Free-Radical Copolymerization Behavior of 5,6-Benzo-2-methylene-1,3-dioxepane and Methacrylic Acid via the in Situ Generation of 3-Methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl Methacrylate and 2-(Acetoxymethyl)benzyl Methacrylate

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ABSTRACT: The copolymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) with methacrylic acid (MAA) using free radical initiator like di-*tert*-butylperoxide resulted in different copolymer structures depending on the monomer feed ratio. The copolymerization proceeded in an unconventional way, i.e., by in situ formation of a new vinyl monomer on mixing BMDO and MAA. In this work, we found a new route to copolymerization by first adding MAA to the double bond of BMDO generating a new vinyl monomer (3-methyl-1,5-dihydrobenzo-[*e*][1,3]dioxepin-3-yl methacrylate) with a double bond and retaining the seven membered ring of BMDO intact. The new structure is stable at 25 °C but underwent ring-opening at higher temperatures like 120 °C, generating further a different vinyl monomer with ester linkages in the side chain (2-(acetoxymethyl)benzyl methacrylate). The resulting new monomer can copolymerize with both MAA and BMDO depending on the monomer feed ratio. The structure of the new monomers and copolymers were characterized using 1D and 2D NMR techniques.

Introduction

Generally, a high molecular weight polymer based on a C−C backbone like vinyl polymers tends to be resistant to hydrolysis, oxidative cleavage, resistant to the enzymatic attack etc. and are therefore not (bio)degradable, whereas heteroatom-containing polymer backbones confer (bio)degradability.[1] First, Bailey and co-workers and later some others studied the free radical ring-opening homopolymerization (RROP) of different cyclic monomers like 2-methylene-1,3-dioxane (MD), 3-methylene dioxepane (MDP), 2-methylene-4-phenyl-1,3-dioxane (MPD), and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) using conventional radical initiators like azobis(isobutyronitrile) (AIBN) and *tert*-butyl peroxide (TBPO) generating polyesters.[2−10] The probability of ring-opening over 1,2-vinyl addition reaction depends on the reaction conditions, ring size, substituent, initiator, etc. Free radical ring-opening copolymerization of cyclic ketene acetals (CKA) with commercial vinyl monomers make possible, the random introduction of ester groups onto the backbone of an addition polymer.[11−16]

We previously have reported the detailed copolymerization behavior of cyclic ketene acetal 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) with vinyl monomers like styrene and methyl methacrylate under atom transfer radical polymerization (ATRP) reaction conditions with an aim to generate degradable vinyl polymers. Detailed 2D NMR characterization of the copolymers showed exclusively (100%) ring-opening polymerization (ROP) reaction of BMDO during copolymerization.[17,18] Later, we showed the formation of new degradable poly(pentafluorostyrene-*co*-ester)s and their utility in making superhydrophobic surfaces using electrospinning technique.[19] Degradable thermoresponsive polymers like (poly(*N*-isopropylacrylamide-*co*-ester)s were also successfully synthesized with varied lower critical solution temperatures (LCST)s by copolymerization of BMDO with *N*-isopropylacrylamide.[20]

In an attempt to make water-soluble degradable materials, free radical copolymerization behavior of BMDO with methacrylic acid (MAA) was studied in the present work. The copolymerization was done by changing the molar ratio of two monomers in the feed. The detailed characterization of the resulting polymers is presented using 1D and 2D NMR techniques and showed an unconventional route to copolymerization.

Experimental Part

Materials. Di-*tert*-butyl peroxide (dtBp) (Aldrich; 98%) was used as received. The solvents, diethyl ether (BASF), methyl *tert*-butyl ether (BASF), *n*-hexane (BASF), and methanol (BASF) were distilled before use. Tetrahydrofuran (THF) was purified by distillation over potassium. The details of synthesis and characterization of 2-methylene-5,6-benzo-1,3-dioxepane (BMDO) is given in our previous reference.[18] Methacrylic acid (MAA; 99%) was used after purification by distillation.

Instrumentation. ^{1}H (400.13 MHz) and ^{13}C (100.21 MHz), NMR spectra were recorded on a Bruker DRX-400 spectrometer. ^{1}H−^{13}C correlation experiments were performed on a Bruker DRX-400 spectrometer, with a 5 mm multinuclear gradient probe and using gs-heteronuclear multiple quantum coherence (HMQC) and gs-heteronuclear multiple bond coherence (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. Four and eight scans were used for HMQC and HMBC experiments, respectively, and four dummy scans was 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 thermogravimetric (TG) and 821 differential scanning calorimetry (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

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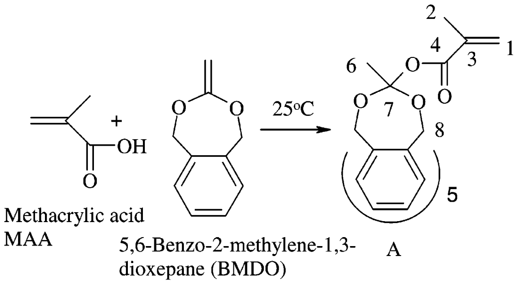
Scheme 1



atmosphere (flow rate = 50 mL/min). A heating rate of 10 °C/min and sample size of 10 ± 1 mg was used in each experiment.

The molecular weights of the polymers were measured by gel permeation chromatography (GPC) using a Knauer system equipped with three linear columns, PSS−SDV (the volume of the bead is 10 μL, the pore sizes of the beads are 10E6 (Å), 10E4 (Å), and 10E3 (Å), respectively, and the sizes of the columns are 8 mm × 600 mm, 8 mm × 600 mm and 8 mm × 300 mm respectively), an UV photometer and a differential refractive index detector. Dimethylformamide (DMF) was used as eluent at a flow rate of 0.24 mL/min at 25 °C. Polystyrene was used as a standard.

