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Synthesis and Characterization of Copolymers of 5,6-Benzo-2-methylene-1,3-dioxepane and Styrene

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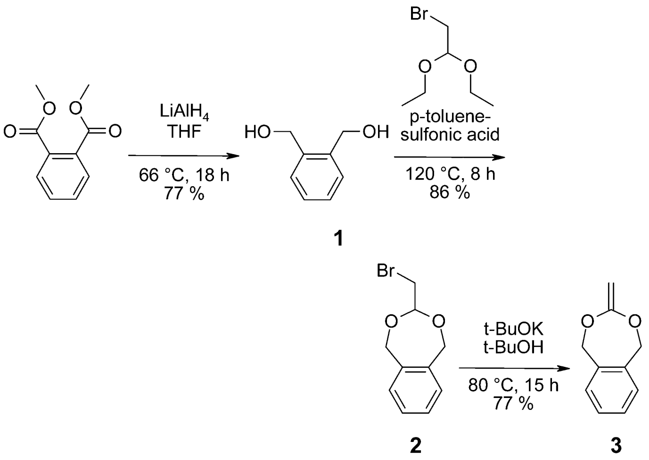
ABSTRACT: Copolymerization behavior of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) with styrene (St) is studied using benzyl bromide/CuBr/1,1,4,7,7-pentamethyldiethylenetriamine radical initiating system. Structural characterization of copolymers was done using 1D and 2D NMR techniques. The copolymer compositions were obtained from ^{1}H NMR spectroscopy. The reactivity ratios for the copolymerization of BMDO with St were determined using Kelen−Tüdõs method and was found to be $r_{\mathrm{BMDO}} = 1.08$ and $r_{\mathrm{St}} = 8.53$. Degradation behavior of the copolymers is also reported.

Introduction

Aliphatic polyesters are important biodegradable and biocompatible materials in the field of medicine, pharmacy and agriculture. There is a continuous development in the synthesis of these polyesters and ring-opening polymerization (ROP) provides a more convenient synthetic route as compared to the traditional step condensation method.[1] However, more recently, there is an ever increasing literature on use of cyclic monomers having an *exo*-methylene group as starting material for the synthesis of polyesters using radical initiators.[2−8] There is always an increasing environmental concern that demands sooner or later all plastic materials to be biodegradable. This radical-initiated method of synthesis of polyesters has its fundamental importance in easy incorporation of biodegradable/hydrolytically unstable ester linkages onto otherwise nonbiodegradable vinyl polymer backbone. This can easily be achieved by radical initiated copolymerization of *exo*-methylene cyclic compounds with vinyl monomers. Much work has already been done on homo- and copolymerization of 2-methylene-1,3-dioxepane (MDO) and its substituted derivatives with vinyl monomers.[2,4−6] Studies with MDO and other *exo*-methylene cyclic compounds clearly shows that the mechanism of reaction after the initiation step with a radical varies with the change in the ring size, initiator, and substituents on the ring.[6−9] 5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) is another interesting cyclic monomer with *exo*-methylene group. It is expected to give good mechanical properties besides introducing hydrolytic/biodegradable ester linkages in vinyl copolymers. It is reported to give quantitative ROP reaction in the presence of both conventional (AIBN) and living radical (ethyl α-bromobutyrate/CuBr/2,2′-bipyridine) initiators giving corresponding polyester.[10−12] Block copolymerization of BMDO with methyl acrylate, methyl methacrylate, and styrene by ATRP is reported by Pan et al.[13,14] Recently we have reported the copolymerization parameters, stereochemical, and compositional assignments of poly(BMDO-*co*-MMA) copolymers.[15] Keeping in mind our broad interest of introducing easily degradable linkages onto vinyl polymer backbones, it would be of interest to study copolymerization behavior of BMDO and a commodity plastic like polystyrene (PS).

Scheme 1



This paper reports detailed studies on copolymerization behavior of BMDO in the presence of styrene (St) as comonomer using benzyl bromide/CuBr/1,1,4,7,7-pentamethyldiethylenetriamine ATRP initiating system. To the best of our knowledge, this is the first attempt to give complete structural characterization and copolymerization parameters for poly(BMDO-*co*-St) copolymers.

Experimental Section

Materials. THF (BASF) was purified by distillation over potassium. *tert*-Butanol (Aldrich) was dried with calcium hydride, distilled and stored under argon. Dimethyl phthalate (Merck), lithium aluminum hydride (Aldrich), potassium *tert*-butyl alcoholate (Aldrich), potassium hydroxide (Riedel-de-Haën), hydrochloric acid (Merck), sulfuric acid (Merck), 1,1,4,7,7-pentamethyldiethylenetriamine (Acros), CuBr (Acros), *p*-toluenesulfonic acid (Aldrich), and silica gel (Merck) were used as received. Diethyl ether (BASF), hexane (BASF), methanol (BASF), and bromoacetaldehyde diethylacetal (Acros) were distilled before use. Benzyl bromide (Merck) was dried with Na_2SO_4 and distilled. Styrene was dried over CaH_2 and distilled.

5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) was synthesized in the laboratory using the literature method of Grewe et al.[16] with some modifications (Scheme 1).

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Synthesis of 1,2-Benzenedimethanol (1). First, 1 L dry THF and 56 g (1.4 mol) $LiAlH_4$ were placed in a predried three-neck flask fitted with a dropping funnel, under argon. To this was added 196 mL (1.2 mol) dimethyl phthalate in 300 mL of THF dropwise with stirring. After completion of the addition of dimethyl phthalate, the reaction contents were refluxed for 18 h. The mixture is hydrolyzed at ice temperature with 1.5 L of water having 400 mL H_2SO_4. After extraction with diethyl ether three times (each time 1 L of diethyl ether), the organic phase was washed with $NaHCO_3$ solution and then with water and then dried over Na_2SO_4. Diethyl ether was evaporated off, and the crude product was recrystallized from 1 L of $CHCl_3$/hexane 1:1 mixture giving 128 g (77%) of **1** as white crystals: mp 64 °C. ^1H NMR (200 MHz, $CDCl_3$): δ/ppm 4.03 (s, 2H, $-CH_2O\mathit{H}$), 4.48 (s, $-C\mathit{H}_2OH$), 7.20 (s, 4H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm 63.69 (2C, $-\mathit{C}H_2OH$), 128.38, 129.52, 139.20 (6C, Ar).

