Synthesis and Characterization of Functionalized Poly(ϵ-caprolactone) Copolymers by Free-Radical Polymerization

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Received May 27, 1997; Revised Manuscript Received December 22, 1997

ABSTRACT: A series of functionalized poly(ϵ-caprolactone) copolymers, poly(ϵ-caprolactone-*co*-vinylphosphonic acid) and poly(ϵ-caprolactone-*co*-dimethyl vinylphosphonate), were synthesized by the free-radical copolymerization of 2-methylene-1,3-dioxepane with two vinyl monomers, vinylphosphonic acid and dimethyl vinylphosphonate. The copolymers have ester groups in the backbone as well as pendant functional groups. The structure of each copolymer was established by ^{1}H and ^{13}C NMR as well as IR spectroscopy. Differential scanning calorimetry indicated that the copolymer had a random structure. NMR study showed hydrogen transfer during the copolymerization. The copolymers have different solubility behavior due to the presence of different pendant functional groups.

Introduction

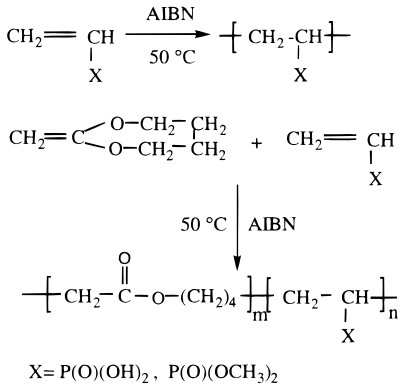
The free-radical ring-opening polymerizations of cyclic ketene acetals have recently evoked a lot of interest. Bailey and co-workers first studied the free-radical ring-opening polymerizations of different cyclic monomers.[1−4] These cyclic monomers could copolymerize with a variety of common monomers to produce copolymers with esters, amides, thioesters, and carbonates in the backbone of the copolymers.[5] One commonly used cyclic ketene acetal is 2-methylene-1,3-dioxepane (MDO), which, in the presence of radical initiators, can undergo quantitative free-radical ring-opening polymerization to produce poly(ϵ-caprolactone). The free-radical copolymerizations of MDO with some vinyl monomers such as styrene also undergo 100% ring-opening polymerizations.[1] The copolymers have aliphatic ester groups in the backbone, which are potentially biodegradable, as well as pendant functional groups originating from the vinyl monomers.

In this paper, two vinyl monomers, vinylphosphonic acid (VPA) and dimethyl vinylphosphonate (VPE), were copolymerized with MDO to introduce phosphonic acid and dimethylphosphonate groups, aimed at forming polymeric-inorganic hybrid materials. Organic polymer−inorganic composite materials are of interest not only for fundamental research concerning biomimetic processes,[6] but also as biomaterials.[7] The presence of ionic groups, such as phosphonic acid and carboxylic acid groups, on the polymer surface is essential for forming polymeric-inorganic hybrid materials.[8−10] The introduction of dimethoxyphosphinyl groups can also provide nucleation sites for hydroxyapatite (HAP) through Ca^{2+} ion accumulation.[11]

Experimental Section

Materials. Chloroacetaldehyde dimethyl acetal, 1,4-butanediol, Dowex 50 (H^+) resin (Dowex 50X2-200), and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Acros. Vinylphosphonic acid (VPA) and triethyl phosphite ($P(OEt)_3$) were obtained from Aldrich. Dimethyl vinylphosphonate (VPE) was provided by Hoechst Celanese Corp., United States. VPE was distilled under vacuum. VPA was dried in a vacuum oven. THF was distilled in sodium using benzophenone as indicator. AIBN was recrystallized in methanol. Other chemicals were used as received.

