Chain Propagation/Step Propagation Polymerization: Synthesis of Defect-Free Telechelomers

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Received October 9, 1991; Revised Manuscript Received March 30, 1992

ABSTRACT: Defect-free poly(oxyethylene-*block*-pivalolactone) telechelomers, represented by $(OE)_{34}$–$(PVL)_m$, where $m = 5$, 12, and 16, were synthesized by sequential anionic ring-opening polymerization of ethylene oxide and pivalolactone with hydroxypivalic acid. These telechelomers exhibited excellent microphase separation, allowing both the hard and soft segments to crystallize. Essentially complete microphase separation occurs for $m = 12$ and 16, and the sample with $m = 5$ showed some microphase mixing in the hard phase. Step polymerization of the $(OE)_{34}$–$(PVL)_m$ telechelomers was achieved by alanine-mediated melt esterification with titanium tetrabutoxide added in catalytic amounts, producing low molecular weight segmented copolymers, represented by $[(OE)_{34}$–$(PVL)_m]_p$. For example, melt esterification of the sample with $m = 16$ produced the pentamer, $[(OE)_{34}$–$(PVL)_{16}]_5$, with $M_n = 16\,000$.

Introduction

In general, multiphase thermoplastic elastomers contain a soft segment and an incompatible hard segment. The soft segments segregate to form an amorphous or semicrystalline soft phase, and the hard segments segregate to form a crystalline hard phase, which acts as a thermally labile physical cross-link. Differential scanning calorimetry (DSC) has proven useful in the study of microphase separation, demonstrating that phase separation usually is incomplete.[1-5] Factors known to enhance microphase separation include a narrow molecular weight distribution,[5-8] a sufficient hard-segment length to permit crystallization,[2,5,8] and a sufficient soft-segment length.[9] Wolfe[10-12] carried out extensive studies of structure/property relationships for poly(ester ether) thermoplastic elastomers and found that these materials ranged from impact-resistant plastics to elastomers, depending upon the nature and length of the polyester hard segment and the polyether soft-segment length.

Lenz,[13] Hall,[14] and Beaman[15] investigated pivalolactone polymerization and showed that a carboxylate anion is preferable in polymerizing pivalolactone smoothly. Carboxylate salts attack pivalolactone at the methylene carbon, opening the ring with acyl-oxygen cleavage (S_N2) to form a carboxylate propagating species. Carboxylate salts give rapid initiation of pivalolactone in tetrahydrofuran and acetonitrile with a linear relationship between polymer molecular weight and percent conversion. Thus, narrow molecular weight distribution polymers are obtained, and the molecular weight is controlled by the stoichiometric ratio of initiator to monomer.

High molecular weight poly(pivalolactone) is a highly crystalline polymer that exists in three crystalline modifications described by Osterhof,[16] and Borri,[17] and Prud'homme.[18]

Poly(pivalolactone) is an excellent choice for a thermoplastic elastomer hard segment due to its high tendency to crystallize, solvent resistance, and narrow molecular weight distribution. Caywood[19] modified a number of poly(alkyl acrylates) by saponifying some of the ester groups by reaction with tetrabutylammonium hydroxide and using the formed carboxylate salts to initiate polymerization of pivalolactone. Sharkey[20,21] synthesized block

and graft copolymers of pivalolactone with isoprene and with isobutylene.

Segmented poly(ester ethers) containing poly(pivalolactone) show promise as thermoplastic elastomers. Yamashita[22] synthesized poly(pivalolactone-*block*-oxytetramethylene-*block*-pivalolactone) triblock copolymers by converting the potassium alkoxide anions of poly(oxytetramethylene) glycol to potassium carboxylate anions with succinic anhydride, followed by pivalolactone polymerization. Inoue and co-workers[23] used aluminum porphyrin catalysts to synthesize low molecular weight versions of poly(β-propiolactone-*block*-oxyethylene) copolymers having monodisperse segments by sequential addition of β-propiolactone and ethylene oxide; however, this method is only useful for the synthesis of low molecular weight diblock copolymers.

Our previous efforts[24-26] focused on the synthesis of a monodisperse telechelomer (a telechelomer is a self-reacting monomer capable of step polymerization only) and its step polymerization to segmented copolymer. This approach, termed chain propagation/step propagation polymerization, utilizes living anionic chain propagation to synthesize the narrow molecular weight distribution segments of the telechelomer sequentially. Then step polymerization of the telechelomer results in a segmented copolymer, and although the overall molecular weight distribution will be large—$M_w/M_n > 2$—within each segmented copolymer the segments should maintain their narrow molecular weight distributions.

