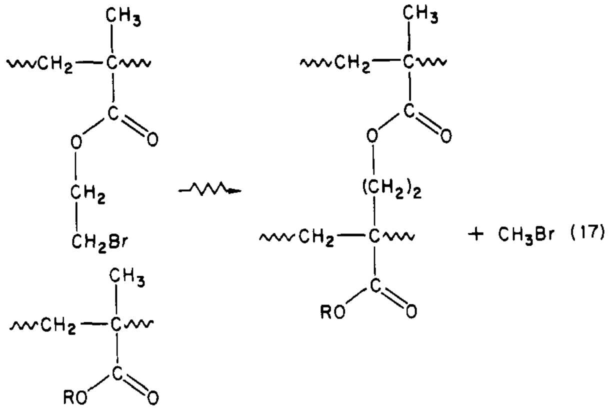
α-bromoacrylate.[8] This characteristic may be related to the ease of CH_3Br elimination. The possible reactions may be


(17)

and others like it.

The ease of cross-linking of the BEMA homo- and copolymers as compared to the CEMA and FEMA polymers may have other explanation. The size of the halogen atoms should govern their rates of diffusion, which are approximately inversely proportional to the square root of their masses. Thus the lighter F· and Cl· atoms can diffuse more readily from their site of formation to react elsewhere. On the other hand, the heavier Br· atom probably reacts in the close vicinity of its site of formation, i.e., hydrogen abstraction. Combination of the two resulting macromolecular radicals would tend to cross-link. We have found in our studies of other halogenated polymers that the bromine-containing polymers generally cross-link much more readily than the chlorine- and fluorine-containing analogues in radiolysis.

In conclusion, PTCEMA has high scission efficiency without tendency of cross-linking. It can be superior to PMMA as an E-beam resist. This optimism should be tempered by the report of Tada[9] that poly(TCEMA) will cross-link at high dose. More work needs to be done for TCEMA polymers at high dose and search for a comonomer to reduce the cross-linking tendency. The bromine-containing systems have no merit for resist applications. The FEMA and CEMA systems are marginal in this respect.

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References and Notes

(1) On leave from the Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India.
(2) A. Todd, *J. Polym. Sci.*, **72**, 223 (1960).
(3) A. A. Miller, E. J. Lawton, and J. S. Balwit, *J. Polym. Sci.*, **14**, 503 (1954).
(4) L. A. Wall, *J. Polym. Sci.*, **17**, 141 (1955).
(5) J. N. Helbert, C. Y. Chen, C. U. Pitman, Jr., and G. L. Hagnauer, *Macromolecules*, **11**, 1104 (1978).
(6) C. Y. Chen, C. U. Pittman, Jr., and J. N. Helbert, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 169 (1980).
(7) C. U. Pitman, Jr., C. Y. Chen, M. Ueda, J. N. Helbert, and J. H. Kwiatkowski, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3413 (1980).
(8) G. N. Babu, A. Narula, S. L. Hsu, and J. C. W. Chien, *Macromolecules*, preceding paper in this issue.
(9) T. Tada, *J. Electrochem. Soc.*, **126**, 1635 (1979).
(10) H. Ito, D. C. Miller, and C. G. Willson, *Macromolecules*, **15**, 915 (1982).
(11) A. Eranian, A. Couttet, E. Datamanti, and J. C. Dubois, *Polym. Prepr., Am. Chem. Soc., Div. Polymer Chem.*, **42**, 779 (1980).
(12) P. B. Ayscough, "Electron Spin Resonance in Chemistry", Methuen and Co.: London, 1967, pp 369-372.

