Notes

Effect of Molecular Weight on the Phase Diagram of Linear Polyethylene in 1-Dodecanol

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Introduction

Flexible-chain molecules can undergo two types of phase separations, one involving liquid–liquid and the other liquid–crystal.[1] Under suitable conditions of temperature, solvent, and concentration, a crystallizable polymer can display both phenomena and the two can overlap in some cases. The shape and location of the binodial, demarcating liquid–liquid phase separation in a temperature–concentration diagram, is well-established to be molecular weight dependent.[1] On the other hand, the liquid–crystal phase boundary is essentially molecular weight independent, except in the limit of very small chain lengths.[2,3] Thus, it can be expected that, in a given solvent, the relation between the binodial and the melting temperature–composition curve can be significantly altered by varying the molecular weight. By using the Flory–Huggins mixing free energy to describe the disordered liquid state, Burghardt has presented numerical calculations describing these different situations.[4]

In the present report we shall demonstrate that by varying the molecular weight of linear polyethylene fractions the binodial can be moved from well above to below the theoretical melting temperature–concentration curve, while concomitantly major changes take place in the experimentally observed melting points. For this study 1-dodecanol was chosen as a typical Θ-type solvent for polyethylene.[5]

Experimental Section

Linear polyethylene fractions were obtained from the Société Nationale Des Pétroles D'Aquitaine and the National Bureau of Standards. The molecular weights used here covered the range 2.13×10^4–2.18×10^5. Measured amounts of polymer and 1-dodecanol (98%, $d = 0.820$; Aldrich) were placed in 1-cm-diameter glass tubes. The tubes were then degassed and sealed under vacuum. The samples were slowly heated up to 160 °C (180 °C for fractions with M above 1×10^5) with occasional shaking. The heating was continued for at least 14 h to ensure complete dissolution. For the phase-diagram measurements, the tubes were rapidly transferred to a bath set at a specified temperature controlled to within 0.1 °C. Cloud points were determined visually by noting the appearance of turbidity as the temperature was decreased at a rate no greater than 10 °C/h.

Solution crystals were obtained by isothermal crystallization at 119.7 °C for 15 h or longer. The melting temperatures of all the samples were determined visually. In addition, the melting temperatures of crystals from some of the more dilute solution were also determined with a Perkin-Elmer DSC-2B differential scanning calorimeter. The temperature scale was calibrated with indium. About 10 mg of the crystallite–solvent suspension was transferred to a large-volume capsule having an O-ring seal. The DSC scan was made with 10 mg of dodecanol in the reference capsule at a heating rate of 10 °C/min. The peak temperature of the observed endotherm was taken as the melting temperature of the crystals. The melting temperatures determined by the two methods agreed to within 1 °C.

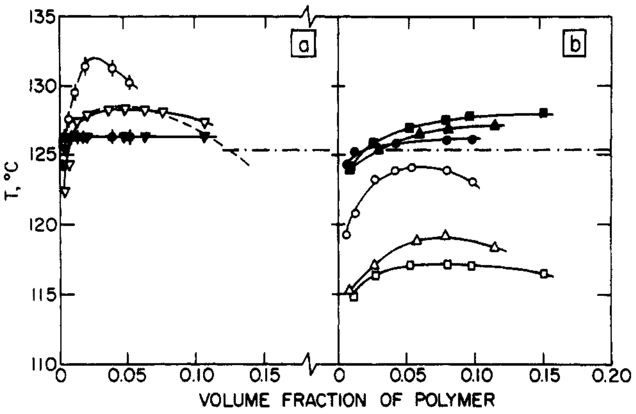

Figure 1. Phase diagrams for linear polyethylene fractions in 1-dodecanol. Temperature–concentration relations for phase equilibria. Solid curves with open symbols are experimental binodials for liquid–liquid phase separation. The dashed curve is a theoretical binodial for $M = 1.2 \times 10^5$. Solid curves with filled symbols represent the experimentally observed melting temperatures; (– · –) theoretical melting temperature–composition relation. For $M_w = 2.18 \times 10^5$ (ϕ, ●); for $M_w = 1.20 \times 10^5$ (▽, ▼); for $M_w = 6.07 \times 10^4$ (○, ●); for $M_w = 3.21 \times 10^4$ (△, ▲); for $M_w = 2.13 \times 10^4$ (□, ■).

Results and Discussion

The experimentally determined binodials and melting temperature–composition curves for the polyethylene fractions in dodecanol are given in Figure 1. From the experimentally determined consolute temperature, T_c, the thermodynamic parameters Θ and ψ_1 were determined in the conventional manner by plotting $1/T_c$ against $(x^{-1/2} + {}^1/_2x)$.[1,6] Here x is the ratio of molar volumes of polymer and solvent. The values of Θ and ψ_1 were found to be 137.0 °C and 1.82, respectively, as compared with 137.3 °C and 1.64 reported by Nakajima et al.[5] From the values of Θ and ψ_1 theoretical binodial curves were generated.[1,6] The calculated binodial for $M_w = 1.2 \times 10^5$ is given by the dashed line in Figure 1a. Very good agreement is found between theory and experiment, as was also the case for the other fractions studied. The consolute temperatures range from 132 °C for $M_w = 2.18 \times 10^5$ to 117 °C for $M_w = 2.13 \times 10^4$. Consequently, depending on the molecular weight, the binodials will lie either above or below the theoretical melting temperature–composition curve. The latter was calculated according to the classical formula[2,7] and is also indicated in Figure 1. In this calculation the melting temperature of the pure species was taken to be 135.4 °C, which is the measured melting temperature of the dried solution crystals. In this manner the finite thickness of the crystallites formed is taken into account. Of particular interest here is the observed melting temperature–composition relations of the actual crystal-

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lites formed. The melting temperatures of the two highest molecular weight fractions, $M_w = 2.18 \times 10^5$ and 1.20×10^5, are given in Figure 1a. Except for the very lowest concentrations, melting occurs within the binodial and the melting temperature is invariant with concentration. This result is to be expected according to the Phase Rule. The melting temperatures are coincident with the intersection temperature of the binodial and the melting temperature curve for a homogeneous melt. Similar results have been reported for other polymer–diluent mixtures crystallizing under the same thermodynamic conditions.[2]

The melting temperature–concentration relations for the three lowest molecular weight fractions, $M_w = 2.13 \times 10^4$, 3.21×10^4, and 6.07×10^4, are given in Figure 1b. The results for these fractions are quite different in that the melting temperatures are now located above the binodial. In this homogeneous region the melting temperature increases with concentration in the conventional manner. On close scrutiny one can note an inversion in the melting temperatures with molecular weight. The melting temperature of the lowest molecular weight fraction is 2 °C greater than the highest one. Although not directly pertinent to the present report, it can be shown that this melting temperature inversion can be attributed to kinetic and morphological factors. For example, when the isothermal crystallization temperature was extended to 4 days, at the same concentration for each of the fractions, the DSC-determined melting temperatures were all the same within experimental error. They corresponded to the value for $M_w = 2.13 \times 10^4$ given in Figure 1b. A similar enhancement of the melting temperature with time has been reported for an unfractionated polyethylene sample crystallized from dodecanol.[8]

In summary, we have been able to verify the major thermodynamic expectations for polymer crystallization from Θ-type solvents. The influence of molecular weight on the morphological consequences resulting from crystallization under these conditions still remains to be explored.[9]

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References and Notes

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