Our[8] analysis of the microphase separation in the telechelomers revealed that considerable microphase mixing occurs, and this microphase mixing can be attributed in part to the irregularity of the copolymer chain due to the initiator fragment and the succinate link. Therefore, a defect-free telechelomer should produce a segmented copolymer and superior microphase separation. The major goal of this work is the synthesis and characterization of a defect-free poly(oxyethylene-*block*-pivalolactone) telechelomer. After the telechelomers are synthesized, their step polymerization to segmented copolymers is addressed, including model studies utilizing homopoly(pivalolactone) telechelomers.
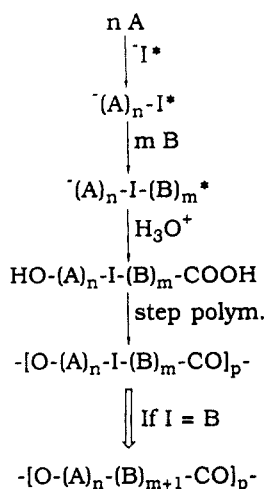
Results and Discussion

The structure of the defect-free telechelomer, represented by $(OE)_n$–$(PVL)_m$, is presented in Figure 1.

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$$H-(OCH_2CH_2)_n-(OCH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CO)_m-OH$$
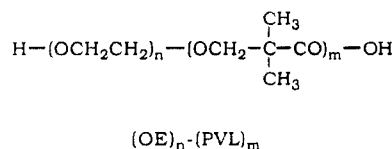
$$(OE)_n-(PVL)_m$$

Figure 1. Structure of the defect-free telechelomer, represented by $(OE)_n-(PVL)_m$.

**Figure 2.** Chain propagation/step propagation polymerization strategy for initiation by a difunctional initiator.

Initiation by hydroxypivalic acid results in defect-free telechelomer, $(OE)_n-(PVL)_m$, since (1) the initiator fragment is identical to the poly(pivalolactone) segment repeat unit and (2) both the hydroxyl and carboxylic acid functionalities are already present. This chain propagation/step propagation polymerization strategy for initiation by a difunctional initiator (Figure 2) is a novel utilization of a difunctional initiator.

Since hydroxy acids are difunctional initiators, it may be possible to achieve the simultaneous polymerization of pivalolactone and ethylene oxide, referred to as dual anionic polymerization, provided that selectivity is achieved on the basis of nucleophilicity. Alternatively, sequential addition of ethylene oxie and pivalolactone should yield the desired telechelomer. First polymerizing pivalolactone is unlikely to succeed because poly(pivalolactone) is insoluble in tetrahydrofuran and decomposes when reacted with a potassium mirror.

Formation of Dianionic Initiator. Hydroxypivalic acid is a sublimable white solid that is easily dried and handled using high vacuum line techniques. To initiate polymerization of ethylene oxide, hydroxypivalic acid must first be converted to the dipotassium salt by reaction with a potassium mirror in tetrahydrofuran. The acidic proton reacts very quickly to form the hydroxy carboxylate salt, which precipitates. The formation of the dipotassium salt requires several days and periodic degassing.

To verify that the dipotassium salt is formed, the reaction of hydroxypivalic acid in tetrahydrofuran with an excess of potassium mirror under vacuum was terminated after varying times, with degassing every 24 h. Back-titrating the products with hydrochloric acid, using phenolphthalein indicator, indicated that after 72 h essentially complete formation of the dianion occurred.

To improve the solubility of the dianion and the reactivity of hydroxypivalic acid, 18-crown-6 was added in a 1:1 molar ratio. The addition of 18-crown-6 in tetrahydrofuran to a potassium mirror under vacuum formed a dark blue solution. Subsequent addition of hydroxypivalic acid in tetrahydrofuran resulted in a violent initial reaction with the immediate loss of the blue color. The
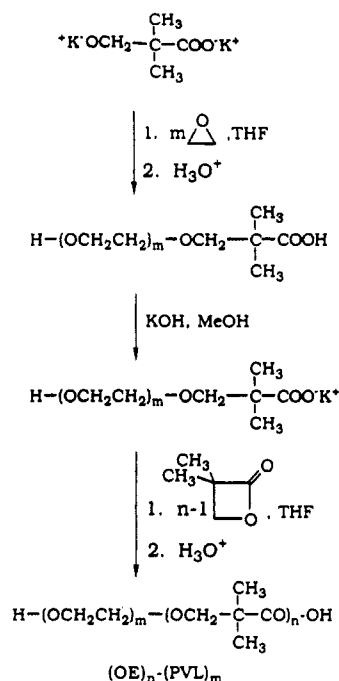
Figure 3. Sequential addition polymerization reaction scheme used to produce defect-free telechelomers $(OE)_n-(PVL)_m$.

formation of the dianion was shortened to 2 days, after which the blue coloration began to re-form; however, substantial precipitation still occurred. Increasing the ratio of 18-crown-6 to hydroxypivalic acid to a 2:1 molar ratio resulted in the formation of a viscous gel due to the formation of aggregates. Attempts to prevent precipitation of the dianion by using larger amounts of tetrahydrofuran and by using N,N,N',N'-tetramethylethylenediamine as the solvent were not successful.

