Synthesis and thermal properties of triblock copolymers of methyl methacrylate using combination of anionic and controlled radical polymerization: Poly(methyl methacrylate) center block bearing different microstructures

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Abstract: ABA and/or ABC type triblock copolymers were synthesized by living anionic and controlled radical polymerization in which poly(methyl methacrylate) was used as central block. The structural composition of these block copolymers were determined by ^{1}H NMR. The block length/molecular weight and microstructure of these polymers were measured by SEC. The microstructure of resultant central alkyl methacrylate block can be tailored from highly syndiotactic to highly isotactic structure by varying the solvent and/or initiator. The thermal and rheological properties of center poly(methyl methacrylate) block and poly(styrene-*b*- methyl methacrylate-*b*- styrene) tri block copolymers were studied in detail.

Introduction

Block copolymers are unique materials whose characteristics may be a hybrid of the individual homopolymers. The properties of the block copolymer, such as thermal behavior, dielectric properties, and solubility, can be controlled through its composition. For example, block copolymer architecture, microstructure and sequential distribution based on poly alkyl acrylates are important parameters that impact the solubility in different solvents [1]. Synthesis of ABA type triblock copolymer can be achieved by three routes: (1) sequential monomer addition, (2) synthesis of AB diblock followed by linking reaction, and (3) successive polymerization of monomers starting from a difunctional macroinitiator. Block copolymerization of dienes and styrene can be initiated from either dienyl or styrenyl anionic species. ABA type triblock copolymers based on dienes and styrene can be synthesized in a controlled manner following above three routes. In the recent years, special attention has been focused on the synthesis of ABA triblock copolymers where the center block is based on poly alkyl methacrylate particularly in the area of polymer blends [2, 3]. Among various combinations, poly(styrene- methyl methacrylate) block copolymers are commonly used as model system, as these polymers are readily accessible, poly(styrene) and poly(methyl methacrylate) have nearly the same glass transition temperature and their physical properties are well-documented in literatures [4, 5]. Poly(styrene-*b*-poly(methyl methacrylate)-*b*-styrene) triblock copolymers have been successfully utilized as ion gel dielectrics [6, 7]. These ion gel

dielectrics comprise self-assembled network of triblock copolymers that are swollen with ionic liquids. These devices have been used as ion gel-gated polymer thin film transistors [8, 9]. This triblock copolymer was also found to be promised for stabilizing and making compatible polymer blends of polystyrene-b-poly(methyl methacrylate) and polystyrene containing lignin [10].

Nearly two decades ago, Teyssie et al demonstrated for the first time a "living" and controlled polymerization of dienes and (meth)acrylate with styrene to develop AB diblock copolymer, and (AB)$_n$ star like polymer [3]. This was achieved using conventional anionic initiator modified with different ligands, and was able to control the electronic and steric environment of the growing ion pair. The possibility of finely controlled molecular architecture (i.e., number average molecular weight with narrow molecular weight distribution) and obtaining high-purity diblock copolymers of alkyl acrylate with styrene, dienes, and 2- and 4-vinylpyridines by using a molar excess of LiCl with respect to initiator has already been demonstrated [2].

However, synthesis of ABA triblock copolymer with B block of polymethacrylate and A block of polystyrene is not possible under anionic polymerization by the utilization of sequential addition of monomers, since the alkyl acrylate enolate anions are not sufficiently basic to reinitiate a second addition of styrene monomer to obtain linear ABA triblock copolymer. Therefore, such types of triblock copolymers architecture can only be synthesized by anionic process employing a linking reaction with the macroanions of AB diblock chains or using controlled radical process such as nitroxide mediated polymerization, atom transfer radical polymerization (ATRP) where the sequence of monomer polymerization is not a critical factor.

Lu and co-workers synthesized poly(methyl methacrylate-*b*-polystyrene-*b*-methyl methacrylate) triblock copolymers were prepared by the combination of an anionic and photo induced charge-transfer polymerization [11]. Poly(styrene-b- poly(methyl methacrylate)-*b*-styrene) triblock copolymers were synthesized by anionic polymerization of MMA using a difunctional initiator, followed by the cationic polymerization of styrene [12, 13]. Nitroxide-based initiators effectively polymerize styrenic monomers by a living free radical mechanism, while acrylates are polymerized efficiently by organo cobalt complexes [14]. In addition, copper halides complexed with either 2, 2'-bipyridine or a 4, 4'-disubstituted 2, 2'-bipyridine can catalyze the polymerization of both styrene and acrylate with a suitable initiator [15]. ATRP, however, is a synthetic polymerization technique that may be useful for producing block copolymers including multi blocks, which are difficult to prepare by conventional anionic methods since it require proper selection and sequential addition of suitable monomer [16]. Percec et al reported controlled polymerization with a low polydispersity (1.1-1.5) of both methyl methacrylate and styrene using arenesulfonyl chlorides with a copper halide/2, 2'-bipyridine complex [17]. Eastwood and Dadmun studied the feasibility of using ATRP for the polymerization of styrene and methyl methacrylate monomers in order to prepare homo, triblock and pentablock copolymers, with both styrene and methyl methacrylate as a center block [18]. Matyjaszewski and co-workers have demonstrated the ability of ATRP to synthesize multi block copolymers without site transformation methods that includes ABA triblock copolymers of poly(methyl methacrylate-*b*-butyl acrylate-*b*-methyl methacrylate) [19] and poly(*tert.* butyl acrylate-*b*-styrene-*b*-*tert.* butyl acrylate) [20], ABC triblock copolymers of poly(*tert.* butyl acrylate-*b*-styrene-*b*-methyl acrylate) [20], and ABCD tetra block copolymers of poly(*tert.* butyl acrylate-*b*-styrene-*b*-methyl acrylate-*b*-methyl methacrylate) [21].

