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Upper Critical Solution Temperatures in Blends of Chlorinated Polyethylenes

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ABSTRACT: Upper critical solution temperatures, UCSTs, were found in binary blends of members of a series of high molecular weight chlorinated polyethylenes, CPE. Miscibilities were determined as a function of blend thermal history by measuring glass-transition temperatures by differential scanning calorimetry. As an example, derivative DSC curves for a 50/50 wt % blend of two CPEs containing respectively 42.2 and 50.7 wt % chlorine showed two peaks when the blend was annealed at 50 °C and one peak when the same blend was annealed at 130 °C. The reproducibility both of phase separation at lower temperatures and rehomogenization at higher temperatures was confirmed by cycling experiments. Phase diagrams of CPE blends showed maxima at 50/50 wt % compositions. The temperature of the UCST was found to depend primarily upon the difference in chlorine contents between the respective CPEs in the blends. In general the critical temperature was lowered as the chlorine content differences decreased, reflecting increased compatibility.

Introduction

Theoretical and experimental interest in miscibility of random copolymers with homopolymers or other copolymers has led to a number of predictions concerning the effects of structure, molecular weight, and temperature in these blends. One important class of mixtures is that in which the random copolymer $(A_xB_{1-x})_{n_1}$ is blended with a second copolymer containing the same monomeric moieties A and B but of different composition and molecular weight, e.g., $(A_yB_{1-y})_{n_2}$. In these formulas x and y represent mole fractions of A; n_1 and n_2 are the respective degrees of polymerization.

The zeroth-order mean-field prediction for this system is that miscibility (at any temperature) can occur only for the condition $|x - y| = 0$ if $n_1, n_2 = \infty$ and the segmental interaction χ_{AB} is greater than 0. If finite molecular weight polymers are employed, the maximum value for miscibility, $|x - y|_{max}$, will itself be finite; moreover, the value of $|x -$

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$y|_{max}$ is a function of χ_{AB} and is given by[1]

$$|x - y|_{max} = (n_1^{-1/2} + n_2^{-1/2})/(2\chi_{AB})^{1/2}$$

We have been interested in applying the theory to several systems in which A ≡ CH_2 and B ≡ CHCl. The chlorinated polyethylenes (CPE) are the simplest of such systems, and we have carried out a comprehensive study in which the quantity $|x - y|_{max}$ has been measured as a function of x for a wide range of conditions.

The purpose of the present paper, however, is to report some unusual findings with respect to temperature effects in these systems, namely the occurrence of a series of upper critical solution temperatures (UCSTs) in blends of appropriate $|x - y|$.

Several reviews[2-4] on critical phenomena in the miscibility of polymers have been published in the last decade. In terms of critical behavior polymer-containing mixtures can be classified into two categories: (1) those constituted from polymers and solvents or from oligomer pairs and (2) polymer–polymer mixtures. Upper critical solution temperature behavior is recognized to be the norm in the former category,[5-7] though exceptions are known. Thus Freeman and Rowlinson[8] found lower critical solution temperature (LCST) behavior in hydrocarbon-containing polymer solutions. It has also become clear that LCST behavior is very common in polymer–polymer systems,[4] and several polymer solutions[9-12] have been found in which the same system displays a UCST at lower temperatures and an LCST at a higher temperature. However, binary mixtures in which both components are high molecular weight polymers have previously only been found to show LCST behavior. In one case Walsh et al.[13] determined the phase boundaries in mixtures of poly(methyl methacrylate) and solution-chlorinated polyethylene using light scattering measurements and found both LCST and UCST behavior in the mixtures. However, it was noticed later[14] that these results were obtained because of an adventitious matching of the refractive indices of the two polymers at certain temperatures.

Zhikuan and Ruona[15] determined the miscibility in blends of chlorinated polyethylene with different degrees of chlorination from the transparency of films cast from solvent. They found the miscibility of the blends of CPEs was dependent upon the degree of chlorination of the polymers and the difference in chlorine content between two CPEs. No temperature effects were studied.

As is well-known, UCST behavior can be predicted by using the Flory–Huggins theory applied to polymer–polymer mixtures; however, this type of mean-field theory is unable to predict LCST behavior. Newer theories of polymer solutions, such as equation-of-state treatments by Prigogine[16] and Flory et al.,[17] and the lattice-fluid theory of Sanchez and Lacombe[18] have been developed and can explain the appearance of LCSTs by taking into account the volume of mixing. McMaster[19] applied an equation-of-state treatment to polymer–polymer mixtures and demonstrated that a small positive interactional energy parameter led to both UCST and LCST behavior when the free-volume effects are very small. He also pointed out that such a case is expected to be uncommon in polymer–polymer systems. The present paper reporting critical phenomena in chlorinated polyethylenes thus describes the first observation of UCST behavior for high molecular weight polymer–polymer blends.

