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# Synthesis and Characterization of Block Copolymers of P(MMA-*b*-*n*-BA-*b*-MMA) via Ambient Temperature ATRP of MMA

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*A binol ester initiator was used as a bifunctional ATRP initiator in combination with PMDETA/copper bromide catalyst system in DMF to synthesize n-butyl acrylate macroinitiator at 50°C. The resulting macroinitiator was used for a detailed investigation of the ATRP of methyl methacrylate (MMA) with CuCl/N,N,N',N',N''-penta-methyldiethylenetriamine (PMDETA) catalyst system in anisole at 30°C. Thus, the MMA polymerization is shown to proceed with first order kinetics, with predicted molecular weight and narrow polydispersity indices. Gel permeation chromatography (GPC) and NMR were used for the characterization of the polymers synthesized.*

**Keywords** ATRP, block copolymers, triblock copolymers, thermoplastic elastomers, binol ester, bifunctional initiator, ambient temperature polymerization, methyl methacrylate, *n*-butyl acrylate

## Introduction

The synthesis of (meth)acrylic block copolymers has industrial significance since a wide range of glass transition temperatures ( $T_g$ ) can be achieved by a simple variation of the alkyl substituent of the ester monomer. The synthesis of block copolymers with well-defined molecular weight and MWD via controlled living radical polymerization is currently being established as a versatile synthetic method (1–7). In atom transfer radical polymerization (ATRP), the development of new/functionalized initiators permits the preparation of a wide range of new materials with improved properties, which are either difficult to prepare or are not available via other polymerization techniques. For example, metal-centered initiators (8) and multi functional initiators (9, 10) have been used to control the topology of the polymer (i.e., star, comb). Macroinitiators (11, 12) have been used to control the composition of the polymers (i.e., block copolymers) and functional initiators (13, 15) have been used to control the functionality of polymers (i.e., chain-end, site-specific).

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Atom transfer radical polymerization has been used for the synthesis of triblock copolymers via two routes (16). The first route involves a simple addition of a second monomer to the reaction medium after the complete consumption of the first monomer. The second route involves the isolation and purification of the first polymer, which, in turn, can be used as a macroinitiator for the growth of the second polymer. The first method is relatively easy to carry out, but it is difficult to obtain a pure block copolymer in this manner (some of the macroinitiator without the appropriate end-group required for initiation will be present as the impurity). In recent years, there have been several reports on the synthesis of acrylic di- and triblock copolymers by ATRP (17). Jerome et al. (18, 19) carried out the synthesis and characterization of poly(MMA-*b*-*n*-BA-*b*-MMA) by a two-step ATRP using the catalyst NiBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. However, several factors were required to be optimized to achieve controlled polymerization. The main requirement in ATRP is efficient initiation (i.e., initiation will have to be fast). To increase the rate of initiation, relative to the rate of propagation, "halide exchange" can be used. Here, an alkyl bromide initiator is used in conjunction with copper chloride. Thus, the -Br end-group initially provides fast initiation, but there after the end-group of the growing polymer chain is predominantly the less labile -Cl group; hence, the rate of initiation is increased relative to the propagation rate, thus improving initiation efficiency (20).

Recently, several reports have been published on the ATRP of hydrophobic (21–23) and hydrophilic (24) monomers at ambient temperature. The presence of 1,2-ethoxyethane in toluene was found to enhance the rate of polymerization of benzyl methacrylate (25). Matyjaszewski et al., (26) has reported on the bulk polymerization *n*-butyl acrylate in the presence of ethylene carbonate. The ATRP of water-soluble acrylate monomers in aqueous media at ambient temperature has also been reported (24, 27). Polymerization at ambient and lower temperature has few advantages, which include the minimization of side reactions and spontaneous thermal polymerization. The synthesis of block copolymers of acrylates and methacrylates at ambient temperature or at any other temperature with narrow polydispersity is a synthetically challenging exercise. In addition it is also important from the point of view of morphological, phase separation, and mechanical property investigations. These properties can be achieved from block copolymers in which one block has a T<sub>g</sub> above room temperature and the other below room temperature. The resulting block copolymers can function as efficient substitutes for the traditional styrene-*b*-butadiene-*b*-styrene (SBS) and styrene-*b*-isoprene-*b*-styrene (SIS) thermoplastic elastomers (TPE). These materials are also expected to resist the UV light and hydrocarbon solvents to a greater extent compared to the styrene-*b*-butadiene analogues.

In this paper, we report on the detailed investigation leading to the synthesis of block copolymers of P(MMA-*b*-*n*-BA-*b*-MMA) by using poly(*n*-butyl acrylate) macroinitiator via ATRP at ambient temperature. The macroinitiator P(*n*-BA) was synthesized using binol ester as the bifunctional initiator along with copper bromide/PMDETA catalyst system in DMF at 50°C following the procedure reported for the polymerization of *n*-BA using 2-ethyl isobromobutyrate as the initiator.

## Experimental

### Materials and Methods

Racemic binaphthol (Gerchem, Hyderabad, India) was used as received. Dichloromethane (DCM, Fischer, Chennai, India), used in the esterification was dried over anhydrous CaCl<sub>2</sub>

and was distilled over anhydrous  $P_2O_5$  before use. Triethylamine (TEA, SRL, Chennai, India) was dried over KOH and distilled before use. Methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA) (Lancaster, Chennai, India) were distilled over  $CaH_2$  under vacuum and stored under nitrogen at  $-20^\circ C$ . 2-bromoisobutyryl bromide, anisole, CuBr, CuCl and PMDETA were purchased from Aldrich India (Bangalore, India) and used without further purification.