It is known that the microstructure of poly alkyl methacrylate play a very important role to forecast the mechanical and thermal properties of the resulting block copolymers (e.g., glass transition temperatures and crystallinities), and thus influence their applications in certain fields such as in ink industry. Therefore, a polymerization process, which is able to readily and precisely control the tacticity of alkyl methacrylate chains in multiblock copolymers, is being required. However, in a strict sense, controlled radical polymerizations mainly yield heterotactic poly alkyl methacrylates or heterotactic-rich polymers.

In this paper, we would like to introduce a novel method to control the microstructure of poly alkyl methacrylate in the formation of ABA/ABC type triblock copolymers where center 'B' block will be poly alkyl methacrylate in a combination of anionic and controlled radical polymerization. The microstructure of resulted central alkyl methacrylate block can be tailored from highly syndiotactic to highly isotactic structure, which in turn affects the thermal and rheological properties and network formation in the melt. In first step, we will examine the feasibility of synthesizing quantitative bromo end functionalized poly(styrene-*b*-methyl methacrylate) diblock macroinitiators using anionic living polymerization. In second step, to prepare triblock copolymers, these bromo monochelic functionalized macroinitiators will be used to initiate the polymerization of styrene and *tert.* butyl 4-vinyl benzoate monomer by controlled radical process, and studied their solution properties in detail. The thermal and rheological properties of center poly(methayl methacrylate) block as well as poly(styrene-*b*-methyl methacrylate-*b*-styrene) tri block copolymers have also been examined.

Results and discussion

The aim of the present work is to evaluate the feasibility of synthesis of triblock copolymers of methyl methacrylate in the central block, which could yield various tunable microstructures. It is well documented in the literature that polymerization of methyl methacylate (pMMA) macro anions in tetrahydrofuran (THF) at -78 °C in the presence of μ-type ligand are "true living" anionic process [22, 23]. This approach offers interesting prospects for the macromolecular engineering in designing macromolecules with well-defined molecular architecture.

Tab. 1. Characteristic data for bromo end functionalized pMMA using functional anionic initiator to different microstructure:

Sample	Initiator	[a]Conversion (%)	[b]MW (M_n, Da)	[b]M_w/ M_n	[a]Microstructure % s %h %i			[c]Tg (°C)	[a]Bromo end functionality (%)
1	DPHLi	100	1100	1.15	69	28	03	82	>99%
2	Sec. BuLi Li-OSi(CH$_3$)$_3$	80.0	5000	1.80	24	01	75	43	>90%
3	Cumyl Potassium	100	3000	1.08	36	58	06	76	>99%

[a]Measured by ^{1}H NMR, [b]Measured by SEC, [c]Determined by DSC.

Obviously, the living pMMA macroanions, instead of being used in block copolymers, can also be end-functionalized by reacting with their terminal carbanion(s) with appropriate electrophiles, which can aid to control the properties of individual microstructures while being used as macro-anions for the preparation of suitable diblock or tri block polymer. Herein, we synthesized and characterized 2-bromo-2-methyl propionyl bromide for the termination and functionalization of living pMMA carbanion. Different molecular weight of living pMMA macroanion was prepared by living anionic polymerization in THF where MMA is being used as monomer, and variable amounts of lithium chloride (LiCl), lithium dimethyl silonate or cumyl potassium was used as initiator. The properties of selective bromo end functionalized pMMA-Br with different tacticity are depicted in Table 1.

^{1}H NMR spectra measured the tacticity and end functionality of bromo end functionalized pMMA rich in syndiotactic and isotactic structure, and are illustrated in Figure 1 and 2. The incorporation of the 2-bromopropionyl group into pMMA was confirmed from the appearance of the dimethyl protons of 2-bromopropionyl end group at around 1.8 ppm.
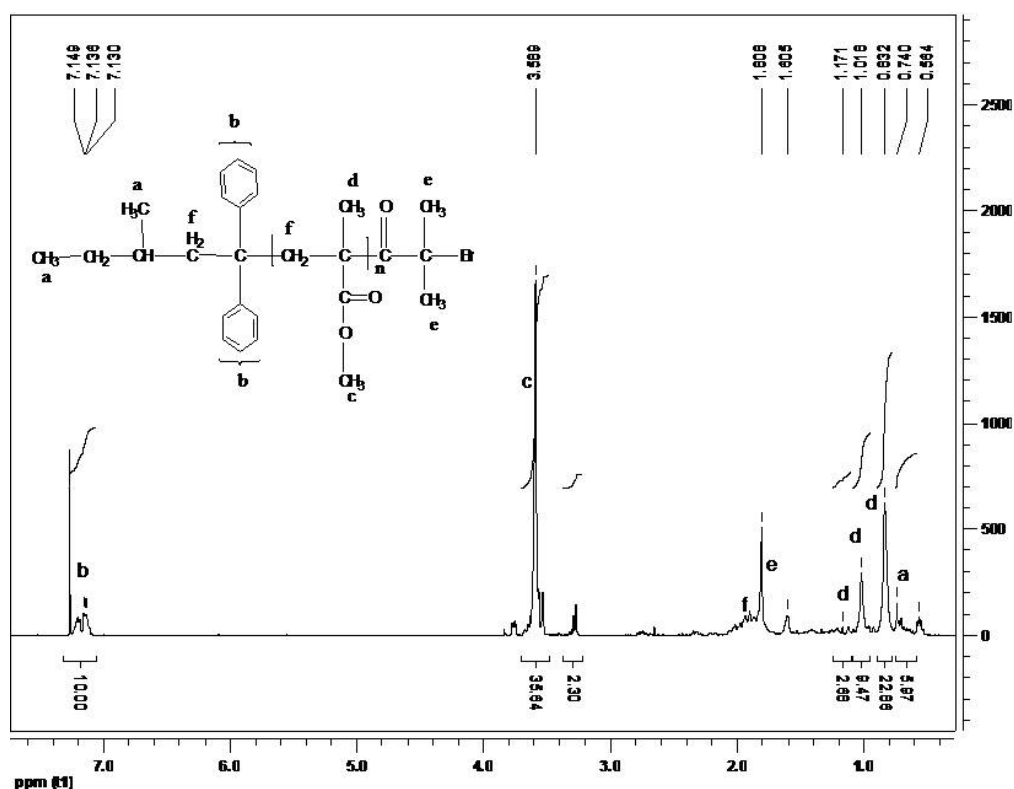

Fig. 1. ^{1}H NMR spectra of pMMA-Br rich in syndiotactic macromer (Table 1, Sample 1).

