Melting of the All-*trans* Planar Modification of Triblock Oligomers α-*n*-Alkyl-ω-*n*-alkoxyoligo(oxyethylene)s

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Melting behavior of the all-*trans* planar modification of triblock oligomers $H(CH_2)_n(OCH_2CH_2)_mO(CH_2)_nH$ (n = 6, 8, and 10; m = 1–4) was studied by differential scanning calorimetry. The melting point, enthalpy of melting, and entropy of melting were measured and compared with those for *n*-alkanes that have similar molecular structures. Structural changes in going from the crystalline phase to the liquid phase were discussed on the basis of the observed thermal behavior.

The oxyethylene chain assumes a helical structure with a repeated *trans–gauche–trans* conformation for the O–CH_2–CH_2–O segment in the solid state.[1] Another structure of the oxyethylene chain, an all-*trans* planar structure, was found for the all-*trans* planar modification of alkyl–oxyethylene diblock oligomers $H(CH_2)_n(OCH_2CH_2)_mOH$ (abbreviated as C_nE_m)[2–5] and alkyl–oxyethylene–alkyl triblock oligomers $H(CH_2)_n(OCH_2CH_2)_mO(CH_2)_{n'}H$ ($C_nE_mC_{n'}$) in the solid state.[6–10] The planar oxyethylene structure results from the competition between the intermolecular packing force of the alkyl block and the intramolecular conformational force of the oxyethylene chain that tends to assume the helical structure in the solid state.[9] The molecular form of the all-*trans* modification of the $C_nE_mC_{n'}$ triblock oligomers, called the γ form, is similar to the molecular form of *n*-alkanes in the solid state, whereas the intramolecular and intermolecular interactions involved in the triblock oligomers and *n*-alkanes are different. Accordingly, comparison of the thermodynamic behavior between the all-*trans* $C_nE_mC_{n'}$ triblock oligomers and *n*-alkanes is of great interest. In this letter, we report the melting point (T_m), enthalpy of melting (ΔH_m), and entropy of melting (ΔS_m) for the all-*trans* planar modification of $C_nE_mC_n$s (n = 6, 8, and 10; m = 1–4), which is one of the stable polymorphs of this homologous series, and compare the thermodynamic quantities obtained with those for *n*-alkanes.[11,12]

The $C_nE_mC_n$ triblock oligomers were synthesized in our laboratory.[7–9] All materials were purified by vacuum distillation. The purity was checked by gas chromatography and IR spectroscopy to be better than 99%. Thermodynamic quantities T_m, ΔH_m, and ΔS_m for $C_nE_mC_n$s were measured with a Shimadzu DSC-50 differential scanning calorimeter equipped with a Shimadzu LTC-50 cooling jacket. Temperature calibration was carried out by using pure samples of biphenyl, benzoic acid, and indium as standard materials. A heating rate of 2.0 K min^{-1} was adopted in this study. The reproducibility of the observed DSC melting curves was confirmed by the measurements on different samples of the same compound. All of the samples studied showed a single transition (melting) peak on the DSC curves in the temperature range from 120 to 320 K.

Figure 1 shows T_m for $C_nE_mC_n$s and *n*-alkanes[11,12] as a function of relative molecular mass (M_r). As most of the *n*-alkanes examined have an intermediate phase (the rotator phase) between the crystalline phase and the liquid phase,[13] the crystalline–rotator phase transition temperatures (T_t) for these *n*-alkanes[11,12] are also shown in the same figure. The melting points T_m for $C_nE_mC_n$s are appreciably lower than T_m and T_t for *n*-alkanes. Figure 1 indicates that the difference between T_m for $C_nE_mC_n$s and T_m for the corresponding *n*-alkanes increases with increasing fraction of the oxyethylene block in the $C_nE_mC_n$ molecule. To examine the factors that lower T_m for $C_nE_mC_n$s, we studied the contributions of the enthalpy and the entropy of melting to T_m. In what follows, we will discuss this problem.

