Polyethylene/deutero-polyethylene phase behaviour

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A study of the phase behaviour of polyethylene/deuterated polyethylene (PEH/PED) has been carried out to address the question of phase segregation. The phase diagram has been determined by differential scanning calorimetry on carefully co-crystallized mixtures of PEH and PED that are of essentially the same molecular weight. The phase diagram for PEH/PED is compared with one determined for the model alkane system $(C_{36}H_{74}/C_{36}D_{74})$ and both are found to be of the type expected for a system forming a series of continuous solid solutions with a narrow liquidus–solidus gap. The relevance of the PEH/PED phase diagram to neutron scattering results, which claim the observation of isotopically driven phase segregation, is discussed.

INTRODUCTION

Recently, there has been an increased interest in polymer isotope mixtures. Mixtures of hydrogenated and deuterated polyethylene have been used extensively in neutron scattering studies[1] to probe the conformation of polymer molecules. The validity of these studies is predicated upon the assumption that the probe molecules mimic the conformation of the host molecules (those of naturally occurring isotopic abundance). Even in the ideal case where the probe and host are isotopically related (no differences in elemental composition, chain structure, molecular weight, molecular weight distribution, etc.) it is not known *a priori* whether the probe will perfectly model the host. In the more usual case, the probe does not relate to the host as a simple isotope and the degree to which the probe will accurately mimic the host is even more uncertain. The simplest and most fundamental way in which to begin to examine the quality of any probe as a mimic is to examine the probe/host phase diagram. For these reasons, it is remarkable that only a schematic diagram of a hypothetical polyethylene/deutero-polyethylene (PEH/PED) system has been presented[2]. Experimental data have been reported for only the paraffinic model system $n\text{-}C_{36}H_{74}/n\text{-}C_{36}D_{74}$ and for the ternary system PEH/PED/benzene[3,4]. Questions concerning solid-solution formation, fractionation, and segregation during crystallization cannot be properly addressed in the absence of a phase diagram.

The determination of phase diagrams of polymeric materials is relatively complicated; many molecular and experimental parameters need to be considered. It is well known[5] that homologous macromolecules differing sufficiently in length segregate under favourable experimental conditions; for PEH of broad molecular weight $(\bar{M}_n = 8530, \bar{M}_w = 153\,000)$ it is known that isothermal crystallization at 129°C can segregate lower molecular weight polymers ($\leqslant 20\,000$) from the higher molecular

weight polymers that have crystallized. Equally well-established is the fact that linear and branched polymer isomers tend to form separate solids[6]. Cooling rates are known to have a major effect on the aforementioned phenomena not only for mixtures, but also for nominally pure components. Obviously, any attempt to verify an isotope effect on the phase diagram of PEH/PED will require that several precautions be taken. Most importantly, the macromolecules need to be true *isotopes*, i.e., identical in chain length distribution and degree of branching.

EXPERIMENTAL

Deuterated and protonated polyethylene were prepared following a previously developed procedure[7]. Ethylene (Liquid Carbonic and ethylene-d_4 (MSD Isotopes) were used as received. Cyclohexane was dried over molecular sieves followed by refluxing over molten potassium for 24 h. Ethyl aluminium sesquichloride $(C_2H_5)_3Al_2Cl_3$ (Aldrich) was used directly as a 25% solution in toluene. Vanadium oxychloride (Aldrich) was diluted to a 0.013 M solution in cyclohexane under dry nitrogen.

Ethylene (deuterated ethylene) was admitted to a 500 ml reaction vessel containing 250 ml of cyclohexane. Following addition of 1 ml $(C_2H_5)_3Al_2Cl_3$ solution, polymerization was initiated at $23 \pm 2°C$ by the addition of the $VOCl_3$ solution, the rate of addition regulated so as to maintain a flow rate of 6 ml s^{-1} of ethylene into the vessel. After approximately 5 min, the reaction was stopped by addition of 1 ml of 2-propanol. The polymer was precipitated by adding the reaction solution to 400 ml of 2-propanol and then vigorously stirring the mixture in a blender. The polymer was filtered on a glass frit and washed with 2-propanol. The polymer was then stirred with ethanol, filtered and then washed with ethanol containing a small amount of antioxidant (Irganox 1010). The low molecular weight tail was removed by extraction with CH_2Cl_2 in a Soxhlet extractor for three hours. Catalyst residues were removed by extraction in a Soxhlet

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* Contribution No. 3694.

extractor using a mixture of t-butanol and HCl. The polymer (*ca.* 2 g) was dried overnight in a vacuum oven at 50°C.