The end functionalization was measured by the comparison of the area of the terminal dimethyl peaks at around 1.8 ppm with the area of the signals due to the pendent H-atoms, the methyl ester peak at 3.6 ppm, and over 90% bromo end group functionalization was achieved in each case (Table 1). pMMA bearing over 68% syndiotactic triads were synthesized in THF at -78 ºC using lithium based monofunctional initiator in the presence of LiCl as an additive (Table 1, Sample 1), while over 75% isotactic rich pMMA is achieved when the polymerization was carried

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out in toluene in the presence of an adduct formed by reaction between sec-butyl lithium and hexamethyl cyclotrisiloxane (lithium silanoate) (Table 1, Sample 2), and relatively higher heterotactic pMMA (~58%) structure can be synthesized when cumyl potassium was used without any ligand in THF at -78 °C (Table 1, Sample 3) .

The molecular weight (MW) and polydispersity index (*Mw/Mn*) of purified pMMA-Br macromers were determined by SEC, and are shown in Table 1. Based on the percentage of conversion and the feed ratio of initiator and monomer, the molecular weight of the macro monomers (end functionalized polymer) were found to be in good agreement with the designed values, indicating good control of the polymerization and the successful preparation of the well-controlled bromo end functionalized pMMA-Br microstructure. Differential Scanning Calorimetry (DSC) was used to measure the glass transition temperature (T_g) of pMMA-Br macromers with different microstructures and molecular weights. The thermal properties of the macromers are presented in Table 1, and the effect of molecular weight and architecture on glass transition temperature is depicted in Figure 3. The T_g of the syndiotactic and isotactic pMMA-Br was found to be significantly different (Table 1, Figure 3) in value, which clearly indicates that this unique approach allows us successful preparation of bromo end functionalization with controllable microstructure. The glass transition temperature increased as the MW increased for the polymers with the same microstructure, and become flat above the MW around 20000 Da (Figure 3). This inclined that above the indicated MW; the macromer form certain organized coil and comparatively rigid mobile chain structure, and thermal properties of the individual microstructure were not dependent on the chain lengths.
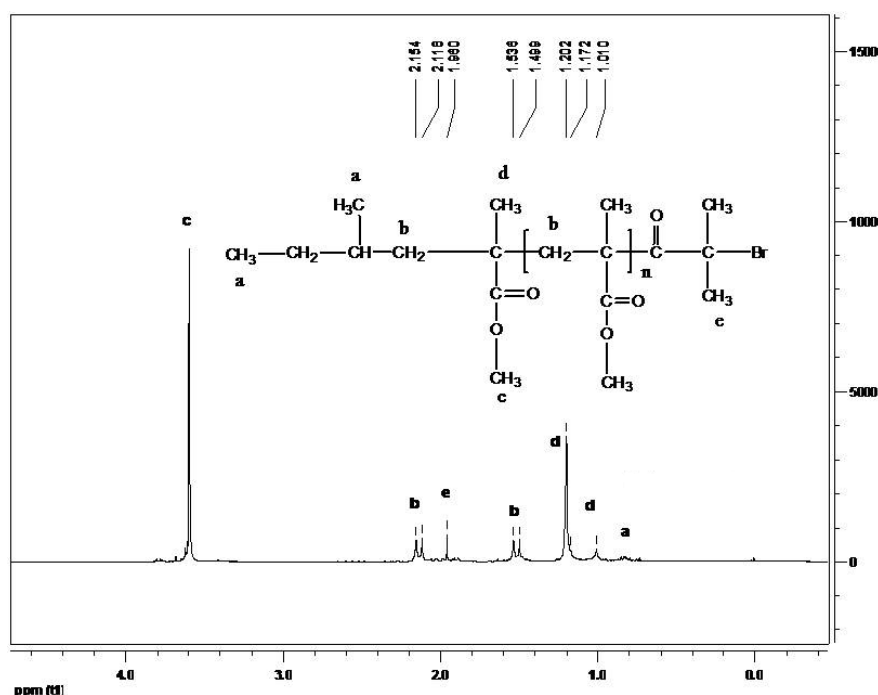

Fig. 2. ^{1}H NMR spectra of pMMA-Br rich in isotactic macromer (Table 1, Sample 2).

This method was then used to explore the synthesis of bromo end functionalized p(St-*b*-MMA)-Br diblock macroinitiators. As expected, several pMMA block bearing highly syndio rich triads to highly isotactic rich triads along with polystyrene or

poly(*tert*. butyl 4-vinyl benzoate) as a third block were prepared and characterized, and is presented in Table 2.
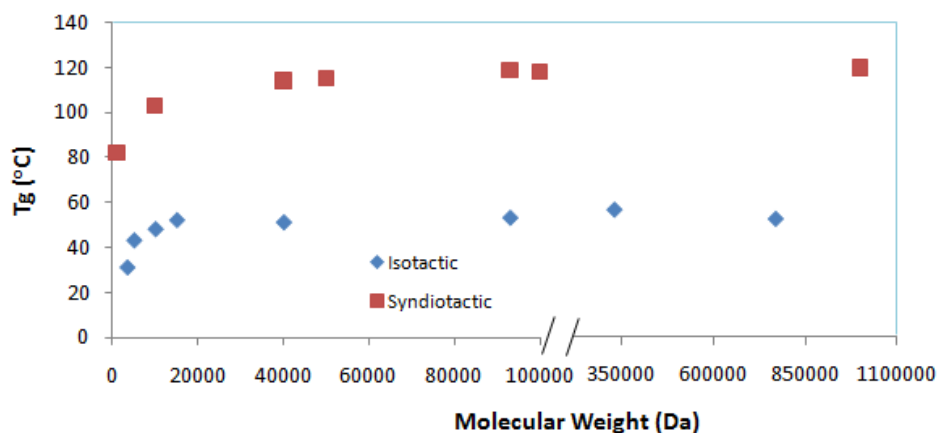

Fig. 3. Effect of molecular weight on Tg in syndiotactic and isotactic pMMA-Br macromers.