Radiolysis of Resist Polymers. 5. Poly(haloalkyl α-chloroacrylates) and Copolymers with Methyl Methacrylate

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ABSTRACT: Homopolymers of 2,2,2-trifluoroethyl α-chloroacrylate (PTFECA) and of hexafluoroisopropyl α-chloroacrylate (PHFPCA) and copolymers with MMA have been synthesized. The homopolymers have $G_s \approx 3.6$ and $G_x = 0$. Their glass transition temperatures are high and the polymers form strong films. These polymers may prove to be excellent candidates for positive electron-beam resist materials, superior to PMMA. A relative comparison of the radiation sensitivity of haloalkyl α-chloroacrylate polymers with homo- and copolymers of methyl α-chloroacrylate is discussed.

Introduction

Research on positive electron-beam resist polymers has mainly been directed toward polymers which are highly sensitive toward radiolytic chain scission without cross-linking. Of course, other considerations such as high T_g, ability to form mechanically strong thin films, and good differential solubility, which depends on molecular weight, are also important.

Poly(methyl α-chloroacrylate) has very high G_s (number of chain scissions per 100 eV absorbed) values of 6-7.4[1,2] Unfortunately, the polymer also tends to cross-link upon irradiation; $G_x \sim 0.6$-0.9. Attempts to eliminate the cross-linking reactions by copolymerizing methyl α-chloroacrylate with methyl methacrylate (MMA) were unsuccessful.[2] Copolymers of all compositions have G_s values lying between that for each corresponding homopolymer but nonzero G_x values.

Halogens placed on the pendant group slightly enhanced G_s without inducing cross-linking.[3] For instance, poly(2,2,2-trifluoroethyl methacrylate)[4-6] and poly(2,2,2-trichloroethyl methacrylate)[6,7] have G_s values of 2.0 and 2.4, respectively, and these G_s values are greater than $G_s = 1.4$ for PMMA. However, based on the G_s and G_r (radical yield) values, dissociative electron capture by halogen atoms on the backbone is more effective in generating radicals than similar capture by halogen atoms on the pendant group. Recently, Tada[8] reported that poly(2,2,2-trifluoroethyl α-chloroacrylate) was found to exhibit

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high sensitivity which is one or two orders magnitude higher than that of PMMA. However, there are no reports on G_s and G_x values on this novel polymer and its copolymers.

Attempts to optimize scission vs. cross-linking for copolymers of methyl α-chloroacrylate and trihaloethyl methacrylates were more promising.[9] Thus poly(94MCA-*co*-6TCEMA) and poly(38MCA-*co*-62TFEMA)[9,10] have G_s values of 2.7 and 3.2, respectively, with $G_x = 0$ in both systems. Thus encouraged, we reasoned that acrylate polymers having halogen atoms on both the backbone and as pendant groups would have enhanced sensitivity toward radiolytic scission but with minimal cross-linking. The results realizing this expectation are reported here.

Experimental Section

Materials. 2,2,2-Trifluoroethyl α-chloroacrylate (TFECA) was synthesized according to the procedure described below.[11]

Methyl 2,3-dichloropropionate (27 g, Aldrich) was added dropwise to 15 g of $Ba(OH)_2 \cdot 8H_2O$ in 30 mL of water kept at 0–5 °C over a period of 3 h. At the end of the reaction, the mixture was acidified with 20% aqueous H_2SO_4 and extracted with ether. The ether was removed under reduced pressure. The dried product was recrystallized from petroleum ether (40–60 °C) to afford 10.5 g (39%) of α-chloroacrylic acid, mp 63–64 °C (lit.[11] mp 64–66 °C). The reaction gave reproducible yields. The acid (15 g) was dissolved in toluene, and 6 mL of triethylamine and 75 g of freshly distilled benzoyl chloride were added to the mixture, while maintaining the reaction below 10 °C. After the reaction mixture was warmed to 50 °C, the excess benzoyl chloride was removed under reduced pressure. About 12 g of liquid was collected, which was redistilled, and the fraction boiling at 35–38 °C (0.18 torr) was collected as α-chloroacrylyl chloride; yield 8.4 g or 56% of theory.