Size exclusion chromatography data were obtained using a DuPont 830 chromatograph with a Wilks infrared detector. The columns consisted of DuPont PSM60 and PSM1000 porous silica packings and the solvent was 1-chloronaphthalene at a temperature of 150°C. Sample concentrations were close to 0.1 wt% and the flow rate was 0.50 ml min^{-1}. Protonated polyethylene was found to have $M_n = 0.92 \times 10^5$, $M_w = 2.23 \times 10^5$ and $M_z = 3.78 \times 10^5$. Deuterated polyethylene had a slightly larger retention time than the protonated polyethylene corresponding to a slight decrease in chain length. Our previous results have shown that the retention time is unaffected by deuteration of branches in branched polyethylene; assuming this result is applicable to linear polymer, we find $M_n = 1.00 \times 10^5$, $M_w = 2.62 \times 10^5$ and $M_z = 4.90 \times 10^5$ for the deuterated polyethylene.

The number of branch points in the PEH was determined by high resolution $^{13}C\{^{1}H\}$ n.m.r. in 1-chloronaphthalene with an external dideuterotetrachoroethane lock at 120°C, to be less than 0.5 branch site per 1000 carbon atoms in the main chain. Branching in highly linear PED cannot be determined by solution n.m.r. methods because of lower sensitivity in the absence of protons. Branching in PED is expected to be very similar to that found for PEH due to the use of an identical synthetic method and an essentially identical degree of polymerization and polydispersity as compared to PEH.

Various mixtures of PEH/PED were prepared by co-dissolution of the components in *p*-xylene under nitrogen at 135°C for 30 min. The total polymer concentration was approximately 1% by weight and 0.1% antioxidant (Irganox 1010) was added. After dissolution the mixtures were quenched to room temperature, the solvent was extracted with hexane, and subsequently the polymer powder was dried overnight under vacuum at 50°C. The mixtures, as well as the pure species, were then heated for 15 min at 160°C in sealed aluminium d.s.c. pans and subsequently cooled down at various rates.

Model compounds n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$ were purchased from Eastman Kodak Co. and MSD Isotopes, respectively, and were used without further purification. Mixtures of n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$ were prepared by blending known amounts of the solid components which were then homogenized at 100°C for 15 min. These mixtures were cooled down at a standard rate of 0.5°C min^{-1} to room temperature.

Differential scanning calorimetry (d.s.c.) was carried out on samples of about 2 mg with typical heating rates of 5°C min^{-1}. The cooling rates used are indicated in the text.

RESULTS

Table 1 lists the thermal properties of PEH, PED, n-$C_{36}H_{74}$ and n-$C_{36}D_{74}$. The as-polymerized PEH has a peak melting temperature of 136.5°C which is 4.0°C higher than as-polymerized PED. The melt-quenched samples show a comparable difference of 4.9°C. The enthalpy of fusion of the as-polymerized PEH is 3.0 kJ mol^{-1} and is 4% higher than that of PED, which is approximately the estimated experimental error. The melt quenched samples both have a value of the enthalpy of fusion that is 60% of the as-polymerized material. The

Table 1 Thermal properties of polyethylene, deutero-polyethylene, $C_{36}H_{74}$ and $C_{36}D_{74}$

Material	T_m (°C)	ΔH_f (kJ mol^{-1})
as-polymerized PEH	136.5	3.0
as-polymerized PED	132.5	2.9
melt-quenched PEH	134.2	1.8
melt-quenched PED	129.3	1.7
$C_{36}H_{74}$	75.4	3.6
$C_{36}D_{74}$	71.6	3.6

heat of fusion of both $C_{36}H_{74}$ and $C_{36}D_{74}$ is 3.6 kJ mol^{-1}. This heat of fusion is the sum of the enthalpy of fusion and the enthalpy of the solid/solid transition just below the melting temperature, for reasons of accuracy. Comparison of the thermal properties of PEH and PED with those of the oligomeric $C_{36}H_{74}$ and $C_{36}D_{74}$ reveals very similar differences between the hydrogenated and deuterated species. For example, in both cases the deuterated isotope has a melting point that is about 4°C lower than the hydrogenated species. The results in *Table 1* indicate that the isotope effect on the thermal properties translates very well from the paraffinic model compounds to the polymer species.

