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Homopolymers and Random Copolymers of 5,6-Benzo-2-methylene-1,3-dioxepane and Methyl Methacrylate: Structural Characterization Using 1D and 2D NMR

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ABSTRACT: Complete structural characterization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) monomer and its homopolymer is carried out using 1D and 2D NMR techniques. Copolymers of BMDO were made with MMA under ATRP reaction conditions. The copolymer compositions were obtained from ^{1}H NMR spectroscopy. The reactivity ratios for the copolymerization of BMDO with MMA were determined using the Kelen−Tüdõs method and was found to be $r_{\mathrm{BMDO}} = 0.53$ and $r_{\mathrm{MMA}} = 1.96$. Compositional and configurational sequence analysis of copolymers is also done.

Introduction

Conventional condensation polymerization and ring-opening polymerization of cyclic esters like lactones and lactides are generally used for the synthesis of polyesters. But 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.[1−7] This radical initiated method of synthesis of polyesters has its fundamental importance in easy introduction 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-dioxolanes (MDL) and its substituted derivatives with vinyl monomers.[1,3−5] Studies with MDL and other exo-methylene cyclic compounds clearly show 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. For example, Bailey et al. showed that 2-methylene-1,3-dioxepane (MDP) (seven-membered ring) gives quantitative ring-opening polymerization reaction to form a polyester in the presence of radical initiators like azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DTBP).[5,6] In comparison to this, five-membered 2-methylene-1,3-dioxolane (MDL) and six-membered 2-methylene-1,3-dioxane (MDA) gave both the ester groups by ring-opening polymerization and acetal groups by vinyl-type addition reactions. But the presence of phenyl ring as a substituent at the 4-position of MDL (2-methylene-4-phenyl-1,3-dioxolane (MPDO)) makes the radical-initiated ring-opening polymerization (ROP) reaction quantitative.[6] MPDO also showed different polymerization behaviors in the presence of different free radical initiator systems. Different from its conventional free radical polymerization, the polymer obtained with living radical initiator (ethyl α-bromobutyrate/CuBr/2,2′-bipyridine) had both addition (polyacetal) and ring-opened (polyester) units.[8]

5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) is another interesting cyclic monomer with an 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. ^{1}H and ^{13}C NMR techniques are used to characterize the resulting polymer, but the present available literature lacks the complete ^{1}H NMR characterization, and also peak assignments to the ^{13}C NMR spectrum are lacking.[9−11] Block copolymerization of BMDO with methyl acrylate, methyl methacrylate, and styrene by ATRP is reported by Pan et al.[12,13]

This paper reports detailed studies on copolymerization behavior of BMDO in the presence of methyl methacrylate (MMA) as comonomer using the 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 of poly(BMDO) using 1D and 2D NMR techniques. Copolymerization parameters, stereochemical, and compositional assignments of poly(BMDO-*co*-MMA) are also reported for the first time.

Experimental Section

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

5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) was synthesized in the laboratory using the literature method of Grewe et al.[14] with some modifications (Scheme 1).

Homo- and Copolymerization of BMDO and MMA. In general, all homo- and copolymerization reactions were carried out under argon in predried Schlenk tubes under ATRP

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Scheme 1

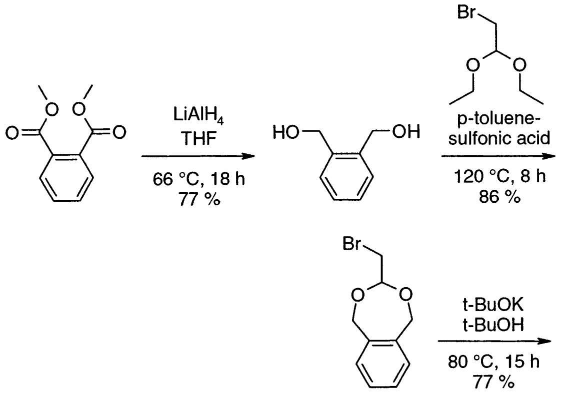


Table 1. Copolymerization Data and Reaction Conditions for MMA−BMDO Copolymers

	feed ratio (molar ratio)					copolymer composition	
run[a]	BMDO	MMA	yield (%)	$M_n \times 10^{-4}$	M_w/M_n	BMDO	MMA
1	100	0	42	0.59	1.8	100	0
2	80	20	46	0.54	2.7	70	30
3	70	30	44	0.87	1.9	53	47
4	50	50	39	1.15	2.3	34	66
5	30	70	40	2.58	1.9	18	82
6	20	80	83	2.02	2.2	10	90
7[b]	0	100	88	9.15	2.4	0	100

[a] Monomer:benzyl bromide:CuBr:ligand = 100:1:1:1; temperature = 120 °C; time = 72 h. [b] Temperature = 90 °C.

reaction conditions. In a typical copolymerization reaction (run 4, Table 1), 28.4 mg (0.2 mmol) of CuBr, 1.85 g (11.4 mmol) of BMDO, 1.2 mL (11.1 mmol) of MMA, 21 μL (0.2 mmol) of benzyl bromide, and 42 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. Homo-poly(BMDO) (PBMDO), poly(MMA) (PMMA), and different copolymers of BMDO and MMA were made by changing the molar ratio of the two monomers in the feed, under similar reaction conditions as described above. Details of reaction conditions with monomer feed ratios are given in Table 1.