Anal. Calcd ($C_8H_{10}O_2$): C, 69.55; H, 7.30. Found: C, 69.18; H, 7.75.

Mass spectrum (EI): *m/z* 121 (4.75), 120 (100), 119 (82.43), 118 (1.55), 104 (10.15), 92 (20.86), 91 (56.98), 90 (3.01), 89 (1.67), 79 (18.46), 78 (6.89), 77 (19.17), 65 (19.39), 51 (2.4), 44 (1.07), 40 (29.57), 39 (6.39).

5,6-Benzo-2-(bromomethyl)-1,3-dioxepane (2). A mixture of 117.44 g (0.85 mol) of **1**, 167.51 g (0.85 mol) of bromoacetaldehyde diethylacetal, and 900 mg of *p*-toluenesulfonic acid was heated at 120 °C for 8 h under argon in a predried flask fitted with a Claisen bridge and dropping funnel for collecting ethanol. When almost all the calculated amount of ethanol was collected, the temperature of the reaction mixture was raised to 160 °C under reduced pressure. The crude product **2** was solidified on cooling the reaction mixture to room temperature. The product was dissolved in $CHCl_3$ and washed with $NaHCO_3$ solution and water. After evaporation of the solvent, crude product was recrystallized from 1.2 L cyclohexane to give about 177 g (86%, white crystals) of **2**. Mp: 98 °C. ^1H NMR (200 MHz, $CDCl_3$): δ/ppm 3.46 (d, 2H, ^3J = 5.24 Hz, $((-CH_2O)_2CHC\mathit{H}_2Br)$, 4.93 (s, 4H, $C_6H_4C\mathit{H}_2O-$), 5.13 (t, 1H, ^3J = 5.12 Hz, $(-CH_2O)_2C\mathit{H}CH_2Br$), 7.16−7.27 (m, 4H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ/ppm 31.45 (1C, $(-CH_2O)_2CH\mathit{C}H_2Br$), 71.74 (2C, $C_6H_4\mathit{C}H_2O-$), 105.81 (1C, $(-CH_2O)_2\mathit{C}HCH_2Br$), 127.40, 127.67, 138.38 (6C, Ar).

Anal. Calcd ($C_{10}H_{11}O_2Br$): C, 49.41; H, 4.56; Br, 32.87. Found: C, 49.14; H, 4.76; Br, 29.75.

Mass spectrum (EI): *m/z* 244 (9.54), 242 (10.06), 150 (16.41), 149 (57.72), 121 (11.65), 119 (11.78), 105 (5.24), 104 (30.51), 93 (36.37), 92 (13.39), 91 (100), 90 (1.47), 89 (2.84), 77 (6.85), 65 (4.33), 43 (1.23).

5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) (3). First, 158.02 g (0.65 mol) of **2** and 78.55 g (0.65 mol) of *t*-BuOK were allowed to react in the presence of 1 L of *t*-BuOH under argon at 80 °C for 15 h. After this, 1 L of diethyl ether was added to the reaction mixture. The insoluble material was removed by passing through silica gel. The organic layer was dried over Na_2SO_4, diethyl ether was removed and the crude liquid obtained was distilled under reduced pressure to give a colorless liquid which solidified to white crystals on standing, giving 82 g (77%) of 3; mp 44 °C. ^1H NMR (200 MHz, $CDCl_3$): δ/ppm 3.71 (s, 2H, $(-CH_2O)_2C{=}C\mathit{H}_2$), 5.04 (s, 4H, $C_6H_4C\mathit{H}_2O-$), 7.05−7.08 (m, 2H, Ar), 7.21−7.23 (m, 2H, Ar). ^{13}C (50 MHz, $CDCl_3$): δ/ppm 69.48 (1C, $(-CH_2O)_2C{=}\mathit{C}H_2$), 71.99 (2C, $-C_6H_4\mathit{C}H_2O-$), 126.14, 127.38, 135.79 (6C, Ar), 164.21 (1C, $(-CH_2O)_2\mathit{C}{=}CH_2$).

Anal. Calcd ($C_{10}H_{10}O_2$): C, 74.06; H, 6.21. Found: C, 72.84; H, 6.97.

Mass spectrum (EI): *m/z* 163 (100), 162 (2.9), 122 (5.84), 121 (73.12), 120 (71.1), 119 (65.41), 104 (22.02), 93 (6.63), 92 (6.92), 91 (4.91), 43 (58.59).

Homo- and Copolymerization of BMDO and St. In general, all homo- and copolymerization reactions were carried out under argon in predried Schlenk tubes under ATRP reaction conditions. In a typical copolymerization reaction (run 5, Table 1), 29 mg (0.2 mmol) of CuBr, 1.83 g (11.3 mmol) of BMDO, 1.3 mL (11.3 mmol) of styrene, 21 μL (0.2 mmol) of benzyl bromide and 43 μL (0.2 mmol) of 1,1,4,7,7-pentamethyldiethylenetriamine were placed in a Schlenk tube under argon. The mixture was degassed by two cycles of freeze−pump−thaw and then placed in a preheated oil bath at 120 °C for 72 h. The reaction mixture was dissolved in chloroform and precipitated in MeOH−HCl. Purification of the copolymers was done by dissolving in $CHCl_3$ and reprecipitation in MeOH. Drying of copolymers was done under vacuum at room temperature until constant weight. Homopoly(BMDO) (PBMDO), polystyrene (PS), and different copolymers of BMDO and St were made by changing the molar ratio of the two monomers in the feed, under similar reaction conditions as described above. Details of the reaction conditions with monomer feed ratios are given in Table 1.

Table 1. Copolymerization Data and Reaction Conditions for St−BMDO Copolymers

	feed ratio (molar ratio)				copolymer composition (molar ratio)	
run[a]	BMDO	St	yield (%)	$M_n \times 10^{-4}$	BMDO	St
1	100	0	42	0.59	100	0
2	80	20	53	0.45	63	37
3	70	30	24	0.96	42	58
4	60	40	46	0.50	36	64
5	50	50	41	1.57	19	81
6	30	70	41	3.21	6	94
7[b]	0	100	63	19.16	0	100

[a] Monomer:benzyl bromide:CuBr:ligand = 100:1:1:1 (molar ratio); temperature = 120 °C; time 72 h. [b] Temperature = 110 °C.