Tab. 2. Characteristic data for ABA or ABC type triblock copolymer synthesized from bromo functionalized p(St-*b*-MMA) macroinitiator:

Sample	[a]Macroinitiator; (p(St-*b*-MMA)-Br MW: M_n [b](M_w/M_n)	Monomer	[a]MW of triblock: M_n (M_w/M_n)	[a]Microstructure of pMMA block % s %h % i			[c]Tg (ºC)
1	4300-*b*-12500 (1.13)	Styrene	4300-*b*-12500-b-4300 (1.13)	80	20	0	MMA:115; St: not distinct
2	5000-*b*-13000 (1.11)	Styrene	5000-*b*-13000-b-5000 (1.11)	61	38	1	MMA:100; St: not distinct
3	7,000-*b*-9,000 (1.18)	Styrene	7,000-*b*-9,000-b-2,800 (1.18)	78	20	2	MMA: 111; St: not distinct
4	7,000-*b*-9,000 (1.18)	Styrene	7,000-*b*-9,000-b-3,800 (1.18)	78	20	2	MMA: 100; St: not distinct
5	7,000-*b*-9,000 (1.18)	*tert*. butyl 4-vinyl benzoate	7,000-*b*-9,000-b-8,000 (1.13)	78	20	2	MMA: 119 St: not distinct

[a]Measured by ^{1}H NMR, [b]Measured by SEC, [c]Determined by DSC.

These bromo end functionalized macroinitiators could be used effectively in ATRP controlled radical polymerization process for the synthesis of various types of triblock polymers where MMA has been used as central block. In this study, p(St-*b*-MMA-*b*-St) or p(St-*b*-MMA-*b*-*t*-BuVB) triblock copolymers were synthesized by initiating styrene or *tert*. butyl 4-vinylbenzoate monomers using an ATRP process. The properties of the resultant triblock copolymers derived from corresponding p(St-*b*-

MMA)-Br macro initiators are depicted in Table 2. Sample 1 to 4 (Table 2) could be denoted as ABA type tri block copolymer in which "A" corresponds to styrene and "B" is methyl methacrylate. On the other hand, sample 5 (Table 2) could be denoted as ABC type triblock copolymers in which "C" corresponds to *tert*. butyl 4-vinyl benzoate. The block length/ MW of extended polystyrene and/or *tert*. butyl 4-vinyl benzoate in these ABA and ABC type triblock copolymers was calculated from the distinct ^{1}H NMR peaks and by SEC. It was found that MW of the corresponding triblock copolymers increases with increase in monomer loading as expected. The MW of ABA type copolymers obtained by ^{1}H NMR closely matched with the value obtained by SEC. Similar finding was observed in ABC type copolymer after the addition of *tert*. butyl 4-vinyl benzoate to p(St-*b*-MMA)-Br for the transformation of individual p(t-BuVB) block, which clearly dictate the successful preparation of ABA and/or ABC type triblock copolymers with well controlled microstructure.

DSC analysis showed that each of the triblock copolymer only has one distinct glass transition temperature (T_g). The presence of single T_g was expected since the T_g of individual homopolymers was in close range. (T_g for the PS homopolymer was 90 °C, and the corresponding value for pMMA homopolymer was about 98 °C). Results shows that pMMA-Br syndiotactic macromers is about 40 °C higher T_g than corresponding isotactic one (Figure 3). Similar trend was observed in tri block copolymers, when syndiotactic portion was reduced with the preparation of heterotacticity (Table 3, Sample 1-2). With a comparable molecular weight of MMA syndiotactic rich structure, it was found that addition of a block length of styrene and/or *tert*. butyl 4-vinyl benzoate, T_g of the corresponding triblock copolymer can be altered (Table 3, Sample 3-5). These results clearly indicate that the stereo regularity of polyacrylate chain plays an important role, and thermal and mechanical properties can be tuned by the proper selection and incorporation of a suitable monomer in the resulting block copolymers.

In this paper, the melt rheological behavior of two poly(St-*b*-MMA-*b*-St) triblock copolymers of a similar molecular weight with a comparable syndiotactic structured polymers (Table 2) were studied and compared.
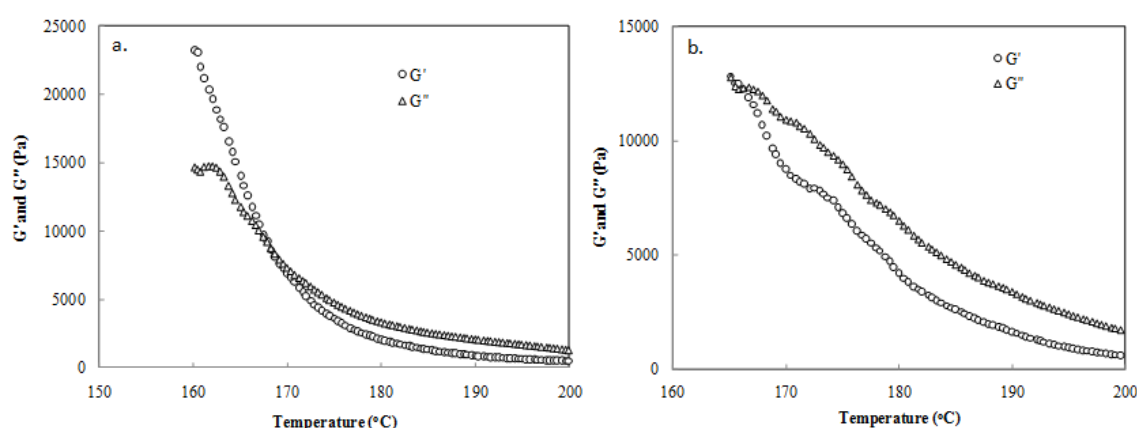

Fig. 4. Isochronal temperature ramp of a) poly(St-*b*-MMA-*b*-St), 80% syndiotactic (Table 2, Sample 1), and b) poly(St-*b*-MMA-*b*-St), 61% syndiotactic (Table 2, Sample 2) at a frequency of 1 Hz and a heating rate of 2.5 °C/min.

