Macromolecules **1992,** *25,* 5591–5596

Quantitative Determination of Microphase Separation: Effect of Hard-Segment Length

K. B. Wagener* and J. C. Matayabas, Jr.[†]

Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida 32611

Received October 7, 1991; Revised Manuscript Received March 30, 1992

ABSTRACT: Microphase separation in a series of triblock poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers, represented by $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$, where m = 5, 7, 9, 12, 16, and 24, was investigated by differential scanning calorimetry. With the poly(oxyethylene) soft-segment length maintained at 24 repeat units, a very distinct transition from phase mixed to essentially complete microphase separation occurs when the poly(pivalolactone) hard-segment length, m, is increased from 9 to 12.

Introduction

Segmented poly(ester ethers) containing poly(pivalolactone) show promise as thermoplastic elastomers. Yamashita[1] synthesized poly(pivalolactone-*block*-oxytetramethylene-*block*-pivalolactone) triblock copolymers by converting the alkoxide anions of a poly(oxytetramethylene) glycol dipotassium salt to carboxylate anions with succinic anhydride, followed by pivalolactone polymerization. Inoue and co-workers[2] 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.

Previously, we[3–5] 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, utilized 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.

In a previous study aimed at gaining a better understanding of microphase separation, we[6] utilized DSC to quantitatively investigate the microphase separation behavior in a series of poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers with the poly(oxyethylene) soft-segment length varying from 4 to 24 repeat units. The B–A–B triblock structure with two poly(pivalolactone) hard segments was chosen because it is the simplest segmented copolymer that can form a two-phase physical network in which the hard-phase domains are covalently linked by the soft segment. This study showed that a minimum of 14 oxyethylene repeat units are required to achieve some degree of microphase separation and that essentially complete microphase separation is achieved when the poly(oxyethylene) soft-segment length is increased to 24 repeat units, with a poly(pivalolactone) hard-segment length of 12 repeat units.

In the present study, the effect of the hard-segment length on microphase separation is examined. The goal is to determine the minimum length of hard segment necessary to achieve a high degree of microphase separation with a constant poly(oxyethylene) soft-segment length of 24 repeat units.

Results and Discussion

Synthesis. A series of poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers, represented by $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$, were synthesized according to the scheme presented in Figure 1. The poly(pivalolactone) hard-segment length (m) varies from 5 to 24 repeat units, and the poly(oxyethylene) soft-segment length was maintained constant at 24 repeat units by beginning with narrow molecular weight distribution poly(oxyethylene) glycol.

The hydroxyl end groups of the poly(oxyethylene) glycol were converted to carboxylic acid end groups in refluxing toluene with excess succinic anhydride, producing α-(hydroxysuccinyl)-ω-((hydroxysuccinyl)oxy)poly(oxyethylene) (HOOC-$(OE)_n$-COOH).

The molecular weight of the poly(oxyethylene) macromolecular initiator, HOOC-$(OE)_n$-COOH, was determined by titration with 0.10 N potassium hydroxide in methanol, giving a number-average molecular weight (M_n) of 1260. This value agreed well with the proton NMR integration of the poly(oxyethylene) methylene singlet and the succinate methylene singlet. The existence of a narrow molecular weight distribution—$M_w/M_n < 1.05$—was confirmed by size-exclusion chromatography.

HOOC-$(OE)_n$-COOH was converted to the dicarboxylate salt KOOC-$(OE)_n$-COOK by reaction with potassium metal in dry tetrahydrofuran under vacuum. Tetrahydrofuran solutions of KOOC-$(OE)_n$-COOK were used to polymerize pivalolactone under dry argon to produce the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers. The length of the poly(pivalolactone) hard-segment block (m) is easily controlled by the stoichiometric ratio of initiator to monomer due to the anionic ring-opening polymerization mechanism, and $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ with m = 5, 7, 9, 12, 16, and 24 were synthesized.

Characterization. The proton NMR of $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ in Silanor-C with 1% trifluoroacetic acid is presented in Figure 2. The average value of m is easily determined by detecting and integrating the proton NMR signals of the 1.23 ppm methyl singlet (a) of the main-chain poly(pivalolactone) segment and the 1.31 ppm methyl singlet of the terminal pivalolactone unit. Additional information regarding the amount of incorporated pivalolactone is obtained from comparison of the poly(oxyethylene) methylene singlet (c) at 3.72 ppm, the poly-

---

[†] Current address: Research Laboratories, Eastman Chemical Co., P.O. Box 1972, Kingsport, TN 37662-5150.

