Controlled Radical Polymerization and Copolymerization of 5-Methylene-2-phenyl-1,3-dioxolan-4-one by ATRP

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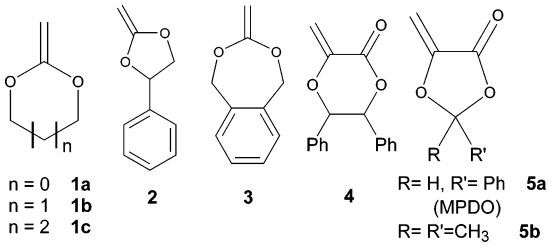
ABSTRACT: The polymerization and copolymerization of a cyclic acrylate, 5-methylene-2-phenyl-1,3-dioxolan-4-one (MPDO), by conventional radical polymerization and atom transfer radical polymerization (ATRP), were determined to occur by 1,2-vinyl addition according to ^{13}C NMR spectroscopy. Copolymerization of MPDO with methyl methacrylate (MMA) or styrene (S) led to copolymers with a much higher MPDO content than originally in the feed, suggesting high reactivity due to its captodative structure. PMPDO−PS copolymers were stable to UV irradiation and basic environments, confirming that copolymerization of MPDO also proceeded by 1,2-vinyl addition rather than ring opening. DSC heating scans of PMPDO−PMMA copolymers show a single T_g that increases with increasing MPDO content.

Introduction

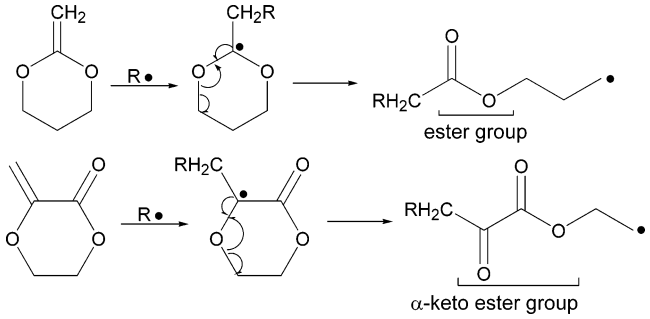
Over the past two decades, significant effort has been devoted to exploring the radical polymerization mechanism of cyclic ketene acetals (CKAs)[1−13] (**1**−**3**, Scheme 1) and cyclic acrylates (CAs)[1,6,13−15] (**4** and **5**, Scheme 1). Because of the presence of ring strain, these monomers can potentially undergo ring-opening polymerization in addition to the more conventional 1,2-vinyl addition. Ring-opening polymerization of CKAs and CAs has generated significant interest because this route incorporates ester and α-keto ester functionality, respectively, into the backbone of the resulting polymers (Scheme 2). These polymers are therefore degradable upon exposure to an acidic or basic environment or to ultraviolet irradiation.[1,3,7,12,13,16,17] For this reason, CKA and CA polymers are attractive candidates in medical and lithographic applications.[1,12,18]

Scheme 2 illustrates the mechanism of radical ring-opening polymerization for both the CKA and CA monomers. Whether ring-opening (as outlined in Scheme 2) is favored over 1,2-vinyl addition during polymerization depends on the relative kinetics of monomer addition and ring opening. The radical polymerization of CKAs has been examined in detail, and the factors that influence the degree of ring opening in these monomers are generally known. To first approximation, the extent of ring substitution and the magnitude of ring strain in the monomer can affect the degree of ring opening dramatically. For example, CKA **1a** undergoes 50% ring-opening polymerization at 60 °C.[9,13] The addition of a phenyl pendant group—which tends to stabilize the propagating radical—to the monomer (CKA **2**) allows for complete ring opening during conventional radical polymerization at 60 °C.[8,9] The increase in monomer ring strain in the case of CKA **1c** greatly favors ring opening during polymerization. Even at low

Scheme 1. Cyclic Monomers that undergo Ring-Opening and/or Addition Free Radical Polymerization



