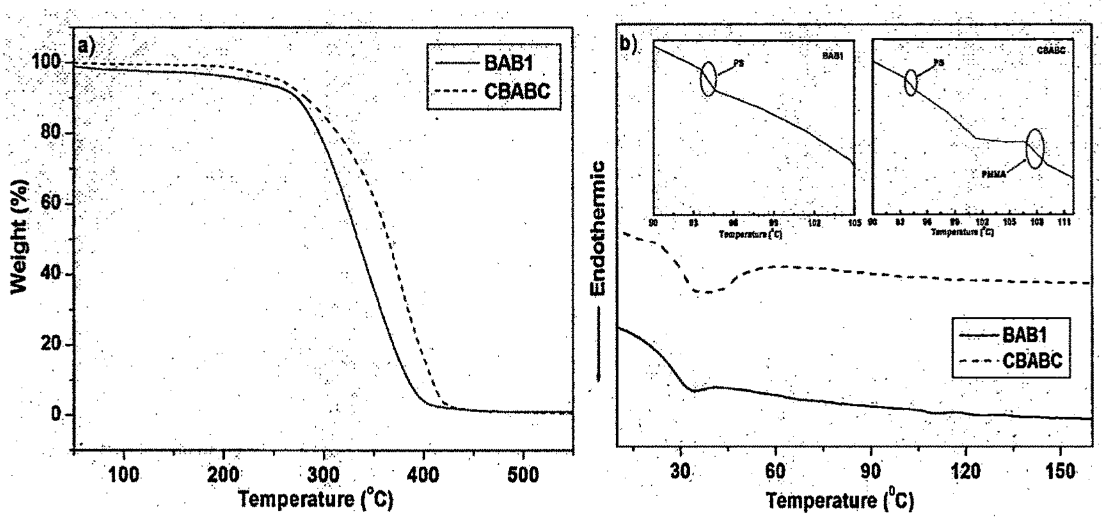


Figure 3.5. (a) TGA of BAB1, triblock and CBABC pentablock copolymer. (b) DSC of BAB1 and CBABC block copolymers.

3.5.2.4. Phase Morphology

The micellization of BAB triblock copolymers in solvents that preferentially dissolve the middle block has been well documented in literature.[43-48] Spherical micelles in these systems consist of a core containing B blocks, surrounded by loops of A block. In the present case we investigated the self-assembly morphology of the synthesized tri- and pentablock copolymers in toluene (Figure 6a and 6b) by TEM, and flower-like micelles were prevalent in both the cases. The acrylate part, in both (less favorable for toluene) of the block copolymers which was stained selectively with iodine vapor, appear dark (inner core) in the micrographs, whereas the brighter zone (shell) represent the PS segment, (more favorable towards toluene). The schematic illustration of the formation of flower-like micelles from the synthesized tri- and pentablock copolymers in toluene is shown in Scheme 3.2. We can clearly see in the IFFT images of the selected areas (6c and 6d) marked by arrows the phase separation between polyacrylate and PS segments in both tri- and pentablock copolymers.

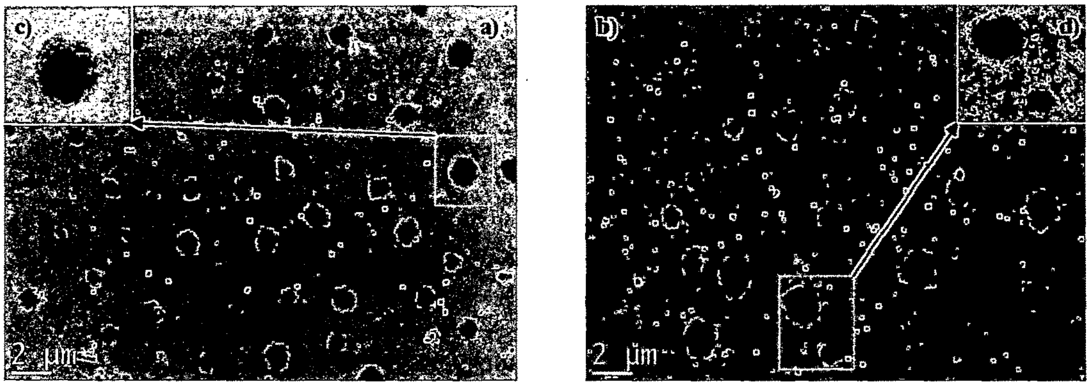
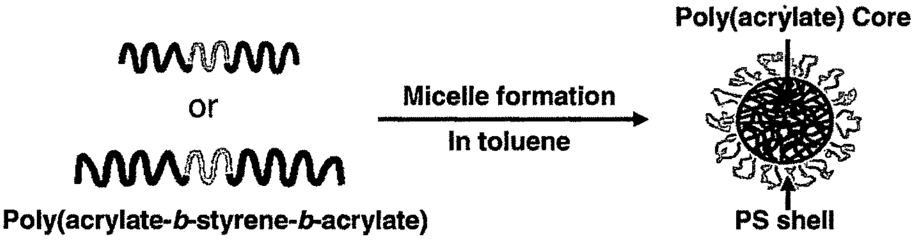