Experimental Procedures

Chlorinated polyethylene (CPE) was prepared by the solution photochlorination of a master batch of polyethylene following the procedure of Walsh et al.[13] The linear high density polyethylene (Pressure Chemical Co., $M_w = 2.4 \times 10^4$, $M_n = 9.4 \times 10^3$) was dissolved in chlorobenzene (5% w/v solution) at 140 °C. Chlorine was bubbled through the solution, and the photoreaction was initiated by a tungsten lamp. CPEs with different chlorine content were obtained by removing aliquots of this solution at appropriate times of reaction. The samples were precipitated with a tenfold excess of methanol and dried at 50 °C for 4 days in a vacuum oven before characterization. Chlorine contents expressed in terms of weight percent were determined by elemental analysis. The molecular weights were measured in tetrahydrofuran solution by GPC. The essential absence of carbonyl groups in the samples was monitored by IR. A range of polymers was prepared in which the chlorine contents were varied systematically by small increments. Characterization data for the five samples referred to in the present paper are shown in Table I. The bracketed values of molecular weights in Table I show the calculated molecular weight relative to that of sample CPE 40.0. The agreement implies that no significant degradation of the polymers occurred during chlorination.

Table I
Properties of Solution-Chlorinated Polyethylenes

sample code	Cl, wt %	molecular weight[a] $M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	T_g, °C[b]
CPE 40.0	40.0	5.67	2.91	1.95	−9.0
CPE 42.2	42.2	5.73 (5.85)[c]	2.84	2.01	−3.4
CPE 46.2	46.2	6.55 (6.27)	3.22	2.03	9.3
CPE 47.9	47.9	6.58 (6.52)	3.20	2.05	16.9
CPE 50.7[d]	50.7	6.35 (6.83)	2.9	2.12	26.2

[a] GPC: relative to polystyrene. [b] Determined from maximum in derivative DSC plot. [c] Calculated; see text. [d] This sample also contains ~2 mol % of CCl_2 units determined by NMR.[22] In samples of lower chlorine content CCl_2 is below the limits of detection.

In preparing a blend the selected CPEs were dissolved in THF (0.5% w/v). The composition of blends studied was 50/50 wt % unless otherwise noted. The mixtures of the CPEs were coprecipitated with a tenfold excess of cold methanol. The precipitated powders were washed several times with cold methanol and then dried at 50 °C for 4 days under reduced pressure. Films were obtained by compression molding at either 50 or 100 °C for 15 min.

The miscibility of the polymers was determined by observing the glass transition temperature behavior of the blends by using a Perkin-Elmer DSC-4 differential scanning calorimeter. Selected thermal histories were imposed by annealing the samples in the DSC. Samples were heated at 200 °C/min to the desired temperatures and annealed for 15 min unless otherwise noted. The samples were then quenched to −40 °C. Thermal analyses of the annealed samples were carried out at a heating rate of 20 °C/min. It was determined that in homogenization experiments in the present systems an annealing time of more than 15 min produced no further changes in the observed glass-transition temperature(s).

Derivative curves of DSC thermograms were used to determine the T_gs. Landi[20] was the first to note the advantage of this technique. when derivative curves are used, the broadening of glass transitions can be more clearly defined and a greater resolution of the T_gs in immiscible blends can be obtained.

Results and Discussion

Several combinations of CPEs from the samples listed in Table I were studied. As an example Figures 1–3 show derivative curves of DSC thermograms for the CPE 42.2–CPE 50.7 mixture. The data shown in Figures 1–3 were all obtained by using the same sample. This blend in film form was stored at 25 °C for 6 days after it was pressed at 100 °C. The first (i.e., top) curve (marked "0 min" in Figure 1) clearly shows two peaks. Since the first peak temperature is slightly higher than the T_g of pure CPE 42.2 (−3 °C) and the second peak temperature is just lower than the T_g of pure CPE 50.7 (26 °C), phase separation in this system is not necessarily complete at 25 °C. The sample was annealed at 120 °C for successively longer periods of time, as shown, and eventually showed a single broad peak

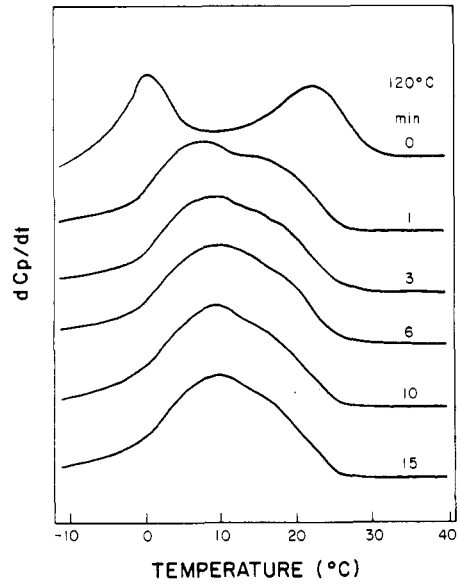

Figure 1. Derivative DSC thermograms of 50/50 wt % blends of chlorinated polyethylene annealed at 120 °C. Annealing times as shown, with sequence starting at top. The chlorine contents of the two polymers are 42.2 and 50.7 wt %, respectively.