0024-9297/92/2225-5591$03.00/0

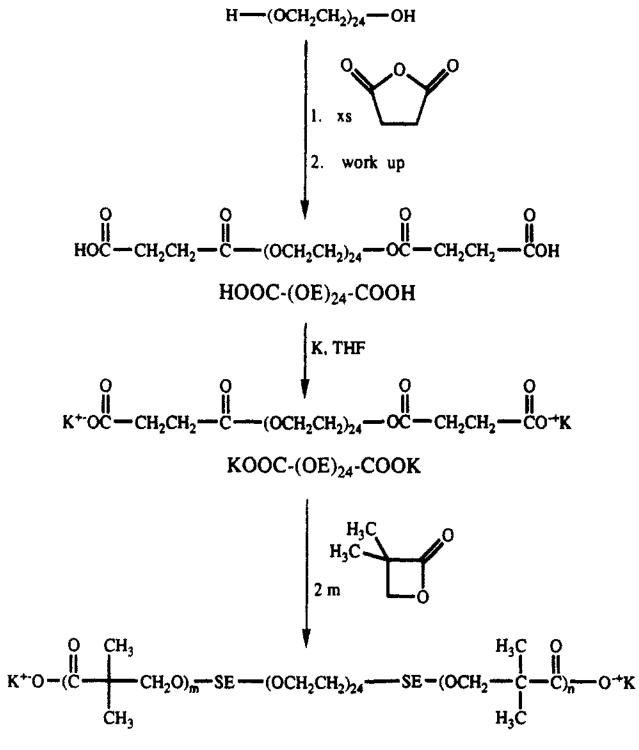

Figure 1. Synthetic scheme for the synthesis of a series of poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers, represented by $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$.

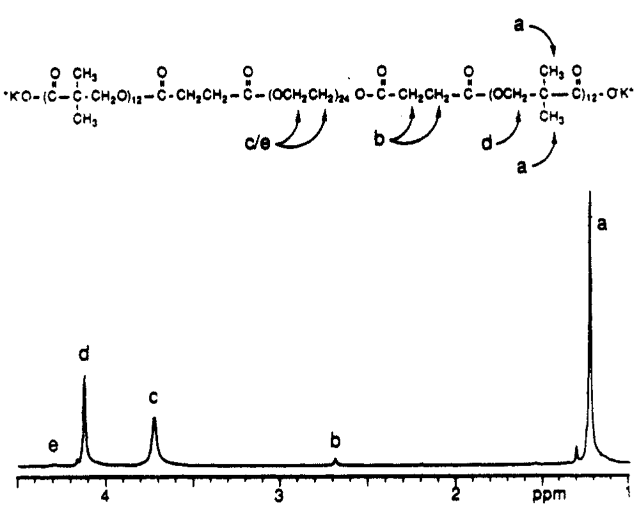

Figure 2. 200-MHz proton NMR of $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ in Silanor-C with 1% trifluoroacetic acid.

Table I
Intrinsic Viscosities ([η]) of $(PVL)_m$-$(OE)_{24}$-$(PVL)_m$ Oligomers and Calculated Number-Average Molecular Weights (M_n)

n	5	7	9	12	16	24
M_n	2400	2900	3100	3900	4500	6100
[η] (dL/g)	0.075	0.081	0.0825	0.084	0.098	0.104

(pivalolactone) methylene singlet (d) at 4.12 ppm, and the succinate link methylene singlet (b) at 2.69 ppm.

Due to the solvent resistance of the poly(pivalolactone) segments, the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers with $m > 7$ are insoluble in most organic solvents including acetone, methylene chloride, chloroform, acetonitrile, dimethyl sulfoxide, and cold *N,N*-dimethylformamide. They are soluble in acidic solvents such as 3-methylphenol, 4-chlorophenol, and methylene chloride with 1% trifluoroacetic acid. The $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers are soluble in hot *N,N*-dimethylformamide and precipitate only slowly on cooling.

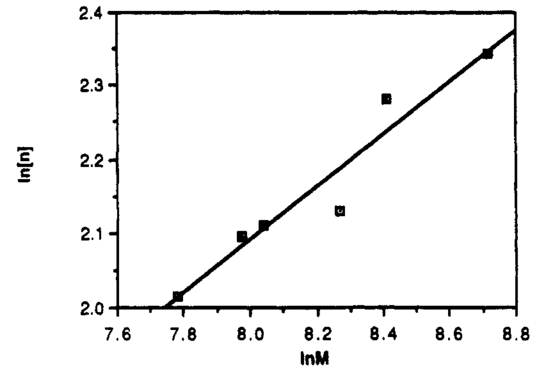

Figure 3. Plot of the Mark–Houwink equation (eq 2) for the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers.