Instrumentation. 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[31] and gs-HMBC[32] 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. Four and eight scans were used for HMQC and HMBC experiments, respectively, and dummy scans of four were used for both experiments. A relaxation delay of 1 s was used for all 1D experiments and 2 s for all 2D experiments. The typical experiment time was about 1.5 and 3.0 h for HMQC and HMBC, respectively.

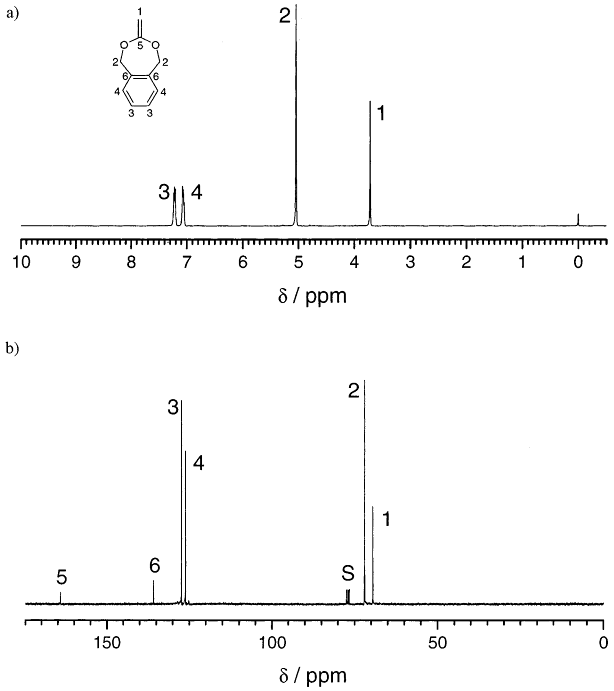


Figure 1. (a) ^1H NMR spectrum of BMDO in $CDCl_3$. (b) ^{13}C NMR spectrum of BMDO in $CDCl_3$.

Results and Discussion

BMDO monomer was synthesized by a slightly modified method of Grewe et al.[14] as shown in Scheme 1. The characteristic resonance signals in ^1H and ^{13}C NMR spectra are shown in Figure 1. The peak positions in ^{13}C NMR are assigned using the 2D $^1H-^{13}C$ HMQC technique. The peaks at 3.83 and 5.12 ppm in the ^1H NMR spectrum are correlated to peaks at 69.37 and 71.83 ppm, respectively, of ^{13}C NMR (Figure 2). The correctness of peak assignments is further confirmed from the $^1H-^{13}C$ HMBC NMR spectroscopic technique. The protons attached to carbon 2 clearly showed two- and three-bond correlation with carbon 5 and carbons 6 and 4 of the aromatic ring (Figure 2) and hence the correctness of the assigned peaks.

Homo- and copolymerization of BMDO with MMA were carried out under ATRP conditions using the benzyl bromide/CuBr/1,1,4,7,7-pentamethyldiethylenetriamine initiator system. Homo-poly(BMDO) (PBMDO) was obtained in the yield of about 40% after 72 h with a molecular weight (M_n) of 5.9×10^3. Structural characterization of the PBMDO obtained under our experimental conditions was done using 1D and 2D NMR spectroscopic techniques. The ^1H NMR spectrum of PBMDO is given in Figure 3. The characteristic ^1H NMR signals of PBMDO were present at 2.66 ($-CH_2C(O)OCH_2-$), 3.02 ($-C(O)OCH_2C_6H_4CH_2-$), 5.20 ($-CH_2C(O)OCH_2-$), and 7.19−7.43 ppm ($-CH_2C_6H_4CH_2-$). Besides the signals of PBMDO, some small signals were also observed at 2.09, 2.34, and between 4.7 and 5.3 ppm. The ^{13}C NMR spectrum showed 10 strong signals of PBMDO. The signals at 172.14 ppm ($-CH_2C(O)OCH_2-$), six signals at 126.46, 128.69, 128.95, 129.83, 133.36, and 139.20 ppm from aromatic carbons, and 64.14 ppm ($-CH_2C(O)OCH_2-$) can be assigned easily, but the remaining two strong signals at 35.12 and 27.14 ppm cannot be assigned unambiguously to either $-C(O)OCH_2C_6H_4CH_2-$ or $-CH_2C(O)OCH_2-$ using only 1D NMR techniques. Further, the two-dimensional $^1H-^{13}C$

