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Quantitative Study of Microphase Separation. Pivalolactone-*block*-oxyethylene Oligomers: Effect of Soft-Segment Length

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ABSTRACT: Block copolymers containing hard segments and soft segments are particularly interesting multiphase copolymers. To investigate the requirements for microphase separation, differential scanning calorimetry analysis has been utilized to achieve quantitative determination of the microphase separation behavior in a series of poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers. With the poly(pivalolactone) hard-segment length maintained at 12 repeat units, a minimum poly(oxyethylene) soft-segment length of 14 repeat units is required to achieve some degree of microphase separation, and essentially complete microphase separation occurs for 24 oxyethylene repeat units. A very distinct transition from partial to essentially complete microphase separation occurs when the soft-segment length is increased from 19 to 24 repeat units.

Introduction

The field of multiphase copolymers has been active since its discovery 30 years ago, wherein segmented copolymers have received much attention recently.[1] While segmented poly(urethane ethers) are perhaps the most investigated and the best understood copolymers of this type,[2-4] there has been a great deal of interest in segmented poly(ester ethers) as well.[5-10]

Copolymers of this type contain a soft segment (a segment having a tendency to be flexible and amorphous) and a hard segment (a segment having a tendency to be glassy or semicrystalline), and these segments form separate phases. However, phase separation usually is incomplete, and investigations have detected the presence of both hard segments in the soft phase[2] and soft segments in the hard phase.[3,4] This phase mixing reduces the effectiveness of the physical cross-link and, therefore, adversely affects the ultimate properties of these copolymers. Phase mixing is obviously a problem, and clearly a better understanding of the microphase separation phenomenon is desirable. However, not much is known about the nature or requirements for microphase separation. Factors known to enhance microphase separation in these systems include a narrow molecular weight distribution for each segment,[4,5,9,10] a sufficient hard-segment length to permit crystallization,[2,4] and segmental incompatability.[1]

We have previously reported the synthesis of α-hydroxy-ω-carboxypoly(oxyethylene-*block*-pivalolactone) telechelomers (a telechelomer is a self-reacting monomer capable of step polymerization only) for polymerization to high molecular weight segmented copolymers of the $(A-B)_x$ type (Figure 1).[8,10] A study of both the telechelomers and their respective copolymers has yielded valuable information regarding their microphase separation behavior. In this paper we report a quantitative study of the microphase separation behavior of triblock poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers of the B–A–B type (Figure 2).

The objective of this study is to determine the minimum length of poly(oxyethylene) soft segment necessary to lead to a high degree of microphase separation with a constant poly(pivalolactone) hard-segment length of 12 repeat units, a length known to induce a high degree of crystallization in the hard-segment homopolymer. We have found that a very distinct transition from partial microphase separation to essentially complete microphase separation occurs when the soft-segment length is increased from 19 to 24 repeat units.

Differential scanning calorimetry (DSC) has proven to be very useful in the study of microphase separation. DSC has been used to qualitatively study microphase separation in a number of multiphase-separated copolymer systems.[11] Additionally, quantitative determination of microphase separation by DSC has been accomplished with poly(urethane ethers)[2,3] The results reported herein are quantitative, combining the techniques described in these previous papers with other factors that have been studied.

Experimental Section

Polymerizations. Narrow molecular weight distribution poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers with varying soft-segment length were prepared by polymerization of pivalolactone with five narrow molecular weight distribution, functionalized poly(oxyethylene) initiators with differing lengths, by using vacuum line and breakseal techniques. Figure 3 displays the reaction scheme for the synthesis of these oligomers, where the functionalized poly(oxyethylene) and poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone) oligomers are represented by HOOC–$(OE)_n$–COOH and $(PVL)_{12}$–$(OE)_n$–$(PVL)_{12}$, respectively.