Recently, Guillet[7,8] showed that [η] is accurately estimated from a single measurement of the viscosity of polymers in the molecular weight range 10^3–10^6 using the Solomon–Ciuta equation:[9]

$$[\eta] = [2\eta_{sp} - 2\ln(t/t_0)](c/2) \qquad (1)$$

Table I presents the molecular weights determined by proton NMR and the measured intrinsic viscosities of the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers (0.005 g/mL solutions in methylene chloride containing 1% trifluoroacetic acid at 30 °C) calculated by eq 1.

For linear polymers, a plot of ln [η] versus ln M_v produces slope = α and intercept = ln K according to the Mark–Houwink equation:[10]

$$\ln [n] = \alpha \ln M_v + \ln K \qquad (2)$$

where K and α are termed the Mark–Houwink parameters. Dondos et al.[11] showed that this relationship also holds for linear block and random copolymers. The error resulting from substituting M_n for M_v is small for narrow molecular weight distribution samples,[44] and from the plot of eq 2 for the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers in Figure 3, $\alpha = 0.35$ and $K = 0.48$ mL/g.

The validity of the calculated Mark–Houwink parameters for the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers was checked by size-exclusion chromatography (SEC) analysis versus polystyrene standards—see Experimental Section for the determination of the Mark–Houwink parameters for polystyrene. The samples were analyzed at concentrations of 0.005 g/mL in methylene chloride containing 1% by volume trifluoroacetic acid. Under these conditions, the $(PVL)_m$-SE-$(OE)_n$-SE-$(PVL)_m$ oligomers gave only weak signals as detected by a differential refractometer. Nevertheless, the peak molecular weights, which should correspond well with M_n for narrow molecular weight distribution polymers, agreed well with the known composition.

Analysis of Microphase Separation. DSC is an excellent method of detecting glass transitions and melting points.[12] For a polymer containing an amorphous soft phase and a crystalline hard phase, DSC evaluation of microphase separation is accomplished by (1) comparing the observed glass transition temperature of the soft phase (T_g^{obs}) of the segmented copolymer with the glass transition of the soft-segment homopolymer (T_g^S) and (2) comparing the observed melting point temperature of the hard phase (T_m^{obs}) with the melting point of the hard-segment homopolymer (T_m^H). The strength of this process lies in its ability to produce a complete description of the microphase separation behavior, providing information about the soft and hard phases.

Analysis of the Soft Phase. The low-temperature DSC scans of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ triblock oli-

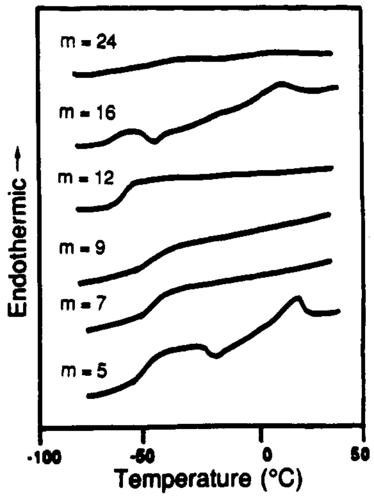

Figure 4. Low-temperature DSC scans of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers.

gomers, with soft-phase glass transitions normalized per gram of sample, are presented in Figure 4. Each sample was quenched from 50 °C to freeze the soft phase into a fully amorphous state at T_g^{obs} and to guarantee that the thermal history of each sample is identical.

Factors known to affect T_g^{obs} include molecular weight, end groups, percent crystallinity, thermal history, and diluents.[12] Thus, with all other factors being equal, an increase in T_g^{obs} is an indication of the presence of a diluent.

Wood[13] demonstrated that the observed glass transition temperature of a single-phase two-component system is the linear weighted addition of the two individual glass transitions:

$$(kW_1 + W_2)T_g^{obs} = kW_1T_g^{(1)} + W_2T_g^{(2)} \qquad (3)$$

where W_1 and W_2 represent the weight fractions of components 1 and 2, $T_g^{(1)}$ and $T_g^{(2)}$ represent the glass transition temperatures of components 1 and 2, and k is a constant. Several researchers[14-17] have attempted to assign physical significance to the constant k, while Wood supports determining k by studying samples of known composition and plotting the results according to the following rearranged form of eq 3:

$$T_g^{obs} = (-1/k)(T_g^{obs} - T_g^{(1)})(W_1/W_2) + T_g^{(2)} \qquad (4)$$

A plot of T_g^{obs} versus $(T_g^{obs} - T_g^{(1)})(W_1/W_2)$ produces a line having slope = $-1/k$ and intercept = $T_g^{(2)}$.