Scheme 1. Synthesis of Functionalized Poly(ϵ-caprolactone) Copolymers



Characterization. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained using a Bruker AF-500 NMR spectrometer. An 85% H_3PO_4 solution and $P(OEt)_3$ were used as reference standards for ^{31}P NMR in D_2O and $CDCl_3$, respectively.[12] FT-IR spectra were obtained on a Nicolet 60SX FTIR spectrometer. Elemental analysis was done by Onedia Research Services Inc., NY. Differential scanning calorimetry (DSC) of the polymers was performed using a TA Instrument, DSC 2929, in N_2 at a heating rate of 20 °C/min. GPC analysis was conducted in NMP or THF with a Waters 150-C ALC/GPC equipped with μ-styrene HT columns of 10^5, 10^5, 10^3, and 10^3 Å pore size at 50 or 35 °C, and a flow rate of 1 mL/min. Polystyrene narrow molecular weight standards were used for calibration.

Synthesis of Monomer. The cyclic ketene acetal used was 2-methylene-1,3-dioxepane. Monomer synthesis was similar to that of Bailey et al.[1] The purity of MDO was examined by GC-MS and found to be 99.99% pure.

Synthesis of Polymers. Homopolymers, poly(ϵ-caprolactone) (P(MDO)), poly(vinyl phosphonic acid) (P(VPA)), poly(dimethyl vinylphosphonate)(P(VPE)), and copolymers, poly(ϵ-caprolactone-*co*-vinylphosphonic acid) (P(MDOVPA) and poly(ϵ-caprolactone-*co*-dimethyl vinylphosphonate) (P(MDOVPE)), were synthesized following Scheme 1 by using AIBN (2 mol %) as initiator. Copolymerization of MDO with VPA without initiator AIBN was also performed to test the stability of MDO in the presence of an acid. The pressure tubes were heated

S0024-9297(97)00728-6 CCC: $15.00 © 1998 American Chemical Society
Published on Web 02/07/1998

Table 1. Polymerization of MDO and Some Vinyl Monomers[a]

monomer(s)	polymer	polymerization time (h)	yield (%)	ester mol % in copolymer	mol wt M_w	mol wt M_n
MDO	P(MDO)	48	70		72 000	42 000[b]
VPE	P(VPE)	48	81		16 000	8000[c]
MDO/VPA						
3:1	P(MDOVPA)1	48	61	32		
1:1	P(MDOVPA)2	48	68	19		
1:3	P(MDOVPA)3	48	59	6		
MDO/VPE						
3:1	P(MDOVPE)1	48	50	60	100 000	21 700[c]
1:1	P(MDOVPE)2	48	62	36	146 000	43 000[c]
1:3	P(MDOVPE)3	48	55	10	150 000	32 700[c]

[a] P(VPA) was synthesized by ref 21. [b] Molecular weight was measured by GPC in THF. [c] Molecular weight was measured by GPC in NMP.

at 300 °C overnight and then transferred into a glovebox. All chemicals were added in the glovebox. The molar feed ratios of comonomers (MDO:vinyl monomer) were 3:1, 1:1, and 1:3, respectively. The reaction mixture was heated neat in an oil bath at 50 °C. After the mixtures were stirred for 48 h, the tubes were removed from the oil bath and different solvents were added into the mixtures to dissolve or disperse the polymers. The polymers with different compositions are listed in Table 1. The purification of the polymers was as follows:

(1) P(MDO) was dissolved in $CHCl_3$ and precipitated in hexane.

^{1}H NMR ($CDCl_3$, ppm): 1.4 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 1.6 (b, 4H, $CH_2COOCH_2CH_2CH_2CH_2$), 2.3 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 4.0 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$).

^{13}C NMR ($CDCl_3$, ppm): 23.6 ($CH_2COOCH_2CH_2CH_2CH_2$), 24.7 ($CH_2COOCH_2CH_2CH_2CH_2$), 25.7 ($CH_2COOCH_2CH_2CH_2CH_2$), 34.3 ($CH_2COOCH_2CH_2CH_2CH_2$), 64.3 ($CH_2COOCH_2CH_2CH_2CH_2$), 173.7 ($CH_2COOCH_2CH_2CH_2CH_2$).

IR (neat, cm^{-1}): 1736 (C═O stretching).

(2) P(VPA) was dissolved in water and precipitated in acetic acid.

