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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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

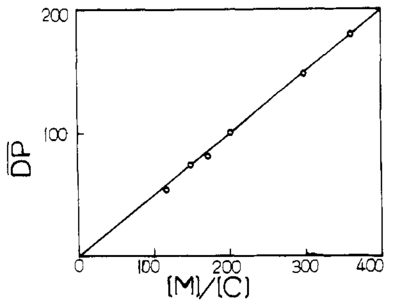


Figure 1. Polymerization of LA by Al/Zn μ-oxo alkoxide at 90 °C.

distilled water successively so that there was no trace of catalyst residue or possible homo-PEO left. Then the structure and composition of the prepolymers were determined by ^{1}H NMR spectroscopy.

Synthesis and Characterization of ABA Block Copolymers. Replacement of the isopropoxy groups of the modified catalyst by reacting with prepolymer was carried out similarly to Teyssie method.[2] After complete replacement, all the solvents were removed under reduced pressure and the residue was dissolved in fresh dried toluene. For block copolymerization a required amount of CL was added into this solution and the system was kept at 90 °C for 36 h with stirring. The $\bar{M}_n$ of the block copolymer was determined with a vapor pressure osmometer (VPO, QX-08) in $CHCl_3$ at 35 °C. The inherent viscosity was measured on a 0.2% (g/dL) solution of polymer in benzene at 30 °C. The molecular weight distribution was obtained in DMF solution by using a Waters C-150 GPC at 45 °C. ^{1}H NMR spectra were obtained with a WH 90 NMR spectrometer in $CDCl_3$ solution.

Results and Discussion

Living Character of LA Polymerization. The AB diblock copolymers of CL and LA have been synthesized successfully due to the perfect living character of CL polymerization by this anionic coordination catalyst, but we failed at first to prepare ABA triblock copolymers directly by adding more CL into this AB diblock intermediate (PCL–PLA-OAl<). It is imperative to know whether the growing PLA–OAl< intermediate has a "living" behavior or not. By adding the same amount of LA to a completely polymerized PLA system it was found that the polymerization continued further with a conversion of monomer of about 95% and the molecular weight of the ultimate polymer nearly doubled. Furthermore, an accurate linear relationship between the mean degree of polymerization ($\overline{DP}$) and the ratio of monomer/catalyst ([M]/[C]) was observed (Figure 1). From these results the conclusion may be drawn that the growing PLA–OAl< chain is "living" in the absence of any chain-terminating impurities. It is suggested that its inactivity in initiating CL copolymerization may be due to some steric hindrance in PLA. As a consequence one may hope to resume the living character of the growing chain by inserting a short linear unsubstituted segment between the PLA chain and the active site. Cyclic ethers such as EO can undergo ring-opening polymerization by Teyssie's catalyst,[5,6] but there is no indication of truly "living" character so we use EO to extend the PLA chain at first and then activate it as follows.

Synthesis of PLA–OCH$_2$CH$_2$–OH Prepolymers. To obtain the active prepolymer-supported catalyst, the following two-step procedure was proposed: Through step 1, the growing PLA chain was extended with ethylene oxide, and thus PEO end-capped PLA was formed as a prepolymer. An exploratory investigation has established that a low temperature should be applied for the capping reaction; otherwise some PEO homopolymer would result at higher temperature. When the reaction was carried out at 15 °C, the chemical structure of the reaction products was studied by ^{1}H NMR with the results shown in Figure 2. The chemical shift peaks at 3.6 and 5.1 ppm in curve 3 obviously showed that the prepolymer so obtained consisted of a $-(CH_2CH_2O)_x-$ as well as a $-(C(O)C(CH_3)HO)_n-$ segment as compared with that of PLA (at 5.1 ppm) and triethylene glycol (at 3.6 ppm). Furthermore, the value of x was found to be 2–4 for different samples. Thus the structure of prepolymer was confirmed to be