Wood's equation has been shown to apply to microphase-separated segmented copolymers having a mostly crystalline hard phase that is rich in component 2 (called the hard segment) and a mostly amorphous soft phase that is rich in component 1 (called the soft segment).[6,18-20] Because this is a two-component two-phase system in which only the amorphous soft phase participates in the glass transition, the individual weight fractions W_1 and W_2 in eq 3 become the weight fractions of the soft and hard segments in the soft phase, M_{SS} and M_{HS} respectively:

$$(kM_{SS} + M_{HS})T_g^{obs} = kM_{SS}T_g^S + M_{HS}T_g^H \qquad (5)$$

where T_g^S and T_g^H represent the glass transition temperatures of the ideally microphase-separated soft and hard segments, respectively.

Solving eq 5 for M_{SS} produces eq 6:

$$M_{SS} = (kT_g^H - kT_g^{obs})/(T_g^{obs} - T_g^S + kT_g^H - kT_g^{obs}) \qquad (6)$$

From eq 6 and noting that $M_{HS} = M_{SS} - 1$, the soft-phase composition is determined from the observed glass transition temperature of the amorphous phase, provided that suitable values for k, T_g^S, and T_g^H are found.

Table II
Results of Quantitative DSC Analysis of the Soft-Phase Microphase Separation of $(PVL)_m$-$(OE)_{24}$-$(PVL)_m$ Oligomers

m	5	7	9	12	16	24
W_S	0.50	0.45	0.38	0.29	0.25	0.18
T_g^{obs} (°C)	-46	-44	-42	-60	-62	-52
$\Delta C_p^{obs}/W_S$ (J/g)	0.76	0.74	0.65	0.79	0.81	0.4
M_{SS}	0.46	0.43	0.39	0.98	1.1	0.6
SR_S				0.95	0.98	0.5

The recorded values for T_g^{obs} and change in heat capacity per gram of soft segment ($\Delta C_p^{obs}/W_S$) of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$, reported in Table II, show a distinct difference in the glass behavior of the soft phase in the samples with $m > 9$. The samples for $m = 5$, 7, and 9 exhibit T_g^{obs} between -46 and -42 °C, and the samples for $m = 12$ and 16 exhibit T_g^{obs} at -60 and -61 °C, respectively, indicating a marked increase in the soft-phase purity in these samples. T_g^{obs} for $m = 24$ is difficult to determine due to the small weight percent of soft phase in this sample, and the error in the reported value of -52 °C, although unknown, is expected to be large. Thus, calculated values for $m = 24$ will be reported with a single significant digit, and very little interpretation will applied to these values.

The values of M_{SS}, also reported in Table II, were calculated according to eq 6, using $k = 0.24$, $T_g^H = 7$ °C, and $T_g^S = -60$ °C, as determined in the previous study.[6] The values of M_{SS} clearly show that substantial microphase mixing occurs for the samples for $m = 5$, 7, and 9. The low-temperature DSC trace for $(PVL)_5$-SE-$(OE)_{24}$-SE-$(PVL)_5$ shows that portions of this material are rich enough in poly(oxyethylene) to permit cold crystallization followed by a melting transition; however, the value of 0.46 for M_{SS} indicates that no microphase separation has occurred. Perhaps a value of 0.24 for k, determined for triblocks containing 12 poly(pivalolactone) repeat units, is inaccurate for this sample.

On the basis of the calculated values of M_{SS}, the soft phase in the samples for $m = 12$ and 16 is nearly pure in soft segment, and the value of 0.98 for M_{SS} of $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ indicates that the soft phase contains 98% by weight poly(oxyethylene) soft segment. The observance of a cold crystallization and the melting of the crystalline regions in the soft phase of $(PVL)_{16}$-SE-$(OE)_{24}$-SE-$(PVL)_{16}$ clearly indicate high soft-segment purity, and a value of 1.1 was calculated for M_{SS}. A value greater than unity for M_{SS} reveals the limitations of estimating T_g^S, the glass transition temperature of the ideally microphase-separated soft segment, with the glass transition temperature of the poly(oxyethylene) initiator HOOC-$(OE)_n$-COOH.