Figure 1 shows d.s.c. heating curves recorded at 5°C min^{-1} of equal weight mixtures of PEH and PED that were prepared by cooling from the melt at various rates. The salient feature of these traces is that they all display one single endothermic peak, even for samples cooled at rates as low as 0.05°C min^{-1}. This observation indicates that no gross segregation of the two species has occurred; evidence for gross segregation would be the presence of multiple melting peaks. As is commonly observed for semi-crystalline polymers, the peak melting temperaure and the enthalpy of fusion increase systematically with
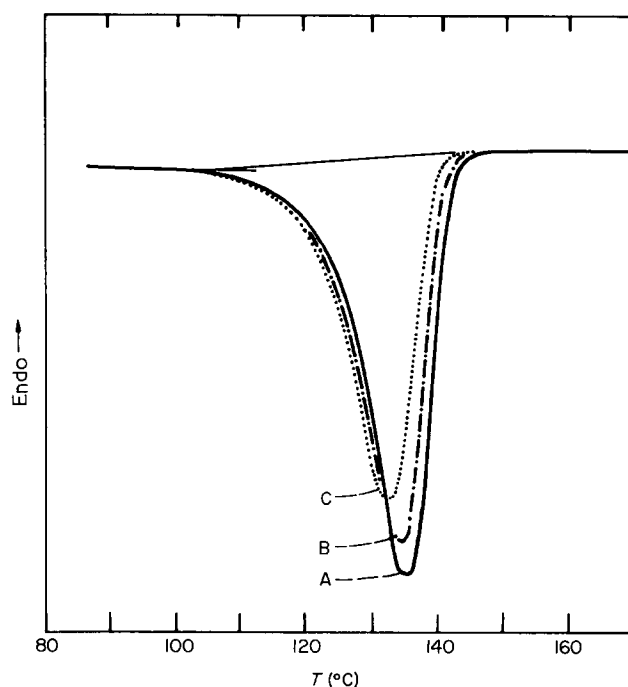
Figure 1 D.s.c. heating curves of 50/50 PEH/PED mixtures cooled at: A, 0.5°C min^{-1}; B, 5°C min^{-1}; C, quenched to room temperature
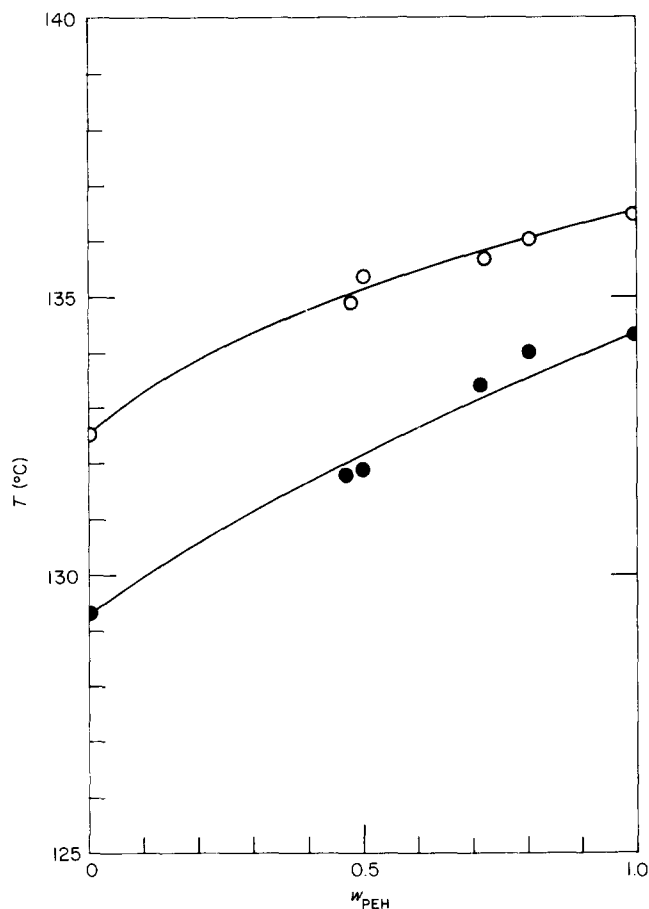
Figure 2 Temperature/composition diagram of the PEH/PED system. (●) Peak melting points of melt-quenched samples. (○) Peak transition temperatures of specimens cooled at 0.5°C min⁻¹
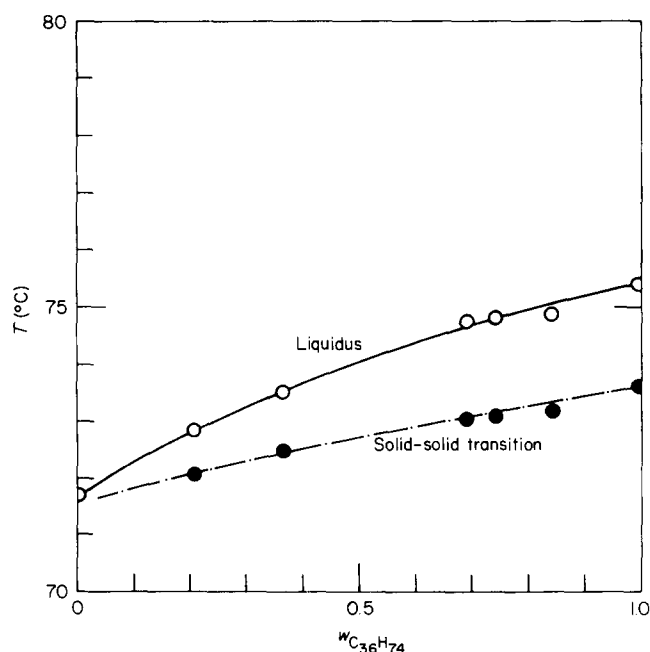