The HOOC–$(OE)_n$–COOH initiators were synthesized by refluxing a toluene solution containing a molar excess of succinic anhydride with one of the five narrow molecular weight distribution poly(oxyethylene) glycols. Number-average molecular weights of the plyethers chosen were 200, 400, 600, 800, and 1000 g/mol, or n = 4, 9, 14, 19, and 24, respectively. A similar method was previously reported for α-methoxy-ω-hydroxypoly(oxyethylene), 1900 g/mol.[12] The products were recovered from the reaction mixture by extraction of a water solution with chloroform, giving yields ranging from 71% (n = 4) to 92% (n = 24). Gel permeation chromatography (in tetrahydrofuran) confirmed complete conversion to a dicarboxylic acid end-capped polyether and the existence of a narrow molecular weight distribution in each case.

These functionalized polyethers were converted into their potassium dicarboxylate salts by reaction with potassium metal in dry tetrahydrofuran under vacuum, and these solutions were used to initiate polymerization of pivalolactone (PVL) under dry argon. The amount of incorporated PVL was calculated by comparing the ^{1}H NMR integrations of the 3.7 ppm methylene singlet of the polyether segment with the 4.4 ppm methylene singlet of the poly(pivalolactone) segment. The hard segment was maintained at 12 PVL units to guarantee its crystallinity. The molecular weight distribution of the PVL segments was also narrow as a result of the anionic ring-opening polymerization procedure.[7-10]

DSC Analysis. All DSC data were obtained with a Perkin-Elmer 7 Series thermal analysis system equipped with a data station. The instrument was calibrated with cyclohexane and indium under dry helium purge gas (25 mL/min) for subambient

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Table I
Glossary of Symbols

T_g^S	glass transition temperature of HOOC–(OE)$_n$–COOH soft-segment model compound
ΔC_p^S	change in heat capacity at T_g^S of HOOC–(OE)$_n$–COOH soft-segment model compound
T_g^{que}	glass transition temperature of melt quenched mixed $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
W_S	weight fraction of poly(oxyethylene) soft segment in $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
W_H	weight fraction of poly(pivalolactone) hard segment in $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
T_g^H	theoretical glass transition temperature of poly(pivalolactone) hard-segment model compound
ΔC_p^H	theoretical change in heat capacity at T_g^H of poly(pivalolactone) hard-segment model compound
T_g^{obs}	glass transition temperature of the soft phase in $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
$\Delta C_p^{obs}/W_S$	change in heat capacity per gram of soft segment at T_g^{obs} of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
M_{SS}	weight fraction of soft segment in the soft phase of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
M_{HS}	weight fraction of hard segment in the soft phase of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
SR_S	soft-segment segregation rate of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer, weight fraction of soft segment in the soft phase with respect to the total weight fraction of the soft segment
T_m	peak melting point of the hard phase of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
M_{HH}	weight fraction of the hard segment in the hard phase of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer
SR_H	hard-segment segregation rate of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomer, weight fraction of hard segment in the hard phase with respect to the total weight fraction of the hard segment

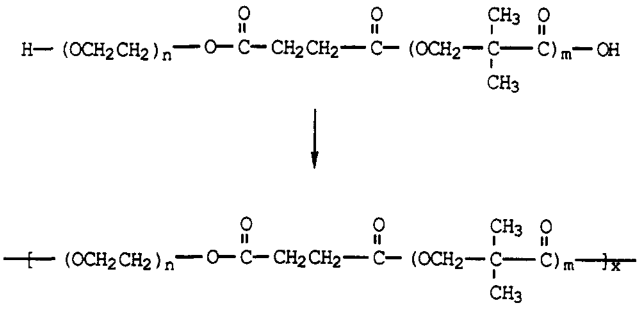

Figure 1. Telechelomer and copolymer.

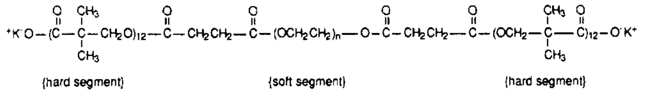

Figure 2. Poly(pivalolactone-*block*-oxyethylene-*block*-pivalolactone).