^{1}H NMR (D_2O, ppm): 1.5 (b, 2H, CH_2CH), 3.5 (b, 1H, CH_2CH), 8−10 (2H, $P(O)(OH)_2$).

^{13}C NMR (D_2O, ppm): 30.2 (CH_2CH), 64.2 (CH_2CH).

^{31}P NMR (D_2O, ppm): 30.1.

IR (KBr, cm^{-1}): 3400−2000 (broad peak, O−H stretching, phosphonic acid).

(3) P(VPE) was dissolved in $CHCl_3$ and precipitated in hexane.

^{1}H NMR ($CDCl_3$, ppm): 1.2−2.8 (b, overlapping peaks, 3H, $CHCH_2$), 3.8 (6H, $P(O)O(CH_3)_2$).

^{13}C NMR ($CDCl_3$): 23.2, 25.0, 27.4, 30.8 (CH_2CH), 52.9 (OCH_3).

^{31}P NMR ($CDCl_3$, ppm): 36.9.

IR (neat, cm^{-1}): 1258 (P═O stretching), 1034 (P−O−C stretching).

(4) The P(MDOVPA) copolymers swelled in water and the hydrogel formed was filtered, followed by washing with water and $CHCl_3$. The NMR and IR spectra were similar except that the relative intensities of the signals varied.

^{1}H NMR (D_2O, swells, ppm): 1.5−1.7 (b, 6H, $CH_2COOCH_2CH_2CH_2CH_2$), 2.2 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 1.5 (b, 2H, CH_2CH, VPA unit), 3.5 (1H, CH_2CH, VPA unit), 4.0 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 5−8 (2H, $P(O)(OH)_2$).

^{13}C NMR (D_2O, swells, ppm): 29.3−32.4 (CH_2CH, VPA unit), 24.6 ($CH_2COOCH_2CH_2CH_2CH_2$), 27.0 ($CH_2COOCH_2CH_2CH_2CH_2$), 28.6 ($CH_2COOCH_2CH_2CH_2CH_2$), 29.3 ($CH_2COOCH_2CH_2CH_2CH_2$), 30.2 (CH_2CH, VPA unit), 60.4, 60.9 ($CH_2COOCH_2CH_2CH_2CH_2$), 64.2 (CH_2CH, VPA unit), 170.6, 171.2, 173.7 ($CH_2COOCH_2CH_2CH_2CH_2$).

P (D_2O, ppm): 30.1, 34.2.

IR (KBr, cm^{-1}): 3400−2000 (O−H stretching, phosphonic acid), 1736 (C═O stretching).

Elemental analysis, P(MDOVPA)1: C, 24.98; H, 5.43. P(MOPVPA)2: C, 31.35; H, 5.73; P(MDOVPA)3: C, 36.87; H, 6.87.

(5) P(MDOVPE) copolymers were dissolved in $CHCl_3$ and precipitated in hexane. All three P(MDOVPE) copolymers have similar NMR and IR spectra, except that the relative intensities of the signals varied.

^{1}H NMR ($CDCl_3$, ppm): 1.4 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 1.6 (b, 4H, $CH_2COOCH_2CH_2CH_2CH_2$), 2.3 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$), 1.2−2.8 (3H, CH_2CH, small peaks overlapping, VPE unit), 3.8 (6H, $P(O)O(CH_3)_2$), 4.0 (b, 2H, $CH_2COOCH_2CH_2CH_2CH_2$).

^{13}C NMR ($CDCl_3$, ppm): 24.7, 25.6, 26.0, 27.3, 28.5, 29.0, 30.8, 31.7, 32.8, 33.9, 34.2 (CH_2CH, VPE unit, $CH_2COOCH_2CH_2CH_2CH_2$), 52.8 (OCH_3, VPE unit), 64.2, 65.0 ($CH_2COOCH_2CH_2$ CH_2CH_2), 171.9, 173.6 (CO).

^{31}P NMR ($CDCl_3$, ppm): 36.9.

IR (neat, cm^{-1}): 1734 (C═O, ester), 1258 (P═O stretching), 1034 (P−O−C stretching).