GPC analysis was performed at room temperature using a Agilent GPC 1100 [Agilent pump equipped with 1100 series auto sampler, three polymer standard service  $5\ \mu m$  columns ( $8 \times 300\ mm$ ) in series (guard column, two  $100\ \text{\AA}$  and  $1000\ \text{\AA}$  columns of  $8 \times 300\ mm$ ) with a Agilent 1000 series RI detector; Germany]. Toluene ( $0.1\ \mu L$ ) was used as a flow marker. THF was used as the eluent at a flow rate of  $1\ mL/min$ . 0.2 wt% solutions of the polymer in THF were used for the measurements. Molecular weights were calculated with PSS software (PSS WinGPC Scientific V 6.10) against linear low-polydispersity PMMA Standards. JASCO FTIR 410 (Japan) infrared spectrometer was used for recording IR spectra. AFM was performed with Nanoscope III (Digital Instruments, Santa Barbara, CA) operating in tapping mode at a resonance frequency of  $\sim 360\ Hz$  Using Si probe with a spring constant of  $\sim 50\ N/m$ . The samples used for this experiment were prepared by spin casting at 2000 rpm on mica substrates from a chloroform solution. DSC was performed with "DSC 2920 modulated DSC" (TA Instrument) with "Thermal analyst" software at a heating rate of  $10^\circ C/min$ . A Bruker 250 (250 MHz for proton) NMR spectrometer was used to record  $^1H$  and  $^{13}C$  spectra.

#### **Synthesis of Bifunctional Initiator 1,1'-Bi-2-naphthol bis(2-bromo-2-methylpropionate)**

1,1'-Bi-2-naphthol bis(2-bromo-2-methylpropionate), a difunctional-initiator was synthesized by reacting 1,1'-bi-2-naphthol with 2-bromoisobutyryl bromide in the presence of triethylamine in dichloromethane. Thus, 2.8 g (10 mmol) of binaphthol was dissolved in 40 mL of dichloromethane (DCM), which was followed by the addition of triethylamine (6.8 mL, 24 mmol). The resulting reaction mixture was cooled to  $0-10^\circ C$ . After this, 2-bromoisobutyryl bromide (3.1 mL, 24 mmol) was added slowly (dropwise). Upon completion of the addition, the reaction mixture was stirred at room temperature. After this, it was poured into cold water and extracted with 120 mL of DCM; the extract was rinsed with water and dried with anhydrous sodium sulphate. The crude product was isolated by removing the solvent via a rotary evaporator and purification was performed by column chromatography with neutral alumina (eluent 10% ethylacetate: 90% hexane). Yield = 75.5%, m.p. =  $132-134^\circ C$ .  $^1H$  NMR ( $\delta$  ppm:  $CDCl_3$ , 400 MHz), 1.3 (s, 6H), 1.55 (s, 6H), 7.34–7.5 (m, 8H), 7.98.0 (dd, 4H).  $^{13}C$  NMR ( $\delta$  ppm:  $CDCl_3$  100 MHz): 170.41(s), 147.15 (2s), 134.00 (2d), 132.31 (2s), 132 (2s), 128.69 (2d), 127.71 (2s), 126.70 (2d), 126.57 (2d), 123.95 (2d), 121.76 (2d), 55.87 (2s), 30.64 (2q), 30.28 (2q).

#### **Synthesis of Poly(*n*-butyl acrylate) Macroinitiator Br-P(*n*-BA)-Br**

A typical atom transfer radical polymerization of *n*-BA was carried out as follows: To a dry Schlenk tube equipped with a magnetic stir bar, CuBr ( $0.096\ g$ ,  $8.37 \times 10^{-2}\ mol$ ) was added. It was then fitted with a rubber septum and was evacuated two times followed by dry nitrogen filling. This was followed by the addition of degassed DMF (2 mL) and

the ligand PMDETA (0.116 g,  $8.37 \times 10^{-2}$  mol) was added with a gas tight syringe. *n*-Butyl acrylate (5.36 g, 5.23 mol) was then added, and the reaction mixture was stirred well. Finally, the initiator [racemic BBiBN] (0.195 g,  $4.186 \times 10^{-2}$  mol) was added to the reaction mixture and the Schlenk tube was placed in an oil bath maintained at 50°C for 4 h with continuous stirring. After this, the resulting solution was precipitated in cold methanol to obtain the macroinitiator Br-P(*n*-BA)-Br. For samples used in the GPC analysis the catalyst residue was removed by passing through neutral alumina column. <sup>1</sup>H NMR: (δ ppm: CDCl<sub>3</sub>, 250 MHz), 4.0 (s, -OCH<sub>2</sub>), 2.3 (s, CH<sub>2</sub>), 0.8–1.88 (m, backbone -CH, CH<sub>2</sub>), 0.96 (s, CH<sub>3</sub>).