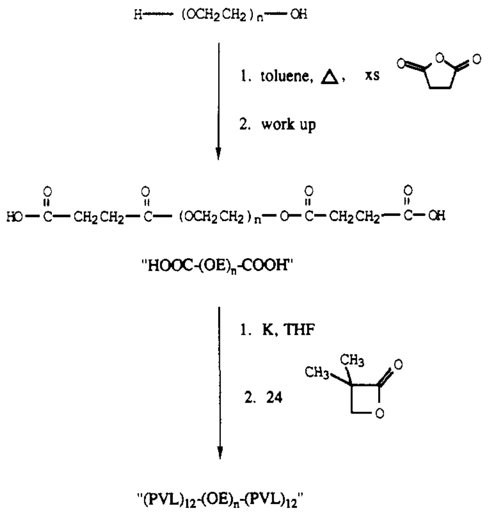

Figure 3. Reaction scheme for the synthesis of $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomers.

operation and with indium and tin under dry nitrogen purge gas (25 mL/min) for operation above 50 °C. All reported DSC results are the average of two to eight scans at 20 °C/min for each sample. In each case, the variance was less than 5%. All reported glass transition temperatures represent the average of recorded temperatures at one-half the height of the glass transition. All reported melting point temperatures represent the average of recorded temperatures at the maximum in the melting point transition.

For subambient operation, each sample was loaded into the DSC pan at room temperature, heated to the quench temperature (either 50 or 250 °C) at a rate of approximately 20 °C/min on a melting point apparatus, and immediately immersed into liquid nitrogen. The Dewar containing liquid nitrogen and the sample was placed into a drybox that covers the DSC with an argon atmosphere, and the sample was quickly transferred to the DSC, which was previously cooled to −150 °C.

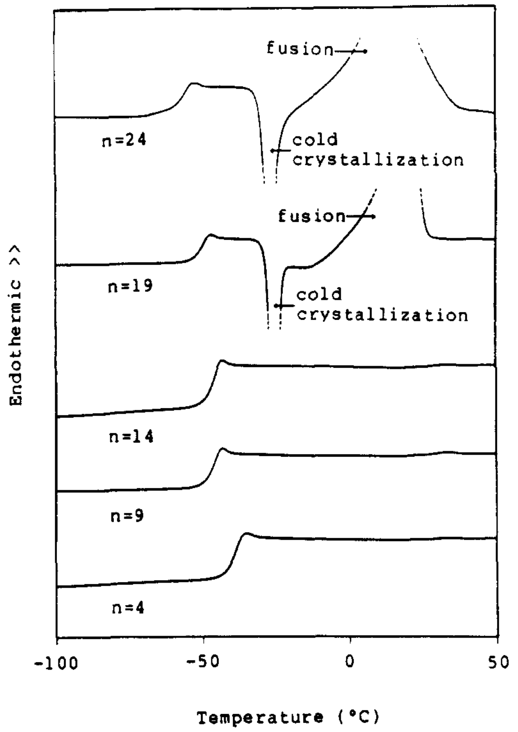

Figure 4. DSC curves of HOOC–(OE)$_n$–COOH soft-segment model compounds.

Results and Discussion

Soft-Segment Model Compounds. To faciliate the understanding of the information presented in this and the following sections, a glossary of symbols is presented in Table I. The HOOC–(OE)$_n$–COOH oligomers serve as model compounds for the ideally microphase-separated soft segments, and their glass transition temperatures (T_g^S) represent the lowest possible glass transition temperatures of the soft phase in the $(PVL)_{12}$–(OE)$_n$–$(PVL)_{12}$ oligomers, assuming that the succinate link will be found in the amorphous region in the well phase-separated triblock oligomers. To guarantee that the samples are fully amorphous, the HOOC–(OE)$_n$–COOH oligomers were quenched with liquid nitrogen from 50 °C and then analyzed in DSC (Figure 4). The values of T_g^S and change in heat capacity (ΔC_p^S), listed in Table II, decrease with

Table II
Glass Transition Temperatures (T_g^S) and Changes in Heat Capacities (ΔC_p^S) of HOOC-(OE)$_n$-COOH Soft-Segment Model Compounds

n	T_g^S, °C	ΔC_p^S, J/g	n	T_g^S, °C	ΔC_p^S, J/g
4	-40	2.1	19	-50	1.4
9	-46	1.8	24	-60	0.83
14	-47	1.6			