2,2,2-Trifluoroethyl α-chloroacrylate was obtained by the reaction of 3.75 g of α-chloroacrylyl chloride with 3 g each of 2,2,2-trifluoroethanol and triethylamine at 0–5 °C. After overnight stirring at this temperature, the reaction mixture was warmed for 10 min. The product was extracted with ether and distilled. The yield of TFECA, bp 40–42 °C (0.22 torr), was 3.49 g (ca. 90%). Anal. Calcd for $C_5H_4O_2Cl_3$: C, 31.9; H, 2.13; Cl, 18.62. Found: C, 30.82; H, 2.01; Cl, 17.93.

Hexafluoroisopropyl α-chloroacrylate (HFPCA) was synthesized from α-chloroacrylyl chloride and hexafluoro-2-propanol by the above method. The crude product was distilled to give 67% of HFPCA monomer, bp 48–51 °C (0.23 torr). Anal. Calcd for $C_6H_3O_2ClF_6$: C, 28.7; H, 1.19; Cl, 14.17. Found: C, 27.9; H, 1.16; Cl, 13.89.

Homopolymerizations in the absence of solvent were initiated by AIBN (0.1 wt % of monomer) at 60 °C according to a previously described method.[2] The polymers were purified by repeated precipitation with methanol from a solution of chloroform and dried at 50 °C in vacuo to constant weight. The molecular weights were obtained with a Waters Associates 201 chromatograph equipped with five μ-Styrogel columns using THF as a solvent and the universal calibration method.[2] The homopolymer of TFECA (PTFECA) has $\bar{M}_n = 1.4 \times 10^5$, $\bar{M}_w = 2.3 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 1.7$. The homopolymer of HFPCA (PHFPCA) has $\bar{M}_n = 9.4 \times 10^4$, $\bar{M}_w = 2.1 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 2.2$. The lower molecular weight of PHFPCA suggests the possibility of chain transfer involving the reactive hydrogen atom in the hexafluoroisopropyl group. The homopolymers are soluble in chloroform, acetonitrile, dioxane, DMF, and THF and can be easily cast into films.

Copolymerizations with MMA were performed by methods similar to those used for homopolymerizations. Two copolymers were obtained. Poly(87MMA-*co*-13TFECA) had $\bar{M}_n = 3.3 \times 10^5$, $\bar{M}_w = 5.3 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 1.6$ and poly(77MMA-*co*-23HFPCA) had $\bar{M}_n = 2.4 \times 10^5$, $\bar{M}_w = 5 \times 10^5$, and $\bar{M}_w/\bar{M}_n = 2.1$. The copolymer compositions were determined by elemental analysis.

Polymer Characterization. The infrared spectra of PTFECA and PHFPCA exhibited peaks at 1770 and 1755 cm^{-1} due to carbonyl absorptions. The double carbonyl bands have been attributed to rotational isomerism of α-haloesters.[12] Lenz et al.[13] reported that the two carbonyl absorptions in the case of poly(methyl α-chloroacrylate) can be correlated with dyad tacticity.