### **Synthesis of ABA Triblock Copolymer (Methyl methacrylate-*b*-*n*-butyl acrylate-*b*-methyl methacrylate)**

To a dry Schlenk tube equipped with a magnetic stir bar, CuCl (0.0055 g,  $9.2 \times 10^{-3}$  mol) was added. It was then fitted with a rubber septum, was evacuated twice, and filled back with dry nitrogen. Following this, degassed anisole (3 mL) and the ligand PMDETA (0.01 g,  $9.2 \times 10^{-3}$  mol), was added using a gas tight syringe. Methyl methacrylate (2.82 g, 4.66 mol), was then added and the reaction mixture was stirred well. The macroinitiator Br-*n*BA-BBiBN-*n*BA-Br (0.445 g,  $4.6 \times 10^{-2}$  mol), was added to the reaction mixture and the Schlenk tube was maintained at room temperature. Samples were withdrawn at the desired time period for analysis. The resulting polymer was precipitated in cold methanol. For samples used in GPC analysis, the catalyst residue was removed by passing through neutral alumina column. <sup>1</sup>H NMR: (δ ppm: CDCl<sub>3</sub>, 250 MHz), 4.0 (s, -OCH<sub>2</sub>, *n*-BA), 3.60 (s, -OCH<sub>3</sub>, MMA), 2.3 (s, CH<sub>2</sub>), 1.5 (s, CH<sub>3</sub>) 0.8–1.88 (m, backbone -CH, CH<sub>2</sub>), 0.96 (s, CH<sub>3</sub>). The composition ratio of the blocks were also determined from the relative intensity of the resonance at 4.0 ppm (-OCH<sub>2</sub> protons of the butyloxy group) corresponding to the *n*-BA monomer and at 3.60 ppm (-OCH<sub>3</sub> of the methyloxy group) corresponding to the MMA monomer. For example, the composition ratio of a MMA-*b*-*n*-BA-*b*-MMA triblock of  $M_n = 60,800$  (GPC) was determined to be 44:12:44.

## **Results and Discussion**

In ATRP, the components (initiator, monomer, catalyst, solvent etc..) present in the initiating system play a crucial role in obtaining control over the polymerization. The structure of the initiator and initiation mechanism affects the molecular weight characteristics of the resulting polymers. The importance of designing appropriate initiating system and experimental procedure to improve the control over MMA polymerization has been demonstrated in the literature (20, 28). Towards the goal of designing a suitable initiating system, we investigated the scope of a novel initiator for the controlled polymerization of MMA in a previous work (29). In this paper, we investigate the synthesis of PMMA at ambient temperature using the bifunctional macroinitiator Br-P(*n*-BA)-Br and characterize the resulting block copolymer by GPC and NMR.

### **Synthesis of 1,1'-Bi-2-naphthol bis(2-bromo-2-methylpropionate) (BBiBN) Initiator**

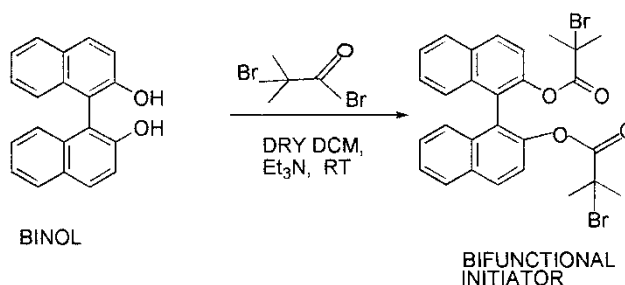
The initiator used in the polymerization of *n*-BA was synthesized by reacting 2-bromo-2-methylpropionyl bromide with 1,1'-bi-2-naphthol in the presence of triethylamine as the

catalyst (Scheme 1). A similar procedure has been reported for the synthesis of allylic esters from allyl alcohol and 2-bromo-2-methylpropionyl bromide (30). The details of this synthesis has been published elsewhere (29).

The ATRP of *n*-BA in 25% v/v DMF at 50°C has been carried out with 2-EiBBr/CuBr/PMDETA/(v/v) catalyst system before (31). We followed the same procedure for the synthesis of the *n*-BA macroinitiator using the BBiBN bifunctional initiator. The characterization of the P(*n*-BA) macroinitiators thus obtained are summarized in Table 1. It was clear from these experiments that relatively narrow dispersed bifunctional macroinitiators based on P(*n*-BA) can be synthesized in about 3 h using the novel binol bifunctional initiator. To characterize the macroinitiator in detail, the initiator fragment present in the macroinitiator can be used. The <sup>1</sup>H NMR as shown in Figure 1 exhibits peaks from the binol fragment in addition to the large characteristic signals from P(*n*-BA). Thus the protons from the para (2) and peri(2) positions of the 1,1'-bi(2-naphthol) derived from BBiBN were seen at 7.8–8.0 ppm. The  $M_n$  for the P(*n*-BA) was determined from the peak area of the 2,6 hydrogens (four protons; para and peri) and butyl ester protons (two protons) of the main chain [ $M_n = \{(\text{integrated area due to bond; } \text{OCH}_2/2)/(\text{integrated area due to the 2,6 hydrogens from the initiator})\} \times 128$ ]. The  $M_n$  calculated from <sup>1</sup>H NMR was observed to be higher than the values from GPC [for example in one case  $M_n$  (GPC) = 15,900,  $M_n$  (NMR) = 21,500].

### Synthesis of (MMA-*b*-*n*-BA-*b*-MMA) at Ambient Temperature

In the literature, it is reported that the activation of a dormant P(*n*-BA) chain-end to a radical species is slower than the activation of a dormant PMMA chain end (14, 18). This results in slow initiation of the macroinitiator and thus poor molecular weight control (i.e., broad polydispersity and/or bimodality). Chambard et al. (32) have analyzed the solvent effect on the activation rate parameters for poly(*n*-BA) macroinitiator in ATRP. In this study, the room temperature synthesis of the symmetric triblock copolymer of (MMA-*b*-*n*-BA-*b*-MMA) via ATRP was investigated. Recently we have established that the ambient temperature polymerization of MMA can be carried out with a reasonable rate of polymerization via ATRP using the system 2-EiBBr (or) [(R) BBiBN]/CuBr/PMDETA/50% v/v in anisole (29, 33, 34). The block copolymerization reported here was carried out under identical conditions as reported before (Scheme 2) except that we employed the macroinitiator Br-P(*n*-BA)-Br. Polymerization was carried out in bulk as well as in 50% v/v anisole solution.