Soft-Segment Segregation. Camberlin and Pascault[21,22] introduced a method of determining the soft-segment segregation (SR_S), which is defined as the weight fraction of soft segment in the soft phase with respect to the total weight of soft segment in the copolymer:

$$SR_S = (\Delta C_p^{obs}/W_S)/\Delta C_p^S \qquad (7)$$

where $\Delta C_p^{obs}/W_S$ represents the observed change in heat capacity per gram of soft segment in the copolymer and ΔC_p^S represents the change in heat capacity at the glass transition of the soft-segment homopolymer. Camberlin and Pascault[21,22] used eq 7 to quantitatively determine the soft-segment segregation of segmented copolymers containing methylenebis(phenyl isocyanate)-based poly-

Table III
Results of Quantitative DSC Analysis of the Hard-Phase Microphase Separation of $(PVL)_m$-$(OC)_{24}$-$(PVL)_m$ Oligomers

m	5	7	9	12	16	24
W_H	0.50	0.55	0.62	0.71	0.75	0.92
M_{HH}				0.98	0.99	0.9
SR_H				0.99	1.0	0.9
T_m^{obs} (°C)	142	152	172	200	201	207
T_m^H (°C)	174	182	190	201	205	215
ρ	0.73	0.76	0.76	0.99	0.94	0.94

urethane and polyurea hard segments and varying soft segments. Brunette et al.[20] used a similar equation to quantitatively determine the soft-phase composition of segmented copolymers containing methylenebis(phenyl isocyanate)-based polyurethane hard segments and poly(oxybutadiene) soft segments.

Equation 7 does not take into account the contribution to ΔC_p^{obs} by the hard segments in the soft phase, and Wagener and Matayabas[23] showed that when this contribution is considered, a slightly different equation results:

$$SR_S = (M_{SS}\Delta C_p^{obs}/W_S)/(M_{SS}\Delta C_p^S + M_{HS}\Delta C_p^H) \quad (8)$$

where ΔC_p^H represents the change in heat capacity at the glass transition of the hard-segment homopolymer. If the multiphase copolymers are very well microphase separated or if ΔC_p^H is very small, then eq 8 reduces to eq 7, and since the change in heat capacity for poly(pivalolactone) is too small to be detected by DSC, eq 7 is valid for microphase-separated poly(pivalolactone-*block*-oxyethylene) copolymers.

The values of SR_S, also in Table II, were calculated according to eq 7, where $\Delta C_p^S = 0.83$ as previously determined.[6] A value of 0.95 for $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ indicates that 95% of the poly(oxyethylene) soft segments in this sample is located in the soft phase, leaving 5% in the hard phase or a mixed interface. A value of 0.98 for $(PVL)_{16}$-SE-$(OE)_{24}$-SE-$(PVL)_{16}$ indicates that essentially all of the soft segments are located in the soft phase.

Determination of the Hard-Phase Composition. Once both M_{SS} and SR_S are known, it is a simple matter to determine the composition of the hard phase. Assuming that only two phases are formed, the weight fraction of the hard segment in the hard phase (M_{HH}) can be estimated:[6]

$$M_{HH} = 1 - [M_{SS}W_S(1 - SR_S)/(M_{SS} - SR_SW_S)] \quad (9)$$

Similar to SR_S, the hard-segment segregation (SR_H) is calculated by the following equation:[6]

$$SR_H = (M_{SS}M_{HH} - SR_SW_SM_{HH})/(M_{SS}W_H) \quad (10)$$

where W_H represents the weight fraction of the hard segment in the copolymer ($W_H = 1 - W_S$).

The calculated values of M_{HH} and SR_H, listed in Table III, indicate high hard-segment purity in all of the microphase-separated samples. A 0.99 value of M_{HH} for $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ indicates that the hard segment of this sample contains 99% by weight poly(pivalolactone) hard segment, and a 1.0 value of SR_H for $(PVL)_{16}$-SE-$(OE)_{24}$-SE-$(PVL)_{16}$ indicates complete microphase separation.

Figure 5 presents the high-temperature DSC scans of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$, showing the hard-phase melting endotherms (T_m^{obs}). The values of T_m^{obs}, listed in Table III, increase with increasing hard-segment length m.