Scheme 2. Ring-Opening Mechanism for CKA and CA Monomers



reaction temperatures (e.g., 50 °C), this monomer undergoes 100% ring opening.[2,3,9,13] Similarly, CKA **3**, also a monomer with seven-membered ring, undergoes complete ring opening during radical polymerization; its resulting propagating species is presumably even more stable than that of CKA **1c** due to the presence of the phenyl ring.[5,19−21]

While the polymerization of CKAs is generally understood, the synthesis of CKA polymers of high molecular weight remains challenging. The CKA polymers that result from conventional radical polymerization typically have low molecular weights (<10 kg/mol) and broad molecular weight distribution, presumably because of the low reactivity of such vinyl-ether-type cyclic monomers. With the recent advent of controlled/"living" radical polymerization techniques, biodegradable CKA polymers with controlled molecular weights and narrow

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molecular weight distributions have been obtained.[22−28] Yet, to our best knowledge, CKA polymers of high molecular weight have not been reported.

In light of these challenges associated with CKAs, we have chosen to focus on the radical polymerization of CA **5a**, 5-methylene-2-phenyl-1,3-dioxolan-4-one (MPDO). In contrast to what had been reported for CKA polymers, we have been able to obtain PMPDO of high molecular weights (>40 000 g/mol). When MPDO is polymerized by a "living" technique, i.e., atom transfer radical polymerization (ATRP),[29−32] the resulting polymer has a narrow molecular weight distribution (PDI < 1.2). Although MPDO is the only CA monomer studied, we expect the controlled polymerization of other CAs—those containing both ester (electron withdrawing) and ether (electron donating) groups in the ring—to yield polymers of high molecular weight and narrow molecular weight distribution due to the stabilizing captodative effect on the active radical carbon.[33]

On the basis of what had been previously reported on CKA polymerization mechanism, we expected the polymerization of MPDO to proceed by ring opening. Yet, we found that MPDO polymerization proceeds solely by 1,2-vinyl addition at all the reaction conditions we explored. In addition to homopolymerization, we also explored the copolymerization of MPDO with methyl methacrylate (MMA) and with styrene (S). During copolymerization, MPDO also undergoes 1,2-vinyl addition rather than ring opening.

Experimental Section

Materials. Methyl methacrylate (Acros, 99%) and styrene (Aldrich, 99%) were passed through a column of activated basic alumina and stored over molecular sieves prior to use. Anisole (Acros, 99%) and benzene (Fisher, 99+%) were dried over CaH_2 and $MgSO_4$, respectively. α,α′-Azoisobutyronitrile (AIBN, Aldrich, 98%) was recrystallized from MeOH. Benzaldehyde (Aldrich, 99.5%), *p*-toluenesulfonic acid (Acros, 99%), diisopropylamine (Acros, 99+%), CuBr (Aldrich, 98%), $CuBr_2$ (Aldrich, 98%), ethyl 2-bromoisobutyrate (EB*i*B, Aldrich, 98%), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) were used as received. β-Chlorolactic acid was synthesized according to a previously reported procedure,[34] and the structure was confirmed by ^{1}H NMR: ($CDCl_3$, ppm) 3.91 (2H, m) 4.61 (1H, t).

Synthesis of 2-Phenyl-5-chloromethyl-1,3-dioxolan-4-one (PCDO). A similar procedure to Bailey et al.[15] using β-chlorolactic acid as a precursor rather than β-bromolactic acid was used to synthesize PCDO. β-Chlorolactic acid (22.66 g, 0.182 mol), *p*-toluenesulfonic acid (0.433 g, 2.5 mmol), benzaldehyde (18.4 g, 0.173 mol), and 130 mL of dry benzene were added to a 250 mL flask. The flask was equipped with a Dean−Stark trap to collect water, and the solution was heated to reflux for 36 h. When the reaction was completed, the benzene solution was washed with an aqueous $NaHCO_3$ solution followed by an aqueous NaCl solution and then dried over $MgSO_4$. Benzene was then removed under partial vacuum, and the remaining solution was distilled to give 15.5 g (40%) of PCDO, which was collected between 140 and 150 °C under vacuum. ^{1}H NMR ($CDCl_3$, ppm) confirms structure: 3.97 (2H, d,d), 4.78, 4.83 (1H, m), 6.45, 6.72 (1H, s) 7.44−7.50, 7.59−7.61 (5H, m).