**Scheme 1.** Atom transfer radical polymerization of *n*-BA with BBiBN bifunctional initiator.

**Table 1**  
Synthesis of P(*n*-BA) macroinitiator in DMF at 50°C

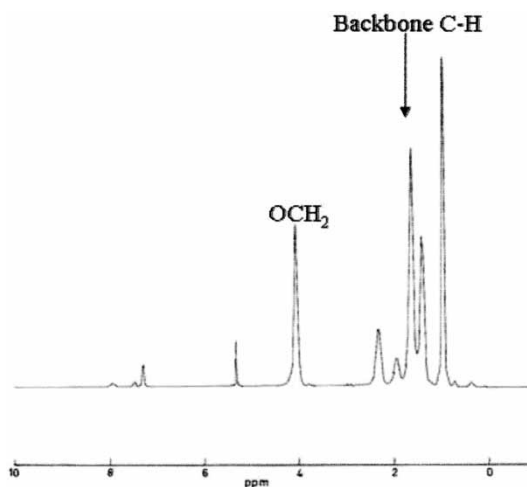
S. No.	Reaction time (min)	M <sub>n</sub> (SEC)	PDI
1 <sup>a</sup>	225	12,000	1.20
2 <sup>a</sup>	240	13,600	1.31
3 <sup>a</sup>	285	13,000	1.15
4 <sup>b</sup>	300	15,900	1.09
5 <sup>b</sup>	330	19,200	1.28

<sup>a</sup>target DP = 125; [Cat]: [L]: [initiator] = [*n*-BA], [1]: [1]: [0.5]/25% v/v DMF at 50°C.

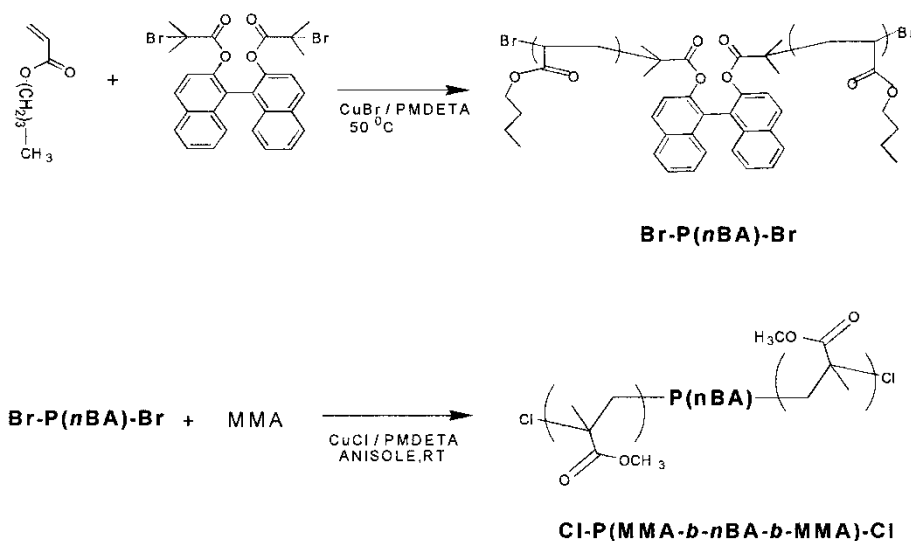
<sup>b</sup>target DP = 200; [Cat]: [L]: [initiator] = [*n*-BA], [1]: [1]: [0.5]/25% v/v DMF at 50°C.

A detailed kinetic analysis was therefore carried out with system ([MMA]:[Br-P(*n*-BA)-Br]:[CuCl]:[PMDETA] = 1000:1:2:2 in 50% v/v anisole) at 30°C. The number average molecular weight (M<sub>n</sub>) and polydispersity index (PDI) of the macroinitiator was 15900 and 1.09, respectively (data from GPC; molecular weight rounded to the nearest hundred). The dependence of monomer conversion as a function of time for this polymerization is shown in Figure 2. The corresponding data are presented in Table 2. Based on the data it was calculated that the rate was approximately first order with respect to the concentration of the monomer. The time vs. ln([M<sub>0</sub>]/[M]) plot was linear with a correlation coefficient of 0.9947. The k<sub>app</sub> calculated from the slope was 1.12 \* 10<sup>-4</sup> s<sup>-1</sup>, which is close to the value reported for the polymerization of MMA using the system [P(*n*-BA)-Br]:[CuCl]:[PMDETA] 25% v/v in benzonitrile (1.1 \* 10<sup>-4</sup> s<sup>-1</sup>) at 100°C.<sup>35</sup> Thus the polymerization reported here at 50°C is faster than the one reported using a similar macroinitiator at 100°C.