Reaction of BMDO with MAA. In a representative example, two monomers, BMDO and MAA, in a 1:1 molar ratio (BMDO (324 mg; 2 mmol) and MAA (172 mg; 2 mmol)) are simply mixed under argon without any initiator, in a predried Schlenk tube. The mixture was stirred at 25 °C for different intervals of time and analyzed as such without any purification, by 1D and 2D NMR techniques. The double bond of BMDO underwent electrophilic addition by acidic vinyl monomer MAA ($pK_a = 4.66$) under study, generating a new vinyl monomer 3-methyl-1,5-dihydrobenzo[*e*][1,3]-dioxepin-3-yl methacrylate (A) keeping the seven membered ring of BMDO intact, as shown in Scheme 1. The product obtained after 30 min, contained structure **A** and unreacted MAA in the molar ratio 99: 1. This was determined from ^{1}H NMR from the ratio of peak intensities at ppm 5.45−6.05 (2 s, 2H, $C\boldsymbol{H}_2{=}C(CH_3)COO-$) of structure A and ppm 10.89 (s, 1H, $-COO\boldsymbol{H}$) from unreacted MAA

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.82 (s, 3H, $CH_2{=}C(C\boldsymbol{H}_3)-$), 1.84 (s, 3H, $-(CH_3)C(OCH_2-)_2(OC(O)-)$, 4.60−4.97 (2d, 4H, $-OCH_2C_6H_4C\boldsymbol{H}_2O-$), 5.45−6.05 (2s, 2H, $C\boldsymbol{H}_2{=}C(CH_3)$-$COO-$), 6.87−7.02 (2 m, 4H, $-OCH_2C_6\boldsymbol{H}_4CH_2O-$), 10.89 (s, 1H, $-COO\boldsymbol{H}$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 17.40 ($CH_2{=}C(\boldsymbol{C}H_3)-$), 20.31 ($-(\boldsymbol{C}H_3)C(OCH_2)_2(OC(O)-$), 64.62 ($-O\boldsymbol{C}H_2C_6H_4\boldsymbol{C}H_2O-$), 117.24 ($-(CH_3)\boldsymbol{C}(OCH_2)_2(OC(O)-$), 125.16 ($\boldsymbol{C}H_2{=}C(CH_3)-$), 125.47−136.21 ($-OCH_2\boldsymbol{C}_6H_4CH_2O-$), 136.11 ($CH_2{=}\boldsymbol{C}(CH_3)-$), 163.18 ($-\boldsymbol{C}OOCCH_3(OCH_2)_2O(C(O))$, 169.55 ($-\boldsymbol{C}OOH$).

The other details of the characterization are given in the text and as Figures 1−5.

Furthermore, the resulting product of BMDO and MAA, i.e., the new vinyl monomer A, is heated at 120 °C for 15 min under Argon. The seven-membered ring of BMDO has the tendency to open up by rearrangement and a new ester group (structure B; 2-(acetoxymethyl)benzyl methacrylate) is formed as shown in the Scheme 2. The product was analyzed as such, without any purification, using various NMR techniques. The product contained 92 mol % of structure B as determined from the ^{1}H NMR spectrum.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.84 (s, 3H, $CH_2{=}C(C\boldsymbol{H}_3)-$), 1.96 (s, 3H, $-C_6H_4CH_2OCOC\boldsymbol{H}_3$), 5.10 (s, 2H, $-C_6H_4C\boldsymbol{H}_2$-$OCOCH_3$), 5.17 (s, 2H, $-C\boldsymbol{H}_2C_6H_4CH_2OCOCH_3$), 5.46−6.03(2s, 2H, $C\boldsymbol{H}_2{=}C(CH_3)-$), 7.2−7.33 (2 m, 4H, $-CH_2C_6\boldsymbol{H}_4CH_2$-$OCOCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.07 ($CH_2{=}C(\boldsymbol{C}H_3)-$), 20.62 ($-C_6H_4CH_2OCO\boldsymbol{C}H_3$), 63.62 ($-C_6H_4\boldsymbol{C}H_2OCOCH_3$), 63.81 ($-C\boldsymbol{H}_2C_6H_4CH_2OCOCH_3$), 125.73−135.90 ($-CH_2\boldsymbol{C}_6H_4CH_2$-$OCOCH_3$), 166.76 ($CH_2{=}C(CH_3)\boldsymbol{C}OOCH_2-$), 170.46 ($-CH_2C_6H_4$-$CH_2O\boldsymbol{C}OCH_3$).

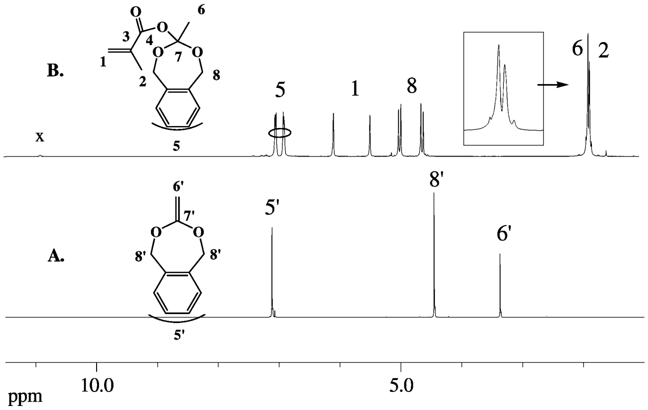


Figure 1. ^{1}H NMR spectra (A) of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and (B) 3-methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl methacrylate (structure A) formed by the addition of MAA to the double bond of BMDO at 25 °C in $CDCl_3$.

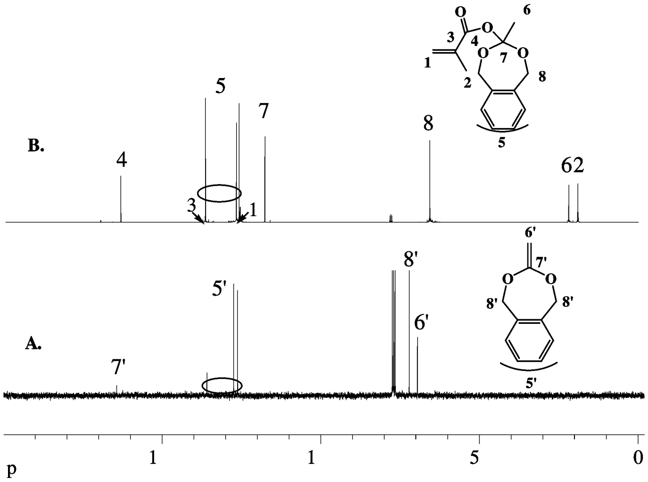


Figure 2. ^{13}C NMR spectra (A) of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and (B) 3-methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl methacrylate (structure A) formed by the addition of MAA to the double bond of BMDO at 25 °C in $CDCl_3$.

The other details of characterization of B are given in the text and as Figures 6 and 7.

Copolymerization Behavior of BMDO with Methacrylic Acid. In general, all homo- and copolymerization reactions were carried out under Argon in predried Schlenk tubes using free radical initiator (di-*tert*-butyl peroxide (dtBp)). In a typical polymerization reaction, 649 mg (4 mmol) of BMDO and 344 mg (4 mmol) of methacrylic acid, 2 mol % of the total monomers of *tert*-butyl peroxide initiator (dtBp) were placed in an Schlenk tube under Argon. The reaction was started by placing the reaction contents in a preheated oil bath at 120 °C. After 6 h of reaction time, the reaction mixture was diluted with DMF and precipitated in about 200 mL of diethyl ether. The polymers were purified by dissolving in DMF and reprecipitation in diethyl ether. The copolymers were dried in vacuum at 40 °C until constant weight. The product was obtained as a white powder ((655 mg; 66%), intrinsic viscosity (0.34 dL/g; DMF; 25 °C), copolymer composition structure B:MAA 70:30 (molar ratio)). The homopolymer and different copolymers of BMDO and MAA were made by changing the molar ratio of the two monomers in the feed, under similar reaction conditions as described above. The feed compositions, the yields, and the copolymer compositions obtained by ^{1}H NMR technique are tabulated in Table 1. The detailed characterization is shown in the Results and Discussion.