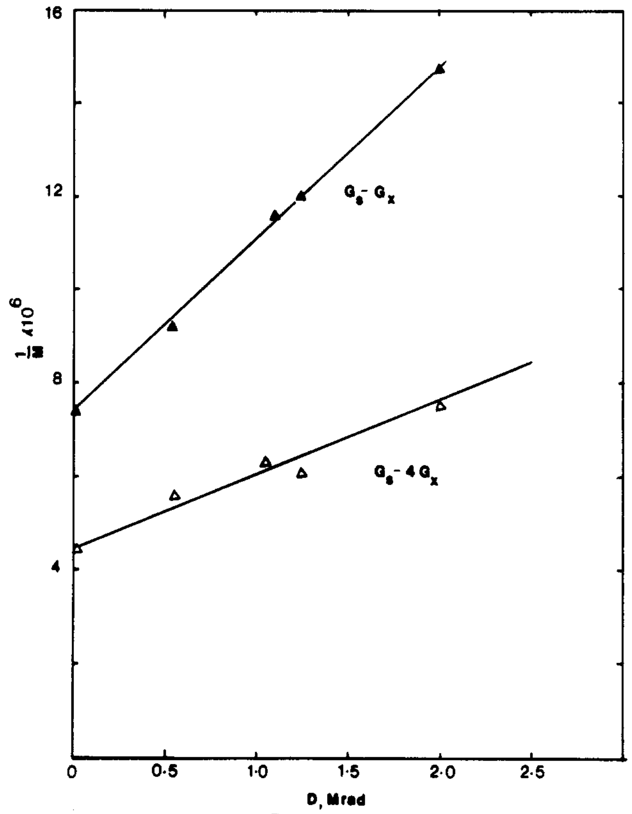


Figure 1. Variation of $\bar{M}_n$ (▲) and $\bar{M}_w$ (△) with γ dose for PTFECA. Solid lines are least-squares fits of experimental data.

Table I
Radiolysis Yields

polymer	$G_s - G_x$	G_s	G_x	G_r
PTFECA	3.6	3.6	0	4.8
P(87MMA-*co*-13TFECA)	1.9	1.9	0	2.6
PHFPCA	3.5	3.5	0	5.3
P(7MMA-*co*-23HFPCA)	2.4	2.4	0	3.2
PMCA[2]	6.5	7.4	0.9	~9
PTFEMA[9]	2.0	2.0	0	3.2
PTFEMA	2.3	2.3	0	
PHFPMA	2.4	2.4	0	3.6
PHFPMA	2.6	2.6	0	

[a] PHFPMA = poly(hexafluroisopropyl methacrylate). The results for PMCA, PHFPMA, and PTFEMA according to references are included for comparison.

The glass transition temperature of PTFECA and PHFPCA, respectively, were 130 and 119 °C. A high glass transition temperature is one of the desirable properties of a resist.

Radiolysis. The γ-irradiation determinations of G_s, G_x, and G_r and ESR measurements were previously described.[2,6]

Results and Discussion

Radiolysis Yields. Polymers were irradiated with a ^{137}Cs γ source to various doses and the changes in molecular weights were determined by GPC. Figures 1 and 2 show the results for the homopolymers. Similar determinations were made on the copolymers. The radiolysis yields are summarized in Table I.

The values of G_s and G_x were determined from the values of $\bar{M}_n$ and $\bar{M}_w$ of the irradiated polymers using the equations of Kilb.[14]

$$\bar{M}_n^{-1} = \bar{M}_{n,0}^{-1} + [(G_s - G_x)D]/100N \quad (1)$$

$$\bar{M}_w^{-1} = \bar{M}_{w,0}^{-1} + [(G_s - 4G_x)D]/200N \quad (2)$$

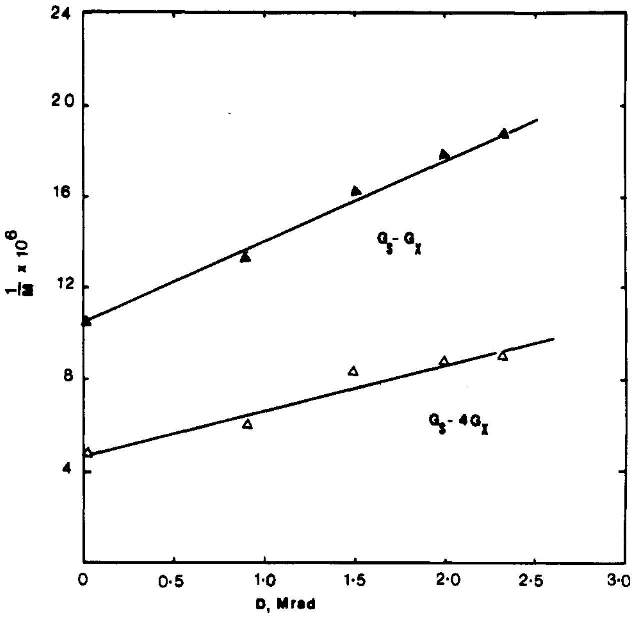


Figure 2. Variation of $\bar{M}_n$ (▲) and $\bar{M}_w$ (△) with γ dose for PHFPCA. Solid lines are least-squares fits of experimental data.