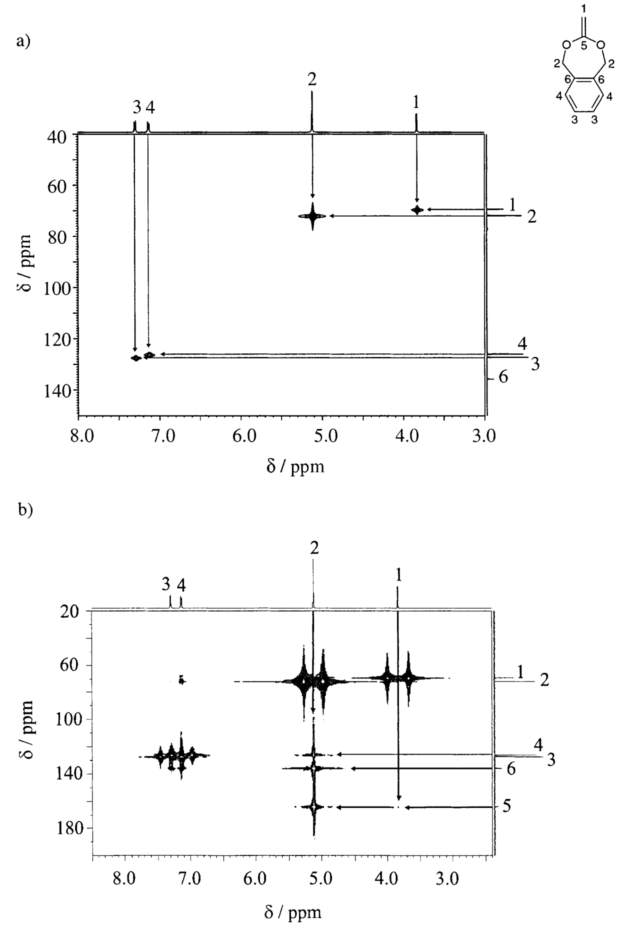


Figure 2. (a) $^1H-^{13}C$ HMQC NMR spectrum of BMDO. (b) $^1H-^{13}C$ HMBC NMR spectrum of BMDO.

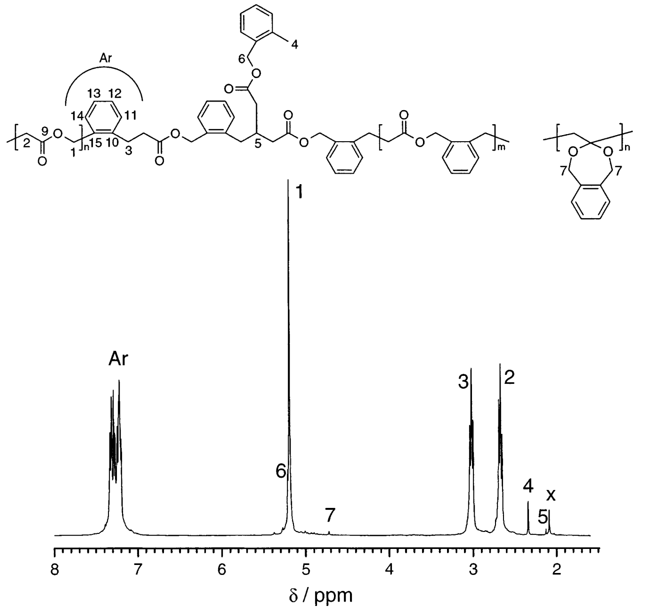


Figure 3. ^1H NMR spectrum of PBMDO in $CDCl_3$.

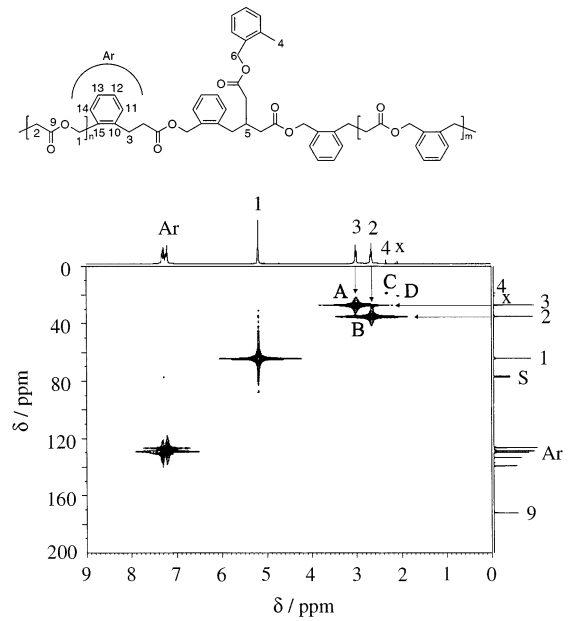


Figure 4. $^1H-^{13}C$ HMQC NMR spectrum of PBMDO.