Figure 3.6. TEM micrographs in toluene (3mg/ml) (a) BAB1 triblock copolymer (b) CBABC pentablock copolymer (c) and (d) Inverse fast Fourier transform (IFFT) images of the selected area (marked by arrows) showing clearly the phase separation between the two phases.



Scheme 3.2. A schematic illustration of the formation of core-shell type flower-like micellar structures from BAB, triblock and CBABC, pentablock copolymer in toluene.

3.6. Conclusions

This work illustrates that ATRP can be successfully used to synthesize BAB and CBABC tri- and pentablock copolymers of styrene, n-butyl methacrylate and methyl methacrylate with controlled molecular weights and narrow molecular weight distributions. The structures of the block copolymers, living nature, thermal and morphological properties of the synthesized polymers have been studied. The block copolymers are synthesized for the first time via solution atom transfer radical polymerization with good control on the molecular weight and the molecular weight distribution resulting in the unique core-shell type flower-like micellar structures in nonpolar solvent. This system can thus be tuned to fit particular monomers or catalyst systems resulting in unique supramolecular structures and offers the control needed to synthesize well-defined polymers for specific applications.

3.7. References

(1) Matyjaszewski, K.; Davis, T. P., Eds. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, 2002.

(2) Lutz, J. F.; Pakula, T.; Matyjaszewski, K., In *Advances in Controlled/Living Radical Polymerization*, Matyjaszewski, K.; Eds., *ACS Symposium Series* 854, *American Chemical Society*: Washington, DC, 2003, Chapter 19, pp. 268.

(3) Matyjaszewski, K.; Ed. *Advances in Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT, ACS Symposium Series* 768, American Chemical Society: Washington, DC, 2000.

(4) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.*, **2001**, 101, 3661.

(5) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. J *Macromolecules*, **1995**, 28, 1721.

(6) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.*, **1995**, 117, 5614.

(7) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.*, **2001**, 101, 3689.

(8) Matyjaszewski, K.; Xia, J. *Chem. Rev.*, **2001**, 101, 2921.

(9) Chiefari, J.; Rizzardo, E. Eds *Handbook of Radical Polymerization.*; Matyjaszewski, K.; Davis, T. P, Wiley-Interscience: Hoboken 2002, Chapter 12, pp. 621.

(10) Lee, J. M.; Kim, O. H.; Shim, S. E.; Lee, B. H.; Choe, S. *Macromol. Res.*, **2005**, 13, 236.

(11) Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.*, **2002**, 124 2874

(12) Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.*, **2002**, 124, 13666.

(13) Yamago, S. *J. Polym. Sci., Part A: Polym. Chem.*, **2006**, 44, 1.

(14) Kwak, Y.; Goto, A.; Fukuda, T.; Kobayashi, Y.; Yamago, S. *Macromolecules*, **2006,** 39, 4671.

(15) Marutani, E.; Yamamoto, S.; Ninjbadgar, T.; Tsujii, Y.; Fukuda, T.; Takano, M. *Polymer*, **2004**, 45, 2231.

(16) Liu, P.; Su, Z. *Polym Bull*, **2005**, 55, 441.

(17) Bottcher, H.; Hallensleben, M. L.; Nub, S.; Wurm, H. *Polym Bull,* **2000**, 44, 223.

(18) Coessens, V.; Pintauer, T. ; Matyjaszewski, K. *Prog. Polym. Sci.*, **2001**, 26, 337.

(19) Kumar, S.; Shah, P. N.; Kang, B. G.; Min, J. K.; Hwang, W. S.; Sung, I. K.; Shah, S. R.; Murthy, C. N.; Ahn, S.; Chang, T.; Lee, J. S. *J Polym Sci Part A: Polym Chem,* **2010**, 48, 2636.