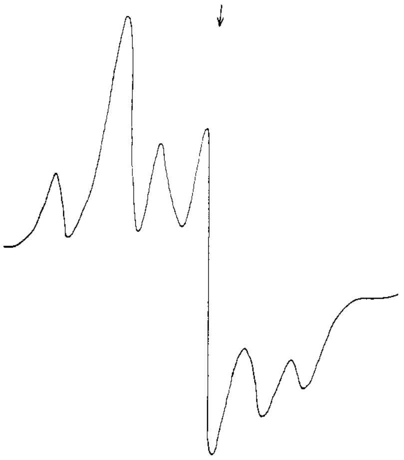


Figure 3. ESR spectra of irradiated PTFECA and PHFPCA. Marker is for DPPH.

where $\bar{M}_{n,0}$ and $\bar{M}_{w,0}$ are the average molecular weights of the unirradiated polymer, $\bar{M}_n$ and $\bar{M}_w$ are the values for the polymer after it has absorbed a γ-ray dose (D), and N is Avogadro's number.

For the homopolymers of fluoroalkyl α-chloroacrylates, the G_s and G_x values lie between those of PMCA and PTFEMA but closer to the latter. However, the tendency toward cross-linking, like in PMCA, is absent in these polymers. In the case of copolymers with MMA, the scission yields are slightly higher than the the arithmetic averages of the G_s values of the homopolymers. Earlier papers of this series showed that changes in radiolysis yields are usually not monotonic functions of copolymer compositions.[2,6,9]

ESR Spectra. The ESR spectra of irradiated PTFECA and PHFPCA are superimposable (Figure 3). They are identical with those obtained from γ irradiation of PMCA (Figure 3a of ref 2). This spectrum had been assigned[2] to two radicals $-CH_2(Cl)\dot{C}(COOR)$ (**I**) and $-CH_2(COOR)\dot{C}CH_2-$ (**II**). The same assignments apply here with R = CH_2CF_3 and R = $CH(CF_3)_2$.

The ESR spectrum (Figure 4) of γ-irradiated poly(87MMA-*co*-13TFECA) is mainly due to radicals I and II, as in Figure 3. However, there are additional peaks which are absent in the irradiated homopolymers. These correspond to some of the resonances of the irradiated PMMA radicals

$$\underset{\text{III}}{-CH_2\dot{C}(CH_3)(COOR)}$$

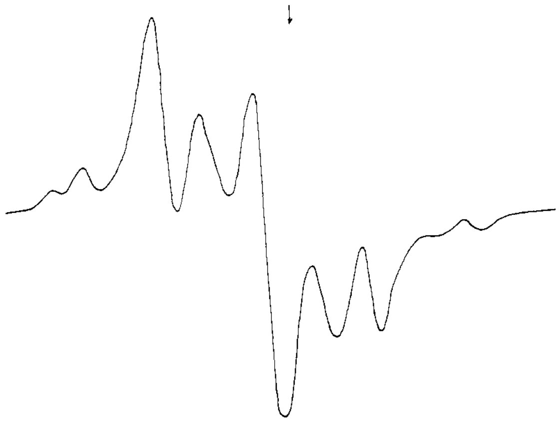


Figure 4. ESR spectrum of irradiated poly(87MMA-*co*-13TFECA). Marker is for DPPH.

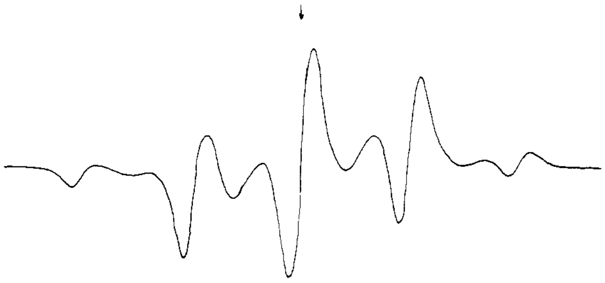


Figure 5. ESR spectrum of irradiated poly(77MMA-*co*-23HFPCA). Marker is for DPPH.