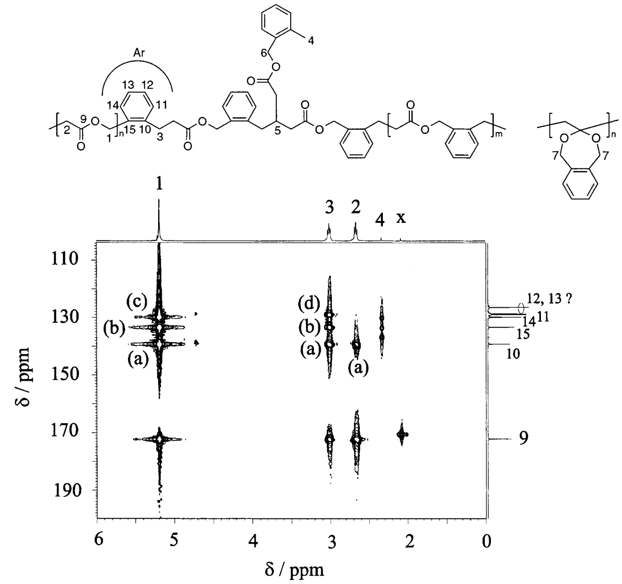


Figure 5. A part of $^1H-^{13}C$ HMBC NMR spectrum of PBMDO: ^1H NMR region 0–6 ppm; ^{13}C NMR region 105–195 ppm.

HMQC (heteronuclear multiple quantum correlation) technique was used for correct and complete ^{13}C NMR peak assignments. From the $^1H-^{13}C$ HMQC spectrum shown in Figure 4, two separate cross-peaks (A and B) can easily be seen by correlation of protons 3 at 3.02 ppm with carbon signal at 27.14 ppm and that of protons 2 at 2.66 ppm with a carbon signal at 35.12 ppm. On the basis of this, the signals at 27.14 and 35.12 ppm could easily be assigned to the carbon atoms attached to the protons 3 and 2 of BMDO repeat units, respectively. It is worthwhile mentioning here that the ^{13}C NMR signal of carbon 3 attached to the benzene ring appears at lower field as compared to that of carbon 2. This is in contrast to their resonance positions in the ^1H NMR spectrum. The correctness of peak assignments in ^1H and ^{13}C NMR spectra is further confirmed by the 2D $^1H-^{13}C$ HMBC NMR technique (Figure 5). The $^1H-^{13}C$ HMBC spectrum clearly shows that the protons attached to carbon atom 2 (at 2.66 ppm) is related to the carbon signals at 172.14 ppm (carbon atom 9), 27.14 ppm (carbon atom 3), and 139.20 ppm (aromatic carbon). This suggests that protons 2 are involved with proton–carbon correlations with carbons 9 and 3 through couplings over two bonds. The correlation peak with carbon signal at 139.20 ppm (Ar region) shows proton–carbon correlations through three bonds and helps in assigning the signal at 139.20 ppm to carbon 10 (Figure