Figure 4 shows a distinct cross-over point of elastic (G') and viscous modulus (G") at 166.2 and 168.3 °C, respectively for 80% and 61% syndiotactic poly(St-*b*-MMA-*b*-St).

The temperature had a significant influence on dynamic modulii of the triblock copolymer; both the elastic modulus (G') and the viscous modulus (G") decreased exponentially as a function of temperature. A slight increase in the gelation point temperature for poly(St-*b*-MMA-*b*-St), 61% syndiotactic, is attributed to larger polystyrene block (Figure 4-b). A consistent higher magnitude of viscous modulus (G") confirmed the liquid-like property of the melt above the gel point. These observations indicate that both poly(St-*b*-MMA-*b*-St) became disordered block copolymer above the cross-over temperature. Furthermore, both copolymers are thermodynamically disordered liquid above these temperatures. The lack of very sharp transitions in the rheological data compared to other block copolymer systems may be due to an overlap of glass transition temperatures of the polystyrene and poly(methyl methacrylate) block. A similar observation has been reported by Fei et al for poly(styrene-*b*-methylacrylate-random-octadecylacrylate-*b*-styrene) [24].
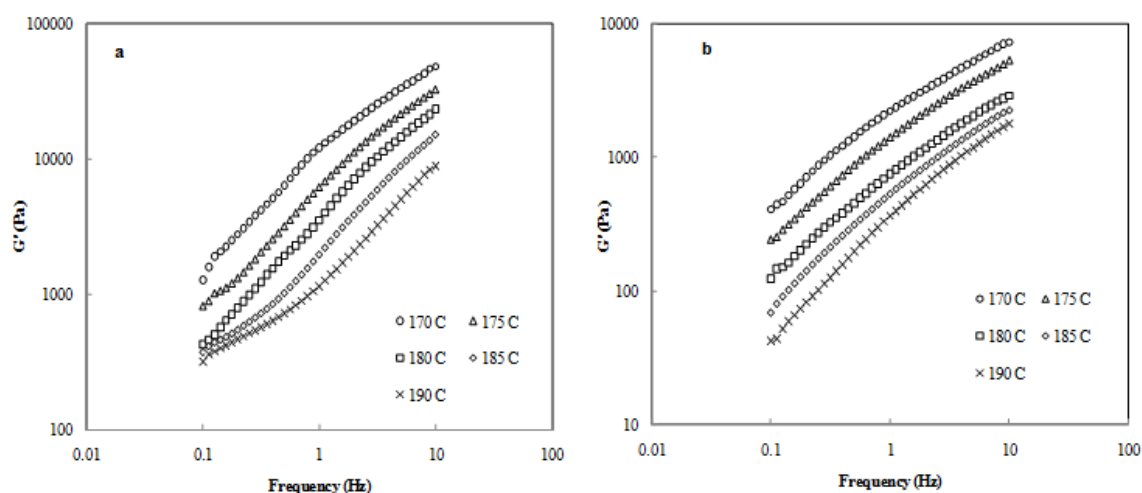

Fig. 5. Effect of temperature on elastic modulus of a) poly(St-*b*-MMA-*b*-St), 80% syndiotactic (Table 2, Sample 1), and b) poly(St-*b*-MMA-*b*-St), 61% syndiotactic (Table 2, Sample 2) polymer.

The temperature dependence of the G', G" and η* poly(St-*b*-MMA-*b*-St) triblock copolymers are illustrated in Figures 5, 6 and 7, respectively. Figure 5 present the variation of G' with temperature as a function of frequency. As the frequency increases, the elastic modulus of the samples increases irrespective of the temperatures being applied. This behavior can be explained on the basis of time-dependent molecular relaxation of the polymers. At lower frequency range, there is enough time for relaxation for the polymer, and they exhibited lower mechanical strength with applied force. However, at higher frequency range, the stress applied to polymers is too fast for molecular rearrangement, and thus flow becomes restricted, resulting in higher mechanical strength. Similar observation has been observed for ATRP synthesized typical ABA triblock copolymer [25]. The 61% syndiotactic triblock copolymer (Figure 4-b) exhibited higher mechanical strength (G') compared to 80% syndiotactic one due to larger polystyrene block (Figure 4-a). The G' systematically decreased in both as temperature was increased from 170 to 190 ºC (Figure 5). The lower G' at higher temperature is an outcome of the cross-link scission which generates more volume for deformations within the polymer.