Hydrolysis of the Copolymer of BMDO and Methacrylic Acid. Copolymer (200 mg) ($M_n = 37\,000$; PDI = 1,7; copolymer composition BMDO:Str B = 44:56 (molar ratio)) was dissolved in 20 mL of 5% NaOH in distilled water in a bottle and was stirred for 24 h under room temperature. After this, 10 mL 10% of HCl

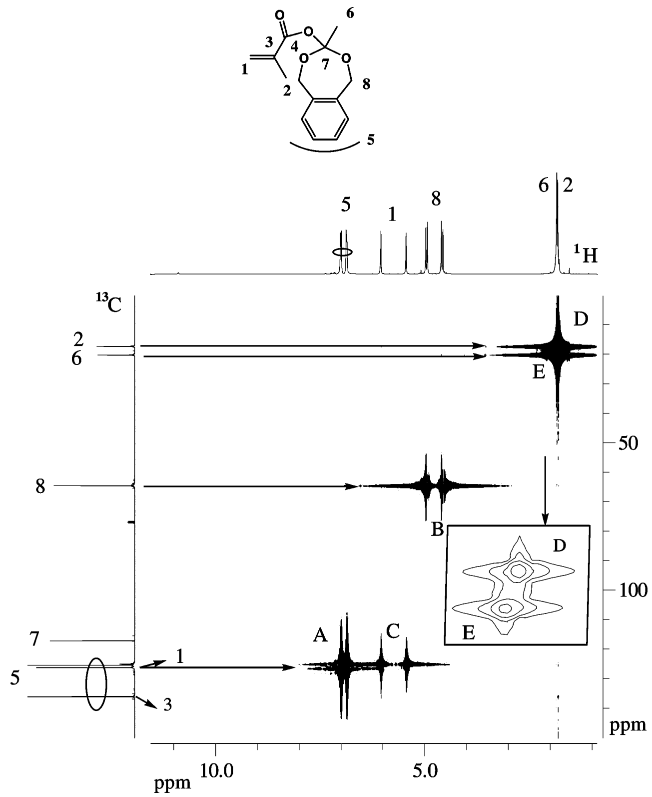


Figure 3. 2D ^{1}H−^{13}C HMQC (heteronuclear multiple quantum coherence) NMR spectrum of 3-methyl-1,5-dihydrobenzo[*e*][1,3]-dioxepin-3-yl methacrylate (structure A) in $CDCl_3$.

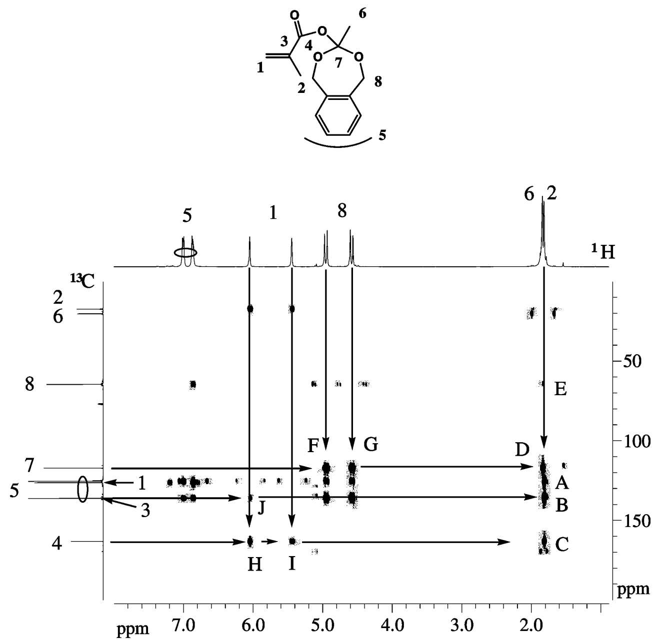


Figure 4. 2D ^{1}H−^{13}C HMBC (heteronuclear multiple bond coherence) NMR spectrum of 3-methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl methacrylate (structure A) in $CDCl_3$.

was added. The mixture was extracted with chloroform, washed with water, and dried with Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure. The remaining solid was dried in vacuum oven at 40 °C. The molecular weight of the remaining solid was measured by GPC ($M_n = 1800$; PDI = 1.1). The results are shown in Figure 14.

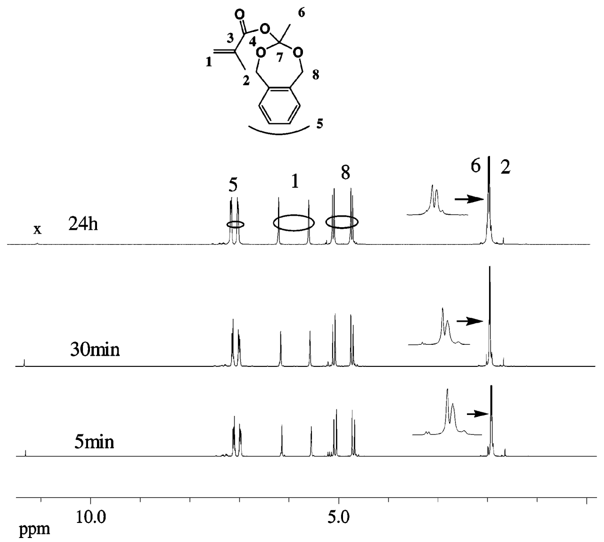


Figure 5. ^{1}H NMR spectra of 3-methyl-1,5-dihydrobenzo[*e*][1,3]-dioxepin-3-yl methacrylate (structure A) after different intervals of time of mixing 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and methacrylic acid (MAA) at 25 °C in $CDCl_3$.