Synthesis of 5-Methylene-2-phenyl-1,3-dioxolan-4-one (MPDO). The procedure outlined by Bailey et al.[15] for the final step of MPDO synthesis was modified as follows: A 100 mL flask containing 4.5 g (21 mmol) of PCDO and 40 mL of dry ether was sealed with a septum under N_2. Diisopropylamine (2.36 g, 23 mmol) was added dropwise via a syringe, and the solution was allowed to stir at room temperature overnight. The precipitated ammonium salts were then removed by filtration, and the remaining solution was washed with water. The solution was subsequently passed through a column of neutral alumina to remove impurities and then placed on a vacuum line where ether and excess diisopropylamine were removed by distillation to give 3.14 g (17.8 mmol, 85%) of MPDO. Anisole was condensed into the flask containing MPDO to protect the monomer from air and moisture as it has been reported to be unstable when isolated.[14,15] ^{1}H NMR ($CDCl_3$, ppm): 4.98 (1H, d), 5.28 (1H, d), 6.68 (1H, s), 7.46 (5H, s). ^{13}C NMR: 92.3 (H_2C=C), 103.2 (O−*C*HPh−O), 126.1, 128.9, 130.8, and 134.5 (aromatic carbons), 143.7 (H_2C=*C*), 162.2 (C=O).

ATRP Homo- and Copolymerization of MPDO. MPDO (2.5 g, 14.2 mmol) in 2 mL of anisole, CuBr (28.6 mg, 0.20 mmol), $CuBr_2$ (2.2 mg, 0.010 mmol), PMDETA (36.4 mg, 0.21 mmol), and an additional 2 mL of anisole were added to a 15 mL flask equipped with a magnetic stir bar. During copolymerization, MMA or S comonomer was also added to the reaction flask. The flask was sealed with a septum and purged with N_2 for 1 h followed by injection of 39.0 mg (0.20 mmol) of EB*i*B. The solution was purged and allowed to stir at room temperature for an additional 30 min. The reaction flask was then placed in an oil bath preheated to 70 °C for 90 min. After the specified time, it was removed from the oil bath and cooled to 0 °C, and the solution was exposed to air. The polymerization medium was diluted with THF and passed through a column of neutral alumina to remove copper salts. It was then concentrated and the polymer precipitated into MeOH. The filtered polymer was dried in vacuo for 24 h.

Conventional Radical Polymerization of MPDO. MPDO (2.5 g, 14.2 mmol) in 2 mL of anisole, AIBN (16.4 mg, 0.10 mmol), and an additional 2 mL of anisole were added to a 15 mL flask equipped with a magnetic stir bar. The reaction flask was sealed and purged with N_2 for 30 min. The flask was then placed in an oil bath preheated to 150 °C and allowed to stir therein for 200 min. The final polymer solution was exposed to air and concentrated by rotary evaporation, and the polymer was precipitated in MeOH. The filtered polymer was dried in vacuo for 24 h.

Degradation of PMPDO−PS Copolymers. PMPDO−PS-I was exposed to basic conditions for hydrolytic degradation experiments. Specifically, 0.1 g of the copolymer was dissolved in a mixture of THF (3 mL) and methanol (1 M KOH, 2.5 mL) in a 20 mL vial. The mixture was heated to 70 °C, and the molecular weight change was monitored by GPC. Photodegradation was carried out on a 2% w/v THF solution of PMPDO−PS-II in a Rayonet photochemical chamber reactor equipped with 12 RPR-254 nm lamps at 40 °C for 25 h.