Block copolymerization decreases the observed melting point (T_m^{obs}) of a crystalline segment, and T_m^{obs} in a block copolymer can be calculated by eq 11:[24]

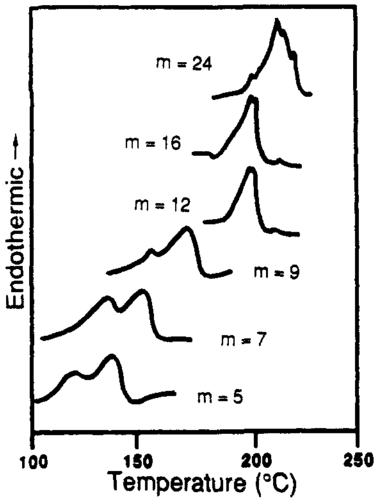

Figure 5. High-temperature DSC scans of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers.

$$1/T_m^{obs} = 1/T_m^H - (R/\Delta H) \ln \rho^H \quad (11)$$

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.[25,26] Wagener and Wanigatunga[27] used eq 11 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, they were able to qualitatively determine the hard-phase composition.

An interesting application of eq 11 is obtained by solving for ρ^H:

$$\rho^H = \exp[(1/T_m^H - 1/T_m^{obs})\Delta H/R] \quad (12)$$

From eq 12, ρ^H can be calculated, and ρ^H should be a very good approximation for M_{HH}. The values of ρ^H for the $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers in Table III were calculated from eq 12 using a value of 3550 cal/mol of repeat unit[28] for ΔH and the T_m^H of homopoly(pivalolactone) with the corresponding molecular weight, also listed in Table III.

The calculated values of ρ^H indicate that the crystalline hard-phase purity increases with increasing hard-segment length for m = 5–12. The values between 0.73 and 0.86 for m = 5, 7, and 9, in contrast to the soft-segment data, indicate that the hard segment has partially microphase separated. For example, the 0.73 value of ρ^H suggests that the crystalline hard phase of $(PVL)_5$-SE-$(OE)_{24}$-SE-$(PVL)_5$ is richer in poly(pivalolactone) hard segment than the 0.50 value, from W_H, that is expected if no microphase separation occurs. The 0.99 value of ρ^H for m = 12 is identical to the M_{HH} calculated from the soft-segment data and indicates that the crystalline hard phase of $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ is completely microphase separated. The 0.94 value of ρ^H for m = 16 also indicates a high degree of crystalline hard-phase purity; however, this value is slightly lower than the 0.99 value of M_{HH}. The

Table IV
Intrinsic Viscosities ([η]), Number-Average Molecular Weights (M_n), and Polydispersities (M_w/M_n) of Polystyrene Standards Used for Universal SEC Calibration

M_n	9000	17500	37000	48900
M_w/M_n	1.06	1.06	1.06	1.06
[η] (dL/g)	0.062	0.105	0.172	0.209

0.94 value of ρ^H for $m = 24$ agrees well with the 0.9 value of M_{HH}.

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 0.3 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 TAS7 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%.

All viscometry data were obtained on an Ace Scientific viscometer, ubderhalden type, using a Haake E2 constant-temperature water bath maintained at 30 ± 0.01 °C.

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.

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 0.5 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. From the viscometry determination of [η] for the polystyrene standards (Table IV), the Mark–Houwink parameters for polystyrene in chloroform containing 1% trifluoroacetic aced were determined, $K = 0.010$ and $\alpha = 0.71$, by a plot of eq 2 (Figure 6).

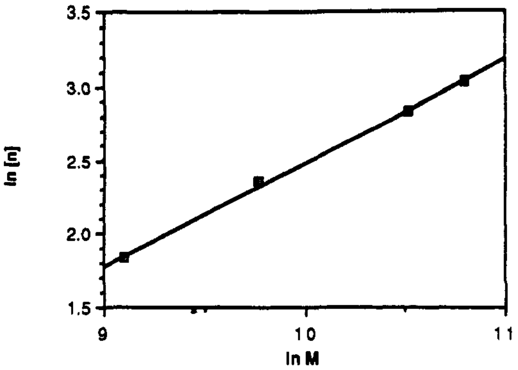

Figure 6. Plot of the Mark–Houwink equation (eq 2) for the polystyrene standards used for GPC universal calibration.

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. 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.

The narrow molecular weight distribution (5% by weight) poly(oxyethylene) glycols were donated in pure form by Union Carbide. When needed dry, the poly(oxyethylene) glycols were dried under vacuum at 100 °C in a modified drying pistol for several days.

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 under reduced pressure at −30 °C.

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

Succinic anhydride (Aldrich) was dried under dynamic vacuum, sublimed under vacuum into an ampule containing a breakseal, flame sealed in the ampule, and sublimed directly into the reaction flask.