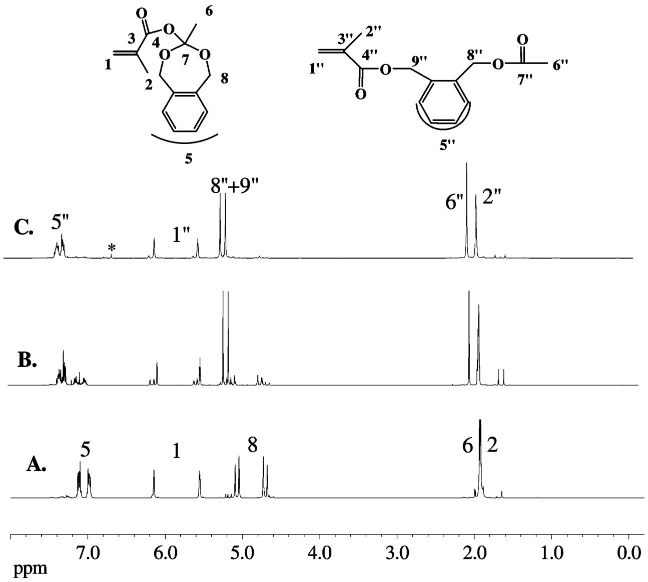
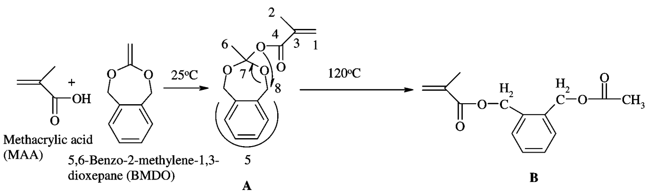


Figure 6. ^{1}H NMR spectra in $CDCl_3$ showing structure transition of the new material (structure A) 3-methyl-1,5-dihydrobenzo[*e*][1,3]-dioxepin-3-yl methacrylate by heating (A) 25 °C for 24 h, (B) 60 °C for 30 min, and (C) 120 °C for 15 min with a pinch of hydroquinone to avoid thermal polymerization (* peaks from hydroquinone).

Scheme 2



Results and Discussions

Previously, we and others showed the copolymerization behavior of a cyclic ketene acetal, BMDO with various vinyl monomers like methyl methacrylate (MMA),[17] styrene (St),[18] pentafluorostyrene (PFS),[19,20] etc. under free radical polymerization conditions. It led to either of the four pathways shown in Scheme 3 depending on the reaction conditions, i.e., the type of the initiator, its amount, temperature of the reaction, monomer

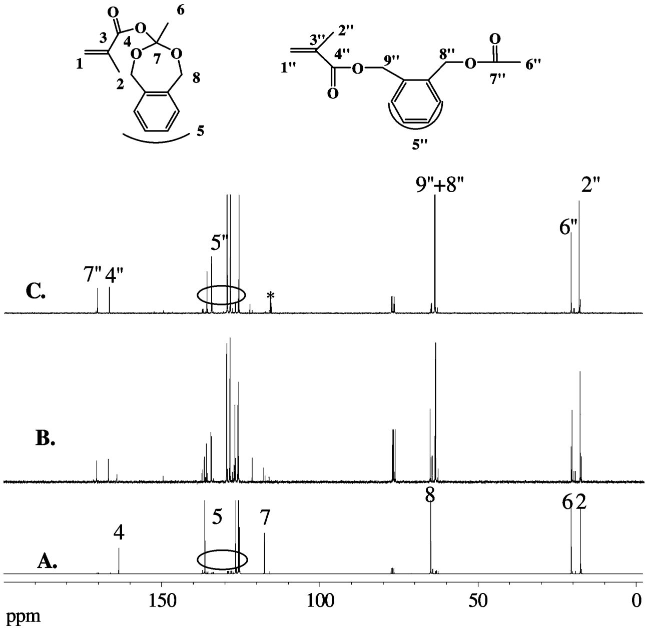


Figure 7. ^{13}C NMR spectra in $CDCl_3$ showing structure transition of the new material (structure A) 3-methyl-1,5-dihydrobenzo[*e*][1,3]-dioxepin-3-yl methacrylate by heating (A) 25 °C for 24 h, (B) 60 °C for 30 min, and C) 120 °C for 15 min with a pinch of hydroquinone to avoid thermal polymerization (∗ peaks from hydroquinone).

Table 1. Copolymerization of 5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) and Methacrylic Acid (MAA) at 120 °C for 6 h

	feed ratio (molar ratio)			copolymer composition^a (molar ratio)		
run	BMDO	MAA	yield (%)	BMDO	B	MAA
1	20	80	98	0	22	78
2	50	50	66	0	70	30
3	80	20	37	44	56	0

[a] Copolymer composition is determined using ^{1}H NMR.

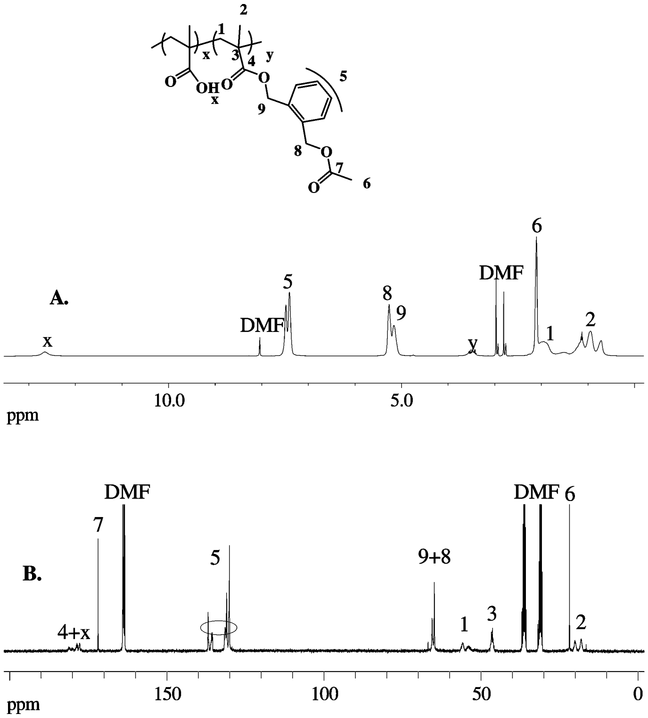


Figure 8. (A) ^{1}H NMR spectrum and (B) ^{13}C NMR spectrum in deuterated dimethylformamide (DMF) of poly(B-*co*-MAA) made using 1:1 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO): methacrylic acid (MAA) in the feed at 120 °C for 6 h.