Characterization. Molecular weights and molecular weight distributions were determined using a GPC system equipped with a Waters 515 HPLC solvent pump, two PLgel mixed-C columns (5 μm bead size, Polymer Laboroatories Inc.) connected in series, an online interferometric refractometer (Optilab DSP, Wyatt Technology Corp.), and a multiangle laser light scattering (MALLS) detector (DAWN-EOS, Wyatt Technology Corp.). THF was used as the mobile phase at a flow rate of 1.0 mL/min at 30 °C. ^{13}C NMR spectroscopy was performed on a Varian INOVA 500 MHz spectrometer, and ^{1}H NMR spectroscopy was performed on a Varian Unity+ 300 MHz NMR spectrometer. The 2D NMR spectroscopy experiments were recorded on a Bruker Avance DMX-500 spectrometer operating at 500.13 MHz (^{1}H) and 127.76 MHz (^{13}C). 2D ^{1}H−^{13}C correlation experiments (edited-HSQC) were acquired in a 5 mm *z*-gradient broad-band inverse probe using Bruker standard pulse sequences provided with the XWIN NMR 3.5 software package. The edited-HSQC experiment was recorded in echo−antiecho mode using the hsqcedetgp pulse program optimized for a C−H coupling constant of 145 Hz.[35] Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 with a heating rate of 10 °C/min. Glass transition temperatures (T_g) were measured on second heat at the extrapolated half heat capacity.

Results and Discussion

Homopolymerization of MPDO. Homopolymerizations of MPDO were carried out in anisole, by both conventional radical polymerization and ATRP, and the

Table 1. Polymer Composition and Molecular Weight Data for PMPDO Homopolymer, PMPDO−PMMA, and PMPDO−PS Copolymers

	monomer feed (mol %)		polymer composition (mol %)[h]			
sample	MPDO	comonomer	PMPDO	comonomer	M_n[i]	PDI
PMPDO[a]	100		100		44 000	1.48
PMPDO[b]	100		100		52 000	1.67
PMPDO[c]	100		100		51 000	1.18
PMPDO−PMMA-I[d]	5	95	5	95	15 400	1.12
PMPDO−PMMA-II[e]	9	91	32	68	11 000	1.29
PMPDO−PMMA-III[f]	14	86	58	42	11 200	1.51
PMPDO−PS-I[g]	6	94	15	85	9500	1.18
PMPDO−PS-II[g]	6	94	12	88	16 000	1.13

[a] $[AIBN]_0/[MPDO]_0 = 1/920$, 60 °C, 400 min. [b] $[AIBN]_0/[MPDO]_0 = 1/142$, 150 °C, 200 min. [c] $[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0/[MPDO]_0 = 1/1/0.05/1.05/71$, 70 °C, 360 min, PMPDO $dn/dc = 0.10$ mL/g (690 nm, THF, 30 °C). [d] $[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0/[MMA]_0/[MPDO]_0 = 1/1/0.05/1.05/150/7.5$, 70 °C, 90 min. [e] $[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0/[MMA]_0/[MPDO]_0 = 1/1/0.05/1.05/138/14$, 70 °C, 90 min. [f] $[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0/[MMA]_0/[MPDO]_0 = 1/1/0.05/1.05/125/21$, 70 °C, 90 min. [g] $[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0/[S]_0/[MPDO]_0 = 1/1/0.05/1.05/200/12$, 90 °C. [h] Determined by peak integration in ^{1}H NMR spectra. [i] Determined by GPC using MALLS.

resulting polymers were characterized by GPC and ^{13}C NMR spectroscopy. The conditions for each polymerization, as well as resulting MW and polydispersity indices (PDI = M_w/M_n), are summarized in Table 1. As shown in the first two entries of Table 1, we carried out two conventional radical polymerizations, one at 60 °C and the other at 150 °C. The ^{13}C NMR spectra of the MPDO monomer (Figure 1a) and the homopolymers synthesized by ATRP (Figure 1b) and conventional radical polymerization at 150 °C (Figure 1c) are shown in Figure 1. The ^{13}C NMR spectra for PMPDO synthesized by conventional radical polymerization, at both 60 °C and 150 °C, and by ATRP are identical, indicating a common mechanism for both polymerization techniques at temperatures as high as 150 °C. More importantly, the absence of the ketone peak of the α-ketoester (190 ppm)[36]—evidence of ring opening—in the ^{13}C NMR spectrum of PMPDO indicates that the polymerizations proceeded by 1,2-vinyl addition. Further evidence that the polymerizations proceeded by 1,2-vinyl addition, and not ring opening, stems from the retention of the peak at ∼100 ppm (labeled d in Figure 1) in the ^{13}C NMR spectra of the polymers. This peak is present in the MPDO monomer spectrum and corresponds to the acetal benzylic carbon. As illustrated in Scheme 3, the benzylic carbon can only remain in its same nuclear environment when the monomer is incorporated by 1,2-vinyl addition. Should MPDO undergo ring-opening polymerization instead, the nuclear environment of this particular carbon would change dramatically. Contrary to previous reports,[1,13−15] our ^{13}C NMR analysis thus indicates *unambiguously* that MPDO undergoes 1,2-vinyl addition rather than ring-opening polymerization.