Hydrolysis of BMDO−Styrene Copolymer. First, 400 mg of copolymer (run 5, Table 1) was dissolved in a mixture of 50 mL of KOH in methanol (5 wt %) and 30 mL of THF in a round-bottom flask and was refluxed for 1 week. After this, 5 mL of concentrated hydrochloric acid was added. The mixture was extracted with chloroform and washed with water. The solvent was evaporated under reduced pressure. The remaining solid was dried under vacuum at room temperature.

Instrumentation. The molecular weights of the polymers were determined by GPC using a Knauer system equipped with two columns, PSS−SDV (linear, 10 μL, 60 × 0.8), a differential refractive index detector, and a UV photometer using $CHCl_3$ as eluent at a flow rate of 0.83 mL/min.

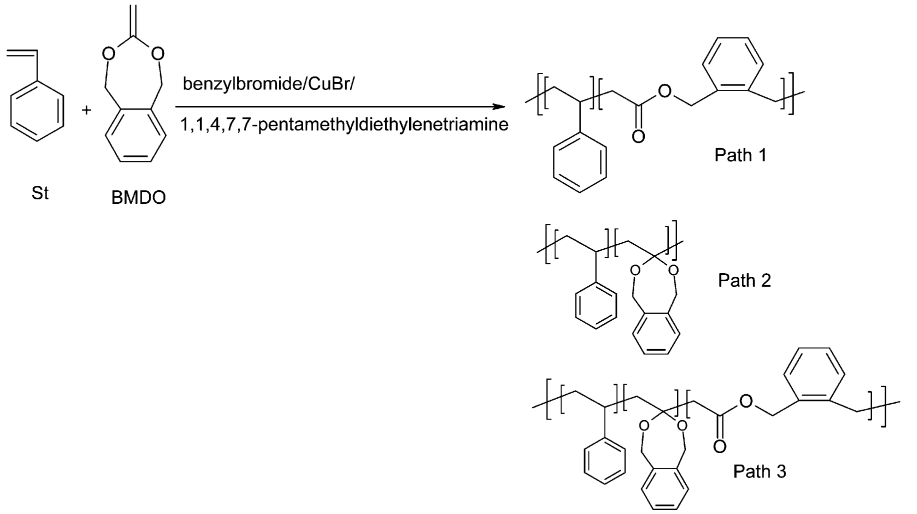
^1H (400.13 MHz), ^{13}C (100.21 MHz), and ^{13}C-DEPT NMR spectra were recorded on a Bruker DRX-400 spectrometer. Tetramethylsilane (TMS) was used as internal standard. $^1H-^{13}C$ correlation experiments were performed on a Bruker DRX-500 spectrometer, with a 5 mm multinuclear gradient probe and using gs-HMQC and gs-HMBC pulse sequences. The HMQC experiment was optimized for C−H coupling of 140 Hz, with decoupling applied during acquisition; while the HMBC experiment was optimized for coupling of 8 Hz, with decoupling during acquisition. 2D NMR data were acquired with 2048 points in t_2, and the number of increments for t_1 was 256. A total of four and eight scans were used for HMQC and HMBC experiments respectively, and four dummy scans were used for both the experiments. A relaxation delay of 1 s was used for all 1D experiments and 2 s for all 2D experiments. Typical experiment times were about 1.5 and 3.0 h for HMQC and HMBC, respectively.

Mettler thermal analyzers having 851 TG and 821 DSC modules were used for the thermal characterization of copolymers. DSC scans were recorded in nitrogen atmosphere at a heating rate of 10° C/min. Thermal stability was determined by recording TG traces in nitrogen atmosphere (flow rate = 50 mL/min) using powdered samples. A heating rate of 10° C/min and sample size of 10 ± 1 mg were used in each experiment.

Results and Discussion

The BMDO monomer was synthesized by a slightly modified version of the method of Grewe et al.[16] The

Scheme 2



detail characterization is mentioned in the experimental part. Copolymerization of BMDO and styrene was carried out under ATRP reaction conditions using benzyl bromide/CuBr/1,1,4,7,7-pentamethyldiethylenetriamine initiator system (Scheme 2). Various copolymers of BMDO with St were made by changing the molar ratio of two monomers in the initial feed. There was no systematic variation of molecular weight with change in copolymer composition, but in general, copolymers with high styrene content had high molecular weights (Figure 1, Table 1). Copolymerization of St with BMDO could lead to copolymers with different structures as shown in Scheme 2 by ring opening reaction of BMDO and/or vinyl addition reaction at its double bond. Therefore, structural characterization of copolymers was done using NMR spectroscopic techniques. The representative ^{1}H NMR of copolymer sample (run 5, Table 1) is shown in Figure 2. The characteristic proton signals of both St and BMDO units were present and are marked in Figure 2 based on the signals of homo PS and that of homo-PBMDO.[15] There are some other minor peaks present at 2.2, 2.4, and 2.5 ppm. ^{13}C NMR spectrum of copolymers showed 10 strong signals of PBMDO (Figure 3). These signals were at 172.5 ppm $(-\mathrm{CH_2}C\mathrm{(O)OCH_2}-)$, six signals at 126.8, 128.9, 129.2, 130.2, 133.7, 139.5 ppm from aromatic carbons, 64.5 ppm $(-\mathrm{CH_2C(O)O}C\mathrm{H_2}-)$, 35.5 ppm $(-\mathrm{C(O)OCH_2C_6H_4}C\mathrm{H_2}-)$, and 27.5 ppm $(-C\mathrm{H_2C(O)OCH_2}-)$. The signals at 172.5 and 64.5 ppm also showed further splitting into some minor signals. The PS signals were present at 41.9−46.6 $(-C\mathrm{H_2CH(C_6H_5)}-)$ and 40.6 ppm $(-\mathrm{CH_2}C\mathrm{H(C_6H_5)}-)$ and aromatic carbons were present between 125.8 and 145.8 ppm. Other small but noticeable peaks were observed at 19.0, 21.1, 29.2, 30.4, 37.6, and 39.9 ppm which will be characterized in the later part using 2D NMR techniques. The absence of signal between 100 and 110 ppm implies the absence of polyacetal linkages. This in turn signifies the quantitative ring opening of BMDO with no traces of vinyl type addition at double bond and hence path 1 (Scheme 2) as the only route of copolymerization. ^{13}C NMR technique gives first indication about the copolymer structure. The presence of a major carbonyl peak at 172.5 ppm with some minor peaks shows the structure to be random with long blocks of comonomeric units. ^{13}C HMQC (heteronuclear multiple quantum correlation) technique was used for complete ^{13}C NMR peak assignments. From the ^{1}H−^{13}C HMQC spectrum shown in Figure 4, six separate cross-peaks (A, B, C, D, E, and F) can easily be seen besides other cross-peaks from BMDO and St units. The cross-peak A is from correlation of protons at 2.4 ppm with carbon signal at 19.0 ppm. A broad peak centered at 2.0 ppm in ^{1}H NMR spectrum showed correlation with three small peaks in ^{13}C NMR spectrum at 21.1 ppm (peak B), 37.6 ppm (peak D), and 46.7 ppm (peak E). The correlation of protons at 2.2 and 2.7 ppm with that of carbon signals at 30.4 and 29.2 ppm gives peaks C and F respectively in HMQC NMR spectrum. The peak at 2.4 ppm in ^{1}H NMR is assigned to the methyl group attached to the phenyl ring, formed as a result of 1,7 hydrogen abstraction by the growing benzyl radical (backbiting reaction) (Scheme 3). The correctness of this peak assignment is confirmed using 2D ^{1}H−^{13}C HMBC NMR technique that clearly showed the correlation of these protons (at 2.4 ppm; proton 8) with aromatic carbon signals (Figure 5). The same backbiting reaction was also observed in the homopolymers of BMDO.[15] The carbon signals at 46.7 and 39.9 ppm are assigned to the linking units $(-C\mathrm{H_2CH(C_6H_5}-))$ (12) and $(-\mathrm{CH_2}C\mathrm{H(C_6H_5}-))$ (6) of PS, respectively. The linking units of BMDO $(-\mathrm{CH_2C(O)}$-