The number average molecular weight (M<sub>n</sub>) increased linearly with conversion, as shown in Figure 3. This indicates that the concentration of growing radical chains was

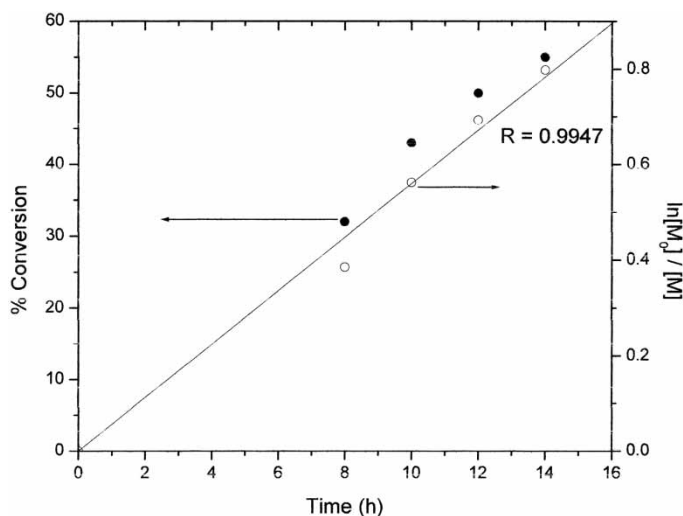


**Figure 1.** <sup>1</sup>H NMR of P(*n*-BA).



**Scheme 2.** Synthesis of PMMA and P(MMA-*b*-*n*-BA-*b*-MMA) from the bifunctional initiator.

constant throughout the polymerization time. The evolution of GPC chromatograms with conversion/time is shown in Figure 4. The  $M_n$  values determined by GPC were close to the expected values. The PDI values obtained were between 1.2 and 1.4. The PDI was observed to increase with reaction time and this is attributed to the presence of a small amount of chain breaking reactions. The resulting block copolymer structure was also confirmed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR of a block copolymer is shown in



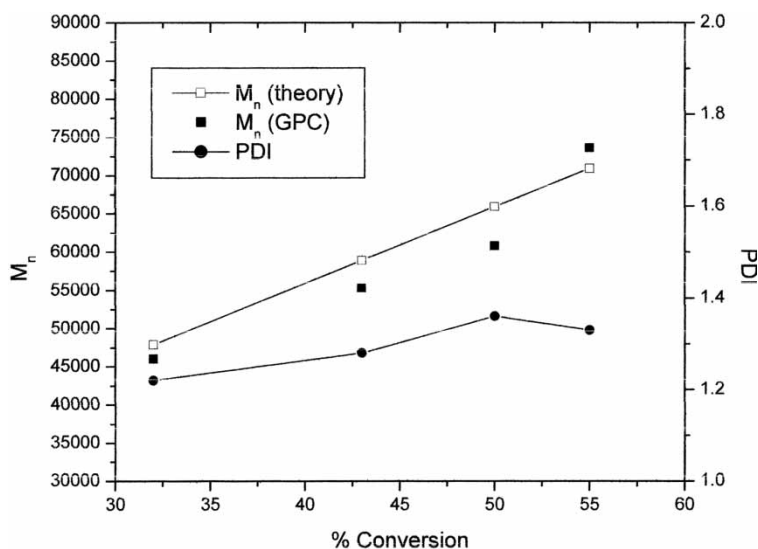
**Figure 2.** Conversion vs. time plot for the ATRP of MMA at 30°C (50% v/v anisole). MMA:Br-P(*n*-BA)-Br:CuCl:PMDETA = 1000:1:2:2. (○)—Expected; (●)—Observed.



**Table 2**  
Ambient temperature polymerization of MMA using Br-P(*n*-BA)-Br as the macroinitiator ( $M_n = 15,900$ , PDI = 1.09)

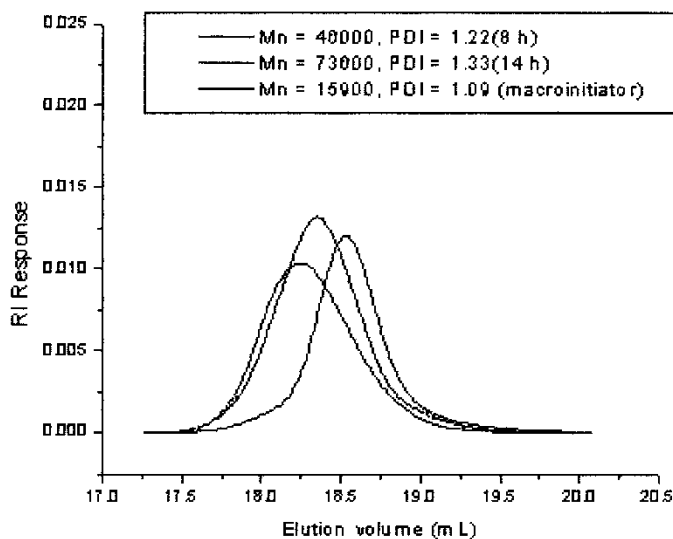
S. No.	Time (h)	% Conversion	$\ln[M_0]/[M]$	$M_n(\text{Theo})$	$M_n(\text{SEC})$	Composition ratio $^1\text{H NMR}$	PDI	f
1	8	32	0.3856	47,900	46,000	40:20:40	1.22	1.04
2	10	43	0.5621	58,900	55,300	41:18:41	1.28	1.06
3	12	50	0.6931	65,900	60,800	44:12:44	1.36	1.08
4	14	55	0.7985	70,900	73,600	44.5:11:44.5	1.33	0.93

Polymerization of MMA, Target DP = 1000; [Cat]:[L]:[macroinitiator] = [MMA], [1]:[1]:[0.5]/[anisole], 1/1 @ RT. PMMA standards. Eluent was THF. Composition ratio of the blocks as determined by  $^1\text{H NMR}$ .



**Figure 3.**  $M_n$  and PDI vs. monomer conversion for the ATRP of MMA at 30°C (50% v/v anisole) MMA:Br-P(*n*-BA)-Br:CuCl:PMDETA = 1000:1:2:2. (■) :  $M_n$ ; (●) : PDI.