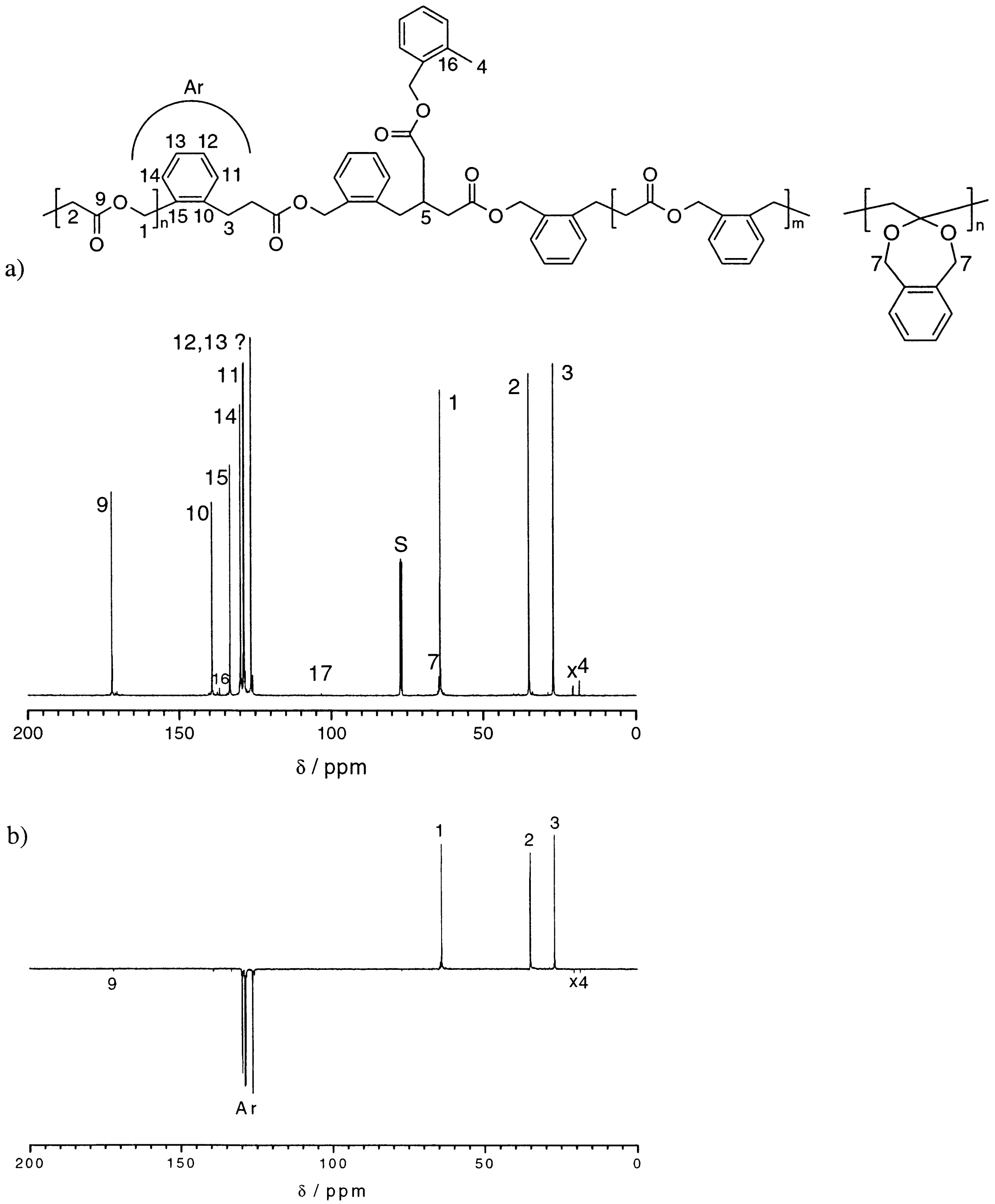
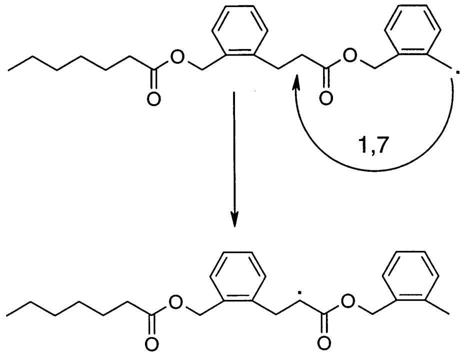


Figure 6. (a) ^{13}C NMR spectrum of PBMDO. (b) A part of DEPT NMR spectrum of PBMDO.

5). The peak at 5.20 ppm is correctly assigned as it shows correlation with the carbonyl carbon and three aromatic signals (139.32, 133.36, and 130.08 ppm) through two- and three-bond correlations. The protons attached to carbon 3 at 3.02 ppm produced correlation peaks with signals from carbons 2 and 9 and three aromatic signals at 139.20, 133.36, and 128.95 ppm. Also, the ^{1}H−^{13}C HMBC NMR technique is used to give correct peak assignments in the aromatic region (126−140 ppm). This can be done using correlation peaks of protons attached to carbons 1, 2, and 3 with ring carbons. All three of these protons showed a common correlation peak with carbon resonance at ppm 139.20 (**a**). The protons attached to carbon 2 can give correlation only with carbon 10 of the aromatic ring through three bonds, and hence the peak at 139.20 ppm is assigned to carbon 10. Similarly, the protons attached to carbons 3 and 1 both should show a common correlation peak with carbon 15 of the aromatic ring through three- and two-bond correlation, respectively. This common peak was observed in the HMBC spectrum at 133.36 ppm (**b**). The third correlation peak shown by protons attached to carbon 1 is with carbon 14 at 129.83 ppm (**c**), and that of protons attached to carbon 3 is with carbon 11 at 128.95 ppm (**d**). The other two peaks in the aromatic region at 128.69 and 126.46 ppm are from carbons 12 and 13 but cannot be distinguished using the HMBC technique. The complete peak assignments in the ^{13}C NMR spectrum of PBMDO are shown in Figure 6. ^{1}H and ^{13}C NMR spectra of PBMDO also showed negligibly small peaks at 4.72 and 103.29 ppm from polyacetal linkages formed from vinyl addition reaction in addition to ROP reaction of BMDO. The correlation of peak at 2.34 ppm in the ^{1}H NMR spectrum