Dual Anionic Polymerization. The dual anionic polymerization approach is interesting; however, there are many undesired reactions that can occur. In practice, only a limited amount of ethylene oxide is incorporated into the product, indicating that the alkoxide anion is reacting with pivalolactone in such a way as to prevent reaction with ethylene oxide. One likely possibility is attack at the methylene carbon of the lactone by the alkoxide anion, thereby converting the alkoxide anion into a carboxlate anion and making further reaction with ethylene oxide impossible.

Sequential Addition Polymerization. Figure 3 presents the sequential addition polymerization reaction scheme used to produce defect-free telechelomers $(OE)_n-$ $(PVL)_m$. Ethylene oxide is vacuum transferred into a suspension of the dipotassium salt of hydroxypivalic acid in tetrahydrofuran, and the reaction mixture is stirred at 5 °C for several days. The product, α-hydro-ω-((hydroxypivalyl)oxy)poly(oxyethylene), $(OE)_n-PVL$, is isolated by evaporation of the tetrahydrofuran, dissolving the residue in water, acidifying with dilute hydrochloric acid, extracting with methylene chloride, and precipitating the product in diethyl ether. Deprotonation of the acid proton produces the potassium carboxylate, which is used to polymerize pivalolactone in tetrahydrofuran under argon. Workup, which includes acidifying, produces the defect-free telechelomer, $(OE)_n-(PVL)_m$.

Control of the Soft-Segment Length. The proton NMR of $(OE)_{34}-PVL$ (Figure 4) is very simple, having three large singlets at 3.7, 4.6, and 1.2 ppm, resulting from the poly(oxyethylene) methylene protons (a), the pivalic acid end-group methylene protons (b), and the pivalic acid methyl protons (c), respectively. The poly(oxyethylene)
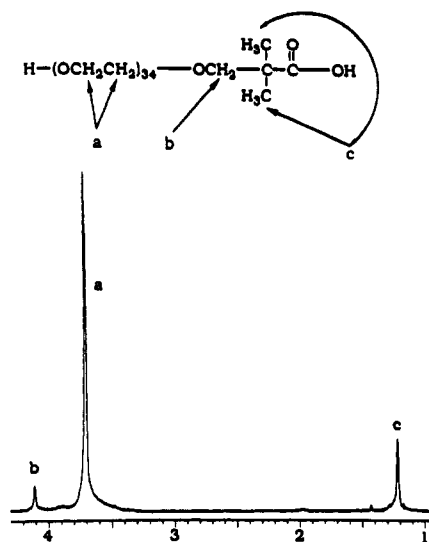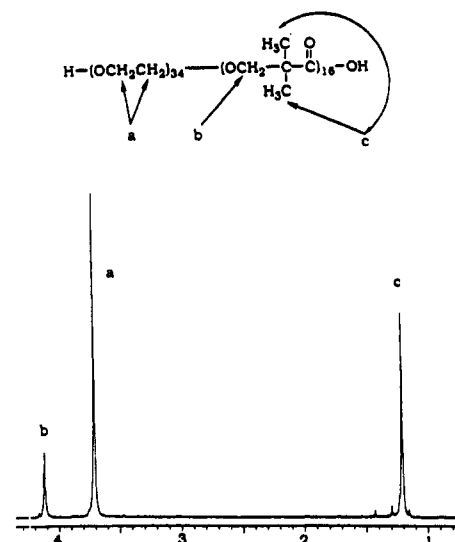
**Figure 4.** 200-MHz proton NMR of (OE)$_{34}$-PVL in Silanor-C.