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Figure 6 show the variation of G'' with frequency as selected temperatures. Following the same trend of G'-ω, the viscous modulus increased with frequency and decreased as a function of temperature. The G'' was significantly higher than that of G' for both samples in the studied temperature range, and therefore, samples exhibited predominating liquid-like properties. The G'' values of 80% syndiotactic polymer was considerably higher than 61% syndiotactic one (Figure 6). The lower values of G'' in the lower frequency range of the sample supported more molecular relaxations as was observed by Kavitha et al [25]. A continuous increase in G'' as frequency increased from 0.1 to 10 Hz has been attributed by restricted flow behavior in limited time frame that hindered the molecular relaxation depending upon applied temperature. The significant drop of the G'' at 190 ºC is due to polymeric chains become free for intermolecular slippage that causes flow.
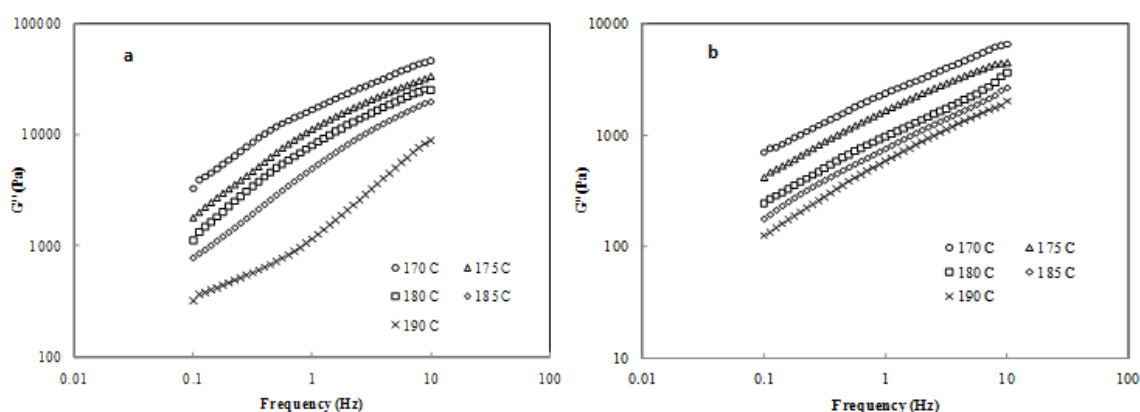

Fig. 6. Effect of temperature on viscous modulus of a) poly(St-*b*-MMA-*b*-St), 80% syndiotactic (Table 2, Sample 1), and b) poly(St-*b*-MMA-*b*-St), 61% syndiotactic (Table 2, Sample 2) polymer.
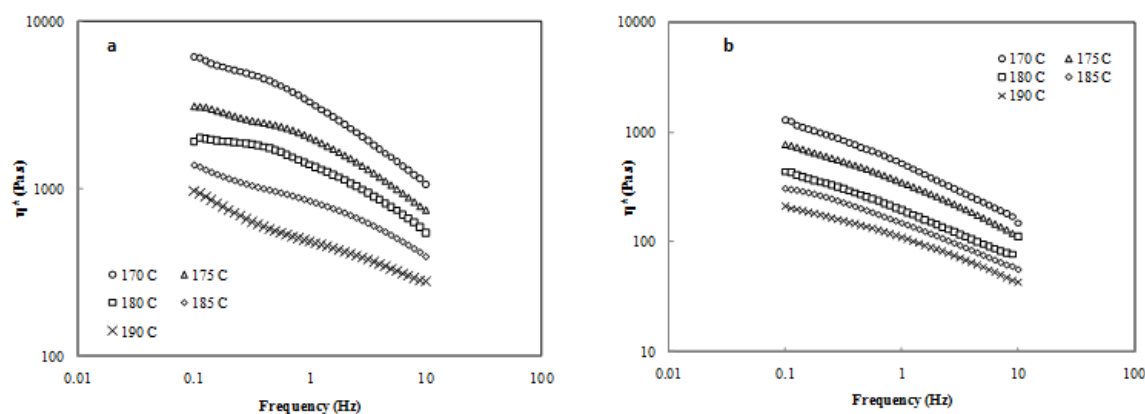

Fig. 7. Effect of temperature on complex viscosity of a) poly(St-*b*-MMA-*b*-St), 80% syndiotactic (Table 2, Sample 1), and b) poly(St-*b*-MMA-*b*-St), 61% syndiotactic (Table 2, Sample 2), polymer.

Figure 7 illustrates the effect of frequency on complex viscosity (η^*) at selected temperatures. The η^* decreased as frequency was increased from 0.1 to 10 Hz. This observation indicated a shear-thinning behavior of the triblock copolymers. The

change of η^* was relatively slower at higher melting temperature than that of low melting temperatures (Figure 7). This is due to thermal cleavage of the cross-links in the polymer which eases molecular slippage among the chains. Furthermore, the change of η^* was prominent at lower frequency range which further confirmed the appearance of a gel network, and supports higher G' and G" data. It also indicates that the dynamic rheological behavior at low frequency was more sensitive to the micro-structural changes of the polymeric materials.

Tab. 3. Regression parameters for equation (1) for triblock copolymer during isothermal heating.

Sample	Temperature (^{o}C)	Slope	Intercept	R^2	S.E.
poly(St-*b*-MMA-*b*-St) (4300-*b*-12500-*b*-4300), 80% syndiotactic	170	0.55	15169	0.98	0.10
	175	0.64	9572	0.98	0.12
	180	0.67	7034	0.98	0.12
	185	0.72	4510	0.99	0.07
	190	0.73	1387	0.98	0.14
poly(St-*b*-MMA-*b*-St) (5000-*b*-13000-*b*-5000), 61% syndiotactic	170	0.49	2268	0.99	0.04
	175	0.52	1586	0.99	0.06
	180	0.57	956	0.98	0.11
	185	0.57	733	0.99	0.04
	190	0.60	554	0.99	0.05

The viscoelastic characteristics of the triblock copolymer melt can be well described by calculated slopes of the linear regression of the power-type relationship of ln ω vs ln G' or G" (eq. 1) which is commonly used to predict the solid or liquid-like characteristics of polymers. Since, the G" was significantly higher than that of G', and therefore, G" was used to determine the liquid-like behavior of the triblock copolymer melt.

$$G' \ or \ G'' = A\omega^{n} \qquad \text{Linear form: } \ln G' \ or \ G'' = \ln A + n \ln \omega \qquad (1)$$

where n is the slope (dimensionless) and A is the intercept (Pa.s^n).

The magnitude of the slope for both 80% and 61% syndiotactic triblock copolymers is presented in Table 3. Rheological data (G'-ω) are fitted adequately ($R^2 > 0.98$). The slopes ranged from 0.55 to 0.73 for poly(St-*b*-MMA-*b*-St), 80% syndiotactic and the corresponding values were found to be 0.49 and 0.60 for 61% syndiotactic polymer. The liquid-like properties increased as slopes are increased systematically with applied temperature (170 to 190 ºC). These data indicated that both copolymers behaved like shear thinning fluid at melt.