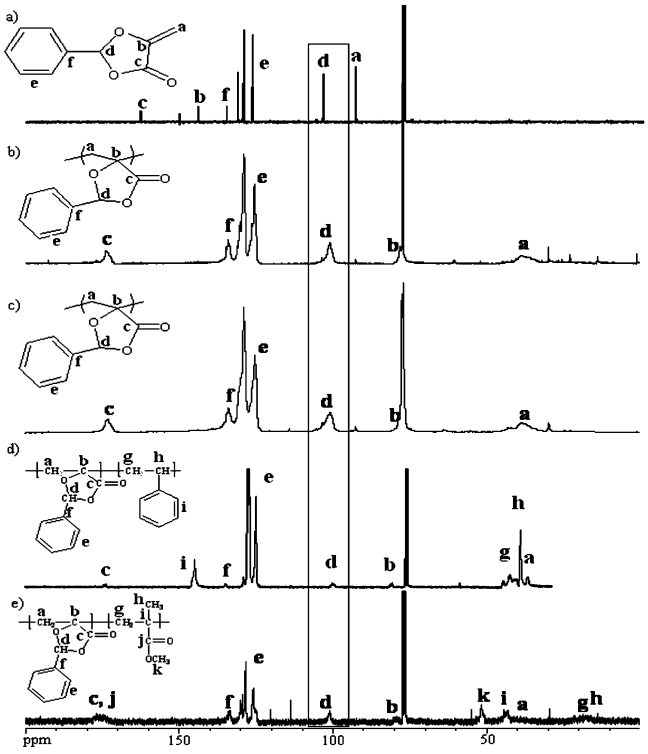
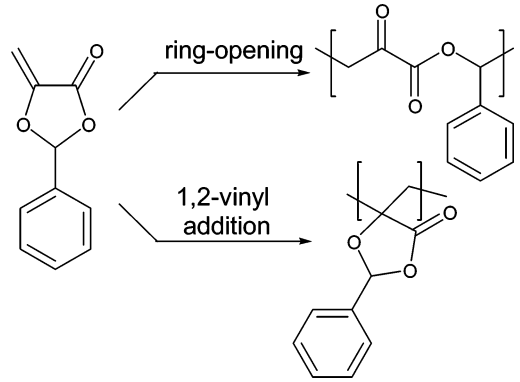


Figure 1. ^{13}C NMR spectra of and peak assignments for (a) MPDO monomer, (b) PMPDO by ATRP, (c) PMPDO by conventional radical polymerization, (d) PMPDO−PS-I, and (e) PMPDO−PMMA-I. The presence of peak d strongly indicates that the MPDO polymerization proceeded by 1,2-vinyl addition rather than ring opening in all cases explored.

Past reports concerning MPDO polymerization mechanism have been ambiguous. For example, Bailey and Feng reported that MPDO and CA **5b** underwent 100% ring opening at 120 °C in *tert*-butylbenzene.[15] They drew this conclusion based on similarities in UV spectra between the resulting PMPDO and pyruvic acid. In another study—at reaction temperatures merely 10 °C higher than the previous study—Bailey et al. concluded that the polymerization of MPDO proceeded by 1,2-vinyl addition instead of ring opening.[1] In a third study by Bailey and co-workers, where the polymerization was carried out at yet a higher temperature of 140 °C,[13] the authors concluded the polymerization of MPDO proceeded by ring opening. Yet, many of these studies were not substantiated by direct structural characterization.