Table I
Results of Polymerization of Ethylene Oxide (OE) under Varying Conditions

init, mol	OE, mol	M_n calc	M_n obs	M_w/M_n	% yield	conditions
0.010	0.20	1000	3780	1.03	82	25 mL of THF, Ar, 5 °C for 1 day, room temp for 2 days
0.010	0.20	1000	1660	1.13	88	25 mL of THF, Ar, 5 °C for 3 days
0.010	0.20	1000	1610	1.10	85	100 mL of THF, Ar, 5 °C for 3 days
0.010	0.20	1000	1570	1.10	60	25 mL of THF, Ar, 5 °C for 2 days
0.005	0.10	1000	1590	1.05	84	50 mL of THF, Ar, 0.005 mol of 18-crown-6, 5 °C for 3 days
0.005	0.10	1000	6430		65	50 mL of TMEDA, Ar, 5 °C for 4 days
0.012	0.22	890	1050	1.30	83	100 mL of THF, vacuum, 5 °C for 3 days

segment length (n) is easily determined by proton NMR integration and verified by titration of the acid end group and SEC.

The polymerization of ethylene oxide to form (OE)$_n$–PVL was conducted at various conditions, and the percent yield, number-average molecular weight determined by titration, and the SEC molecular weight distribution of each product, (OE)$_n$–PVL, are listed in Table I. Due to the insolubility in THF of the dipotassium salt of hydroxypivalic acid, the rate of initiation is expected to be slower than that of similar homogeneous initiators, resulting in broader molecular weight distributions. The products in Table I result from precipitations from diethyl ether, which favors the higher molecular weight material, and all have molecular weights higher than that predicted by the stoichiometric ratio (M_n obs). However, some molecular weight control is obtained by varying the conditions. The addition of 18-crown-6 gave the best results, producing (OE)$_n$–PVL with M_n = 1590 and M_w/M_n = 1.05 in good yield, 84%.

Control of the Hard-Segment Length. Once (OE)$_n$–PVL is formed, the polymerization of pivalolactone to build the hard segment of the telechelomer is straightforward. The acid proton is easily removed with potassium hydroxide in methanol to form the carboxylate salt, which is used to polymerize pivalolactone in tetrahydrofuran

Figure 5. 200-MHz proton NMR of (OE)$_{34}$-(PVL)$_{16}$ in Silanor-C.
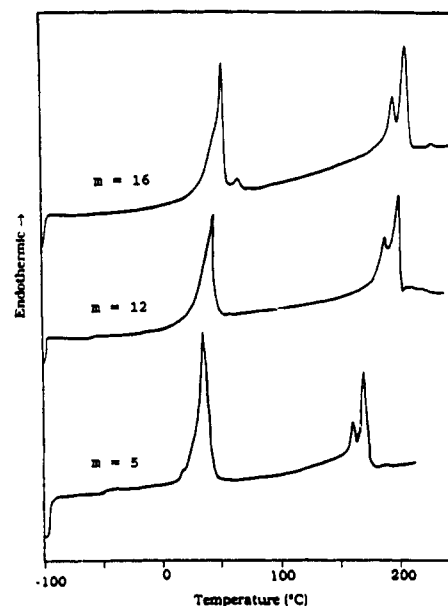
Figure 6. DSC curves of the (OE)$_n$-(PVL)$_m$ defect-free telechelomers.

under argon. The poly(pivalolactone) hard-segment length is controlled by the ratio of carboxylate to pivalolactone, and (OE)$_n$-(PVL)$_m$ telechelomers were synthesized with a constant poly(oxyethylene) soft-segment length, n = 34, and varying poly(pivalolactone) hard-segment length, m = 5, 12, and 16.

The proton NMR of (OE)$_{34}$-(PVL)$_{16}$ (Figure 5) is identical to the proton NMR of (OE)$_{34}$-PVL (Figure 4), except for the heights and integrations of the poly(pivalolactone) singlets at 4.6 (b) and 1.2 ppm (c). The poly(pivalolactone) segment length (m) is easily determined by proton NMR integration and verified by SEC analysis.

Analysis of Microphase Separation. Figure 6 presents the DSC curves of the (OE)$_{34}$-(PVL)$_m$ defect-free telechelomers. Each sample shows a weak glass transition around –50 °C and two melting endotherms, a high-temperature endotherm for the hard phase and a lower temperature endotherm for the soft phase. Although the samples were quenched from 50 °C, the soft phase of these telechelomers exhibits crystallization, indicating that a high degree of microphase separation exists.