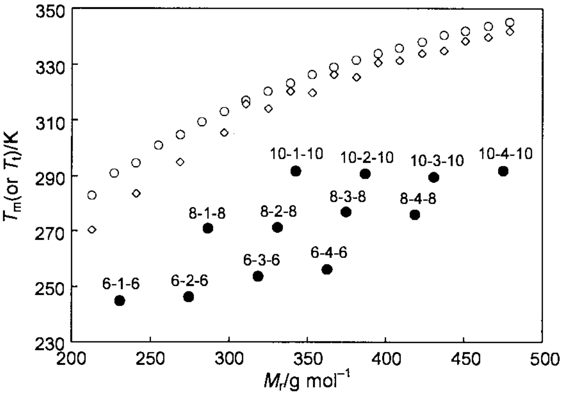

Figure 1. T_m for the $C_nE_mC_n$ oligomers (●), and T_m (○) and T_t (◇) for *n*-alkanes. The $C_nE_mC_n$ oligomers are denoted by *n-m-n* in the figure.

The plots of ΔH_m for $C_nE_mC_n$s and *n*-alkanes and the enthalpy of melting of the rotator phase (ΔH_{ro}) for *n*-alkanes are shown against M_r in Figure 2, where ΔH_m for *n*-alkanes that have the rotator phase is defined as a sum of the enthalpy of crystalline–rotator phase transition and the enthalpy of rotator–liquid

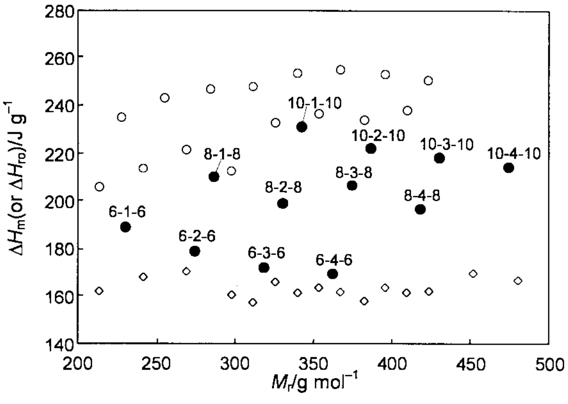

Figure 2. ΔH_m for the $C_nE_mC_n$ oligomers (●), and ΔH_m (○) and ΔH_{ro} (◇) for *n*-alkanes. The $C_nE_mC_n$ oligomers are denoted by *n-m-n* in the figure.

phase transition. In Figure 2, the values of ΔH_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s are between the values of ΔH_m and ΔH_ro for *n*-alkanes, and decrease in general with increasing fraction of the oxyethylene block in the $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ molecule. The latter observation indicates that the oxyethylene block lowers ΔH_m of $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s. This can be explained by an effect of the force that operates a transformation of the less stable planar structure of the oxyethylene block into the stable helical structure. This structure restoration force opposes the intermolecular packing force in the alkyl blocks, leading to an increase of the Gibbs energy of crystals of $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s and resulting in the decrease of ΔH_m. It is expected therefore that with increasing fraction of the oxyethylene block in the $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ molecule, the planar oxyethylene structure becomes less stable. For the $\mathrm{C}_6\mathrm{E}_m\mathrm{C}_6$ oligomers, for example, ΔH_m decreases from 190 J g^{-1} for $\mathrm{C}_6\mathrm{E}_1\mathrm{C}_6$ to 170 J g^{-1} for $\mathrm{C}_6\mathrm{E}_4\mathrm{C}_6$ (Figure 2), and a conformational transformation eventually takes place between $\mathrm{C}_6\mathrm{E}_4\mathrm{C}_6$ and $\mathrm{C}_6\mathrm{E}_5\mathrm{C}_6$ from the all-*trans* planar γ form to the extended/helical/extended triblock β form.[8]

The plots of ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s and *n*-alkanes are shown against M_r in Figure 3, where the entropy of melting of the rotator phase (ΔS_ro) for *n*-alkanes is also plotted. The value of ΔS_m for *n*-alkanes is given as a sum of the entropy of crystalline–rotator phase transition and the entropy of rotator–liquid phase transition. Figure 3 shows that the values of ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s are not appreciably different from those of ΔS_m for *n*-alkanes. The plots indicate that the values of ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s tend to decrease with increasing fraction of the oxyethylene block in the molecule.