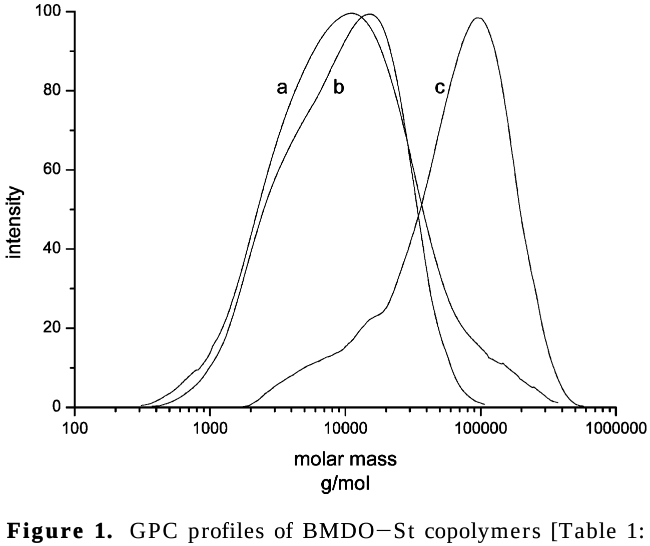


Figure 1. GPC profiles of BMDO−St copolymers [Table 1: (a) run 2; (b) run 4; (c) run 6].

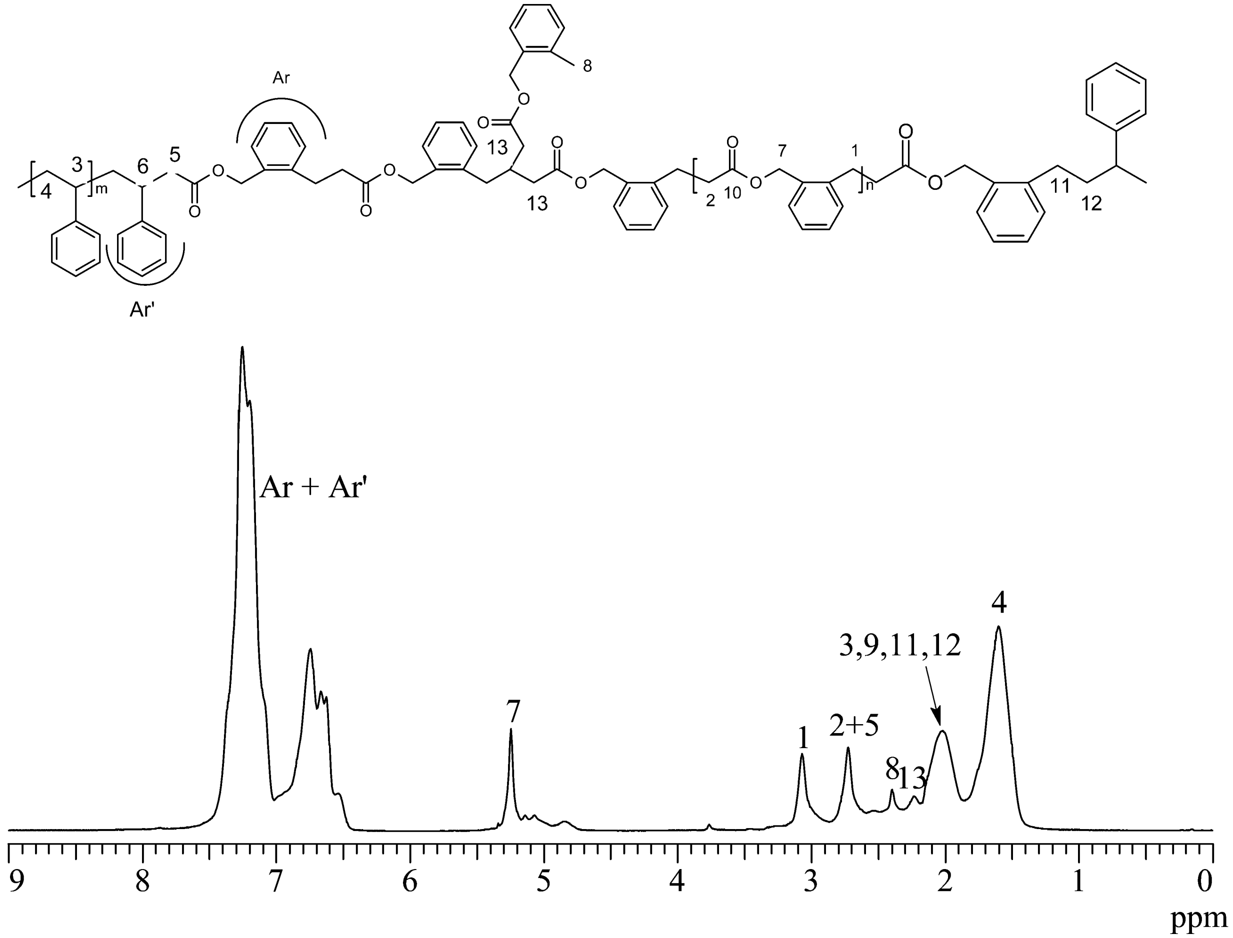


Figure 2. ^{1}H NMR spectrum of BMDO−St copolymer in CDCl$_3$ (run 5; Table 1).