Table III
Melt Quenched Mixed Glass Transition Temperatures (T_g^{que}) and Soft-Segment Weight Fractions (W_S) of (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ Oligomers

n	W_S	T_g^{que}, °C	n	W_S	T_g^{que}, °C
4	0.08	-5	19	0.26	
9	0.13	-14	24	0.29	
14	0.19	-20			

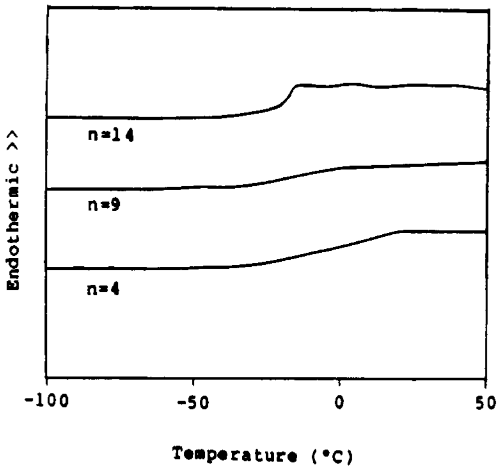

Figure 5. DSC curves of melt quenched mixed (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers.

increasing molecular weight. The samples for n = 4, 9, and 14 are completely amorphous, having only T_g^S. The higher molecular weight samples, n = 19 and 24, tend to crystallize on heating, displaying a cold crystallization exotherm followed by the endothermic melting of the crystalline regions. However, in both cases, n = 19 and 24, the quenching procedure gives fully amorphous samples at T_g^S since $\Delta H_{cryst} \approx \Delta H_{fus}$ (68 and 69 J/g, for n = 19 and 24, respectively).

Melt Quench Mixing of (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ Oligomers. The purpose of melt quench mixing is to obtain the glass transition temperature of each oligomer frozen into a homogeneous and fully amorphous state (T_g^{que}). This procedure allows for the calculation of the constant (k) in Wood's equation[2] and provides a reference glass transition temperature of the amorphous regions in the completely phase mixed samples. The values of T_g^{que} represent the highest possible glass transition temperatures of the amorphous regions in the (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers. In order to obtain T_g^{que} (Figure 5), the (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers were quenched with liquid nitrogen from 250 °C, a temperature above T_m (discussed in later sections) and below T_{dec} (determined by thermogravimetric analysis). Unfortunately, the samples for n = 19 and 24 could not be quenched to a fully amorphous and homogeneous state, and no definitive T_g^{que} could be obtained. T_g^{que} and soft-segment weight fractions (W_S) of each triblock oligomer are presented in Table III.

The glass transition temperature of the ideally microphase-separated hard segment (T_g^H) and k are determined by the linear plot of Wood's equation (Figure 6):[13]

$$T_g^{que} = (-1/k)(T_g^{que} - T_g^S)(W_S/W_H) + T_g^H \quad (1)$$

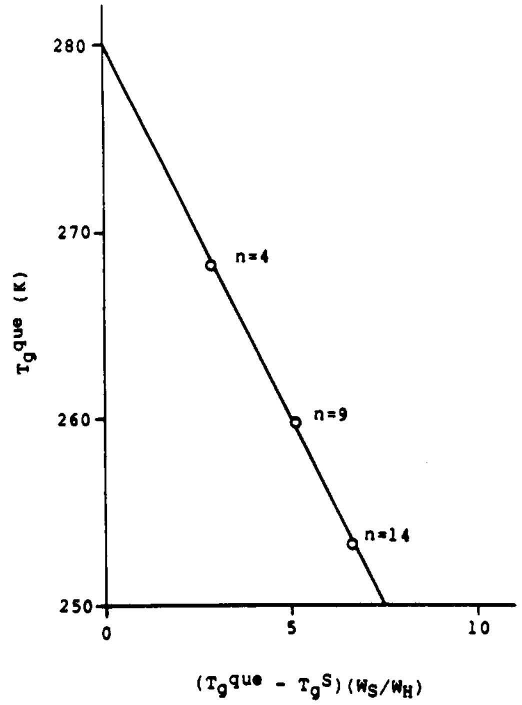

Figure 6. Plot of Wood's equation (eq 1) for the melt quenched mixed (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers.