The creep and recovery behavior of melt copolymers of poly(St-*b*-MMA-*b*-St), 80% and 61% syndiotactic triblock copolymers were studied at 180 ºC, and are shown in Figure 8. The experiments were performed starting with a low stress of 1 Pa and increased gradually to 15 Pa. For both samples, the strain increased with time indicating the sample started to flow immediately when the stress was applied (Figure 8). After the stress was removed, both polymers tried to regain the strain slowly. The recovery was found to be a function of applied stress. The strain recovery shortened as the applied stress was increased.

During each creep and recovery test, the segmental mobility of the polymer at different stages of deformation happened. During creep, as the stress increased, a faster strain was observed, indicating higher mobility for poly(St-*b*-MMA-*b*-St), 61% syndiotactic polymer (Figure 8-b). The large deformation is a consequence of the broken structure of the melt. During recovery, the sample had more time to rebuild structure. It was observed that poly(St-*b*-MMA-*b*-St), 80% syndiotactic polymer regained only 18% of its original strain during recovery time of 300 sec whereas poly(St-*b*-MMA-*b*-St), 61% syndiotactic polymer retained almost 53% of its original strain (Figure 8-a, b). These data clearly indicate that poly(St-*b*-MMA-*b*-St), 80% syndiotactic polymer lost its original structure more severely than that of poly(St-*b*-MMA-*b*-St), 61% syndiotactic polymer at similar stress level. It is further confirms that at low strains both triblock copolymer had a time dependent melt rheological response, a thixotropic behavior [26].
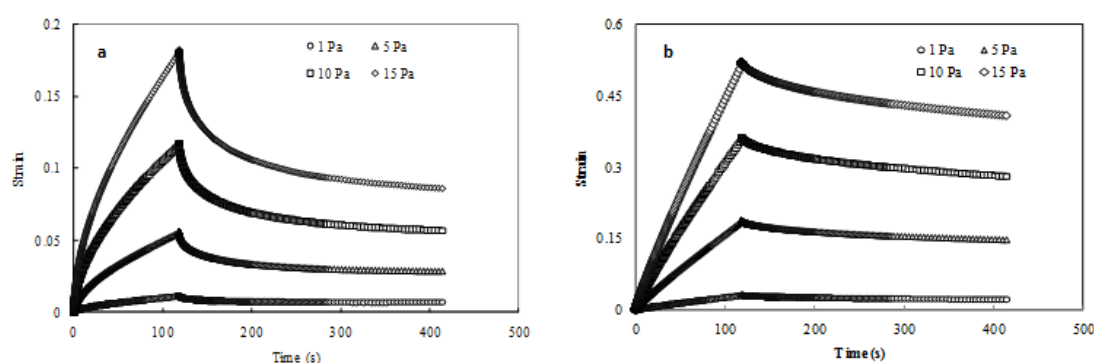

Fig. 8. Creep and recovery of poly(St-*b*-MMA-*b*-St), a) 80% and b) 61% syndiotactic triblock copolymers at 180 °C.

The detail comparative thermal and melt rheological behavior study of syndiotactic, isotactic and atactic poly(St-*b*-MMA-*b*-St) triblock copolymers are currently underway in our laboratory, and will be reported separately.

Conclusions

We have successfully synthesized and characterized bromo end functionalized poly(St-*b*-MMA)-Br macroinitiators, and subsequently prepared various tri block copolymers in a controlled fashion. We showed that this controlled synthetic process is very efficient for the formation of ABA/ABC type triblock copolymers with moderate MW of individual block. It could also be very useful for the formation of asymmetric ABA and/or ABC type triblock copolymers where terminal block of polystyrene or *tert.* butyl 4-vinyl benzoate could bear variable MW. The thermal properties of various block copolymers can be controlled by changing the tacticity of the central MMA block. The variable MW of triblock copolymers with comparable syndiotacticity played a significant role in variations of dynamic rheological modulii. Copolymer containing larger polystyrene block showed higher mechanical strength (G'>G'') which is duly supported by higher glass transition temperature. Both copolymers, however, showed predominating liquid-like shear-thinning behavior during melt due to disordered state of the block copolymer at higher temperature.

Experimental section

Materials

Styrene (St), methyl methacrylate (MMA) (99%) and lithium chloride (LiCl) (99.99%) were purchased from Sigma Aldrich and purified as required for the living anionic polymerization. *Tert.* butyl 4-vinylbenzoate (*t*-BuVB) was prepared by reacting 4-vinylbenzoyl chloride with tert-butanol in dry diethyl ether in presence of potassium *tert*-butoxide following previously published literature procedure [27].

Copper (I) chloride (99%), 2,2'-bipyridine (99%) and anisole ($\geq$ 99%) were purchased from Sigma-Aldrich and used as received. N,N,N′,N″,N″-pentamethyldiethylenetriamine ($\geq$ 98%) and 2-bromo-2-methyl propionyl bromide were also purchased from Aldrich and was purified by distillation under atmospheric pressure, and the middle fraction was collected to use for the reaction. Tetrahydrfuran (THF) was purified by refluxing over fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent). It was further distilled over oligomers of styryl lithium under reduced pressure immediately before use. Oligomeric α-methyl styryllithium (α-MSLi) was prepared by reacting *sec*-BuLi with a slight molar excess of α-methylstyrene (α-MS) in THF at -20 ^{o}C temperature, and used as a monofunctional initiator.

Structural Characterization

^{1}H NMR spectra were used to measure the microstructure of these polymers in CDCl$_3$ solution on a **Bruker** DRX spectrometer (400 MHz), and tetramethylsilane was used as internal reference. All chemical shifts were reported in parts per million (ppm). The molecular weight (MW) and polydispersity index (PDI) of functionalized pMMA, diblock and triblock polymers were determined by size exclusion chromatography (SEC) with a system consisting of Varian liquid chromatograph equipped with a refractive index, UV and light scattering detectors. The samples were eluted with THF, passing through three SEC columns (Supelco, G6000-4000-2000HXL) with a flow rate of 1.0 mL/min and the system was calibrated with narrow dispersed MW polystyrene/polymethyl methacrylate standards.