Scheme 2



(HMQC correlation at 18.65 ppm (C), Figure 4) with three carbon resonances through two- and three-bond correlations in the aromatic region in the HMBC NMR spectrum shows the presence of some amount of backbiting reaction during ROP (Scheme 2). This peak at 2.34 ppm is formed as a result of backbiting leading to the formation of side chains with methyl group attached to the benzene ring. This is also confirmed from the 2D DEPT NMR experiment (Figure 6). The DEPT spectrum showed a negative signal for this methyl carbon. The amount of side chains was determined quantitatively from ^{1}H NMR and was found to be about 1 side chain per 28 repeat units of BMDO. Also, the peak observed at 2.09 ppm in ^{1}H NMR (×) (negative peak in DEPT experiment) showed only one correlation with a minor signal in the carbonyl carbon region in the HMBC NMR spectrum. This shows the presence of $CH_3-C(O)-$ type end groups in very small amount. Previous reported literature[9−11] on ROP of BMDO in the presence of conventional radical initiators like AIBN, DTBP, and ATRP initiators like ethyl α-bromobutyrate/CuBr/2,2′-bipyridine has not mentioned any side reactions. The NMR characterization mentioned in this literature is not complete.

Different copolymers of BMDO with MMA were made by changing the molar ratio of two monomers using the benzyl bromide/CuBr/1,1,4,7,7-pentamethyldiethylenetriamine ATRP initiator system. These copolymers showed an increase in molecular weight (M_n) with decrease in the amount of BMDO in the feed with unimodal GPC curves (Table 1). Structural characterization of copolymers was done using NMR spectroscopic techniques. The representative ^{1}H NMR of copolymer sample (run 4) is shown in Figure 7. Six sets of characteristic proton signals of both MMA and BMDO units were observed as marked in Figure 7. All the signals in ^{1}H NMR spectra of copolymers showed splitting in contrast to that of homopolymer signals. The splitting of peaks shows their sensitivity to compositional and configurational sequences in the copolymers. The copolymer composition was determined by taking the ratio of peak areas of methoxy protons of MMA at 3.60 ppm to that of peak at 5.08 ppm ($-CH_2C(O)OCH_2-$) of BMDO. It is observed that the mole fraction of BMDO was less 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[15] method (Figure 8) (runs 2−5, Table 1) and found to be $r_{BMDO} = 0.53$ and $r_{MMA} = 1.96$.

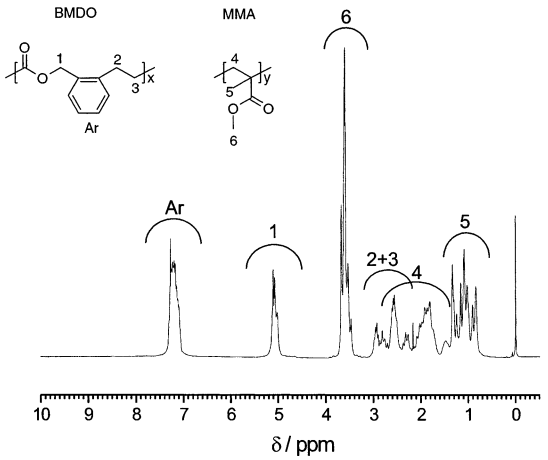


Figure 7. ^{1}H NMR spectrum of BMDO−MMA copolymer (run 5, Table 1) in $CDCl_3$.