Block copolymerization decreases the observed melting point (T_m^{obs}) of a crystalline segment, and T_m^{obs} in a block

Table II
Results of DSC Analysis of Microphase Separation of
$(OE)_{34}-(PVL)_m$ Defect-Free Telechelomers

		hard phase			soft phase		
m	W_H	T_m^{obs}, °C	T_m^H, °C	ρ^H	T_g^{obs}, °C	T_m^{obs}, °C	ρ^S
5	0.25	142	174	0.73	-50	38	1.00
12	0.45	199	201	0.91	-53	42	1.04
16	0.52	207	205	1.09	-52	50	1.13

copolymer can be calculated by eq 1:[27]

$$1/T_m^{obs} = 1/T_m^H - (R/\Delta H) \ln \rho^H \tag{1}$$

where T_m^H represents the melting point of the hard-segment crystalline homopolymer, ΔH represents the heat of fusion per mole of repeat unit of the crystalline hard segment, and ρ^H represents the hard-segment crystalline sequence propagation probability. This equation has been used to calculate T_m^{obs} of the poly(hexamethylene sebacate) segment due to block copolymerization with a poly-(dimethylsiloxane) segment.[28,29] In a previous study, we[8] used eq 1 to calculate the upper and lower limits of the poly(pivalolactone) hard segment in their poly(oxyethylene-*block*-pivalolactone) telechelomers. The upper limit, with $\rho^H = 1$, equals T_m^H, and the lower limit was calculated using $\rho^H = W_H$. The lower limit is the T_m^{obs} expected if no microphase separation occurs, and the upper limit is the T_m^{obs} expected for complete microphase separation. From this range, we were able to qualitatively determine the hard-phase composition.

An interesting application of eq 1 is obtained by solving for ρ^H:

$$\rho^H = \exp[(1/T_m^H - 1/T_m^{obs})\Delta H/R] \tag{2}$$

From eq 2, ρ^H can be calculated, and ρ^H should be a very good approximation for the hard-phase purity. The calculated values of ρ^H for the $(OE)_{34}-(PVL)_m$ defect-free telechelomers (Table II) were calculated using a value of 3550 cal/mol of repeat unit[30] for ΔH and the peak melting of homopoly(pivalolactone) with the corresponding molecular weight (Table II) for T_m^H. The values of ρ^H show that the samples for $m = 12$ and 16 have very high hard-segment purity. The 0.73 value of ρ^H for $(OE)_{34}-(PVL)_5$ indicates that hard-segment microphase mixing occurs in this sample.

Because the soft phase of the $(OE)_{34}-(PVL)_m$ telechelomers also exhibits crystallization, eq 2 can also be applied to the soft phase of these materials:

$$\rho^S = \exp[(1/T_m^S - 1/T_m^{obs})\Delta H/R] \tag{3}$$

where T_m^S represents the melting point of the soft-segment crystalline homopolymer, ΔH represents the heat of fusion per mole of repeat unit of the crystalline soft segment, and ρ^S represents the soft-segment crystalline sequence propagation probability. In this case, ρ^S should be a good approximation for the soft-segment purity. The values of ρ^S for the $(OE)_{34}-(PVL)_m$ telechelomers, listed in Table II, were calculated from eq 3 using a value of 1980 cal/mol of repeat unit for ΔH^{31} and a value of 37.4 °C for T_m^S.[32] The values of ρ^S for the $(OE)_{34}-(PVL)_m$ telechelomers are all greater than unity, indicating essentially complete soft-phase microphase separation occurs for the soft segments capable of crystallizing.

Step Polymerization of Telechelomers. The $(OE)_{34}-(PVL)_m$ telechelomers exhibit excellent microphase separation; however, they do not have thermoplastic characteristics due to their low molecular weights and lack of more than one hard segment per polymer molecule. The
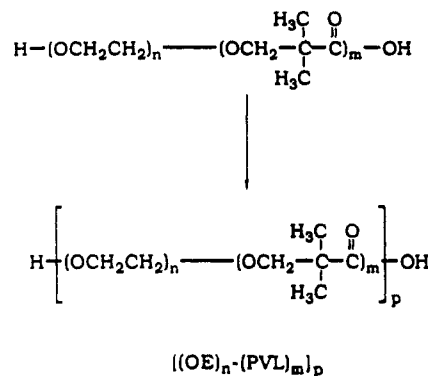

$[(OE)_n-(PVL)_m]_p$

Figure 7. Step polymerization of the telechelomers to segmented copolymers, represented by $[(OE)_n-(PVL)_m]_p$.
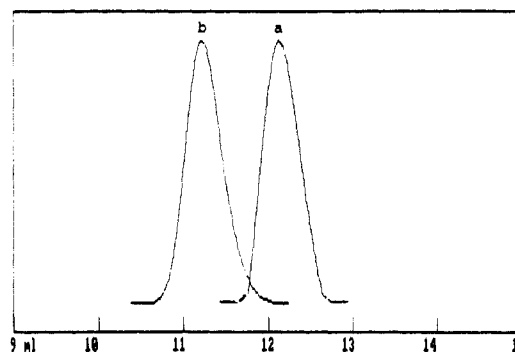

Figure 8. SEC trace of $(OE)_{34}-(PVL)_{16}$ with $M_n = 3200$ (a) and $[(OE)_{34}-(PVL)_{16}]_5$ with $M_n = 16\,000$ (b).

step polymerization of the telechelomers to $[(OE)_n-(PVL)_m]_p$ segmented copolymers (Figure 7) represents an important aspect in the synthesis of poly(oxyethylene-*block*-pivalolactone) thermoplastic elastomers.