In the case of poly(77MMA-*co*-23HFPCA), irradiation yielded a spectrum (Figure 5) which is nearly all due to radical III. Comparison of Figures 3 and 5 showed that radicals I and II must be present only in small amounts (if any) in this sample.

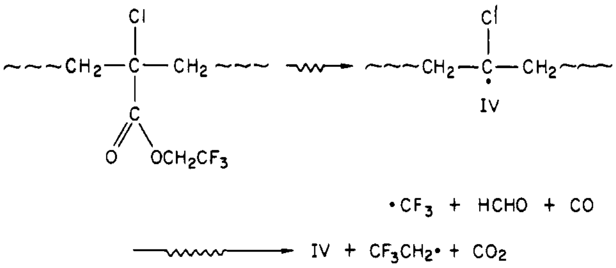
Radiolysis Mechanism. The very high efficiency of radical formation in the radiolysis of PMCA may be attributed to the dissociative electron capture by the chlorine atom.

$$\text{PMCA} \xrightarrow{e^-} \underset{\text{II}}{-\dot{C}H_2C(COOR)CH_2-} + Cl^-$$

$$\text{II} \rightarrow -CH_2C(COOR){=}CH_2 + \underset{\text{I}}{\dot{C}(Cl)(COOR)CH_2-} \quad (3)$$

The other primary and secondary radiolysis processes have been previously discussed in detail.[2]

In the radiolysis of poly(haloalkyl methacrylates), it was proposed[6] that interaction with electromagnetic radiation led to the formation of halogen atoms, various haloalkyl radicals, and CO, or CO_2, leading to radical IV.



$$\sim\sim\sim CH_2-C(Cl)(C(=O)OCH_2CF_3)-CH_2\sim\sim\sim \rightsquigarrow \underset{\text{IV}}{\sim\sim\sim CH_2-\dot{C}(Cl)-CH_2\sim\sim\sim} + \cdot CF_3 + HCHO + CO \quad (4)$$

$$\rightsquigarrow \text{IV} + CF_3CH_2\cdot + CO_2 \quad (5)$$

The fact that the formation of radical II in PTFECA and PHFPCA does not produce cross-links may be attributed

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to the stability of radical II due to the presence of the electron-withdrawing fluorinated side chain. Further, the side-chain substitution stabilizes the radical I to an even greater degree. Under these circumstances, the possible reactions are the recombination of I with electron or chain scission.

In the previous study on copolymers of MCA and MMA, the ESR spectrum of III was obtained upon irradiation when the MCA content is less than 0.2. The results of Figures 4 and 5 are in consonance.

In conclusion, PTFECA and PHFPCA have high efficiency toward radiolytic chain scission without cross-linking. They are excellent candidates as positive electron-beam resist materials. The copolymers with MMA are also superior to PMMA.

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References and Notes

(1) J. N. Helbert, C. Y. Chen, C. U. Pittman, Jr., and Q. L. Hagnauer, *Macromolecules*, 11, 1104 (1978).

(2) G. N. Babu, A. Narula, S. L. Hsu, and J. C. W. Chien, *Macromolecules*, in press.

(3) C. U. Pittman, Jr., E. Wallace, Jr., T. V. Jayaraman, P. Wang, and M. Veda, Proceedings of the IUPAC 28th Macromolecular Symposium, July 12–16, 1982, Amherst, MA, p 443 and references therein.

(4) C. U. Pittman, Jr., C. Y. Chen, M. Ueda, J. N. Helbert, and J. H. Kwiatowski, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3413 (1980).

(5) H. Ito, D. C. Miller, and C. G. Willson, *Macromolecules*, **15**, 915 (1982).