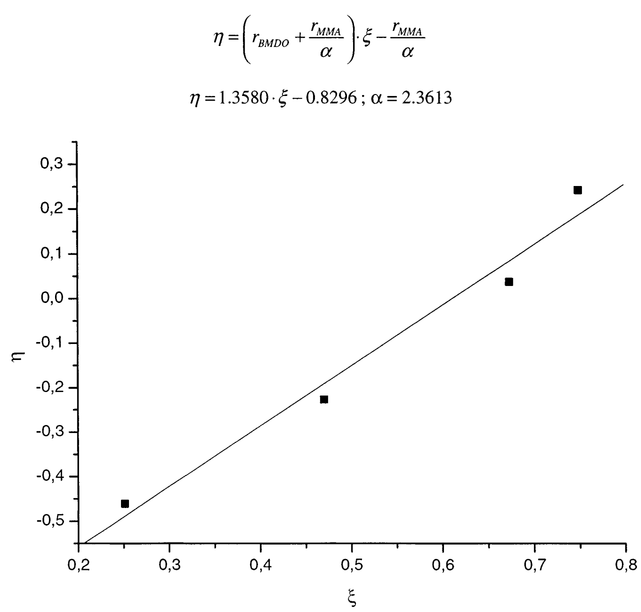
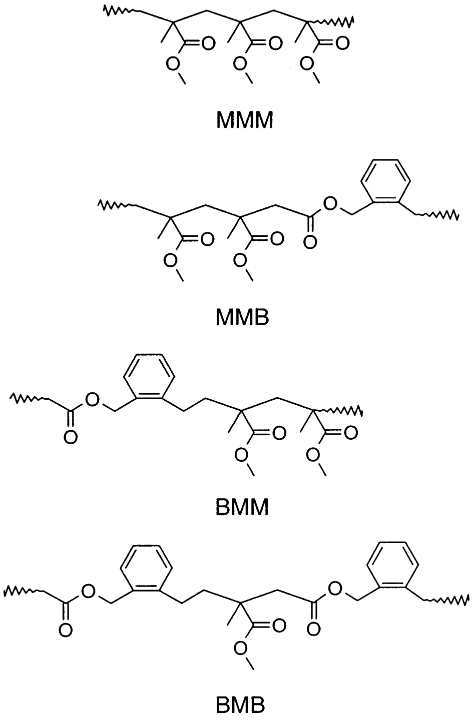


Figure 8. Kelen−Tüdõs plot for BMDO-MMA copolymers. $F = M_{BMDO}/M_{MMA}$ (monomer feed); $f = m_{BMDO}/m_{MMA}$ (copolymer composition); $\eta = [(F/f)(f - 1)]/(\alpha + F^2/f)$; $\xi = (F^2/f)/(\alpha + F^2/f)$; $\alpha = [((F^2/f))_{min}((F^2/f))_{max}]^{1/2}$.

An attempt has been made to study compositional and configurational sequencing in BMDO−MMA copolymers. The methoxy peak of the MMA unit between 3.4 and 3.8 ppm was observed as four peaks in all copolymers in contrast to a single peak in PMMA homopolymer. The intensity of the peak centered at 3.60 ppm decreased with decrease in MMA content in the copolymer. The other three peaks centered at 3.47, 3.53, and 3.67 ppm increased with increase in MMA content until about 66 mol % of MMA in the copolymer and then decreased with further increase in the MMA content. On the basis of this, the peak at ppm 3.60 is assigned to the MMM (MMA, MMA, MMA) triad, and other three peaks are from MMB (MMA, MMA, BMDO), BMM (BMDO, MMA, MMA), and BMB (BMDO, MMA, BMDO) triads (Scheme 3). To distinguish further between these three triads (BMM, MMB, BMB) and to distinguish between the influence of carbonyl and benzylic methylene groups in causing chemical shifts, a 50:50 molar ratio (in monomer feed) copolymer of MMA with 2-methylene-1,3-dioxepane (MDO)[5] was used. In this copolymer, the three additional peaks of methoxy protons of MMA from MMD (MMA, MMA, MDO), DMM (MDO, MMA, MMA), and DMD (MDO, MMA, MDO) were observed at lower field to that of MMM triad. This shows the effect of carbonyl group and methylene group in the triad MMD is to give a downfield shift. Therefore,

Scheme 3



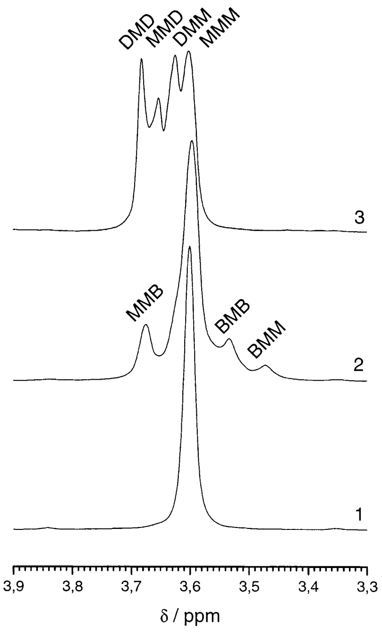


Figure 9. A part of ^{1}H NMR spectra of PMMA (1, run 7, Table 1), BMDO−MMA copolymer (2, run 4, Table 1), and MDO−MMA copolymer (3); methoxy proton region.