The polymerizations we carried out—whether by conventional radical polymerization or by ATRP—

Scheme 3. Two Possible Mechanisms for MPDO Homopolymerization



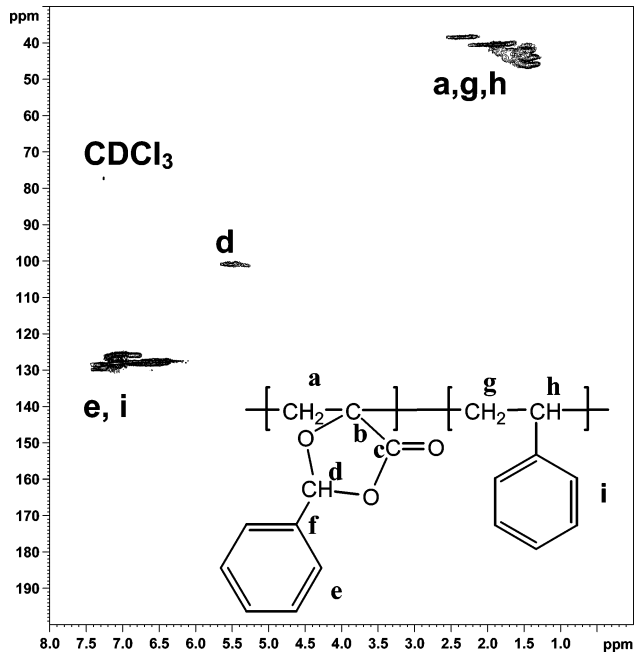


Figure 2. ^{1}H and ^{13}C HSQC NMR spectrum of PMPDO−PS-I (in $CDCl_3$).

always resulted in the 1,2-vinyl addition product of PMPDO as verified by ^{13}C NMR (see Figure 1). In contrast to polymers derived from CKAs, however, conventional radical polymerization of MPDO led to polymers with high molecular weights. We attribute the ability to achieve high molecular weights in PMPDO to the increased stability of the active carbon radical due to the captodative effect. Homopolymerization of MPDO by ATRP also resulted in high molecular weight polymers; the "living" nature of ATRP yielded polymers with lower polydispersity (PDI < 1.2), as compared to polymers formed by conventional radical polymerization (see Table 1).

Copolymerization of MPDO with MMA and Styrene. We successfully copolymerized MPDO with both MMA and S by ATRP. The conditions for the copolymerization of MPDO with either MMA or S in anisole, along with the resulting polymer compositions and molecular weights, are listed in Table 1. Copolymerizing MPDO with either MMA or S did not alter the mechanism by which MPDO polymerized. In particular, results from ^{13}C NMR analysis of the statistical copolymers (representative spectra shown in Figure 1d,e) are analogous to those of PMPDO homopolymers; the acetal benzylic carbon (labeled d) from the MPDO monomer is retained while the α-keto carbonyl carbon is absent. Furthermore, we also carried out 2D NMR analysis on PMPDO−PS-I (representative spectrum shown in Figure 2). We are able to cross correlate the proton peak at 5.5−6.5 ppm with the acetal benzylic carbon signal at ∼100 ppm—a further indication that the five-membered ring in the MPDO monomer is retained on copolymerization. This is, again, in contrast with what had previously been reported for the copolymerization of MPDO with MMA.[14] In that particular report, structural characterization of the statistical copolymer was not presented. Rather, that MPDO ring opens during copolymerization was supported by photodegradation studies. With detailed NMR characterization at hand, we speculate that the decrease in molecular weight during the degradation studies observed by Chung and co-workers[14] was a result of random scission

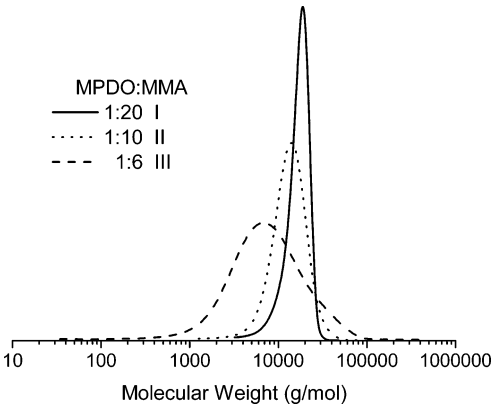


Figure 3. GPC traces (RI) of PMPDO−PMMA-I, -II, and -III by ATRP.

along the PMMA segments[37,38] and not photocleavage of the bond between carbonyl groups[14] in the ring-opened form of PMPDO segments.