Thermal Properties

Thermal analysis of all these polymers was carried out on a TA (Q100) Differential Scanning Calorimeter (DSC) (TA Instruments, Newcastle, DE, USA) calibrated with indium under an ultra high purity nitrogen atmosphere using a flow rate of 50 ml/min. Approximately 10 mg samples were employed and were encapsulated in aluminum pans. An empty aluminum pan was used as a reference in all measurements. Samples were heated at 10 ºC/min over a range of 0-175 ºC, and T$_g$ was taken as the midpoint of the transition during the second heating cycle. Analysis of the data was performed using TA Instruments Universal Analysis Software.

Melt Rheology

Rheological measurements of polymer samples were performed on a controlled-stress rheometer (AR 2000Ex, TA Instruments, New Castle, DE, USA) with parallel plate geometry (40 mm diameter) in the melt state (170-190 ºC). The temperature range was chosen because the range was above gel point (G' and G'' cross over point 168.3 ºC). The width of the gap between two plates was 1000 µm. The sample

temperature was internally controlled by a Peltier system attached with a water circulation unit. Specimens were compression-molded under vacuum into disks and loaded into the rheometer. For each test, samples were placed at the centre of the rheometer plate for five minutes for complete melting and temperature equilibration before the actual measurements. A stress sweep test was initially conducted to determine the linear viscoelastic range (LVR) of samples. The frequency ranges used during testing were 0.01 to 10 Hz. The domain of linear viscoelasticity was established by the oscillatory stress sweep tests for each sample. Rheology Advantage software (TA Instruments, New Castle, DE, USA) was used to acquire data. The deviation did not exceed 5% between duplicate runs, as the experiment was repeated. The average of the triplicate runs was reported as the measured value. The creep and recovery behavior was measured using parallel plate rheometer. The sample was allowed to stand at 180 $^{\circ}$C for 5 min. In the creep step, selected shear stress was applied instantaneously and the applied stress was released after 2 min with a recovery phase time of 3 min.

Preparation of bromo end functionalized poly(methyl methacrylate) (pMMA-Br)

Reaction flask was equipped with three-way stop cock bearing rubber septum for the addition of the required reagents. Polymerization was carried out under argon (>99.999%) atmosphere. One molar equivalent of dried LiCl with respect to initiator was first introduced into the reaction flask followed by addition of freshly purified THF. A slight molar excess of diphenylethylene with respect to the required amount of Sec. butyl lithium initiator was added to THF solution. The 0.2M initiator solution was added drop wise to THF (500 ml) until the initiator color persists; usually 3-4 drops of initiator (0.2M) solution is required to get a persistent red color. The solution was cooled to -78 $^{\circ}$C, followed by the addition of required quantity of freshly purified MMA and the polymerization reaction was continued for 15 min at -78 $^{\circ}$C. Polymerization was terminated by adding 2 molar excess of freshly distilled 2- bromo-2- methyl propionyl bromide with respect to the initiator (Sec BuLi) at -78 $^{\circ}$C, and solution was stirred for 1 h at -78 $^{\circ}$C. The pMMA-Br was recovered by precipitation into cold methanol. The product was further purified to remove excess of 2- bromo-2-methyl propionyl bromide from polymer by dissolving polymer in THF and re precipitated in cold methanol. Product was then dried under vacuum for 48 h at 40 $^{\circ}$C.

Preparation of bromo end functionalized AB diblock copolymer of poly(styrene-b-methyl methacrylate) [p(St-b-MMA)-Br]

Bromo end functionalized diblock copolymer of styrene and MMA was prepared by anionic polymerization by successive addition of styrene and methyl methacrylate monomer respectively. Briefly, 2 molar excess of 2-bromo-2-methyl propionyl bromide with respect to the initiator (Sec BuLi) was used to terminate the polymerization reaction. An aliquot of the reaction mixture was withdrawn for SEC analysis in order to determine the MW of first polystyrene block. The copolymer was recovered by precipitation into methanol. The product was further purified by dissolving in THF and reprecipitated in cold methanol in order to remove trace amount of excess terminating reagent. Product was then dried under vacuum for 48 h at 40 $^{\circ}$C. This diblock macroinitiator was then used for the synthesis of tri block copolymer.

Preparation of ABA/ABC triblock polymer using an extension of [p(St-b-MMA)-Br] diblock copolymer by ATRP

ABA or ABC triblock polymers were synthesized from bromo end functionalized AB diblock copolymer using ATRP process. In a typical polymerization, 5 g p(St-*b*-MMA)-Br (M_n: 7000-b-9000 Da) was transferred in a 250 ml one neck flask equipped with a three way stop cock bearing a rubber septum. The bromo functionalized copolymer was dried further under vacuum for 30 minutes at room temperature, and then 15 ml dried anisole was added into the reaction flask to dissolve the polymer, followed by the addition of 0.03 g (0.30 mmol) CuCl (I) and 0.05 g (0.29 mmol) of N,N,N′,N″,N″-pentamethyldiethylenetriamine. In case of ABA type triblock polymer, 2.5 g (24.00 mmol) styrene, and in preparation of ABC type polymer 2.5 g (12.25 mmol) *tert*. butyl 4-vinylbenzoate was added to the reaction flask under argon atmosphere. The polymerization was carried out at 90 ^{o}C for 12 h, while the solution was being agitated with a magnetic stir. After polymerization, the crude triblock polymer was dissolved in chloroform and the solution was passed through a column packed with silica to remove inorganic salts from the polymer. The filtrate was concentrated under vacuum and the polymer solution was precipitated in ethanol/hexane (1:1). Polymer was then dried for 18 h in vacuum oven at 50 ^{o}C. Yield: ABA; 6.3 g (84%).

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