Figure 5. This exhibits a new peak at 3.6 ppm corresponding to methoxy group of the PMMA in addition to the other characteristic peaks of P*n*-BA at 4.0 ppm and 0.8–1.8 ppm, confirming the formation of the block copolymer. Block copolymerization could also be confirmed by DSC measurements. The *n*-BA block with an  $M_n$  of 15,900 was observed to exhibit  $T_g \sim -55^\circ\text{C}$  and the MMA block (the  $M_n$  of this block varies from 15,000 to 23,800 depending on the sample) at  $\sim 60^\circ\text{C}$  with the heating rate being



**Figure 4.** GPC of P(MMA-*b*-*n*-BA-*b*-MMA) at 30°C.

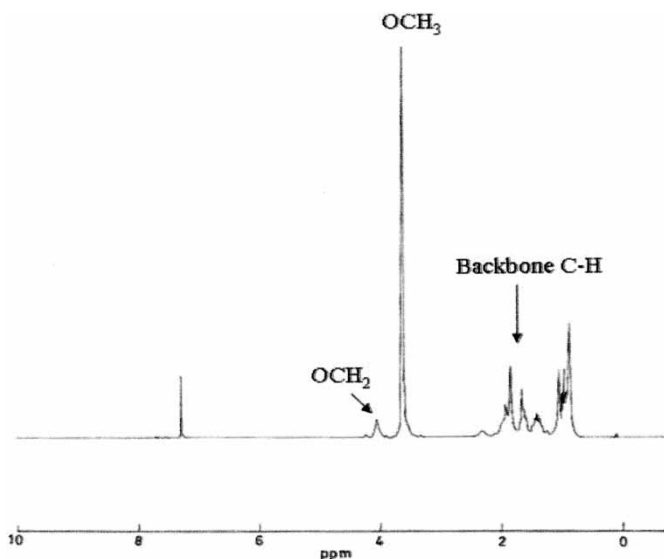


Figure 5.  $^1\text{H}$  NMR of poly(MMA-*b*-*n*-BA-*b*-MMA).

$10^\circ\text{C}/\text{min}$  (data not shown). The  $T_g$  of the MMA block is unusually low when compared with that predicted by the Flory-Fox equation (based on this equation it must be in the vicinity of  $80^\circ\text{C}$ ). This is probably due to the fact that the molecular weight of the MMA block is well below the critical molecular weight for entanglement ( $\sim 27,800$ ) and therefore the Flory-Fox equation can not be used to predict the expected  $T_g$ . The AFM of one of the block polymers exhibiting lamellar morphology is shown in  $[\text{P}\{(\text{MMA})_{150}\text{-}b\text{-}(\text{n-BA})_{124}\text{-}b\text{-}(\text{MMA})_{150}\}]$ .

Based on the above results the block copolymerization of MMA with Br-P(*n*-BA)-Br macroinitiators (as shown in Table 1) were investigated in solution as well as in bulk. The details of the results from these investigations are presented in Table 3. It can be seen from these results that triblock copolymers with a reasonably long MMA blocks can be synthesized by the method reported here in a reasonably short span of time as 2 h. It was observed that bulk polymerization of MMA was faster than polymerization from solution under these conditions. Assuming that the mechanism of polymerization in the bulk, as well as in anisole solution, are the same (that is  $k_p$  is assumed to be the same for bulk as well as solution polymerization) this can be attributed to the concentration of monomer and initiator available for polymerization ( $\text{Rate} = k_p \times [\text{monomer}] [\text{initiator}]$ ). The solution polymerization was slow compared to the bulk and conversion was also low (Figure 6).

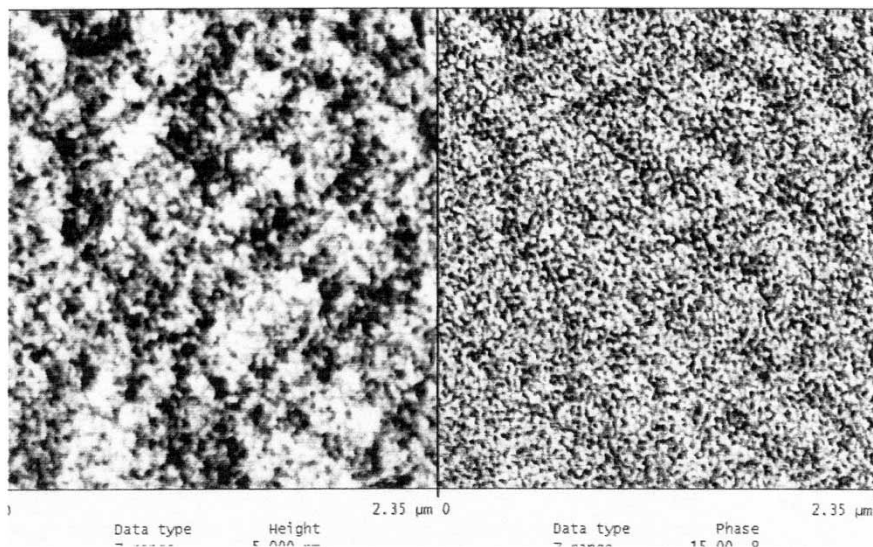
## Conclusion

The synthesis of P(MMA-*b*-*n*-BA-*b*-MMA), a thermoplastic elastomer, via ambient temperature ATRP of methyl methacrylate with CuCl/PMDETA catalyst system is reported. It is observed that the above polymerization proceeds with a reasonable rate of polymerization in bulk, resulting in block copolymers with a  $M_n$  in the vicinity of 100,000 within few hours of polymerization. Polymerizations in solution (50% v/v anisole) are

**Table 3**  
Polymerization of MMA using various Br-P(*n*-BA)-Br macroinitiators

S. No.	Macroinitiator M <sub>n</sub> (PDI)	Reaction time (h)	% Conversion	M <sub>n</sub> (theo)	M <sub>n</sub> (SEC)	PDI	Solvent system
1	12,000 (1.20)	11	74	86,500	88,100	1.38	anisole
2	13,600 (1.31)	12	53	66,600	94,000	1.26	anisole
3	13,000 (1.15)	02	49	62,000	90,900	1.28	bulk
4	13,600 (1.31)	02	43	55,600	70,200	1.20	bulk
5	19,200 (1.28)	02	51	70,600	75,300	1.19	bulk

Target DP = 1000:[Cat]:[L]:[macroinitiator] = [1]:[1]:[0.5]. PMMA standards.  
Eluent used was THF.