Figure 3 shows GPC curves for the PMPDO−PMMA copolymers. Consistent with living radical polymerizations, the molecular weight distributions of the copolymers are relatively narrow (PDI < 1.6; Table 1). We did, however, observe a slight increase in polydispersity with increasing MPDO feed concentration. Strangely, increasing the MPDO in the monomer feed also consistently decreased the overall yield of the polymers. In fact, yields as low as 3% were recorded for the homopolymerization of PMPDO. Additionally, copolymer molecular weights exceeded their theoretical values; a good indication that initiation was incomplete.

Polymer compositions were obtained by integrating the aromatic peaks of PMPDO and the methyl ester peak of PMMA in the ^{1}H NMR spectra (see Figure 4) and are summarized in Table 1. The chloroform solvent peak, which appears at 7.28 ppm, is excluded from the integration. We found the copolymer compositions, especially at higher MPDO feed concentrations, to be significantly different from the feed compositions. In fact, a monomer feed of 10 mol % MPDO resulted in a copolymer with 32 mol % PMPDO. That MPDO is preferentially incorporated into the copolymer was also observed during the synthesis of PMPDO−PS. These observations indicate that MPDO is much more likely to add to a growing carbon radical compared to either MMA or S. As discussed earlier, the presence of both an electron-withdrawing and electron-donating substituent on the cyclic radical of MPDO has a strongly stabilizing effect. Consequently, the formation of a stabilized MPDO cyclic radical not only favors conversion of MPDO over MMA and S but also prevents its ring opening.[39]

To further confirm that MPDO copolymerization in fact did proceed by 1,2-vinyl addition and not ring opening, we also carried out some degradation experiments on PMPDO−PS copolymers. Unlike the PMPDO−PMMA copolymers examined by Chung and co-workers,[14] the PS segments in our copolymers are stable upon exposure to UV and basic environments. Any decrease in molecular weight during these degradation studies must therefore be attributed to MPDO—only the ring-opened product contains α-ketoester groups in the polymer backbone that are both photo- and hydrolytically cleavable—degradation. Hydrolytic degradation of PMPDO−PS-I copolymer was carried out under basic conditions. After 50 h, only a slight decrease of the molecular weight was observed (Figure 5), suggesting

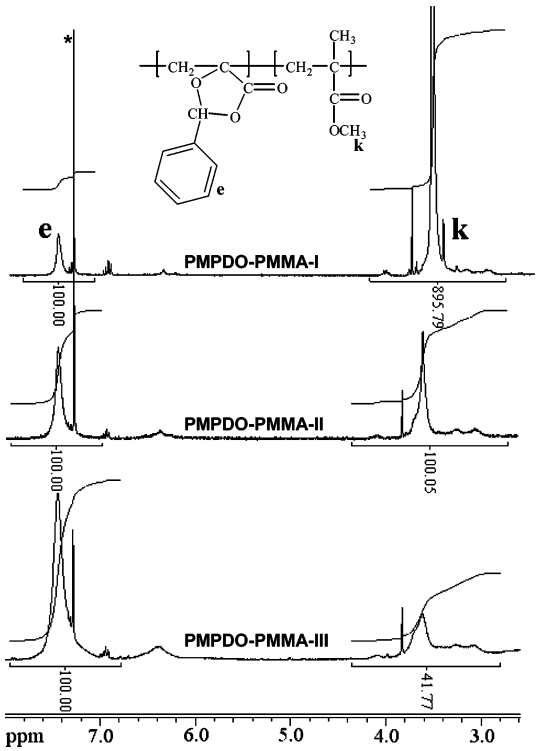


Figure 4. ^{1}H NMR spectra of and peak assignments for PMPDO−PMMA-I, PMPDO−PMMA-II, and PMPDO−PMMA-III. Integrations from which polymer compositions were obtained are indicated. * indicates the chloroform solvent peak, which was excluded from the integration.