Elemental analysis, P(MDOVPE)1: C, 50.81; H, 7.90; P(DOPVPE)2: C, 43.89; H, 7.56. P(MDOVPE)3: C, 37.67; H, 6.75.

For each polymer, the polymerization time and yield are listed in Table 1.

Comonomer Composition. The comonomer composition for each copolymer was calculated from elemental analysis (C%), assuming that the copolymer compostion is $(C_6H_{10}O_2)_x(C_2H_3R)_{1-x}$, where R is $P(O)(OH)_2$ and $P(O)(OCH_3)_2$, respectively. Each comonomer composition is represented by ester mol % (x) and is listed in Table 1.

Hydrolytic Stability. The hydrolytic stability of the copolymer P(MDOVPA) was examined at various pHs for different time periods. The copolymer P(MDOVPA)2 was used for all the studies. P(MDOVPA)2 (0.1 g) was placed in 2 mL of distilled water. The pH of the water was adjusted by either adding 0.1 M HCl or 0.1 M NaOH to 2, 7, and 12, respectively. The sample at each pH was taken out and dried after 2, 7, and 14 days, respectively. IR spectra were recorded for all the samples.

Results and Discussion

Comonomer Composition. As shown in Table 1, the ester mol % is less than 50% for all 1:1 comonomer feed ratios, similar to the results Bailey et al. obtained for the copolymerizations of MDO with other vinyl monomers.[1] The ^{1}H NMR technique was also used to measure the comonomer composition of P(MDOVPE) copolymers because of the distinguishing peaks of the two comonomers in the ^{1}H NMR spectrum (4.0 and 3.8 ppm for MDO and VPE, respectively). The ester mol % of P(MDOVPE)2 obtained from NMR (36%) is close to that from elemental analysis (33%).

Copolymer Structure and Sequence Distribution. Usually the cationic polymerization of cyclic ketene acetals gives polyacetals or mixtures of polyesters and polyacetals.[13] The possibility of cationic polymerization of MDO with acidic monomer VPA (4:1, 1:1, and 1:4 molar rations) was tested by IR and ^{1}H

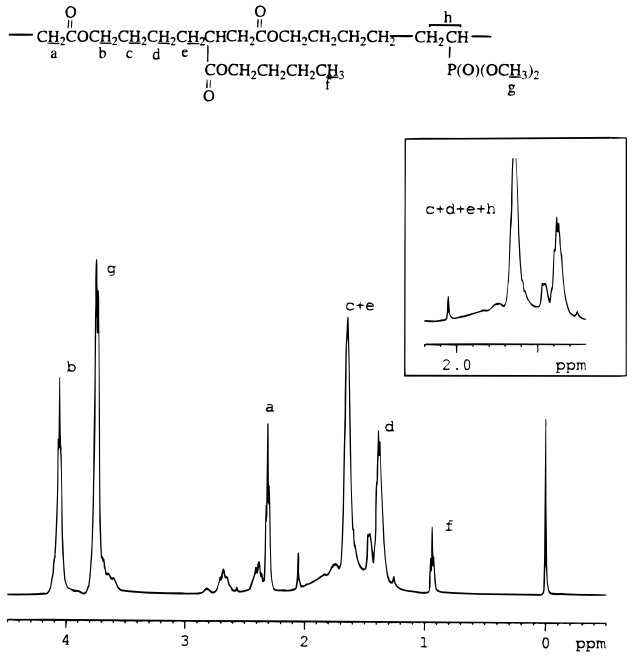


Figure 1. ^{1}H NMR spectrum of P(MDOVPE).

NMR spectra. The reaction mixture did not turn viscous after 48 h, and the product was soluble in chloroform. The IR spectrum of the reaction mixture showed the formation of ester (1736 cm^{-1}, C═O stretching); however, the ^{1}H NMR spectrum was very complicated. The cationic polymerization of MDO catalyzed by VPA only gave low-molecular-weight products, as found in some cationic polymerizations of MDO.[14] During the free-radical polymerization of MDO with VPA, the cationic polymerization of MDO was also possible. This side reaction would affect the feed ratio of MDO to VPA, but the side-reaction product was separated from the free-radical product due to its low molecular weight and its solubility in chloroform.