**Figure 6.** Tapping Mode AFM of P{(MMA)<sub>150</sub>-b-(nBA)<sub>124</sub>-b-(MMA)<sub>150</sub>.

observed to be relatively slower. A novel macroinitiator based on *n*-BA is synthesized from a binol ester using a reported procedure. The macroinitiator and block copolymers are characterized by FTIR, NMR, and GPC.

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### References

1. Matyjaszewski, K. (1997) Mechanistic and Synthetic Aspect of Atom Transfer Radical Polymerization. *J. Macromol. Sci. Pure Appl. Chem.*, A34 (10): 1785–1801.
2. Sawamoto, M. and Kamigaito, M. (1997) Metal Complex-mediated Living Radical Polymerization: Features, Scope and Precision Polymerization Synthesis. *J. Macromol. Sci. Pure Appl. Chem.*, A34 (10): 1803–1814.
3. (a) Matyjaszewski, K. Ed. (1998); *Controlled Radical Polymerization*; Washington, DC: American Chemical Society; Vol. 685; (b) Matyjaszewski, K. Ed. (2000) *Controlled Radical Polymerization: Progress in ATRP, NMP and RAFT*; Washington, DC: American Chemical Society, Vol. 768.
4. Pattern, T.E. and Matyjaszewski, K. (1998) Atom Transfer Radical Polymerization and Synthesis of Polymeric Materials. *Adv. Mater.*, 10 (12): 901–915.
5. Pattern, T.E. and Matyjaszewski, K. (1999) Copper(I)-Catalyzed Atom Transfer Radical Polymerization. *Acc. Chem. Res.*, 32 (10): 895–903.
6. Matyjaszewski, K. (1999) Transition Metal Catalysis in Controlled Radical Polymerization: Atom Transfer Radical Polymerization. *Chem. Eur. J.*, 5 (11): 3095–3102.
7. Collins, J.E. and Fraser, C.L. (1998) Transition Metals as Templates for Multifunctional Initiators: Bulk Atom Transfer Radical Polymerization of Styrene Using Di-, Tetra and Hexa Functional Ruthenium Tris(bipyridene) Reagents. *Macromolecules*, 31 (19): 6715–6717.

8. Paik, H.J., Gaynor, S.G., and Matyjaszewski, K. (1998) Synthesis and Characterization of Graft Copolymers of Poly (Vinyl chloride) with Styrene and (Meth)acrylates by Atom Transfer Radical Polymerization. *Macromol. Rapid Commun.*, 19 (1): 47–52.
9. Beers, K.L., Gaynor, S.G., Matyjaszewski, K., Sheiko, S.S., and Moller, M. (1998) The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization. *Macromolecules*, 31 (26): 9413–9415.
10. Jankova, K., Chen, X., Kops, J., and Batsberg, W. (1998) Synthesis of Amphiphilic PS-b-PEG-b-PS by Atom Transfer Radical Polymerization. *Macromolecules*, 31 (2): 538–541.
11. Gaynor, S.G. and Matyjaszewski, K. (1997) Step-growth Polymers as Macroinitiators for “Living” Radical Polymerization: Synthesis of ABA Block Copolymer. *Macromolecules*, 30 (14): 4241–4234.
12. Coessens, V., Pintauer, T., and Matyjaszewski, K. (2001) Functional Polymers by Atom Transfer Radical Polymerization. *Prog. Polym. Sci.*, 26 (3): 337–377.
13. Percec, V., Barboiu, B., and Kim, H.-J. (1998) Arenesulfonyl Halides: A Universal Class of Functional Initiator for Metal-Catalyzed “Living” Radical Polymerization of Styrenes(s) Methacrylates, and Acrylates. *J. Am. Chem. Soc.*, 120 (2): 305–316.
14. Haddleton, D.M. and Waterson, C. (1999) Phenolic Esters-Based Initiators for Transition Metal-Mediated Living Polymerization. *Macromolecules*, 32 (26): 8732–8739.
15. Shipp, D.A., Wang, J.L., and Matyjaszewski, K. (1998) Synthesis of Acrylates and Methacrylates Block Copolymers Using Atom Transfer Radical Polymerization. *Macromolecules*, 31 (23): 8005–8008.
16. Matyjaszewski, K., Shipp, D.A., Mcmurtry, G.P., Gaynor, S.G., and Pakula, T. (2000) Simple and Effective One Pot Synthesis of (Meth)acrylic Block Copolymers through Atom transfer Radical Polymerization. *J. Polym. Sci. Part A: Polym. Chem.*, 38 (11): 2023–2031.
17. Moineau, G., Minet, M., Dubois, Ph., Teyssie, Ph., Senninger, T., and Jerome, R. (1999) Controlled Radical Polymerization of (Meth)acrylates by ATRP with  $\text{NiBr}_2(\text{PPh}_3)_2$  as Catalyst. *Macromolecules*, 32 (1): 22–35.
18. Moineau, G., Minet, M., Dubois, Ph., Teyssie, Ph., Senninger, T., and Jerome, R. (1999) Synthesis and Characterization of Poly(methyl methacrylate)-block-poly(n-butylacrylate)-block-poly(methyl methacrylate) Copolymers by Two-Step Controlled Radical Polymerization (ATRP) Catalyzed by  $\text{NiBr}_2(\text{PPh}_3)_2$ , 1. *Macromolecules*, 32 (25): 8277–8282.
19. (a) Matyjaszewski, K., Wang, J.-L., and Grimaud, T., and Shipp, D.A. (1998). Controlled/“Living” Atom Transfer Radical Polymerization of Methyl methacrylates using Various Initiation Systems. *Macromolecules*, 31 (5): 1527–1534; (b) Matyjaszewski, K., Shipp, D.A., Wang, J.-L., Grimaud, T., and Pattern, T.E. (1998) Utilizing Halide Exchange to Improve Control of Atom Transfer Radical Polymerization. *Macromolecules*, 31 (20): 6836–6840.
20. Haddleton, D.M., Kukulj, D., Duncalf, D.J., Heming, A.M., and Shooter, A.J. (1998) Low-Temperature Living “Radical” Polymerization (Atom Transfer Polymerization) of Methyl Methacrylate Mediated by Copper (I) *N*-alkyl-2-pyridylmethanimine Complexes. *Macromolecules*, 31 (16): 5201–8251.
21. Xia, J.H., Gaynor, S.G., and Matyjaszewski, K. (1998) Controlled/“living” Radical Polymerization. Atom Transfer Radical Polymerization of Acrylates at Ambient Temperature. *Macromolecules*, 31 (17): 5958–5959.
22. Carlmark, A., Vestberg, R., and Johnson, E.M. (2000) Atom Transfer Radical Polymerization of Methyl Methacrylate from a Multifunctional Initiator at Ambient Temperature. *Polymer*, 43 (15): 4237–4242.
23. Wang, X.-S., Lascelles, S.F., Jackson, R.A., and Armes, S.P. (1999) Facile Synthesis Well Defined Water Soluble Polymers via Atom Transfer Radical Polymerization in Aqueous Media at Ambient Temperature. *Chem. Commun.*, 18: 1817–1818.
24. Haddleton, D.M., Perrier, S., and Bon, S.A.F. (2000) Copper (I) Mediated Living Radical Polymerization in the Presence of Oxyethylene Groups:  $^1\text{H}$  NMR Spectroscopy to Investigate Solvent Effects. *Macromolecules*, 33 (22): 8246–8251.