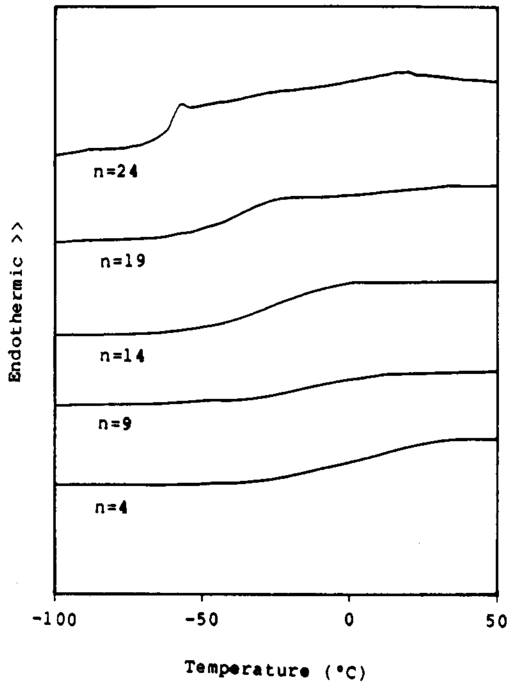

Figure 7. Low-temperature DSC curves of (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers.

where W_S and W_H represent the soft- and hard-segment weight fractions, respectively, and were determined from the known compositions of the triblock oligomers, neglecting the succinate link. The data points, n = 4, 9, and 14, are collinear, having a correlation of 0.99, and the following values are calculated from the slope and intercept: k = 0.24 and T_g^H = 7 °C.

Analysis of the Soft Phase. The low-temperature DSC curves of the (PVL)$_{12}$-(OE)$_n$-(PVL)$_{12}$ oligomers (Figure 7) were obtained under conditions identical with those of the soft-segment model compounds. The samples were quenched from 50 °C to guarantee that the soft phase is totally amorphous without affecting the hard phase. The glass transition temperatures (T_g^{obs}) and changes in heat

Table IV
Glass Transition Temperatures (T_g^{obs}), Changes in Heat Capacities per Gram of Soft Segment ($\Delta C_p^{obs}/W_S$), and Calculated Weight Fractions of Soft Segment in the Soft Phase (M_{SS}) of $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ Oligomers

n	T_g^{obs}, °C	$\Delta C_p^{obs}/W_S$, J/g	M_{SS}
4	-5		0.08
9	-14		0.13
14	-28	0.94	0.30
19	-38	0.87	0.49
24	-59	0.79	0.98

capacity per gram of soft segment ($\Delta C_p^{obs}/W_S$) are reported in Table IV.

With the values of k, T_g^H, and T_g^S evaluated, the weight fraction of the soft segment in the soft phase (M_{SS}) is determined by another form of Wood's equation:[2,13]

$$M_{SS} = (kT_g^H - kT_g^{obs})/(T_g^{obs} - T_g^S + kT_g^H - kT_g^{obs}) \tag{2}$$

The calculated values of M_{SS}, also reported in Table IV, increase with increasing soft-segment length and decreasing T_g^{obs}.

Since T_g^{obs} is the same as T_g^{que} and M_{SS} is equal to W_S for $n = 4$ and 19, it can be concluded that these two samples are not microphase separated. T_g^{obs} is lower than T_g^{que} and higher than T_g^S for $n = 14$ and 19, indicating that these samples are partially microphase separated. In addition, M_{SS} is higher than W_S and lower than unity for $n = 14$ and 19, supporting this conclusion. Because $n = 19$ possesses a higher M_{SS} and a smaller differential between T_g^{obs} and T_g^S, this sample contains less hard segments in the soft phase than the sample for $n = 14$. Since for $n = 24$, T_g^{obs} of the triblock oligomer has a value of -59 °C, which is nearly equal to the T_g^S of the model compound for the ideally microphase-separated soft segment (-60 °C), it is evident that the soft phase of this sample is nearly free of hard segments. The calculated value of 0.98 for M_{SS} predicts that the soft phase of $(PVL)_{12}$-$(OE)_{24}$-$(PVL)_{12}$ contains only 2% hard segment.