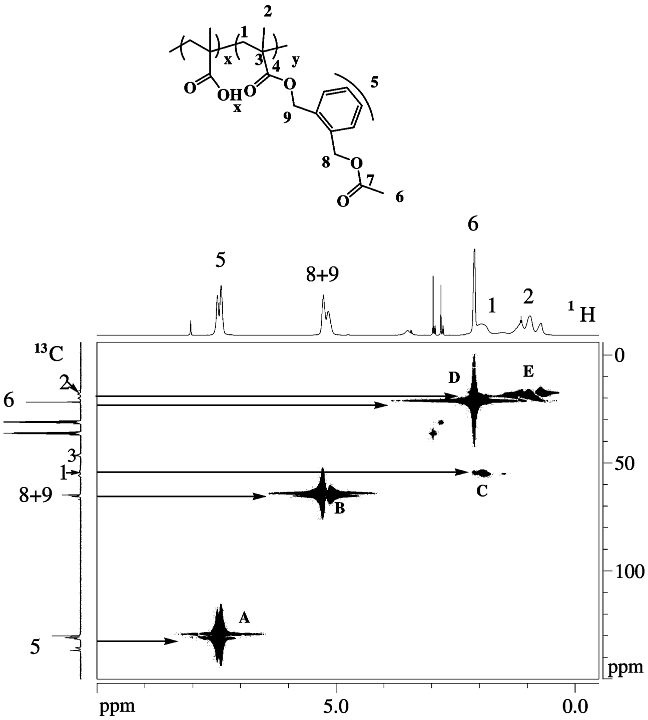


Figure 9. 2D ^{1}H−^{13}C HMQC (Heteronuclear Multiple Quantum Coherence) NMR spectrum of poly(B-*co*-MAA) made by using a 1:1 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO):methacrylic acid (MAA) in the feed at 120 °C for 6 h in deuterated dimethylformamide(DMF).

feed ratio, etc. In an attempt to generate new degradable water-soluble vinyl polymers by free radical ring-opening copolymerization of BMDO and methacrylic acid (MAA), we observed some unexpected results, different from the simple copolymerization of BMDO and MAA; i.e., the results obtained were not in accordance with the four paths shown in Scheme 3. We found another path (the fifth in Scheme 4) during copolymerization generating some new and unexpected copolymers shown at a later part of this work. A systematic study is further carried out to establish the structure of the new product obtained. First, the two monomers BMDO and MAA in 1:1 molar ratio are simply mixed under argon without any initiator for different intervals of time. The addition of acidic vinyl monomer, MAA ($pK_a = 4.66$), to the double bond of BMDO took place, generating a new vinyl monomer 3-methyl-1,5-dihydrobenzo-[*e*][1,3]dioxepin-3-yl methacrylate (A), keeping the seven membered ring of BMDO intact, as shown in Scheme 1. The new material was obtained as a colorless highly viscous liquid and was characterized without any purification using different NMR spectroscopic techniques. The representative ^{1}H and ^{13}C NMR of the new vinyl monomer (A) formed after 30 min of mixing at room temperature (25 °C) is shown in Figures 1 and 2, respectively. With our previous experience on BMDO,[16−17] the signals at ppm 7.02 and 6.87 ($-CH_2C_6\boldsymbol{H}_4CH_2-$; 5) were assigned to the aromatic protons of BMDO. The protons ($-C\boldsymbol{H}_2C_6H_4C\boldsymbol{H}_2-$; 8) as compared to BMDO (8′), split into two signals at ppm 4.94 and 4.57. The peaks at ppm 6.05 and 5.45 were assigned to the double bond protons ($C\boldsymbol{H}_2{=}C(CH_3)-$; 1) and are shifted upfield as compared to the double bond protons of the starting BMDO which disappeared at ppm 3.4 (6′). Also in the lower ppm region between ppm 1.75−1.9 two overlapping peaks were seen which are assigned to the two methyl groups, i.e., methyl group of MAA and methyl group generated by addition MAA to the double bond of BMDO

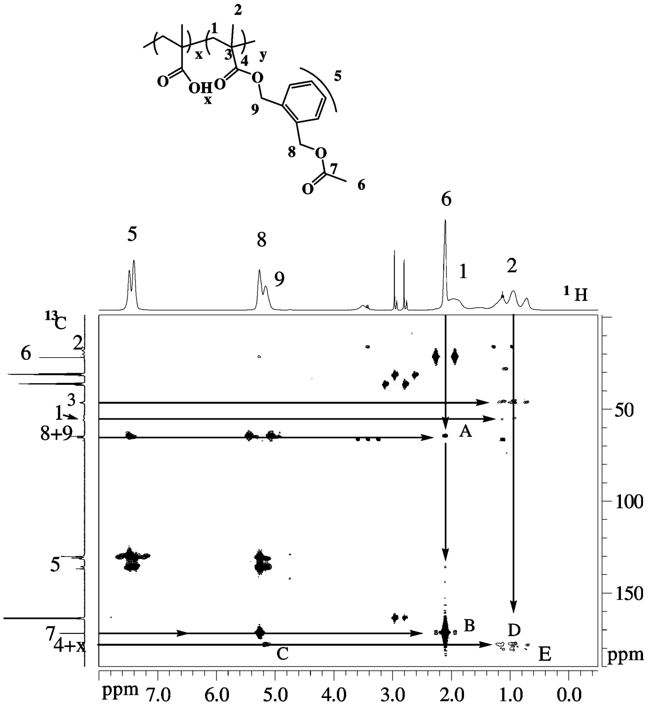


Figure 10. 2D $^1H-^{13}C$ HMBC (heteronuclear multiple bond coherence) NMR spectrum of poly(B-*co*-MAA) made by using a 1:1 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO):methacrylic acid (MAA) in the feed at 120 °C for 6 h.

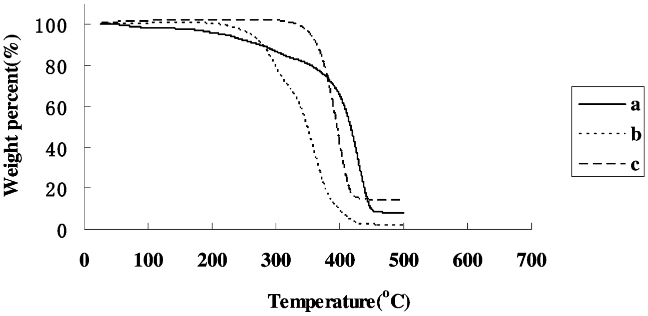


Figure 11. Thermogravimetric analysis (TGA) thermograms of copolymers with (a) B:MAA 70:30 (molar ratio), (b) B:MAA 22:78 (molar ratio), and (c) B:BMDO 56:44 (molar ratio).

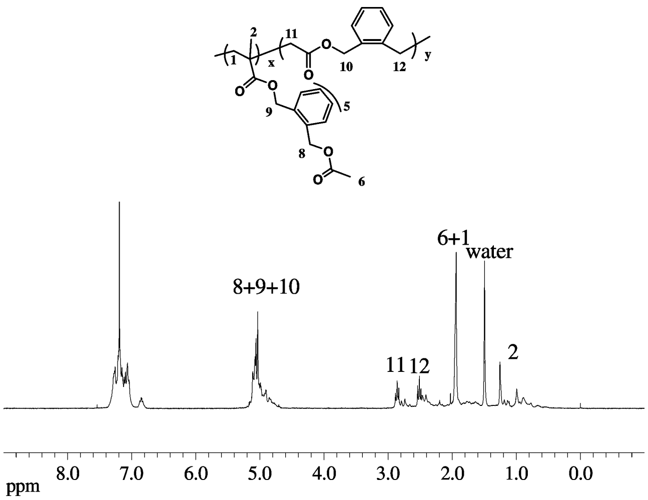


Figure 12. ^1H NMR spectrum in dimethylformamide (DMF) of poly-(B-*co*-BMDO) made using 80:20 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO):methacrylic acid (MAA) in the feed at 120 °C for 6 h.