The free-radical polymerization of cyclic ketene acetals has two possibilities forming two different structures. One is the ring-opening producing the polyester, and the other is ring retention producing polyacetals.[1] Free-radical copolymerizations of MDO with the two vinyl monomers resulted in 100% ring opening, as in the free-radical polymerization of MDO.[1] The structures of the polymers were elucidated by their NMR and IR spectra. The NMR spectra could be obtained when the polymer was swollen in a solvent, although the peaks were broader. The NMR spectra of all copolymers indicate the presence of both comonomer units. In the ^{1}H and ^{13}C NMR spectra of the copolymers (Figures 1−4), all the peaks from MDO units are observed (^{1}H NMR: 1.4, 1.6, 2.3, and 4.0 ppm, ^{13}C NMR: 24.7, 25.6, 28.5, 34.2, 64.3, and 173.7 ppm), although there are some shifts due to the formation of the copolymers and the solvents for the NMR spectra. P(MDOVPA) has a broad peak at 5−8 ppm (P═O(OH)$_2$) in the ^{1}H NMR spectrum when the polymer concentration is large in D_2O. Backbone H's and C's of P(MDOVPA) are observed in the NMR spectra: 1.5 ppm (C*H*$_2$CH) and 3.5 ppm (CH$_2$C*H*) (Figure 3) and 30.2 ppm (*C*H$_2$CH) and 64.2 ppm (CH$_2$*C*H) (Figure 4). ^{1}H and ^{13}C NMR spectra of P(MDOVPE) have very characteristic peaks from OCH$_3$ in the VPE unit: ^{1}H, 3.81 ppm (Figure 1); ^{13}C, 52.8 ppm (Figure 2). The IR spectra (Figure 5) of all the copolymers show ester peaks (1734 cm^{-1}), and in the IR spectra of P(MDOVPA), O−H stretching is observed at 2400−3500 cm^{-1} (Figure 5a).

On the basis of the solubility differences, measures were taken to ensure that the copolymers were separated from any homopolymers during the purification outlined in the Experimental Section. However, the DSC studies of P(MDOVPE) copolymers showed that no

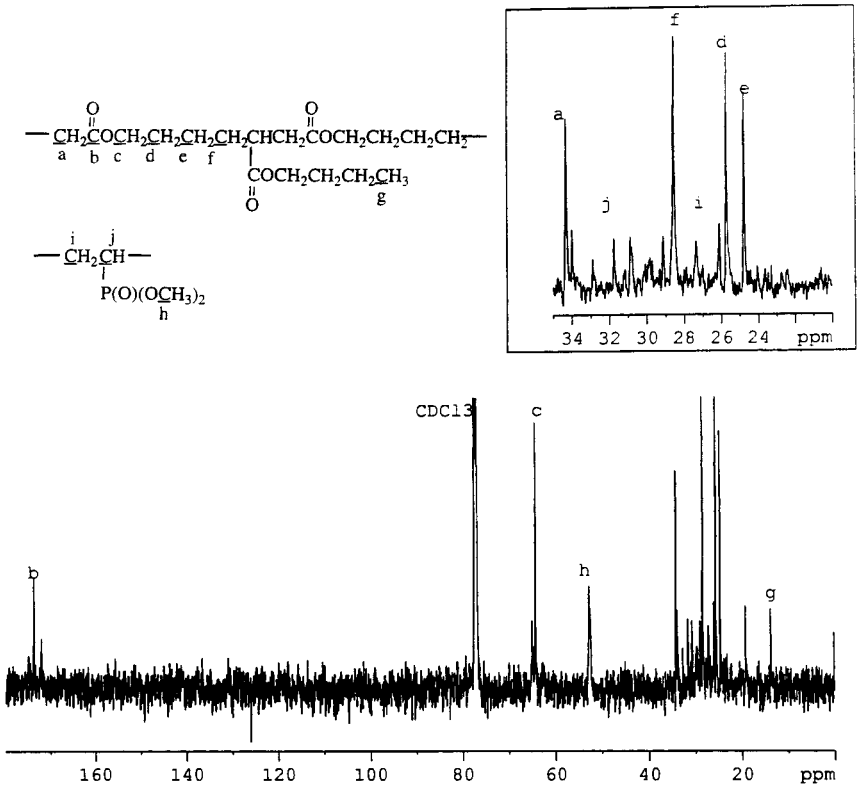


Figure 2. ^{13}C NMR spectrum of P(MDOVPE).