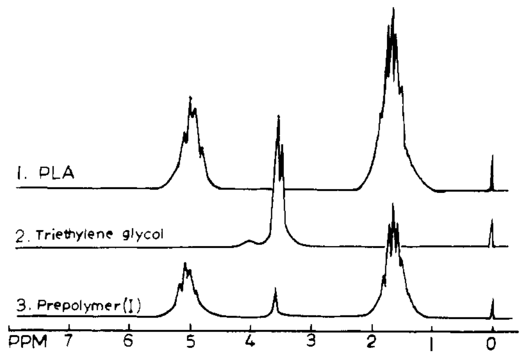
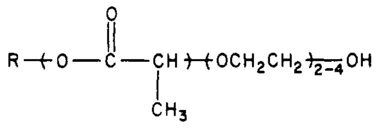
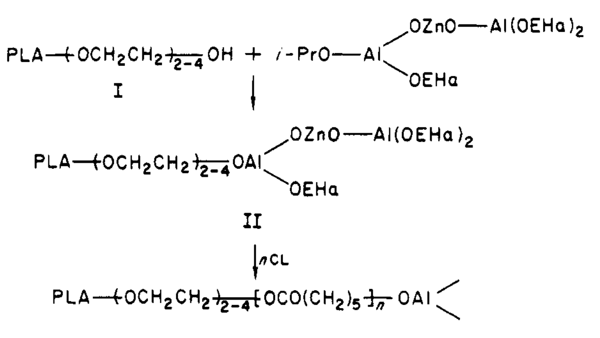


Figure 2. ^{1}H NMR spectra.



$$\mathrm{R\!-\!\!\left[O-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{CH}\right]\!\!-\!\!\left[OCH_2CH_2\right]_{2-4}OH}$$

Through step 2 the isopropoxy group of the modified bimetallic catalyst was replaced by reacting with the prepolymer (I), with the results that the prepolymer was reactivated to II as follows:



Three of the four isopropoxy groups of the Al/Zn μ-oxo isopropoxide catalyst were replaced by carboxylate groups (OEHa) after reacting with 2-ethylhexanoic acid to form the modified bimetallic catalyst, which was then added to the prepolymer (I) in a 1:1 ratio to form II, which was end-capped by bimetallic entities carrying only one potential insertion site for CL polymerization, the other three Al–O bonds being inactive. It is imperative to carry out the replacement reaction at temperatures as low as possible with short duration in order to avoid harmful side reactions such as esterification and degradation. Our results showed that the reaction would reach as high as 94% replacement without any degradation and structural change for 5 h at 110 °C. If the time of reaction was extended to 8 h the degree of replacement would increase 1% only but the inherent viscosity of the prepolymer nI) would drop by 10% (see Figure 3).

The results of CL polymerization initiated by the reactivated prepolymer-supported catalyst (II) are given in Table I. The CL was indeed block copolymerized onto the prepolymer as proved by the increase of the molecular weight of the ultimate polymers, but the polymerization rate and conversion were somewhat lower.

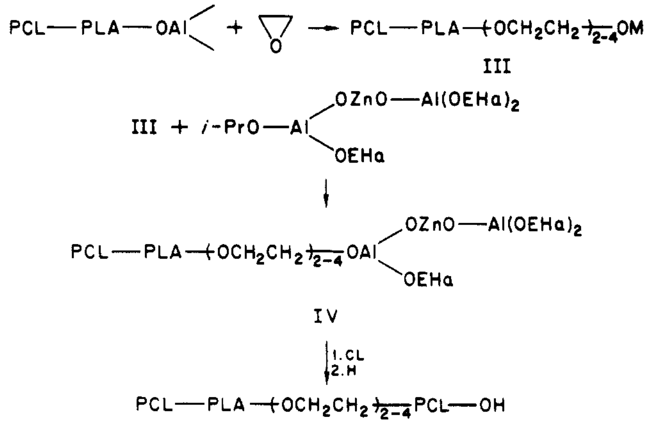
Table I
CL Polymerization Initiated by PLA-$(OCH_2CH_2)_{2-4}$-OAl in Toluene at 90 °C

	test no. 3-04	test no. 3-05
Before Block Copolymerization		
PLA prepolymer		
$\bar{M}_n \times 10^{-4}$	1.0	1.0
[η], dL/g	0.30	0.30
wt, g	3.0	3.0
CL		
wt, g	3.0	5.0
After Block Copolymerization		
CL		
$\bar{M}_n \times 10^{-4}$	1.4	1.6
[η], dL/g	0.38	0.42
wt, g	5.5	7.4
CL conversion, %	83	88

Table II
Preparation of ABA Triblock Copolymers

	test no. 4-04	test no. 4-05	test no. 4-06
Before Block Copolymerization			
prepolymer (III)			
$\bar{M}_n \times 10^{-4}$	3.3	3.2	3.8
[η], dL/g	0.50	0.51	0.56
[LA]/[CL]	23/77	30/70	40/60
wt, g	5.0	5.0	5.0
CL			
wt, g	3.0	3.0	3.0
After Block Copolymerization			
CL			
wt, g	6.8	7.1	6.9
CL conversion, %	43	50	40
$\bar{M}_n \times 10^{-4}$	3.9	3.8	4.3
[η], dL/g	0.58	0.56	0.63
[LA]/[CL]	20/80	25/75	35/65