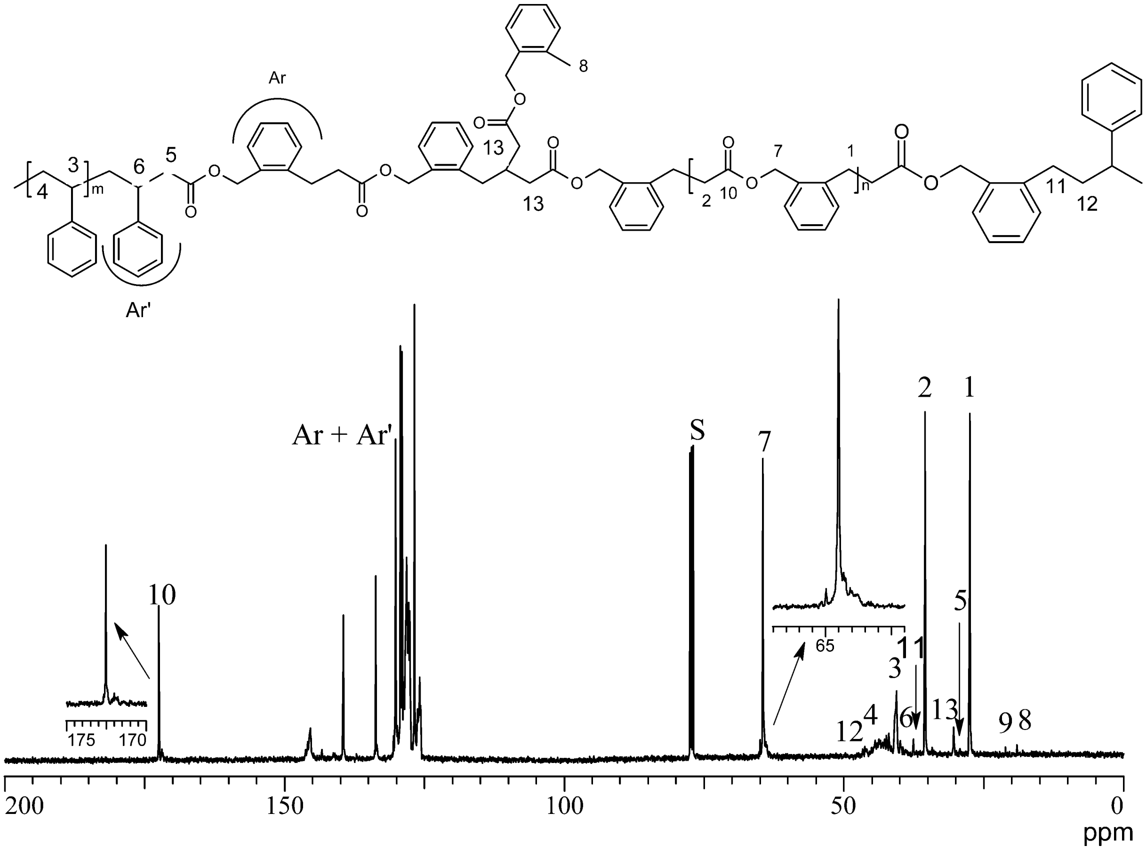


Figure 3. ^{13}C NMR spectrum of BMDO−St copolymer in CDCl$_3$ (run 5; Table 1).

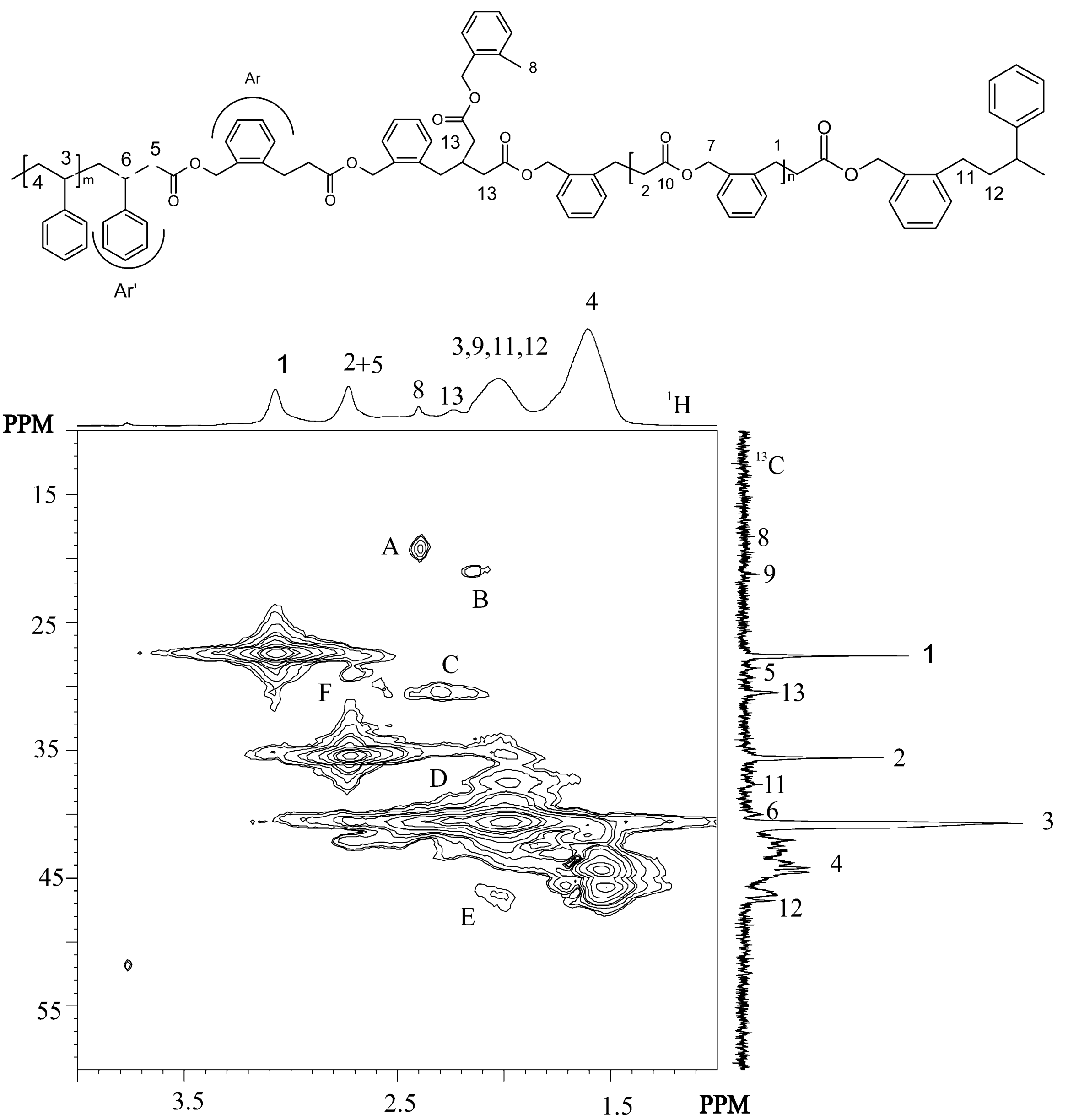
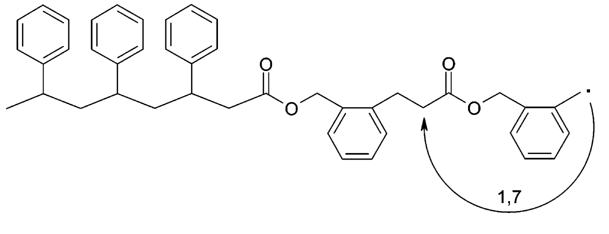