The *gem*-dimethyls that give the poly(pivalolactone) hard segment excellent solvent resistance also make the sterically hindered carboxylic acid very difficult to step polymerize. We[26] were unable to polymerize pivalolactone based telechelomers using a number of standard solution polyesterification reagents, including 1-methyl-2-bromopyridinium chloride/tri-*n*-butylamine, *N,N'*-bis-(2-oxo-3-oxoazolidinyl)phosphorodiamidic chloride/triethylamine, triphenyl phosphite, hexachlorocyclotriphosphatriazene, trifluoroacetic acid/methylene chloride, and methanesulfonic acid/phosphorus pentoxide. Several attempts at melt esterifications also were unsuccessful, including heating without catalyst and heating with antimony trioxide or titanium tetrabutoxide.

We[26,32] have previously shown that alanine-mediated polymerization, the first example of amino acid or zwitterionic catalyzed polyesterification, is successful in step polymerizing similar telechelomers. Melt esterifications of the $(OE)_n-(PVL)_m$ telechelomers using 1 mol % of tetrabutoxide and DL-alanine, at temperatures between 180 to 250 °C, produced low molecular weight segmented copolymers, represented by $[(OE)_n-(PVL)_m]_p$. For example, a segmented copolymer with $M_n = 16\,000$ by SEC (Figure 8) was produced from $(OE)_{34}-(PVL)_{16}$.

The methyl region of the proton NMR of $[(OE)_{34}-(PVL)_{16}]_5$ product (Figure 9) contains several small peaks, evidence that this product contains a significant amount of partially decomposed poly(pivalolactone) segments. The DSC scan of $[(OE)_{34}-(PVL)_{16}]_5$ is presented in Figure 10. The segmented copolymer produced from alanine-mediated melt esterification shows, relative to that of the original telechelomer in Figure 6, a slight decrease in the hard-phase melting point with a large decrease in the heat of fusion, resulting in a much smaller signal. The melting
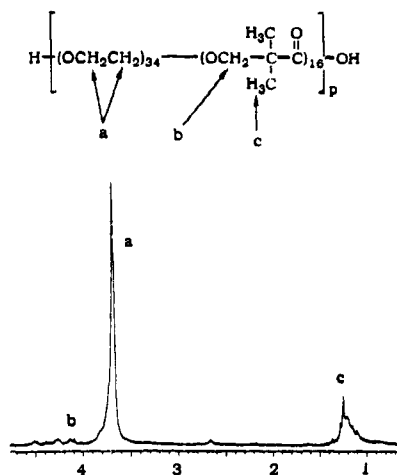
Figure 9. 200-MHz proton NMR of [(OE)$_{34}$-(PVL)$_{16}$]$_5$ in Silanor-C.
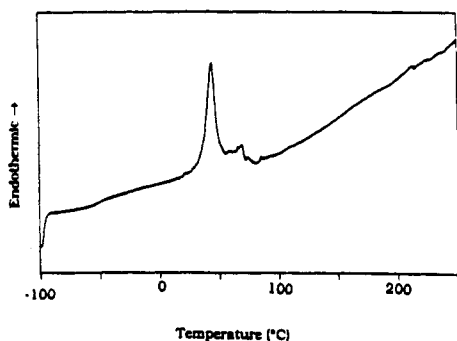

Figure 10. DSC scan of [(OE)$_{34}$-(PVL)$_{16}$]$_5$.

point of the soft phase also decreased slightly, relative to that of the telechelomer.

Experimental Section

Instrumentation. NMR data were obtained on a Varian XL-200, and all chemical shifts are reported in units of ppm downfield from tetramethylsilane internal standard. Silanor-C or chloroform-*d* was used to make dilute solutions of the samples (about 0.003 g/mL), and to samples containing poly(pivalolactone) trifluoroacetic acid was added until a clear solution formed. All NMR sample solutions were filtered through glass wool prior to analysis.