(20) Ahn, J. H.; Shin, Y. D.; Nath, G. Y.; Park, S. Y.; Rahman, M. S.; Samal, S.; Lee, J. S. *J. Am. Chem. Soc.,* **2005**, 127, 4132.

(21) Hadjichristidis, N. ; Pispas, S.; Floudas, G. *Block Copolymers: Synthetic Strategies, physical Properties, and Applications*, 1st ed. Hoboken, New Jersey, John Wiley & Sons, Inc., 2003, Chapter 1, pp. 12.

(22) (22) Shin, W. J.; Kim, J. Y.; Lee, J. S. *Macromol. Res,* **2010**, 18, 742.

(23) Nath, G. Y; Samal, S.; Park, S. Y.; Murthy, C. N.; Lee, J. S. *Macromolecules,* **2006**, 39, 5965.

(24) Hirao, A.; Tsunoda, Y.; Matsuo, A.; Sugiyama, K.; Watanabe, T. *Macromol. Res.,* **2006**, 14, 272.

(25) Chen, W. H.; Liaw, D. J.; Wang, K. L.; Lee, K. R.; Lai, J. Y. *Polymer,* **2009**, 50, 5211.

(26) Li, G. H.; Cho, C. G. *Macromol. Res.*, **2002**, 10, 339.

(27) Lutz, J. F. *Polym. Int.,* **2006**, 55, 979.

(28) Ogawa, M.; Nitahara, S.; Aoki, H.; Ito, S.; Narazaki, M. ; Matsuda, T. *Macromol. Chem. Phys*, **2010**, 211, 1369.

(29) Datta, H.; Singha, N. K. *J Polym Sci Part A: Polym Chem,* **2008**, 46, 3499.

(30) Choi, J. H.; Oh, S. B.; Chang, J.; Kim, Il; Ha, C. S.; Kim, B. G.; Han, J. H.; Joo, S. W.; Kim, G. H.; Paik, H. J. *Polym Bull,* **2005**, 55, 173.

(31) Park, B. J; Hong, M. K.; Choi, H. J. *Colloid Polym Sci,* **2009**, 287, 501.

(32) Peng, H.; Fan, Z. ; Cheng, S. *Polym. Eng. Sci.,* **2005**, 45, 1508.

(33) Weidisch, M.; Michler, G. H.; Arnold, M.; Fischer, H. *J. Mater. Sci.,* **2000**, 35, 1257.

(34) Weidisch, R. ; Michler, G. H.; Arnold, M.; Hofmann, S.; Stamm, M.; Jerome, R. *Macromolecules,* **1997**, 30, 8078.

(35) Kim, Y. M.; Jeong, J. M.; Kim, J. G.; Kim, Y. J.; Lim, S. Y. *J. Korean Phys. Soc.,* **2006**, 48, 250.

(36) Davis, K. A.; Matyjaszewski, K. *Macromolecules,* **2001**, 34, 2101.

(37) Shipp, D. A.; Wang, J. L.; Matyjaszewski, K. *Macromolecules,* **1998**, 31, 8005.

(38) Lutz, J. F.; Pakula, T.; Matyjaszewski, K. *Macromol. Chem. Phys.,* **2002**, 203, 1385.

(39) Matyjaszewski, K.; Shipp, D. A.; Wang, J. L.; Grimaud, T.; Patten, T. E. *Macromolecules,* **1998**, 31, 6836.

(40) Matyjaszewski, K.; Shipp, D. A.; Mcmurtry, G. P.; Gaynor, S. G.; Pakula, T. *J Polym Sci Part A: Polym Chem,* **2000**, 38, 2023.

(41) Ramakrishnan, A.; Dhamodharan, R. *Macromolecules,* **2003**, 36, 1039.

(42) Davis, K. A.; Matyjaszewski, K. *Macromolecules,* **2000**, 33, 4039.

(43) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules,* **1991**, 24, 1975.

(44) Kotaka, T.; Tanaka, T.; Hattori, M.; Inagaki, H. *Macromolecules,* **1978**, 11, 138.

(45) Tsitsilianis, C.; Sfika, V. *Macromol. Rapid Commun.,* **2001**, 22, 647.

(46) Saito, R.; Ishizu, K. *Polymer* **1997**, 38**,** 225.

(47) Krause, S. *J. Phys. Chem.,* 1964, 68, 1948.

(48) Honda, S.; Yamamoto, T.; Tezuka, Y. *J. Am. Chem. Soc.,* **2010**, 132, 10251.