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

Synthesis of HOOC-(OE)$_n$-COOH. In a 250-mL round-bottom flask fitted with a condenser, magnetic stirbar, and calcium sulfate drying tube, 10.0 g (10 mmol) of poly(oxyethylene) glycol (1000 g/mol) and 10.0 g (100 mmol) of succinic anhydride were refluxed for 24 h in 100 mL of toluene with stirring. The toluene was removed under reduced pressure. The resulting white residue was dissolved in 100 mL of deionized water, stirred for 30 min, filtered, and then extracted with four 25-mL portions of methylene chloride. The combined methylene chloride extracts were washed with two 25-mL portions of deionized water and dried over anhydrous sodium sulfate for at least 2 days before being filtered. The methylene chloride was evaporated to a concentrated solution and transferred to a drying pistol. The product was dried to a constant weight under vacuum while heating and refluxing water, resulting in a 92% yield. Molecular weight: 1260 (NMR) and 1260 (titration). Elemental analysis: theoretical, 52.7% C and 8.3% H; found, 52.1% C and 8.4% H.

Synthesis of KOOC-(OE)$_n$-COOK. After drying under high vacuum at 100 °C for several days, 1.15 g (0.91 mmol) of HOOC-(OE)$_n$-COOH was dissolved in 75 mL of dry tetrahydrofuran by vacuum transfer. The flask containing HOOC-(OE)$_n$-COOH in tetrahydrofuran was sealed and attached to a 250-mL reaction flask containing a sidearm for potassium metal and a magnetic stirbar. Approximately 1 g of potassium was placed into the sidearm, and the flask was flame sealed and taken to high vacuum. The potassium was distilled into the reaction flask under dynamic vacuum, forming a mirror, and the sidearm was removed by flame sealing. The stopcock to the dynamic vacuum was closed, and the tetrahydrofuran solution of HOOC-(OE)$_n$-COOH was allowed to pour onto the mirror, with immediate bubbling. The reaction was periodically degassed to remove hydrogen. After 24 h, the tetrahydrofuran solution was decanted into a second round-bottom flask and evaporated under reduced pressure, resulting in 1.2 g of a white powder which was dried by high vacuum and stored under argon.

Synthesis of (PVL)$_m$-SE-(OE)$_n$-SE-(PVL)$_m$. Macromolecular initiator KOOC-(OE)$_n$-COOK was quickly weighed (1.0 g) and placed into a round-bottom flask with a stirbar, and the flask was attached to the vacuum line. The flask was taken to high vacuum, and 40 mL of dry tetrahydrofuran was vacuum transferred into the flask. This initiator solution (0.020 mmol/mL) was stored under argon.

To a 250-mL round-bottom flask with a magnetic stirbar under argon was added 10 mL of the initiator solution by syringe. With stirring, pivalolactone (9.9 mmol/mL) was added by syringe to obtain initiator to monomer ratios of 1:5, 7, 9, 12, 16, and 24. The reaction was stirred under argon overnight, and the product was isolated by evaporation of the tetrahydrofuran under reduced pressure. Elemental analysis: $(PVL)_5$-SE-$(OE)_{24}$-SE-$(PVL)_5$ theoretical, 54.3% C, 7.9% H, and 3.3% K; found, 54.6% C, 8.2% H, and 1.4% K; $(PVL)_7$-SE-$(OE)_{24}$-SE-$(PVL)_7$ theoretical, 54.8% C, 7.9% H, and 2.7% K; found, 55.0% C, 8.1% H, and 1.3% K; $(PVL)_9$-SE-$(OE)_{24}$-SE-$(PVL)_9$ theoretical, 55.5% C, 7.9% H, and 2.5% K; found 55.5% C, 8.3% H, and 1.1% K; $(PVL)_{12}$-SE-$(OE)_{24}$-SE-$(PVL)_{12}$ theoretical, 56.5% C, 8.0% H, and 2.0% K; found 55.7% C, 8.0% H, and 1.1% K; $(PVL)_{16}$-SE-$(OE)_{24}$-SE-$(PVL)_{16}$ theoretical, 57.0% C, 8.0% H, and 1.7% K; found 55.3% C, 8.0% H, and 1.0% K; $(PVL)_{24}$-SE-$(OE)_{24}$-SE-$(PVL)_{24}$ theoretical, 57.7% C, 8.0% H, and 1.3% K; found 57.1% C, 8.0% H, and 1.0% K.