All DSC and TGA data were obtained on a Perkin-Elmer 7 Series thermal analysis system equipped with a TAC7 microcontroller and a PE7500 computer equipped with Perkin-Elmer TαS7 software. Both instruments were calibrated by a two-point method. The TGA was calibrated with nickel and perkalloy Curie point standards with dry nitrogen purge gas (50 mL/min). The DSC was calibrated with cyclohexane and indium with dry helium purge gas (25 mL/min) for subambient operations and with indium and tin with dry nitrogen purge gas (25 mL/min) for operation above 50 °C. Reported melting point temperatures represent the peak of the melting endotherm, and reported glass transitions represent the temperature of the midpoint of the glass transition. All reported DSC results are the average of 2–8 scans, at a rate of 20 °C/min, of each sample. In each case reported, the variance was less than 5%.

Polymerizations of ethylene oxide were maintained at 5 ± 1 °C using a Precision Scientific Precision Lo-Temptrol low-temperature bath containing Sears antifreeze pumped through a copper coil immersed in an insulated 2-propanol bath.

Vacuum line experiments were performed on a high-vacuum line (10^{-6} mmHg) constructed by the University of Florida Glass Shop using two Sargent Welch Model D-1400 vacuum pumps, an Ace Glass mercury diffusion pump, two Ace Glass cooling traps, an Ace Glass mercury manometer, Ace Glass high-vacuum stopcocks, and an argon inlet with a mineral oil bubbler. Argon was passed through a concentrated sulfuric acid bubbler, a sodium hydroxide column, and a calcium sulfate column.

All SEC data were obtained on a Waters 6000A liquid chromatograph, equipped with a concentration-sensitive differential refractometer detector. All data were collected and analyzed on a Zenith Model 48 personal computer equipped with a Metra-Byte multi-IO card and an Epson dot matrix printer. Sample solutions of 0.005 g/mL in methylene chloride containing 1% by volume trifluoroacetic acid were filtered through 0.45-μm filters and analyzed using TSK 5000- and 3000-Å columns. For analysis of poly(oxyethylene) polymers, the instrument was calibrated with narrow molecular weight distribution poly(oxyethylene) glycols. For analysis of poly(oxyethylene-*block*-pivalolactone) polymers, the instrument was calibrated with narrow molecular weight distribution polystyrene standards by universal calibration.

Chemicals. All solvents used were reagent or HPLC grade. Tetrahydrofuran was refluxed over potassium–sodium alloy (2:1) overnight, distilled onto fresh potassium–sodium alloy (2:1), degassed, and stored under reduced pressure for vacuum distillation into the reaction flask. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine was degassed, vacuum distilled onto calcium hydride and stirred overnight, vacuum distilled onto a potassium mirror, and vacuum distilled into the reaction vessel. Anhydrous diethyl ether was taken from freshly opened containers only. All solvents used in SEC and viscometry analysis were filtered through 0.5-μm filters prior to use.

Pivalolactone, donated in pure form by Dr. H. K. Hall, was dried over calcium hydride at reduced pressure overnight and then distilled at reduced pressure just before use.

Ethylene oxide (Aldrich) was cooled to –30 °C, opened in the hood, and poured onto calcium hydride, degassed, vacuum distilled onto fresh calcium hydride, and stored in a sealed flask under vacuum at –30 °C.

Potassium metal (Aldrich) was cut in hexane, placed into a sidearm of the reaction flask evacuated to high vacuum, and distilled directly into the reaction flask.

Hydroxypivalic acid (American Tokyo Kasie) was dried in a vacuum desiccator containing calcium sulfate for several days, transferred to an ampule containing a breakseal, dried by dynamic high vacuum for several days, and flame sealed in the ampule.

Gold Label 18-crown-6 (Aldrich) was used as received from unopened 1-g containers, and all transfers were done in a glovebag under argon. Reagent grade 18-crown-6 (Aldrich) was purified by precipitating its complex with nitromethane with high vacuum. To a dried solution of 18-crown-6 in diethyl ether, nitromethane was added, forming a white precipitate that was filtered, placed into a vacuum desiccator under dynamic vacuum for several days, placed into a round-bottom flask, kept under dynamic high vacuum (10^{-6} mmHg) for several days, and stored under argon. Subsequent transfers were conducted in a glovebag under argon.

DL-Alanine (Aldrich) was reprecipitated from water, vacuum sublimed, and stored in a desiccator containing calcium sulfate.

Titanium tetrabutoxide (Aldrich) was vacuum distilled and stored under argon.

Standarized potassium hydroxide solutions in methanol were made from fresh containers of potassium hydroxide and standardized with dried potassium biphthalate with phenolphthalein indicator.