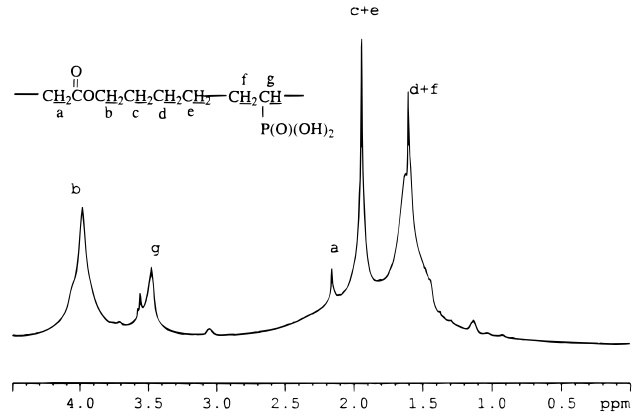


Figure 3. ^{1}H NMR spectrum of P(MDOVPA).

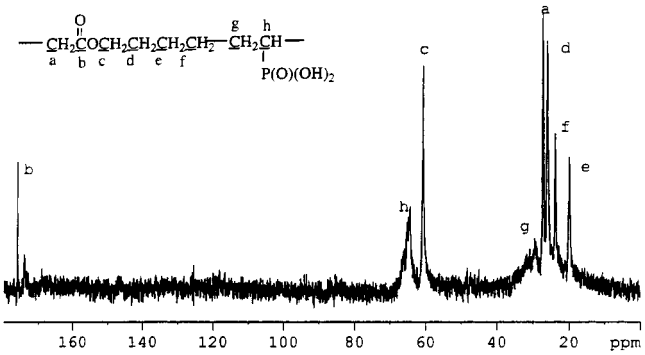


Figure 4. ^{13}C NMR spectrum of P(MDOVPA).

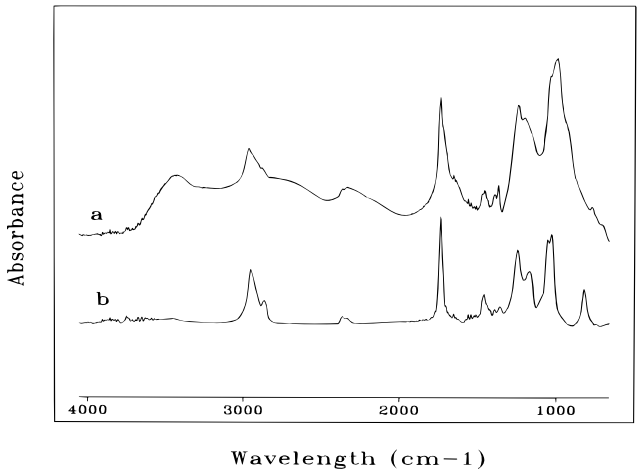
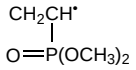


Figure 5. FTIR spectra of the polymers: (a) P(MDOVPA) and (b) P(MDOVPE).

homopolymers were present in the purified samples. All the copolymers are proposed to be random copolymers based on the DSC thermograms. The DSC thermogram of each copolymer showed a single T_g. The latter is between the T_g's of the two homopolymers from the comonomers constituting the copolymer (Table 3). The T_g of P(MDOVPA) was not obtained because it decomposed before it reached the glass transition temperature.