Preparation and Characterization of ABA Block Copolymers. The preparation of ABA block copolymer (PCL–PLA–PCL) was based upon the reactivated AB diblock copolymer (PCL–PLA–OAl<) and carried out according to the following procedure:



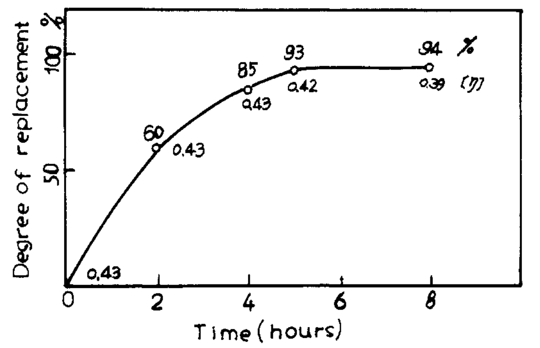


Figure 3. Change in degree of replacement and [η] of the prepolymer with the reaction time at 110 °C.

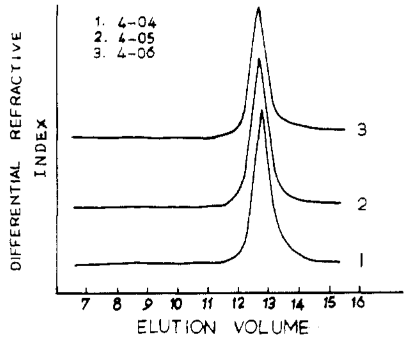


Figure 4. GPC curves of ABA block copolymer.

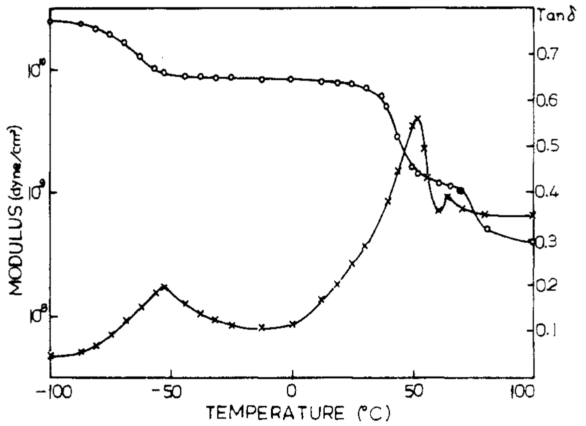


Figure 5. Modulus–temperature and tan δ–temperature curves of ABA block copolymer 4–05.

Copolymer samples with different compositions and segment lengths have been synthesized under the conditions summarized in Table II. From the molecular weight determinations, it is evident that ABA triblock copolymers are actually formed. From the GPC curves of these samples shown in Figure 4 the sharp single peak indicates the monodispersion of molecular weight and absence of any AB diblock copolymer or PCL homopolymer. The two-phase system of these triblock copolymers is evident from Figure 5, which shows two glass transition temperatures,

Table III
Physical and Mechanical Properties of ABA Block Copolymers As Compared with the AB Block Copolymers

polymer no.	[CL]/[LA]	$\bar{M}_n \times 10^{-4}$ (total)	PCL/PLA/PCL	mp, °C	tensile strength, kg/cm²	elongation at break, %	$\bar{M}_w/\bar{M}_n$
12-03	100/0	4.5		63	273	133	1.12
12-06	0/100	1.3			220	250	
12-05	88/12	4.0	35000/5000/0	65	229	100	1.09
12-04	72/28	3.9	29000/10000/0	64	220	380	1.14
4-04	80/20	3.9	24000/9000/6000	66	230		1.28
4-05	75/25	3.8	20000/11000/6000	65	240	600	1.20
4-06	65/35	4.3	21000/17000/5000	65	240	500	1.26

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i.e., one for the PLA at +53 °C and another for the PCL at −53 °C. Table III shows some physical and mechanical properties of ABA and AB block copolymers for comparison. It is interesting to find that the elongation at break of the ABA block copolymer is much higher than that of the AB block copolymer of similar CL/LA ratio with the highest value of 600% without sacrifice of tensile strength.