(6) G. N. Babu, A. Narula, P. H. Lu, X. Li, S. L. Hsu, and J. C. W. Chien, *Macromolecules*, in press.

(7) T. Tada, *J. Electrochem. Soc.*, **126**, 1635 (1979).

(8) T. Tada, *J. Electrochem. Soc.*, **130**, 912 (1983).

(9) G. N. Babu, P. H. Lu, S. L. Hsu, and J. C. W. Chien, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 195 (1984).

(10) MCA = methyl α-chloroacrylate, TCEMA = 2,2,2-trichloroethyl methacrylate, and TFEMA = 2,2,2-trifluoroethyl methacrylate. Number preceding the monomer is its mole percent in the copolymer.

(11) C. S. Marvel, J. Dee, H. G. Cooke, Jr., and J. Cowan, *J. Am. Chem. Soc.*, **62**, 3495 (1940).

(12) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957).

(13) G. R. Denver, F. E. Karasz, W. J. MacKnight, and R. W. Lenz, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2151 (1975).

(14) R. W. Kilb, *J. Phys. Chem.*, **63**, 1838 (1959).

Synthesis of ABA Triblock Copolymers of ϵ-Caprolactone and DL-Lactide

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ABSTRACT: The growing AB block copolymer intermediate (PCL–PLA–OAl<) was extended with ethylene oxide at room temperature to form a HO-terminated PEO end-capped prepolymer which further reacted with a modified Teyssie catalyst and replaced its isopropoxy groups to form an active prepolymer-supported catalyst, PCL–PLA–$(OCH_2CH_2)_{2-4}$–OAl<. It has been proved that this prepolymer-supported catalyst is able to initiate CL polymerization in toluene at 90 °C. ABA triblock copolymers with different segment lengths have been synthesized. This new synthetic method provides a potential pathway from polylactide to form block copolymers with lactone.

Introduction

Over the past few years, an increasing level of interest has been focused on ABA triblock copolymers where A is a crystallizable polymer segment and B is an elastomeric polymer segment. Examples are the polyurethane and polyether–ester elastomers. However, use of a crystallizable polylactone as an A segment and an amorphous polylactide as a B segment to prepare ABA triblock copolymers has received little attention. Teyssie et al.[1,2] have made block copolymers based upon ϵ-caprolactone (CL) by using bimetallic μ-oxo alkoxide as catalyst.

We have been working on the ring-opening block copolymerization of CL and DL-lactide (LA) and have used Teyssie's catalyst to synthesize the corresponding AB diblock copolymers through a living sequential copolymerization process as described previously.[3,4] Owing to their microphase separation, morphology, and narrow molecular weight distribution, the AB diblock copolymers showed several advantages over the corresponding random copolymers, especially when used as biodegradable drug release delivery materials. The AB diblock copolymers provide various controllable periods of biodegradation and drug release as the length of the A and B segments varies. In this paper, we report the synthesis and some properties of the ABA triblock copolymers with poly(ϵ-caprolactone) (PCL) as A and polylactide (PLA) as B.

Experimental Section

Materials. The preparation and purification of CL and LA were performed according to our previous methods.[4] Ethylene oxide (EO) was a commercial reagent dried over CaH_2 at 4 °C for 48 h and purifed by distillation. Preparation of aluminum zinc μ-oxo isopropoxide and the replacement of its isopropoxy groups with 2-ehylhexanoate (EHa) were carried out according to Teyssie's method.[2]

Synthesis and Identification of HO-Terminated PEO-Capped Prepolymers. To prepare PCL–PLA–$(OCH_2CH_2)_{2-4}$–OH prepolymer, CL and LA were allowed to block copolymerize sequentially according to our previous method without the termination step in order to get a "living" intermediate. Onto this intermediate a required amount of EO cooled to 0 °C was added through a syringe and the contents were kept at 15 °C for 24 h. Before being reprecipitated in petroleum ether, the reaction mixture was washed with enough 0.5 N HCl and

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