Soft-segment segregation rate (SR_S) is defined as the weight fraction of soft segment in the soft phase with respect to the total weight fraction of the soft segment. This parameter is termed a rate due to the time dependence of microphase separation. For microphase-separated copolymers, SR_S is approximated by the following equation:[3,14-16]

$$SR_S = (\Delta C_p^{obs}/W_S)/\Delta C_p^S \tag{3}$$

Equation 3 is valid provided that the sample is in fact microphase separated and that the following assumption is made:[14]

$$M_{SS}(\Delta C_p^S) + M_{HS}(\Delta C_p^H) \approx M_{SS}(\Delta C_p^S) \tag{4}$$

where M_{HS} is the weight fraction of hard segment in the soft phase ($M_{HS} = 1 - M_{SS}$). This assumption is valid in the case of these triblock oligomers due to (1) the ΔC_p^H of poly(pivalolactone), 1200 g/mol, is too small to be observed by DSC, (2) according to Couchman and Karasz's theoretical results,[17] the small value of k indicates that ΔC_p^H is much smaller than ΔC_p^S, (3) estimation of ΔC_p^H from the melt quenched studies produced a value of 10^{-3} J/g, and (4) in the case of $n = 24$, M_{SS} is much greater than M_{HS}.

The values of SR_S calculated by eq 3 for the microphase-separated $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ oligomers, $n = 14$, 19, and 24, are presented in Table V. SR_S for $n = 19$ shows only a slight increase from SR_S of $n = 14$, and SR_S for $n = 24$ indicates that 95% of the soft segments are in the soft phase, leaving 5% in the hard phase or a mixed interface.

Table V
Calculated Soft-Segment Segregation Rates (SR_S) of $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ Oligomers

n	SR_S
14	0.58
19	0.60
24	0.95

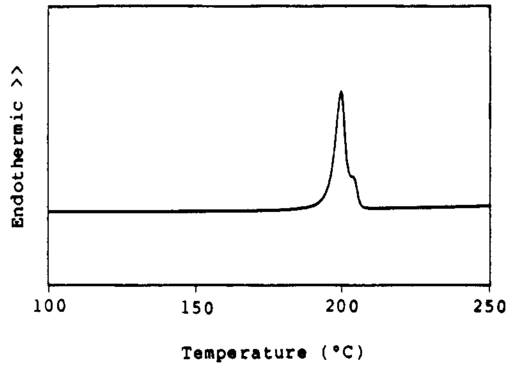

Figure 8. DSC curve of poly(pivalolactone), 1200 g/mol, hard-segment model compound.

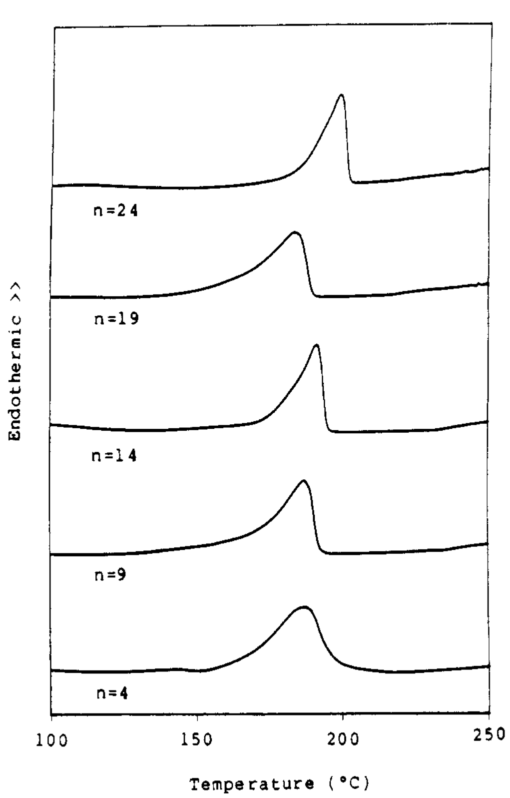

Figure 9. High-temperature DSC curves of $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ oligomers.