Figure 4. Part of the ^{1}H−^{13}C HMQC NMR spectrum of BMDO−St copolymer (run 5; Table 1): ^{1}H NMR region 1−4 ppm; ^{13}C NMR region 10−60 ppm.

Scheme 3



OCH$_2$−C$_6$H$_4$−*C*H$_2$−) (11) and (−*C*H$_2$C(O)OCH$_2$−) (5) are assigned at 37.6 and 29.2 ppm respectively. (−*C*H$_2$C(O)OCH$_2$−) (13) units of BMDO branches are assigned at 30.4 ppm. In DEPT the suggested signals for carbons 5, 11, and 12 appeared as negative peaks with respect to the signal of CDCl$_3$ thereby showing them to be from CH$_2$ groups (Figure 6). The signals from the linking units were so weak that no correlation originating from these peaks could be seen in 2D HMBC/COSY techniques. Therefore, the suggested assignments of these peaks could not be reconfirmed using 2D NMR techniques. The copolymer composition was determined by taking the total peak areas of aromatic protons of BMDO and St units together (I_{Ar}) and that of −OC*H*$_2$−C$_6$H$_4$− protons of BMDO at 5.1 ppm (I_{BMDO}) using the following formula:

$$I_{\mathrm{BMDO}} = 2x \Leftrightarrow x = \frac{I_{\mathrm{BMDO}}}{2}$$

$$I_{\mathrm{Ar}} = 4x + 5y \Leftrightarrow y = \frac{I_{\mathrm{Ar}} - 4x}{5} = \frac{I_{\mathrm{Ar}} - 2I_{\mathrm{BMDO}}}{5}$$

$$(x{:}y = \text{molar ratio of BMDO:St})$$

It is observed that the mole fraction of St was more in copolymers as compared to that in the initial feed (Table 1). The reactivity ratio of the two monomers is calculated using the Kelen−Tüdõs[17] method (Figure 7) and