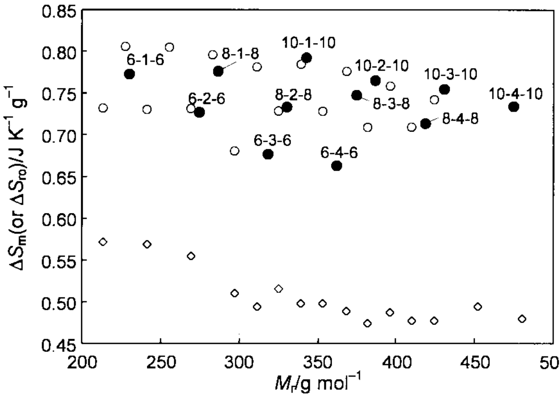

Figure 3. ΔS_m for the $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ oligomers (●), and ΔS_m (○) and ΔS_ro (◇) for *n*-alkanes. The $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ oligomers are denoted by *n-m-n* in the figure.

For flexible linear molecules, ΔS_m can be expressed as a sum of the three terms, ΔS_v, ΔS_d, and ΔS_c,[14–17] where ΔS_v is a change in entropy due to the increase in volume on melting, ΔS_d is a change in entropy due to the occurrence of long-range disorder including the changes of the position and the orientation of molecules, and ΔS_c is a change in entropy due to the increased conformational freedom of molecules in the liquid. Since the magnitudes of ΔS_v for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s and *n*-alkanes are most probably not appreciably different, we will consider only the two terms, ΔS_d and ΔS_c, for discussing the observed values of ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s in comparison with those for *n*-alkanes.

The entropy change ΔS_d is related to the randomness of the molecular configurations in the liquid. If the molecules bear an amphiphilic character, they are likely to associate to form molecular aggregates in the liquid, resulting in the structural organization. Accordingly, the increase of the fraction of the hydrophilic oxyethylene block in the $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ molecule should give rise to a decrease of ΔS_d, which then contributes to lowing ΔS_m. The term ΔS_c, on the other hand, is related to the flexibility of the molecule. As the oxyethylene chain is more flexible than the alkyl chain,[18] the increase of the fraction of the oxyethylene block in the $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ molecule leads to the increase of ΔS_c. This term thus contributes to the raising of ΔS_m. The above discussions show in result that the observed similar values of ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s and *n*-alkanes can be explained as a consequence of the canceled contributions of ΔS_d and ΔS_c to ΔS_m for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s. This result indicates that the lower melting points for the all-*trans* $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ oligomers than for *n*-alkanes are ascribed to the higher Gibbs energy of crystals for the former. As mentioned before, the high Gibbs energy for $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$s, which results from the weakened intermolecular packing force caused by an effect of the structure restoration force in the oxyethylene block, lowers the values of ΔH_m.

The thermodynamic quantities T_m, ΔH_m, and ΔS_m observed for the all-*trans* $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ oligomers have revealed their melting behavior. Further systematic studies on the all-*trans* planar modification of $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_n$ oligomers with other *n* and *m* values and asymmetric triblock oligomers $\mathrm{C}_n\mathrm{E}_m\mathrm{C}_{n'}$ are now in progress in this laboratory. These studies should provide us with more interesting and important knowledge of intramolecular and intermolecular forces acting on flexible linear molecules in the solid and liquid phases.

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