Conclusion

The "living" behavior of LA polymerization by Teyssie's catalyst has been proved, yet the growing PLA–OAl< intermediate could not initiate the block copolymerization of CL directly. Instead, HO-terminated PEO end-capped polylactide was prepared and reactivated by the modified catalyst as the real active prepolymer to initiate the CL block copolymerization. Thus, it provides a pathway to the synthesis of ABA triblock copolymers of lactone and lactide. The ABA block copolymers of CL and LA prepared by this synthetic method show some interesting properties over the AB diblock copolymers such as the high value of elongation at break. Such ABA block copolymers may be considered as a potential new biomedical material with biodegradable and tough membrane-forming properties for sustained release drug delivery system.

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Model Hydrocarbon Polymers: Rheological Properties of Linear Polyisoprenes and Hydrogenated Polyisoprenes

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ABSTRACT: Hydrogenated polyisoprenes (HPI) with nearly monodisperse molecular weight distributions were prepared by reacting H_2 with anionically prepared linear polyisoprenes (PI) in the presence of a Pd/$CaCO_3$ catalyst. Effects of chemical microstructure on rheological properties were explored with PI and HPI samples of various 3,4 contents (isopropenyl and isopropyl branch frequencies). At low 3,4 content the HPI's are good models for conventional equimolar ethylene–propylene copolymers. They have similar average composition, density ρ, glass transition temperature T_g, plateau modulus $G_N{}^\circ$, melt viscosity–intrinsic viscosity relationship, and temperature coefficient of viscosity. The temperature dependence within either the PI series or the HPI series was independent of chemical microstructure at a fixed interval of temperature above T_g. Variations in plateau modulus with microstructure for the two series confirmed, at least qualitatively, the expected roles of the characteristic ratio C_∞ and molecular weight (or volume) per backbone bond m_0 in determining $G_N{}^\circ$. The shift in modulus scale with temperature for HPI was inconsistent with the classical theory for entangled melts, $b_T \propto \rho T$, but in good agreement with a recent prediction: $b_T \propto \rho^d T C_\infty{}^{2d-3}$, $d \sim 2.0$–2.3.

Introduction

Copolymers of ethylene and propylene comprise an important class of commercial products. For approximately equimolar compositions and approximately random sequence distributions, the EP copolymers are substantially amorphous at and above room temperature.[2] With incorporation of small amounts of a diene monomer they form the basis of the EPDM elastomers. Even without addition of the third monomer, however, the structure of the commercial products can be complicated. Made with Ziegler–Natta catalysts, the copolymers have chemical microstructures and compositional distributions which vary with catalyst and conditions. Also, the distribution of molecular weights is typically broad ($\bar{M}_w/\bar{M}_n \gtrsim 2$), and long-chain branching may be present in some cases. With such materials it is very difficult to examine each of these factors in isolation.

On the other hand, a 1:1 ethylene–propylene microstructure can be obtained by the hydrogenation of polyisoprene (PI). Isoprene can be polymerized anionically to form chains of known and highly uniform architecture. Polymerization in nonpolar solvents gives predominantly 1,4 head-to-tail addition ($\sim$92%, the remainder being 3,4 addition). Hydrogenation should give a strictly alternating EP microstructure ($r_1 = r_2 = 0$), interrupted occasionally by isopropyl side groups ($\sim$16/1000 backbone carbons from the 3,4 content of the precursor PI). Such polymers are potentially useful as model materials to provide a better understanding of conventional EP copolymers.

The present paper reports the preparation, characterization, and viscoelastic properties of linear hydrogenated polyisoprene (HPI) and compares the results, extrapolated to 0% isopropyl groups in some cases, with those for substantially linear commercial EP copolymers of similar average microstructure. The behavior of HPI with long branches (hydrogenated samples of three-arm star polyisoprene) will be discussed in a later paper.

Experimental Section

A. Polymerization and Hydrogenation. Isoprene (Aldrich, Gold Label) was polymerized in cyclohexane at 50 °C with initiation by *sec*-butyllithium (Alfa Ventron). The "capped-bottle" procedure of Hsieh was used, as described earlier for butadiene polymerization[3] and modified slightly for isoprene.[4] The 3,4 content was increased in selected cases by adding small amounts of tetrahydrofuran to the polymerization solvent. After completion of polymerization ($\sim$4 h) the polyisopropenyl anions were ter-

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