The molecular weights of the polymers P(MDO), P(VPE), and P(MDOVPE) were measured by GPC (Table 1). The P(MDOVPA) copolymers are not soluble in any solvents or mixture of solvents tried. Molecular weight of these copolymers were not measured. The molecular weight of the copolymers P(MDOVPE) were around the 10^4-10^5 range, but the molecular weight distribution was high. This was probably caused by the poor mixing in the bulk polymerization. Free-radical bulk polymerization makes heat dissipation difficult. Local hot spots may result in a broad molecular weight distribution due to chain transfer to the polymer.[15] The molecular weight of P(VPE) was much lower than that of the copolymers P(MDOVPE). This can be explained by the stability of the free-radical



due to the resonance interaction of the substituent group $O{=}P(OCH_3)_2$ and the low reactivity of the monomer as a consequence of the bulky substituent, which could hinder propagation.[15]

The free-radical polymerization of MDO undergoes intramolecular hydrogen transfer during propagation.[16] Hydrogen transfer was also observed during the free-radical copolymerization of MDO with vinyl monomers. A branched ester structure in the copolymers was also formed, as discussed previously.[16] This is confirmed by the ^{1}H and ^{13}C NMR spectra of P(MDOVPE)1 (Figures 1 and 2, respectively), which has a high ester percentage. Comparing these spectra with the ^{1}H and ^{13}C NMR spectra of P(MDO), the characteristic methyl peaks resulting from hydrogen transfer (0.94 ppm, Figure 1; 13.9 ppm, Figure 2) in the ester unit were observed.[16]

Solubility. The solubility of each polymer in a different solvent is listed in Table 2. P(MDO) is soluble in $CHCl_3$ as are most polyesters. P(VPA) is soluble in most polar solvents. P(VPE) is soluble in polar solvents as well as in less polar solvents such as $CHCl_3$. All the copolymers have both hydrophilic (pendant functional groups) and hydrophobic (ester and vinylene) parts. The solubility of the copolymer depends on its intermolecular or intramolecular interactions and its interactions with the solvent.

Like P(VPE), P(MDOVPE) has very good solubility in all solvents tried. When the hydrophilic VPE unit is in high percentage (P(MDOVPE)2 and P(MDOVPE)3), the copolymer was soluble in water, but P(MDOVPE)1 was not soluble in water due to the larger amount of hydrophobic ester groups.

P(MDOVPA) has hydrophilic phosphonic acid groups. The polymer is not soluble in any of the solvents or mixtures of solvents tried. It swells considerably in water and in some polar organic solvents such as DMSO, NMP, and methanol, and with drying it shrinks. This might be caused by intra- and intermolecuar hydrogen bonding between the ester in the backbone and the pendant phosphonic acid groups, as found in some amphiphilic block and graft copolymers with ester and pendant carboxylic acid groups.[17,18] However, the gel formation was not broken in alkaline solution or in salt solution with high ionic strength, or by the addition of urea. Therefore, the gel formation was caused not only by hydrogen bonding but also by some chemical cross-linking. ^{31}P NMR of P(MDOVPA) showed a major peak at 30.1 ppm and a shoulder at 34.2 ppm (Figure 6a). The major peak is the same as that of P(VPA) (Figure 6b). The shoulder was found to be close to the ^{31}P of phosphoester.[12] We propose that transesterification of phosphonic acid and ester in the backbone occurred. The ester could be hydrolyzed to an acid and an alcohol in the presence of phosphonic acid and a trace of moisture (also see the following hydrolytic stability studies). Further reaction of phosphonic acid and

Table 2. Solubility of the Polymers[a]

polymer	solvent MeOH	$CHCl_3$	DMSO	NMP	*m*-Cresol	H_2O	HOAc
P(MDO)	−	+	−	−	O	−	−
P(VPA)	+	−	+	+	−	+	−
P(VPE)	+	+	+	+	+	+	+
P(MDOVPA)	O	−	O	O	O	O	−
P(MDOVPE)1	+	+	+	+	+	−	−
P(MDOVPE)2	+	+	+	+	+	+	+
P(MDOVPE)3	+	+	+	+	+	+	+

[a] Solubility test was done using 10 mg of sample in 1 mL of solvent: +, soluble; −, not soluble; O, swelling.