Figure 3 Partial phase diagram of the binary system n-$C_{36}H_{74}$/n-$C_{36}D_{74}$

decreasing cooling rates. Very similar results were obtained for mixtures of different compositions, as well as for the pure constituents.

The peak transition temperatures in the d.s.c. curves

were used to construct the temperature/composition diagram of the PEH/PED system. *Figure 2* includes the peak melting temperatures of the slowly cooled (−0.5°C min⁻¹) and quenched samples. Clearly, the diagram is of the solid-solution type with melting points varying smoothly with composition. The position of the solidus is difficult to establish in an accurate manner; however, it is possible to estimate the width of the solidus–liquidus gap by comparison of the width of the melting endotherms of the pure constituents with those of the mixtures. Typically, melting of PEH and PED occurs over a range of about 25°C. This range is quite comparable to that observed for the 50/50 mixture (*Figure 1*), which should exhibit the maximum temperature difference between liquidus and solidus. In fact, there is no experimental evidence for the schematic phase diagram proposed by Schelten *et al.*[2] that exhibits widely separated flat liquidus and solidus curves.

It is instructive to compare the present PEH/PED diagram with the phase diagram of the system n-$C_{36}H_{74}$/n-$C_{36}D_{74}$. The phase diagram of the alkane system (*Figure 3*) determined in this study, matches the results of Stehling *et al.*[3] within experimental error. The resemblance between the oligomeric and polymeric phase diagrams is striking. Stehling *et al.*[3] and Krimm and Ching[4] have discussed the consequences of the C_{36} phase diagram with respect to segregation during solidification from the melt. The conclusion that emerged from their respective works is that finite compositional heterogeneity does exist, due to the finite (albeit small) width of the solidus/liquidus gap, but is only significant at intermediate concentrations. The generality of this conclusion is supported by Spells and Sadler[8] who report that in a mixture of 10% n-$C_{32}H_{66}$/90% n-$C_{32}D_{66}$ no neutron scattering evidence was found for segregation and furthermore, the molecules are arranged randomly within the crystals.

In view of the neutron scattering results for the paraffinic systems and the close resemblance between the polymer and paraffin phase diagrams (*Figures 2* and *3*), it seems remarkable that segregation of PEH and PED molecules reported so frequently in the literature has been attributed to an isotope effect. Arguments[1,2] concerned with differences in crystal growth rates of the two materials are invalid, since the driving force for crystallization is related to the equilibrium melting temperature of the two components in the mixture, and not to those of the pure species. From the results presented here, it is apparent that the origin of phase segregation in PEH/PED mixtures as deduced from the neutron scattering experiments is not predominantly due to isotope effects. The observed segregation more likely reflects differences in molecular weight distribution, the degree of branching, or perhaps the presence of voids[9,10]. The lack of observations of segregation in other polymeric isotope systems[11–14] seems to corroborate this view.

ACKNOWLEDGEMENTS

Mandelkern and K. E. Russell, and Drs D. M. Sadler and J. M. Guenet.

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