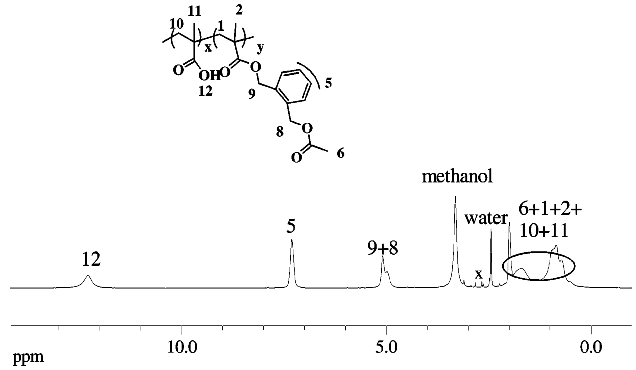


Figure 13. ^1H NMR spectrum in methanol of poly(B-*co*-MAA) made using 20:80 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO):methacrylic acid (MAA) in the feed at 120 °C for 6 h.

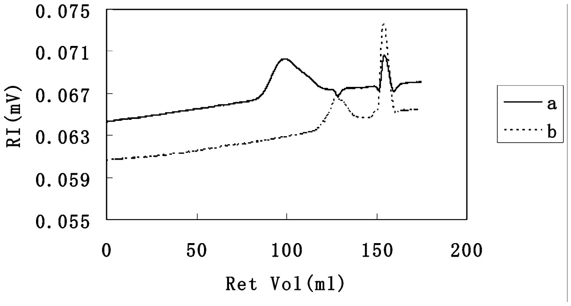
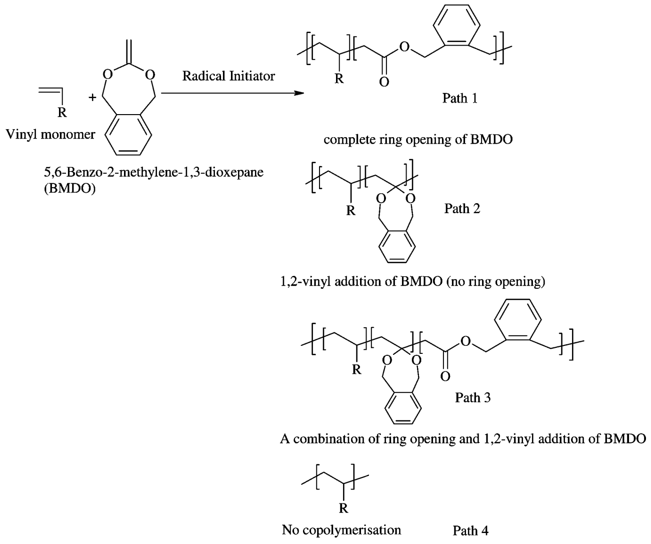


Figure 14. Gel permeation chromatography(GPC) curves of poly(B-*co*-BMDO) made using 80:20 molar ratio of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO):methacrylic acid (MAA) in the feed at 120 °C for 6 h (a) before hydrolysis and (b) after hydrolysis showing the degradability of the copolymers.

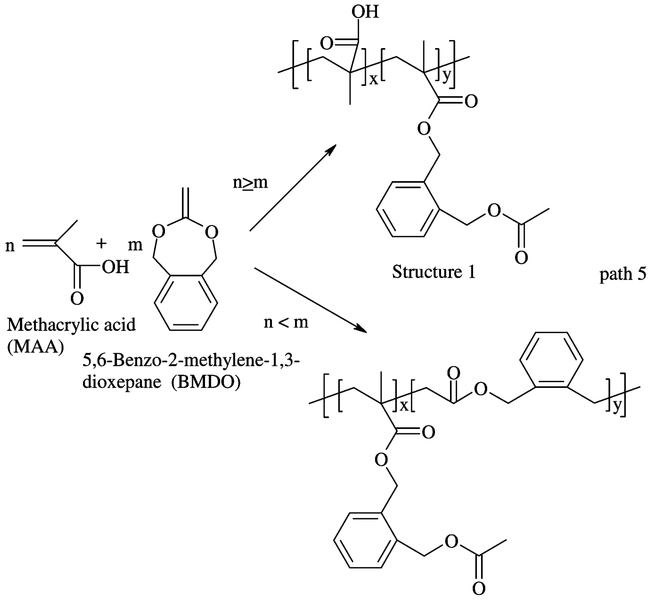
(protons 2 and 6). A very negligible peak at around ppm 11 from the acidic proton (−COO***H***) (marked *x* in Figure 1) from methacrylic acid was found. This could be from the unreacted MAA. The purity of the new material A was as much as 99%, which was determined from ^1H NMR from the ratio of peak intensities at ppm 5.45−6.05 (2s, 2H, $C\boldsymbol{H}_2{=}C(CH_3)COO-$) of structure A and ppm 10.89 (s, 1H, −COO***H***) from unreacted MAA.

The ratio of the peak areas of the protons 8:5:1:2+6 as determined from the ^1H NMR spectrum was in accordance with structure A (3-methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl methacrylate). In the ^{13}C NMR spectrum (Figure 2), a major peak observed at ppm 163.4 was assigned to the carbonyl group ($CH_2{=}C\ (CH_3)\boldsymbol{C}OO-$) (4) of structure A (Scheme 1). The other peaks in ^{13}C NMR ($-CH_2\boldsymbol{C}_6H_4CH_2-$; 5), ($-\boldsymbol{C}H_2C_6H_4\boldsymbol{C}H_2-$; 8), ($\boldsymbol{C}H_2{=}C\ (CH_3)-$; 1) are assigned unambiguously using 2D $^1H-^{13}C$ HMQC NMR correlation studies shown in the Figure 3 having cross-peaks A, B, and C, respectively. The peak at ppm 117.2 does not show any correlation in the HMQC NMR spectrum and therefore is assigned to the quaternary carbon 7. The methyl proton peaks were split into two clear peaks between ppm 17−20 (protons 2 and 6) which showed unambiguous correlations with ^1H peaks at ppm 1.82 (D) and 1.87 (E) respectively. The correctness of the assignment is confirmed by $^1H-^{13}C$ HMBC NMR correlation technique (Figure 4). The proton at ppm 1.82 produced correlation peaks with signals from carbons 1A, 3B, and 4C. While the proton at ppm 1.84 produced correlation peaks with signals from carbon atom at ppm117.24 (7) (D) and carbon atom at ppm 64.7(8) (E). This clearly showed the peak at ppm 1.82 be from carbon 2 and the one at ppm 1.87 from the carbon 6. The peak at ppm 117.2 besides showing correlation with the carbon 6 (D) also showed two more correlation peaks with signals from protons 8 (F and G), thereby showing the correctness of assignment of this peak as carbon

Scheme 3



Scheme 4



7. Carbon 3 showed no correlation in 2D HMQC NMR spectrum but showed correlations with proton 1 (J) and proton 2 (B) in 2D HMBC NMR spectrum.