Conclusions

Quantitative determination of the microphase separation in a series of $(PVL)_m$-SE-$(OE)_{24}$-SE-$(PVL)_m$ oligomers was achieved by DSC analysis. The poly(oxyethylene) soft-segment length was maintained at 24 repeat units, and the poly(pivalolactone) hard-segment length (m) was varied from 5 to 24 repeat units. For shorter hard-segment lengths, the soft phase is microphase mixed; however, the crystalline hard phase appears to exhibit a small degree of microphase separation. A very distinct transition from microphase mixed to essentially complete microphase separation occurs when m is increased from 9 to 12. Complete microphase separation occurs for $(PVL)_{16}$-SE-$(OE)_{24}$-SE-$(PVL)_{16}$. In this series, the hard segment is the major component, and microphase separation occurs to a larger extent in the hard phase than in the soft phase.

Acknowledgment. Financial support for this research was provided by the Army Research Office. Pivalolactone was donated in pure form by Dr. H. K. Hall, University of Arizona. We give special thanks to Mr. Jason Portmess for conducting viscosity experimentation and establishing the SEC universal calibration.

References and Notes

(1) Yamashita, Y.; Toshioki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 425.
(2) Yusada, T.; Aida, T.; Inoue, S. *Macromolecules* **1984**, *20*, 1717.
(3) Wagener, K. B.; Wanigatunga, S. *Macromolecules* **1987**, *20*, 1717.
(4) Wagener, K. B.; Wanigatunga, S. In *Chemical Reactions on Polymers*; Benham, J. L., Kinstle, J. F., Eds.; American Chemical Society: Washington, DC, 1988; p 153.
(5) Wagener, K. B.; Wanigatunga, S. *Macromolecules* **1989**, *22*, 2090.
(6) Wagener, K. B.; Wanigatunga, S.; Matayabas, J. C., Jr. *Macromolecules* **1989**, *22*, 3211.
(7) Price, G. J.; Moore, J. W.; Guillet, J. E. *J. Polym. Sci., Part A* **1989**, *27*, 2925.
(8) Kilp, T.; Guillet, J. E. *Macromolecules* **1977**, *10*, 90.
(9) Solomon, O. F.; Ciuta, I. Z. *Bull. Inst. Polit. Gh. Gh. Dej. Buc.* **1968**, *30*, 3.
(10) Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; John Wiley & Sons: New York, 1979.
(11) Dondos, A.; Rempp, P.; Benoit, H. *Makromol. Chem.* **1974**, *175*, 1659.
(12) Turi, E. A. *Thermal Characterization of Polymeric Materials*; Academic Press: New York, 1981.
(13) Wood, L. A. *J. Polym. Sci.* **1958**, *28*, 319.
(14) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 493.
(15) Di Marzio, E. A.; Gibbs, J. H. *J. Polym. Sci.* **1959**, *60*, 121.
(16) Couchman, P. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 117.
(17) Kelly, F. M.; Bueche, F. *J. Polym. Sci.* **1961**, *50*, 599.
(18) Miller, J. A.; McKenna, J. M.; Pruckmayr, G.; Epperson, J. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 1727.
(19) Leung, L. M.; Koberstein, J. T. *Macromolecules* **1986**, *19*, 706.
(20) Brunette, C. M.; Hsu, S. L.; Rossman, M.; MacKnight, W. J.; Schneider, N. S. *Polym. Eng. Sci.* **1981**, *21*, 668.
(21) Camberlin, Y.; Pascault, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 415.
(22) Pascault, J. P.; Camberlin, Y. *Polym. Commun.* **1986**, *27*, 230.
(23) Wagener, K. B.; Matayabas, J. C., Jr. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 243.
(24) Mandelkern, L., Ed. *Crystallization of Polymers*; McGraw-Hill: New York, 1964; p 79.
(25) O'Malley, J. J. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 1353.
(26) O'Malley, J. J.; Staffer, W. *J. Polym. Eng. Sci.* **1977**, *17*, 510.
(27) Wagener, K. B.; Thompson, C.; Wanigatunga, S. *Macromolecules* **1988**, *21*, 2668.
(28) Borri, C.; Bruckner, S.; Cresenzi, V.; Fortuna, G. D.; Mariano, A.; Scarazzato, P. *Eur. Polym. J.* **1971**, *7*, 1515.

Registry No. (PVL)(OE) (block copolymer), 133451-97-5; (PVL)($KO_2C(OE)_nCO_2K$) (block copolymer), 142396-15-4; $HO_2C(CH_2)_2CO(OCH_2CH_2)_nOCO(CH_2)_2CO_2H$, 37684-51-8; $HO_2C(CH_2)_2CO(OCH_2CH_2)_nOCO(CH_2)_2CO_2H{\cdot}2K$, 142396-14-3.