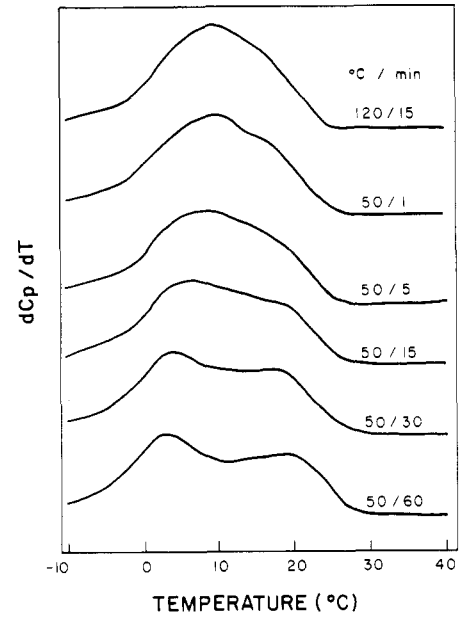

Figure 2. Derivative DSC thermograms of same sample as in Figure 1 with annealing conditions as shown, with sequence starting at top.

with a maximum at 11 °C. This peak temperature is reasonably close to the average of the maxima for the component CPEs. Note that the peak becomes sharper with increasing annealing times. These results suggest immediately that a single phase can be obtained at a temperature *above* a critical point, i.e., UCST behavior. In further experiments this temperature was found to be in the vicinity of 125 °C, although the precise location is subject to some uncertainty.

To confirm the reversibility of these effects the sample was then annealed at 50 °C for extended periods of time. Results are shown in Figure 2. As can be seen, the broad peak bifurcates, revealing that a phase separation in this system occurs at 50 °C (i.e., some 24 °C above the T_g of the highest T_g component). The procedures were repeated in a second cycle, and the reversibility of both phase separation at lower temperature and homogenization at higher temperature was confirmed. The results of the

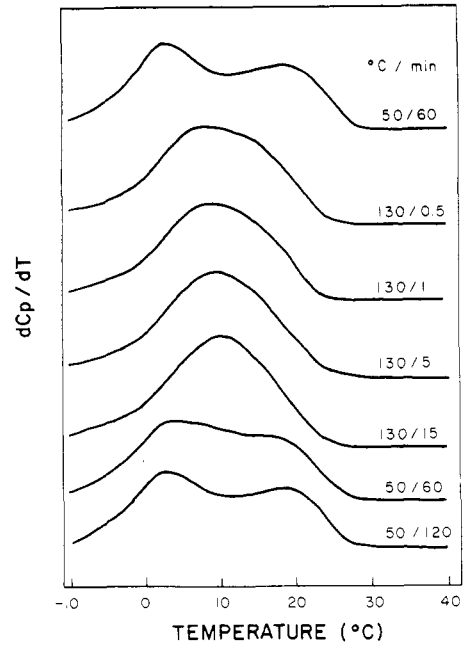

Figure 3. Derivative DSC thermograms of same sample as in Figures 1 and 2 in second cycle of homogenization and phase separation. Annealing conditions as shown, with sequence starting at top.

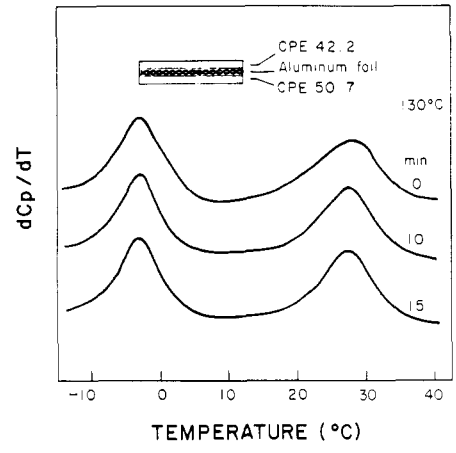

Figure 4. Derivative DSC thermograms of a "model" system consisting of chlorinated polyethylenes with chlorine contents of 42.2 and 50.7 wt % with aluminum foil separation, see text. Annealing times at 130 °C as shown.

second annealing procedure are shown in Figure 3. The sample annealed at 130 °C for 15 min shows one peak again, which is slightly sharper since the annealing temperature was some 10 °C higher. Finally, when the sample was cooled and held at 50 °C, the individual T_gs reappear.