Also, the characteristic double bond hydrogen peak $((-CH_2O)_2C{=}C\boldsymbol{H_2})$ (6′) at ppm 3.77 in ^1H NMR (Figure 1A) and the corresponding carbon peak $((-CH_2O)_2C{=}\boldsymbol{C}H_2)$ at ppm 69.5 in ^{13}C NMR (Figure 2A) from BMDO disappeared, a signature of change in the structure of BMDO on mixing with MAA. It is noted that there is only one carbonyl peak around 163.18 ppm (a minor negligible signal is seen at ppm 179.55 from unreacted MAA impurity), in ^{13}C NMR (shown in Figure 2) having three-bond correlations in $^1H-^{13}C$ HMBC NMR with protons at 6.05/5.45 ppm $(C\boldsymbol{H_2}{=}C(CH_3)-)$ (cross-peaks H and I) and at 1.82 ppm $(CH_2{=}C(C\boldsymbol{H_3})-)$ (cross-peak C), also speaks in favor of the correct characterization of the new vinyl monomer formed with only one ester group and with intact seven membered ring of BMDO (structure A; Scheme 1). Some litertaure is available on cationic ring-opening polymerization of cyclic ketene acetals using initiators like H_2SO4, $TiCl_4$, BF_3, etc. Depending on the temperature, either 1,2 vinyl addition at the double bond or a mixture of 1,2 vinyl addition and formation of ester linkages in the backbone by ring opening of BMDO is reported using cationic initiators.[20−23] In the present work, mixing BMDO with the acidic monomer MAA led to a new product, i.e., a new vinyl monomer characterized above with no ring-opening reaction. Figure 5 shows the ^1H NMR spectra of the product formed after mixing BMDO and MAA for different intervals of time at 25 °C. The reaction was in fact very fast and finished in 5 min of time and the ratio of peak intensities of the protons 8:5:1:2+6 remained the same even after 24 h and matched with that of structure A. The new vinyl monomer was stable at room temperature (25 °C) under argon.

Interestingly, the resulting product of BMDO and MAA; i.e., the new vinyl monomer A is sensitive to heating, even protected under argon. The seven-membered ring has the tendency to open up by rearrangement and a new ester group is formed. The new structure B is shown in Scheme 2. The ring-opening reaction of A was found to be dependent upon temperature. At higher temperature (120 °C) which we generally use for radical ring-opening polymerization of BMDO or its copolymerization with other vinyl monomers, the complete ring opening of structure A was observed after 15 min itself to give another new vinyl monomer having structure B (Scheme 2). At lower temperature of 60 °C, the ring opening was a slow process and gave a mixture of opened and unopened structures after 30 min. Figures 6 and 7 show ^1H and ^{13}C NMR spectra of the product formed after heating structure A for 15 min at 120 °C and for 30 min at 60 °C. ^1H NMR spectrum (Figure 6) showed 75 mol % of the opened structures at 60 °C after 30 min. Because of the ring-opening, in ^{13}C NMR spectrum (Figure 7) two new ester peaks around ppm 170.46 and ppm 166.76 were found, which were assigned to the carbon atoms 7″ and 4″ respectively of the new structure B. The complete disappearance of the quaternary carbon peak (7) at 120 °C also signified the opened structure B. After establishing the behavior of a simple reaction mixture of BMDO and MAA at different temperatures (25 and 120 °C), the copolymerization behavior of the two monomers BMDO and MAA was studied using radical initiator like dtBP. The reaction of BMDO and MAA (1:1 molar ratio) was carried out for 6 h using 50:1 molar ratio of total monomers:initiator at 120 °C. The resulting product was obtained as white powder in a yield of about 66% and was soluble in THF and DMF. The intrinsic viscosity was measured in DMF at 25 °C after adding 50 mM LiBr as salt and was determined to be 0.3406 dL/g. The structural characterization is done using various 1D and 2D NMR techniques. The respective ^1H NMR of the polymer sample is shown in Figure 8. The NMR peak signals from BMDO units were observed at different positions as was expected from the conventional ring-opening copolymerization as reported previously with other vinyl monomers in accordance with Scheme 3. We tried to analyze the obtained NMR data during copolymerization based on our studies described above for the mixture of BMDO and MAA showing the formation of structure B at 120 °C. The two overlapping peaks between ppm 5−5.4 were assigned to methylene $-C\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}-$(8, 9) protons (Figure 8). Many overlapping peaks were seen in the lower ppm region between ppm 0.5 − 2.3 and are assigned to the protons $-C\boldsymbol{H_2}C(CH_3)-$(1), $-CH_2C(C\boldsymbol{H_3})-$(2), and $-OCOC\boldsymbol{H_3}$-(6) obtained after vinyl polymerization of the monomer with structure **B**. The peak at ppm 12.5 showed the presence of free −COOH groups (marked X) also in the polymer. The peaks in ^{13}C NMR spectrum are assigned using 2D HMQC technique and the corresponding correlations are shown in the Figure 9. In ^{13}C NMR spectrum in Figure 8B no peak was seen around 100−120 ppm, also clearly ruling out the paths 2 and 3 of Scheme 3 and also ruling out the formation of corresponding polymer from structure A with retainment of the BMDO ring. Further more, besides one peak from DMF in the carbonyl carbon region, a single sharp peak is observed at ppm 169.8 and a multiplet in the region around ppm 175−178 was seen. The peaks in ^{13}C NMR ($-CH_2\boldsymbol{C}_6H_4CH_2-$;5), ($-\boldsymbol{C}H_2C_6H_4\boldsymbol{C}H_2-$;8 + 9), ($-\boldsymbol{C}H_2CCH_3$-;1), ($-OCO\boldsymbol{C}H_3$;6), and ($-CH_2C\boldsymbol{C}H_3$-;2) are assigned unambiguously using 2D-HMQC NMR techniques shown in Figure 9 having cross-peaks A, B, C, D, and E respectively. The further confirmation of the structure proposed for the resulting polymer is done using HMBC technique (Figure 10). In HMBC spectrum, proton 6 in the ^{1}H NMR spectrum showed two clear cross-peaks with carbon 8 at ppm 63.4 (A) and one signal in the carbonyl carbon region at ppm 169.8 (B). This suggests that the carbonyl carbon peak at ppm 169.8 is from the new ester group (7) from BMDO after ring-opening of the protonated structure A. The carbon peaks in the region around ppm 175.5−177 showed correlations with the proton peak 9 (C) and with the peaks in the ppm region 0.6−1.2 (D) and therefore is assigned to the carbonyl carbon (4) attached to the polymer backbone. The characterization clearly showed the copolymerization of BMDO with MAA does not follow any of the conventional routes given in the literature until now but followed via in situ formation of structure A and afterward simultaneous ring opening of the seven-membered ring with the formation of structure B and its further polymerization giving ester linkages in the side chain (structure 1 in Scheme 4). A small amount of acid protons are seen at ppm 12.5(X; Figure 8A) in the ^{1}H NMR and also some extra peaks in the ^{13}C NMR spectrum between ppm 181−183 (X; Figure 8B). The carbon peaks in the region around ppm 181−183 showed ^{1}H−^{13}C correlations with proton peaks in the lower ppm region; i.e., ppm 0.8−1.2 (E) in HMBC NMR spectrum (Figure 10), showed the presence of some amount of methacrylic acid units also in the copolymer, giving copolymer structure of the type shown in Scheme 4. This also shows that the lower ppm region 0.8−1.2 besides having protons from structure B (i.e., protons 1, 2 and 6) should also have contribution from aliphatic protons $-CH_2-$ and $-CH_3-$ of MAA unit in the copolymer. An attempt has been made to determine the ratio of the two types of units (molar ratio B:MAA) using ^{1}H NMR technique. The peak at ppm 12.5 was taken as characteristic peak of MAA unit and the peaks at ppm 5.0−5.2 for $-OCH_2-$ protons of the units from structure B. The two units are determined to be in the molar ratio B:MAA = 70:30. Thermal stability of the resulting polymer was checked by thermogravimetric analyzer and was found to be stable until 200 °C and thereafter showed a two step degradation as shown in Figure 11a. The first heating cycle in the DSC chromatogram showed a melting peak at around 48 °C. The glass transition temperature was noted from the second heating cycle and was 36 °C with no melting peak in the second heating cycle was observed.