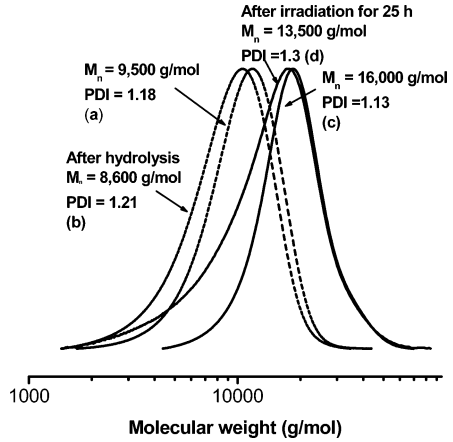


Figure 5. GPC traces (RI) of PMPDO−PS-I: (a) before hydrolysis; (b) after hydrolysis for 50 h (polymer:THF:methanol:KOH = 0.1 g:4 mL:2.5 mL:0.13 g) and of PMPDO−PS-II; (c) before irradiation; (d) after irradiation for 25 h (polymer: THF = 0.1 g:5 mL).

the absence of any hydrolytically cleavable ester groups in the polymer backbone. The small decrease of the molecular weight was probably due to a decrease in the hydrodynamic volume of the polymer chain stemming from the hydrolysis of the ester group in the MPDO ring.[40] Figure 5 also shows that the molecular weight of PMPDO−PS-II remains unchanged despite having been exposed to UV irradiation for 25 h. That these PMPDO copolymers are not susceptible to either photo- or hydrolytic degradation is a further indication that MPDO did not ring open during copolymerization.

Figure 6 contains DSC heating scans of PMMA, PMPDO−PMMA-I, and PMPDO−PMMA-II. The PMMA homopolymer, made by ATRP, exhibits a glass transition temperature, T_g, at ≈104 °C (0.24 J/(g °C)). While we have attempted on several occasions to measure the T_g of pure PMPDO, no apparent glass transition was detected <200 °C. The copolymers, however, exhibit measurable T_gs that appear to increase with increasing MPDO content. Specifically, PMPDO−PMMA-I (8% PMPDO by mass) copolymer reveals a single T_g at ≈104 °C while PMPDO−PMMA-II (44% PMPDO by mass) exhibits a T_g at ≈122 °C. The heat capacities associated with these transitions—0.17 and 0.20 J/(g °C), respectively—are similar to that observed for the PMMA homopolymer, suggesting that the measured glass transitions are representative of the entire polymer samples and not merely segments of the polymers.

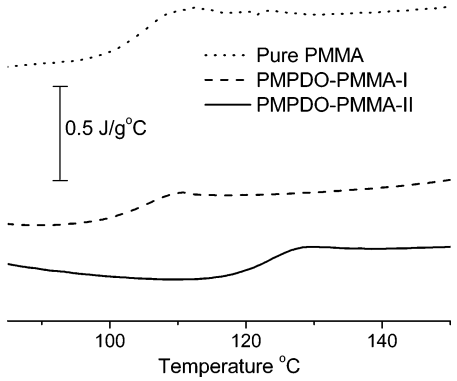


Figure 6. DSC traces for PMMA, PMPDO−PMMA-I, and PMPDO−PMMA-II.

Conclusions

^{13}C NMR structural analysis has allowed us to unambiguously determine the radical polymerization mechanism of MPDO. Specifically, the polymerization of MPDO—whether homo- or copolymerization and regardless of polymerization conditions explored—proceeded by 1,2-vinyl addition rather than ring-opening polymerization. During the copolymerization with MMA or with S, MPDO incorporates significantly faster into the copolymer. This observation suggests that MPDO is a much more reactive monomer than either MMA or S. The stability of PMPDO−PS during photo- and hydrolytic degradation further confirms that MPDO was incorporated into the copolymer through 1,2-vinyl addition and not ring opening. Thermal analysis carried out on the copolymers revealed a single glass transition temperature that increases with increasing PMPDO content.

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