The CPEs used in these studies were of sufficiently high chlorine content to largely or completely eliminate crystallinity. Nevertheless, it is known that glass transitions of very imperfectly crystalline polymers such as PVC may be influenced by thermal treatment.[21] To ensure that the effects reported above were not caused by an interference in T_g behavior stemming merely from crystallization (or simply annealing), a further experiment was devised. In this the two pure CPE components were separated in a DSC sample cup by a thin aluminum foil to prevent mixing and were subjected to an annealing protocol similar to that described above. The derivative curves of the model system are shown in Figure 4. It is obvious that the glass-transition temperatures of the pure CPEs are not changed by annealing at 130 °C for 15 min and that neither crystallinity nor a general smearing of the T_g thermogram

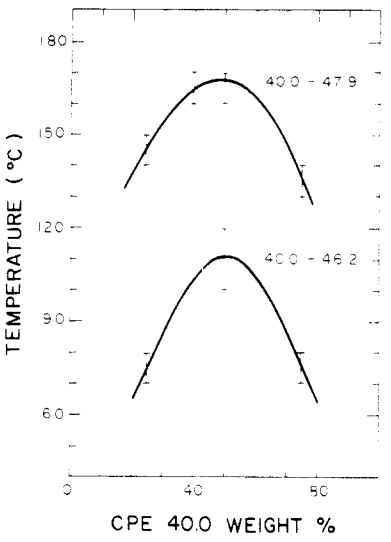

Figure 5. Phase diagrams of blends of CPEs containing 40.0 and 47.9 wt % chlorine and 40.0 and 46.1 wt %, chlorine respectively.

was responsible for the effects described. These results support our conclusion that the phenomena shown in Figures 1–3 represent true UCST behavior.

This was confirmed in two other CPE blends, and Figure 5 shows the respective phase diagrams for these systems. Both blends show characteristic convex curves, with maxima at about 50/50 wt % composition. The UCSTs of the two blends differ by about 60 °C and that with the smaller chlorine content difference is lower, indicating greater miscibility, as expected.

The differences in chlorine content between the two CPEs in all the blends studied is less than 10%. Therefore these systems represent mixtures of polymers that are quite similar in structure. According to the calculations of McMaster,[19] both UCST and LCST behavior might be anticipated for polymer blends when the free-volume difference between two polymers is very small and the interactional energy parameter, X_{12}, is small and positive. Because of the similarity of the blend constituents, we can indeed expect the free-volume effect to be small in this system. We note that Zhikuan and Ruona[15] obtained positive values of X_{12} in mixtures of chlorinated octadecanes.

None of the blends of CPEs studied here clearly displayed an LCST. Any LCST in this system almost certainly lies above the UCST, and its observation may well have been impeded by incipient degradation of the polymers in the vicinity of 200 °C. To directly observe a consolute point in amorphous polymer–polymer blends, the critical temperature must be in an interval essentially bounded by the degradation temperature (or that at which other chemical changes occur) and the glass-transition temperature of the blend. In the present system the observed UCST increased with increasing $|x - y|$ as anticipated, i.e., as the differences in the structures of the components become larger. If an LCST is also present, it would be expected that it would decrease as $|x - y|$ increased, and in principle the consolute points would merge. (For $|x - y|$ exceeding this value, an "hourglass" phase diagram would obtain.) In the present case we can conclude that such a double consolute point, if present, must lie above 200 °C. Evidence for the possible presence of this phenomenon is the fact that in similar experiments, using, however, CPEs of higher average chlorine content,[23] LCSTs are observed below the degradation temperature but above the T_g. Because the former temperature is not a strong function of chlorine content in these CPEs (in fact it decreases somewhat for polymers of higher chlorine content), we conclude that the double consolute point must also decrease, but to a greater degree, with increasing chlorine content to make the observation of an LCST possible. In contrast, in these higher chlorine CPEs UCSTs were not observed, a fact we attribute to the relative proximity of the T_g and the consequent difficulty of attaining thermodynamic equilibrium in the comparatively restricted available temperature interval. Moreover, it could be that the double consolute point has decreased to the extent that it now lies below the blend T_gs.

Modern theories emphasize free-volume effects on the miscibility of polymer blends and hence account for the prevalence of LCSTs. However, we can expect that such effects are far less important in blends of copolymers whose structural differences are small. This together with the fact that the low T_gs for these systems permit the study of phase behavior over a comparatively wide temperature interval can rationalize the ready observation of UCSTs in the present systems.

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