Changing the molar ratio of BMDO and MAA in the initial feed changes the copolymer structure. It was found that the addition of MAA to the double bond of BMDO has precedence over copolymerization and the resulting new monomer B can copolymerize with both MAA and BMDO. ^{1}H of the copolymer with monomer feed ratio 80:20 of BMDO:MAA, made in 6 h (yield 37%) is shown in Figure 12. the product was soluble in DMF, THF, $CHCl_3$. A significant change in the peak positions in NMR spectrum (Figure 12) of the product was obvious on comparing it with Figure 8A (^{1}H NMR of the sample with feed ratio BMDO:MAA 50:50). Besides the aromatic protons around ppm 7, the protons ($-OC\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}O-$) from structure B + $-OCH_2-$ from ring-opening polymerization of BMDO) around ppm 5 obtained as multiplet and also two characteristic multiplet peaks at ppm 2−3 ($-C\boldsymbol{H_2}COOCH_2C_6H4C\boldsymbol{H_2}-$) of BMDO by ring-opening polymerization were clearly found in the spectrum. The proton 11 from BMDO is attached to an asymmetric carbon in the copolymer and the random nature of the copolymers might have led to the splitting of these peaks in the region around ppm 2−3. This showed the formation of structure 2 in Scheme 4 exclusively. No −COOH peak was seen in the NMR spectra, ruling out the presence of MAA type of units in the copolymer. The copolymer composition was determined by using the peak intensities at ppm 2.6−3 I_{BMDO} ($-C\boldsymbol{H_2}COOCH_2C_6H_4-$ of BMDO) and ppm 4.6−5.2 I_{BMDO}($-CH_2COOC\boldsymbol{H_2}C_6H_4$-) + I_B($-COOC\boldsymbol{H_2}C_6H_4C\boldsymbol{H_2}OCO-$) in ^{1}H NMR. The molar ratio of B:BMDO (56:44) in the copolymer is found to be higher as compared to that in the feed, which suggests the relative higher reactivity of B over BMDO during copolymerization. The resulting polymer with higher content of structure B and no MAA units was found to be highly thermally stable (up to 300 °C), as shown in Figure 11c. The glass transition temperature was 29 °C.

Further polymerization behavior was studied by taking more MAA in the initial feed, i.e., 20:80 molar ratio of BMDO:MAA. The 98% of the copolymer was obtained after 6 h reaction time at 120 °C. the product was soluble in MeOH and DMF. ^{1}H NMR spectrum (Figure 13) looked similar to that obtained for 1:1 molar ratio of BMDO:MAA in the feed, i.e., Figure 8A. The presence of peak at ppm 12.5 showed the presence of free −COOH groups from MAA units in the copolymer. The integration of the peak intensities at around ppm 7 and the total peak intensities between ppm 0.3 and 2.2 gave a copolymer composition of B:MAA 22:78 molar ratio. The structure from the BMDO units after conventional ring-opening polymerization was present in a very negligible amount (path 1, Scheme 3). The corresponding peaks are marked with and X in the ^{1}H NMR spectrum (Figure 13). The peaks were too small to be integrated with any accuracy. The intrinsic viscosity of the polymer was very high (0.833 dL/g) at 25 °C in DMF. The product obtained showed weight loss at low temperatures like 150 °C in thermogravimetric analysis (in Figure 11b) No clear glass transition could be seen in the DSC for this sample.

The hydrolytic degradation behavior of the sample made with more BMDO in the feed (BMDO:MAA = 80:20) with copoylmer structures giving ester linkages in the backbone (structure 2; Scheme 4) was studied under basic conditions as described in the experimental part. The GPC curves of the copolymer samples before and after hydrolysis are shown in the Figure 14. The high molecular weight peak of poly(B-*co*-BMDO) disappeared after hydrolysis and shifted to a low molecular weight region, thereby showing the hydrolytic degradation capability of new copolymer synthesized and the presence of ester linkages on the polymer backbone.

Conclusions

The copolymerization of BMDO with MAA does not follow any of the conventional routes of copolymerization of cyclic ketene acetals with vinyl monomers known until now, i.e., 1,2-vinyl addition at the double bond of BMDO giving poly acetal rings and /or free-radical ring-opening polymerization generating ester linkages in the backbone. Instead, this work showed a new route to copolymerization by first addition of MAA to the double bond of BMDO generating a new vinyl monomer (3-methyl-1,5-dihydrobenzo[*e*][1,3]dioxepin-3-yl methacrylate), which is unstable at higher temperatures like 120 °C and rearranged into a new structure (2-(acetoxymethyl)benzyl methacrylate) with vinylic double bond and ester linkages in the side chain. Different monomer ratio in the feed generated different structures with ester linkages either in the backbone or as the side chain. The new polymers depending on their structure could be used as pH sensitive functional materials. Further studies in this direction are in progress.

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