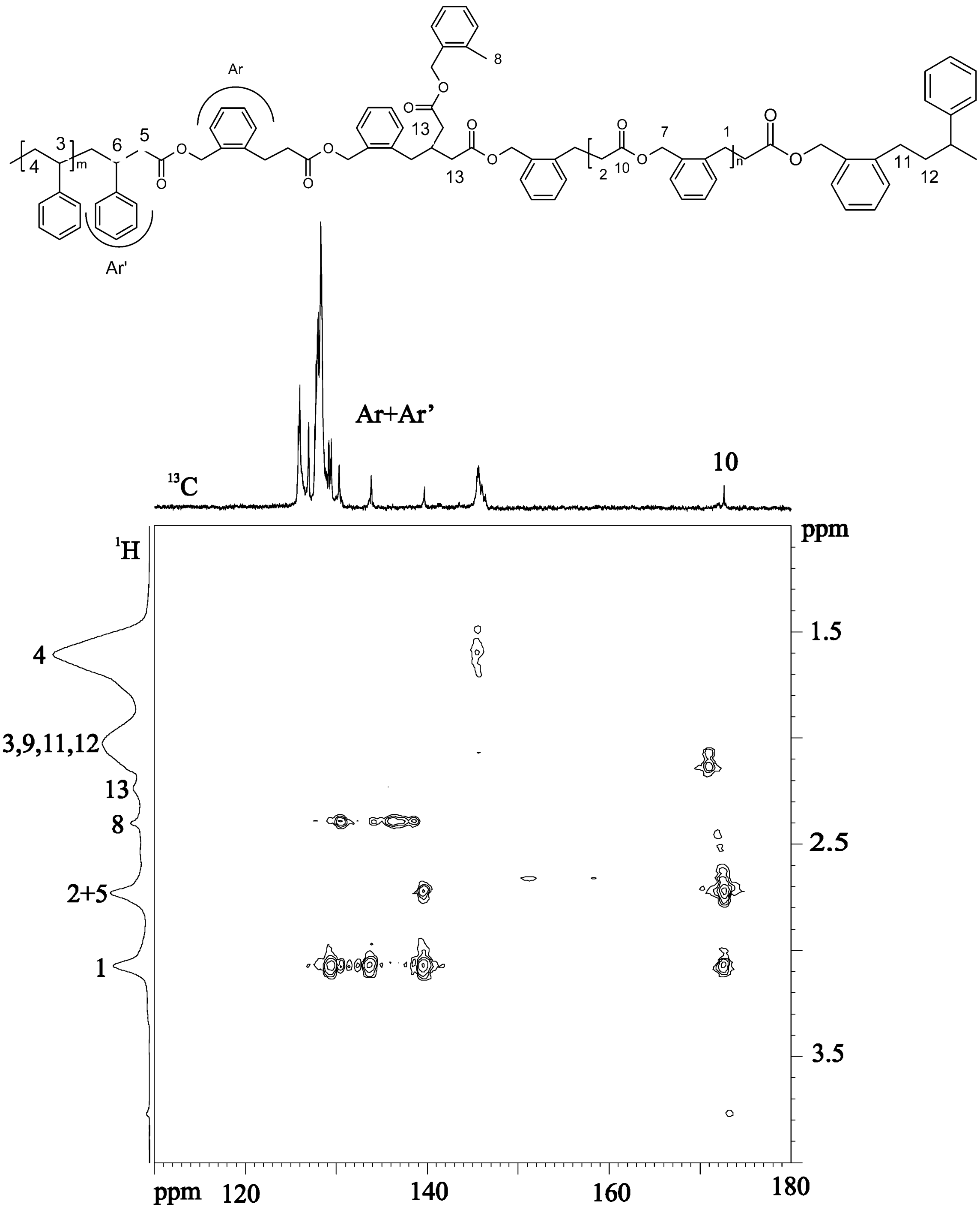


Figure 5. Part of the ^{1}H$-$^{13}C HMBC NMR spectrum of BMDO$-$St copolymer (run 5; Table 1); ^{1}H NMR region 1$-$4 ppm; ^{13}C NMR region 110$-$180 ppm.

found to be $r_{\mathrm{BMDO}} = 1.08$ and $r_{\mathrm{St}} = 8.53$. The high value of reactivity ratio for styrene and BMDO combined with 1D and 2D NMR characterization suggests the copolymer structure to be random with long blocks of monomeric units. The comparatively high reactivity ratio of styrene could be due to the higher stability of the corresponding styryl radical as compared to BMDO radical. BMDO radical is destabilized as compared to styryl radical due to the presence of two electron-rich oxygen atoms as its neighbors. It is worth to note the change in the reactivity ratio values from 0.021:22.6 (r_{MDO}:r_{St})/only homopolymerization of St[6,18] to 1.08:8.53 (r_{BMDO}:r_{St}) with change in the structure of the starting exo methylene cyclic monomer from MDO to BMDO. This may be due to the difference in the stability of the corresponding alkyl/benzyl radicals generated.

Thermal characterization of copolymers was done using TGA and DSC techniques. The glass transition values for the copolymers are listed in Table 2. Single glass transition was obtained for copolymers having low mole fraction of the comonomer units (runs 2 and 6, Table 2). With an increase in the amount of comonomer, for example St in the copolymers (runs 3$-$5, Table 2), two glass transitions were observed having values between the glass transition values for the homopolymers PS and PBMDO. With further increase in the

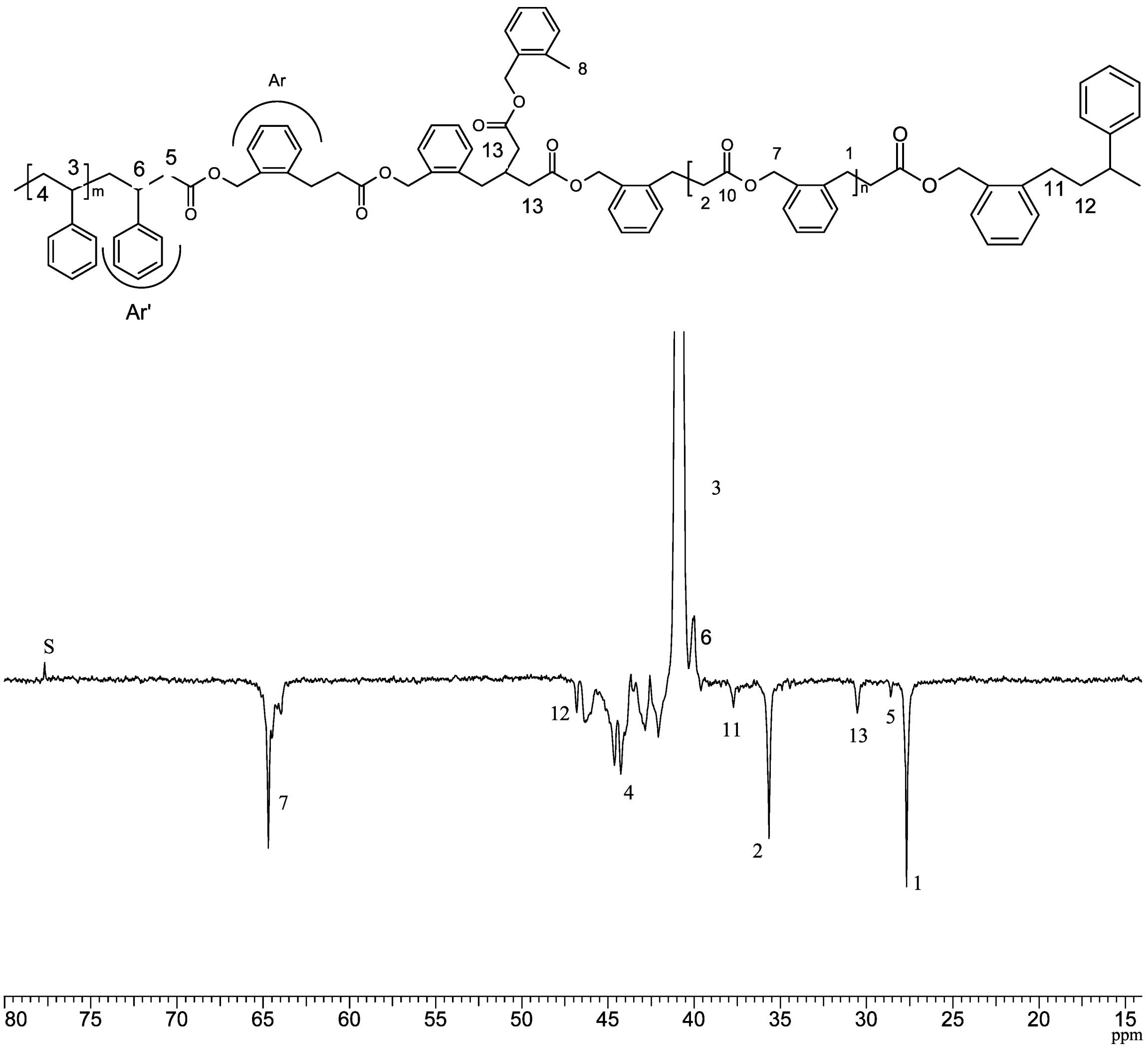


Figure 6. Part of the (15−80 ppm) DEPT NMR spectrum (run 5; Table 1).