25. Matyjaszewski, K., Nakagawa, Y., and Jasieczek, C.B. (1998) Polymerization of *n*-Butyl Acrylate by Atom Transfer Radical Polymerization. Remarkable Effect of Ethylene Carbonate and Other Solvents. *Macromolecules*, 31 (5): 1535–1541.
26. Wang, X.-S., Jackson, R.A., and Armes, S.P. (2000) Facile Synthesis of Acidic Copolymers via Atom Transfer Radical Polymerization in Aqueous Media at Ambient Temperature. *Macromolecules*, 33 (2): 255–257.
27. Ando, T., Kamigaito, M., and Sawamoto, M. (1997) Design of Initiator for Living Radical Polymerization of Methyl Methacrylate Mediated by Ruthenium (II) Complex. *Tetrahedron*, 53 (45): 15445–15457.
28. Dayananda, K. and Dhamodharan, R. ATRP of Methyl Methacrylate Using a Novel Binol Ester-Based Bifunctional Initiator. *J. Polym. Sci. Part A: Polym. Chem.*, 42 (4): 902–915.
29. Husseman, M., Malmstrom, E.E., McNamara, M., Mate, M., Mecerreyes, D., Benoit, D.G., Hedrick, J.L., Mansky, P., Huang, E., Russell, T.P., and Hawker, C.J. (1999) Controlled Synthesis of Polymer Brushes by “Living Free Radical Polymerization Techniques. *Macromolecules*, 32 (5): 1424–1431.
30. Carrot, G., Daimanti, S., Manuszak, M., Charleux, B., and Vairon, J.-P. (2001) Atom Transfer Radical Polymerization of *n*-Butyl Acrylate from Silica Nanoparticles. *J. Polym. Sci. Part A: Polym. Chem.*, 39 (24): 4294–4301.
31. Chambard, G., Klumperman, B., and German, A.L. (2000) Effects of Solvent on The Activation Rate parameters for Polystyrene and Poly(Butyl Acrylate) Macroinitiators in Atom Transfer Radical Polymerization. *Macromolecules*, 33 (12): 4417–4421.
32. Ramakrishnan, A., Dhamodharan, R., and Ruhe, J. (2002) Controlled Growth of PMMA Brushes on Silicon Surfaces at Room Temperature. *Macromol. Rapid Commun.*, 23 (10–11): 612–616.
33. Ramakrishnan, A. and Dhamodharan, R. Facile Synthesis of ABC and CBABC Multiblock Copolymer of Styrene, *tert*-Butyl Acrylate and Methyl Methacrylate via Room Temperature ATRP of MMA. *Macromolecules*, 36 (4): 1039–1046.
34. Garcia, M.F., Jose Luis de la Fuente, Fernandez-Sanz, M., and Madruga, E.L. (2001) The Importance of Solvent Polar Character on the Synthesis of PMMA-*b*-PBA Block Copolymers by Atom Transfer Radical Polymerization. *Polymer*, 42 (23): 9405–9412.