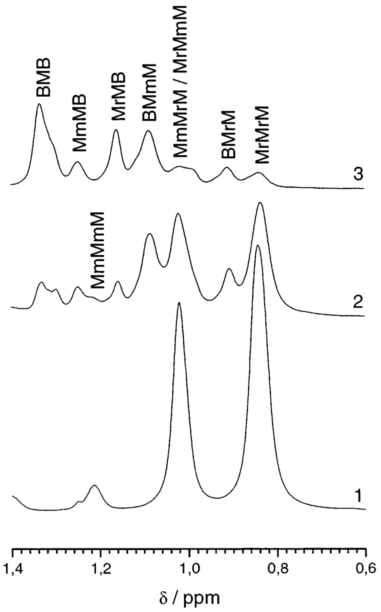


Figure 10. A part of ^{1}H NMR spectra of PMMA (1, run 7, Table 1), BMDO−MMA copolymer (2, run 5, Table 1), and BMDO−MMA copolymer (3, run 3, Table 1); α-methyl protons region.

the peak observed at 3.67 ppm in MMA−BMDO copolymers is assigned to the MMB triad (Figure 9). The presenceof two peaks at higher field as compared to MMM triad showed the influence of benzylic hydrogen in shifting methoxy peaks to lower ppm. Hence, the peak at 3.47 ppm is from the BMM triad, and the peak at 3.53 ppm is given to BMB triad having two neighboring groups with opposite effect on chemical shifts (i.e., benzylic methylene and carbonyl group) within a distance of six bonds. Splitting of the BMDO unit peak (5.01−5.10 ppm) ($-CH_2C(O)OCH_2-$) is also assigned to the occurrence of compositional triad sequences like BBB, BMM, MMB, and MBM. The peak centered at 5.10 ppm is assigned to the BBB triad unit because of its increase in intensity with increase in the amount of BMDO units in the copolymer. It is not possible to differentiate between other two peaks in the present work. The α-methyl resonance signals, 0.83−1.33 ppm in Figure 10, show a complex spectrum. These signals show high chemical shift variation due to the presence of both compositional and tacticity effects. The different triads that are possible and distinguishable by NMR are MrMrM, MmMrM (or MrMmM), MmMmM, BMB, MmMB, MrMB, BMmM, and BMrM. The α-methyl region in copolymers showed mainly eight peaks. The peaks at 0.83, 1.02, and 1.21 ppm are assigned to MrMrM, MmMrM (or MrMmM), and MmMmM triads, respectively, on the basis of the comparison with pure PMMA made under similar experimental conditions. The intensity of these peaks decreased with increase in BMDO content in the copolymer. This divides the 0.83−1.33 ppm region into the mm, mr, and rr tacticity region. The resonance signal at 1.33 ppm that decreased with an increase in MMA content is assigned to the BMB triad. Because BMDO is tacticity insensitive, the BMB triad is expected to appear only at one position. Considering the MMB triad, the tacticity effects between the two M units affect the chemical shift, and hence it appears as two peaks at 1.16 (MrMB) and 1.25 ppm (MmMB). The intensity of these two peaks increased with an increase in BMDO content until it is 80 mol % in the copolymer. Similarly, the triad BMM shows two resonances at 0.91 and 1.09 ppm, corresponding to BMrM and BMmM tactic sequences. These two resonances first increased and then decreased with variation in composition. Many overlapping resonance signals in the methylene proton region 1.48−3.0 ppm were found in copolymer samples. It was observed that the signals centered at 2.93 and 2.58 ppm increased with increase in BMDO content in the copolymer. Therefore, they could be assigned to methylene protons of BMDO homopolymer sequences (2.93 ppm, $-C(O)OCH_2C_6H_4CH_2-$; 2.58 ppm ($-CH_2C(O)OCH_2-$)). These protons further showed diad compositional sensitivity, and a BM diad for $-C(O)OCH_2C_6H_4CH_2-$ was observed at 2.81 ppm. The ratio between BB and BM diad keeps on decreasing with increasing mole fraction of BMDO units in copolymers. ($-CH_2C(O)OCH_2-$) also showed diad sensitivity with occurrence of diad MB at 2.3 ppm. Methylene protons of MMA showed both compositional and configurational sensitivity, resulting into overlapping peaks with homo BB and diad MB of ($-CH_2C(O)$-OCH_2-).

Conclusions

Complete structural characterization of BMDO monomer and homopolymer is given using 1D and 2D NMR techniques. The peaks are assigned in ^1H and ^{13}C NMR spectra unambiguously using 2D HMQC and HMBC techniques. The previous reported literature[9−11] claims quantitative ring-opening polymerization of BMDO without any mention of backbiting reactions. In the present study, the detailed analysis by NMR showed the occurrence of backbiting reaction in a very small amount, leading to the formation of branches. Various copolymers of BMDO having different amounts of vinyl monomers like MMA in the copolymer chain were also made under ATRP reaction conditions. The complex proton spectra of BMDO−MMA copolymers have been analyzed in terms of compositional and configurational sequences. Reactivity ratios for copolymerization of BMDO with MMA are also determined. Such copolymers of MMA and BMDO could be highly useful as biomaterials for various applications. We are currently exploring the mechanical properties and degradability behavior of these copolymers.

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