General Procedure for Dual Anionic Polymerization. In a typical experiment using vacuum line and breakseal techniques, 5 mL (100 mmol) of ethylene oxide was vacuum transferred into a 250-mL reaction vessel, at dry ice/2-propanol temperature, containing a magnetic stirbar and having attached ampules containing (1) 0.04 mol (2.5 mL) of pivalolactone and (2) 0.005 mol of the dipotassium salt of hydroxypivalic acid suspended in 25 mL of tetrahydrofuran. The contents of the ampules were allowed to mix in the reaction vessel, magnetic stirring was begun, and the reaction temperature was maintained at 5 °C by a constant-temperature bath. The reaction was given a static argon atmosphere with a valve to release any sudden pressure. After 2 days, the reaction vessel was evacuated to remove tetrahydrofuran and any unreacted pivalolactone and ethylene oxide. The product was isolated by hydrolysis, extraction with methylene chloride, and precipitation in diethyl ether.

General Procedure for Sequential Addition Polymerization. In a typical experiment using vacuum line and break-

seal techniques, 10 mL (200 mmol) of ethylene oxide was vacuum transferred into a 250-mL reaction vessel containing a magnetic stirbar and having an attached ampule containing 10 mmol of the potassium salt of hydroxypivalic acid and 5 mmol of 18-crown-6 in 25 mL of tetrahydrofuran. The contents of the ampule was added to the reaction vessel, magnetic stirring was begun, and the reaction temperature was maintained at 5 °C by a constant-temperature bath. The reaction was given a static argon atmosphere open to a mineral oil bubbler to release any sudden pressure. After 3 days, the reaction vessel was evacuated to remove tetrahydrofuran and any unreacted ethylene oxide. The reaction vessel was removed from the vacuum line, and the solid residue was dissolved in water, acidified with dilute hydrochloric acid, and extracted with four 25-mL portions of methylene chloride. The methylene chloride extracts were combined, dried over magnesium sulfate, and added to 500 g of cold diethyl ether, precipitating $(OE)_n$–PVL.

One gram of $(OE)_n$–PVL was dissolved in methanol and titrated with 0.01 N potassium hydroxide in methanol with phenolphthalein as an indicator. The resulting solution was rotovapped, and the residue was dried with a drying pistol. Under argon, the dried residue was dissolved in 25 mL of dry tetrahydrofuran, and pivalolactone was added in a molar ratio based upon the amount of base needed in the titration. After 1 day, the reaction was evacuated to remove tetrahydrofuran and unreacted pivalolactone. Methylene chloride was added to dissolve as much of the residue as possible. The resulting solution was shaken with 3 N hydrochloric acid and separated. The $(OE)_n$–$(PVL)_m$ telechelomer was isolated by precipitation in diethyl ether or by evaporation of the methylene chloride solvent.

General Procedure for Alanine-Mediated Step Polymerization. The telechelomer and an equal molar amount of DL-alanine were placed in a three-necked polymerization reactor fitted with a mechanical stirrer, argon/vacuum inlet, and syringe inlet with stopcock. The flask was evacuated and maintained at a slightly elevated temperature to dry the contents. Then the flask was given an argon atmosphere and heated to 200 °C by a salt bath. After the telechelomer melted, mechanical stirring was begun, and the reaction mixture was stirred for 1 h. The flask was evacuated for 0.5 h at 200 °C to remove any unreacted DL-alanine. Titanium tetrabutoxide (1 mol %) was added by syringe to the reaction, and the reaction temperature was slowly increased to 25 °C over a period of 1 h. Then vacuum was applied at 250 °C for 0.5 h. The reaction was allowed to cool, and the resulting product was dissolved in methylene chloride—or dissolved in boiling N,N-dimethylformamide and cooled—and added to a large volume of diethyl ether. The product was isolated by filtration and dried in a vacuum desiccator.

Conclusions

Defect-free telechelomers, $(OE)_n$–$(PVL)_m$, are produced by initiation with the dipotassium salt of hydroxypivalic acid in sequential anionic chain propagation polymerization of ethylene oxide and pivalolactone. The DSC analysis of microphase separation of $(OE)_{34}$–$(PVL)_m$ defect-free telechelomers indicates that these materials exhibit excellent microphase separation, allowing both the hard and soft segments to crystallize. Essentially complete microphase separation occurs for $m = 12$ and 16. In the case for $m = 5$, the hard segment is the minor component, and microphase separation is not complete.

Alanine-mediated melt esterification of the $(OE)_n$–$(PVL)_m$ defect-free telechelomers with titanium tetra-butoxide was successful in producing low molecular weight polymers containing a substantial amount of decomposed poly(pivalolactone) segment.

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