Hard-Segment Model Compound. Poly(pivalolactone) (PPVL), 1200 g/mol, serves as the model compound for the ideally microphase-separated hard phase of each triblock oligomer. The DSC scan of PPVL (Figure 8) shows a sharp endothermic melting peak at 201 °C; the shoulder to the main peak is reported to be the melting of a second crystalline structure.[8,9] The T_g of PPVL was not observed, even for the melt quenched sample scanned from -150 to 220 °C, due to a combination of its small ΔC_p and high degree of crystallinity.

Analysis of the Hard Phase. The DSC curves of the melting of the hard phase in the $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ oligomers (Figure 9) were obtained under conditions

Table VI
Melting Points of the Hard Phase (T_m), Weight Fractions of the Hard Segment (W_H), and Calculated Weight Fractions of Hard Segment in the Hard Phase (M_{HH}) of $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ Oligomers

n	W_H	T_m, °C	M_{HH}
4	0.92	196	
9	0.87	187	
14	0.81	191	0.88
19	0.74	183	0.85
24	0.71	200	0.98

identical with the melting of PPVL, and the peak melting point temperatures (T_m) are reported in Table VI. Each sample has a single peak endotherm, indicating that there exists only one type of crystalline hard phase and that the soft segments that exist in the hard phase are thoroughly mixed with the hard segments.

From the estimated values of the soft segment and soft-phase microphase separation, it is a simple matter to calculate the weight fraction of the hard segment in the hard phase (M_{HH}):[13]

$$M_{HH} = M_{SS}W_S(1 - SR_S)/(M_{SS} - SR_S W_S) \qquad (5)$$

From the values of W_H and M_{HH} for the $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ oligomers (Table VI) it is clear that as the value of M_{HH} increases, T_m of the hard phase also increases. Since the sample for $n = 24$ has a T_m that is only 1 °C below the T_m of PPVL, the hard phase is predicted to be nearly free of soft segments, and the calculated value of 0.98 for M_{HH} concurs with this information. Since SR_S for $n = 14$ and 19 are approximately equal, the five more oxyethylene repeat units did not appreciably aid the segregation of soft segments, and it follows that the additional oxyethylene units also increase the content of the soft segment in the hard phase of $n = 19$, resulting in a higher T_m and M_{HH} for $n = 14$ compared to $n = 19$. Recalling that the samples for $n = 4$ and 9 were found to be homogeneous, T_m can be correlated with W_H in these samples, and $n = 4$ has a higher W_H and a higher T_m than $n = 9$. The overall order of T_m follows the expected increasing order $n = 19$, 9, 14, 4, and 24, according to the increasing weight fraction of the hard segment from M_{HH}, for $n = 14$, 19, and 24, and W_H, for $n = 4$ and 9.

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

$$SR_H = (M_{SS}M_{HH} - SR_S W_S M_{HH})/M_{SS}W_H \qquad (6)$$

The values of SR_H (Table VII) increase with increasing soft segment length. SR_H for $n = 24$ indicates that the hard phase of this sample contains 99% of the total hard segment. Despite the fact that the hard phase in the sample for $n = 19$ has more soft-segment content than the hard phase in the sample for $n = 14$, SR_H increases with increasing soft-segment length. It is important to note that SR_H determines only what percent of the total hard segment is located in the hard phase, as opposed to the soft phase, and provides no information concerning the amount of soft segment present in the hard phase.

Table VII
Calculated Hard-Segment Segregation Rates (SR_H) of $(PVL)_{12}$-$(OE)_n$-$(PVL)_{12}$ Oligomers

n	SR_H
14	0.68
19	0.77
24	0.99

Conclusions

A minimum length of 14 oxyethylene repeat units is required to achieve some degree of microphase separation. Estimated values of the soft-segment and hard-segment segregation rates increase with increasing soft-segment length for the microphase-separated samples, approaching unity for $n = 24$. A very distinct transition from partial microphase separation to essentially complete microphase separation occurs when the soft-segment length is increased from $n = 19$ to 24. For the partially microphase-separated samples, phase mixing of the soft segment into the hard phase is an equally important consideration as the presence of hard segment in the soft phase.

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Registry No. (PVL)(OE) (block copolymer), 107558-01-0; $(PVL)(HO_2C(OE)_nCO_2H)$ (block copolymer), 118520-10-8.

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