Table 2. Thermal Characterization of St−BMDO Copolymers

	T_g (°C)		dec temp (°C)	
run	T_{g1}	T_{g2}	T_i	T_f
1	16		338	413
2	18		343	401
3	22	80	342	427
4	17	75	344	432
5	22	87	350	435
6		99	357	435
7		108	398	432

amount of St (run 6), a single glass transition close to glass transition value of homo polystyrene is obtained. The presence of two glass transition temperatures could be due to the immiscible blocky random structure of the copolymers as discussed above. Thermal stability of copolymers was determined using thermo gravimetric analyzer. Homopoly(BMDO) showed two-step degradation with major weight loss in the temperature range 300−450 °C. St−BMDO copolymers showed one step degradation and T_i (extrapolated initial decomposition temperature) and T_f (extrapolated final decomposition temperature) values for thermal decomposition of these copolymers are reported in Table 2. There is a decrease of about 50 °C in T_i on incorporation of about 20 mol % BMDO units onto PS backbone. Further increase in mol % of BMDO in the copolymers had a negligible effect on T_i value. The change in T_f value is not significant until 50 mol % incorporation of BMDO units in the copolymers. Preliminary studies are carried out for studying the hydrolytic degradation behavior of these copolymers. The St−BMDO copolymers were found to be hydrolytically degradable and leads to significant decrease in the molecular weight. The polymer left after hydrolysis showed bimodal GPC curves with the peaks shifted to significantly lower molecular weights (Figure 8). This also reconfirms the random incorporation of ring-opened BMDO units into the PS chain. Detailed hydrolytic and biodegradation studies of these copolymers are in progress.

Conclusions

Different copolymers of BMDO having different amounts of vinyl monomer (St) in the copolymer chain were made under ATRP reaction conditions. The structural characterization of copolymers was done using 1D and 2D NMR techniques. The ring opening of BMDO is found to be the only path for its incorporation in the copolymer backbone under ATRP reaction conditions. No traces of vinyl type addition at double bond of BMDO during its copolymerization with St is detected. Reactiv-

$$\eta = \left(r_{BMDO} + \frac{r_{St}}{\alpha}\right)\cdot\xi - \frac{r_{St}}{\alpha}$$

$$\eta = 2.7759\cdot\xi - 1.6927;\ \alpha = 5.0385$$

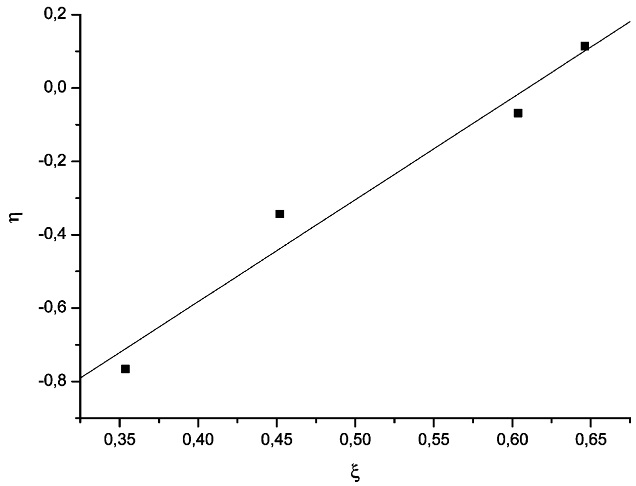


Figure 7. Kelen–Tüdõs plot for BMDO–St copolymers.

$$F = \frac{M_{\mathrm{BMDO}}}{M_{\mathrm{St}}}\ \text{(monomer feed)};\quad f = \frac{m_{\mathrm{BMDO}}}{m_{\mathrm{St}}}\ \text{(copolymer composition)}$$

$$\eta = \frac{\frac{F}{f}(f-1)}{\alpha + \frac{F^2}{f}};\quad \xi = \frac{\frac{F^2}{f}}{\alpha + \frac{F^2}{f}};$$

$$\alpha = \sqrt{\left(\frac{F^2}{f}\right)_{\min}\left(\frac{F^2}{f}\right)_{\max}}$$

ity ratios for copolymerization of BMDO with St are also determined. Reactivity ratio values and structural characterization using NMR showed the copolymers to be random with long blocks of comonomeric units. There was no significant change in thermal degradation behavior of PS on incorporation of low mole % of BMDO units. Although detailed biodegradation studies of these copolymers are in progress, preliminary degradation studies are encouraging and provide a step toward a degradable vinyl polymer, polystyrene.

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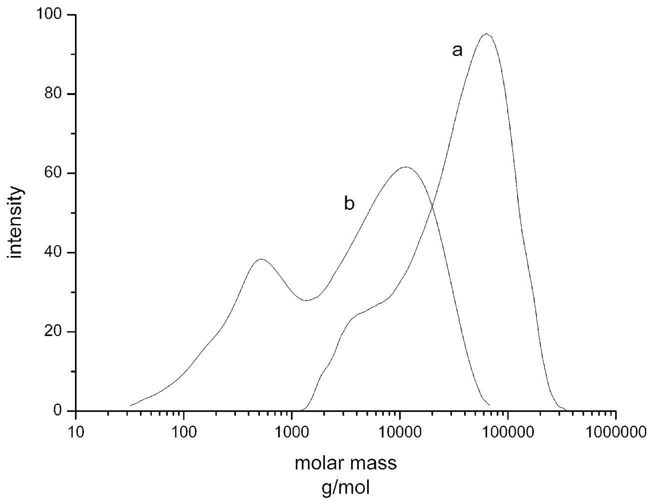

Figure 8. GPC traces of St–BMDO copolymer (run 5, Table 1): (a) before hydrolytic degradation; (b) after hydrolytic degradation.

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