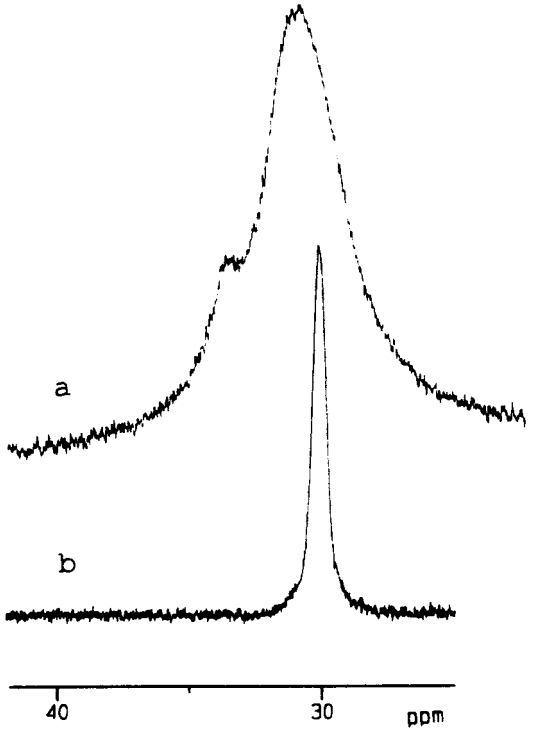


Figure 6. ^{31}P NMR spectra of the polymers: (a) P(MDOVPA) and (b) P(VPA).

Table 3. Thermal Analysis of the Polymers

polymer	P(MDO)	P(VPA)	P(VPE)	P(MDOVPA) 1	2	3	P(MDOVPE) 1	2	3
T_g (°C)	−57		18	74	89	132	−19	9	16

alcohol would result in the formation of a phosphoester, and this would lead to the cross-linking of the copolymer.[19]

Hydrolytic Stability Studies. The chain scission of P(MDOVPA) resulted in the formation of acids and alcohols, but the gel still remained. Because of the insolubility of the polymer and its hydrolysis products, the molecular weight decrease after hydrolysis was not measured. The hydrolysis was determined by FT-IR analysis. After 14 days, the ester absorbance (1736 cm^{-1}, C═O stretching) disappeared, and a carboxylic acid absorbance (1665 cm^{-1}, −COOH, internal hydrogen bonding with $-P(O)(OH)_2$) (Figure 7) appeared. The hydrolytic stability of P(MDOVPA) decreased due to the presence of the acidic functional groups, $-P(O)(OH)_2$, analogous to the observed decrease in the stability of poly(ϵ-caprolactone) due to the presence of acidic end groups, −COOH.[20]

Conclusions

Homopolymers, P(MDO), P(VPA), and P(VPE), and copolymers, P(MDOVPA) and P(MDOVPE), were successfully synthesized by the free-radical polymerizations. The pendant hydrophilic functional groups, $-P(O)(OH)_2$ and $-P(O)(OMe)_2$ from the vinyl monomers, VPA and VPE, respectively, were incorporated into the ester backbones. When the feed ratio of the comonomers MDO and the vinyl monomer were varied, copolymers with a different ester percentage or percentage of functional groups were obtained. These copolymers are amorphous with extensive glass transition temperatures. Applications of these copolymers for making polymeric-inorganic composites are underway.

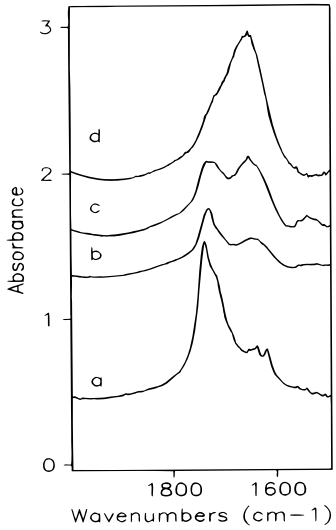


Figure 7. FTIR spectra of P(MDOVPA)2 and its hydrolyzed products at pH = 7 after different time periods (day): (a) 0, (b) 2, (c) 7, and (d) 14.

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MA9707289