Letters

Order—disorder transformations in ionic complexes of poly (ethylene oxide)

In the course of investigations into the thermal properties of ionic complexes of poly(ethylene oxide)[1] we have observed well defined order—disorder transformations in some of the samples. Order—disorder transformations are, of course, well known in other systems. The 'λ' transition in certain alloys and the 'Curie point' at which ferromagnetism disappears are examples of this type of critical phenomenon. However, to the writer's knowledge, such well defined behaviour as reported here (see Figure 1) has not been reported previously for a linear polymer system. The possibility that the order—disorder transformations are involved in morphological changes in the sample is of particular interest.

The complexes are the open chain analogues of the so-called crown ether macrocyclic complexes. They are formed when 4 mol of the repeating unit of poly(ethylene oxide) are com-

Figure 1 Thermograms of ionic complexes of poly(ethylene oxide). A, Sodium iodide/PEO 600 000 (crystallized from solution); B, ammonium thiocyanate/PEO 6000 (crystallized at 51°C)

plexed with 1 mol of certain alkali metal or ammonium salts[2,3]. Complexation occurs by donation of lone pair electrons of the ether oxygen atoms to the cation. Complexes with the thiocyanates of sodium, potassium and ammonium and with sodium iodide are readily prepared by evaporation of solvent from methanol solutions. In the present work poly(ethylene oxide) of molecular weight 600 000 and 6000 was used. The complexes crystallize to form spherulites having high degrees of crystallinity (i.e. 85 to 90% as determined by X-ray diffraction) with a similar morphology to the uncomplexed polymer. X-ray fibre photographs show that highly ordered crystalline lattices may develop. The fibre repeat distance for the potassium thiocyanate complex, for example, is 8.1 Å (ref 2) compared with 19.3 Å for poly(ethylene oxide). The melting temperature of the pure polymer (76°C) is enhanced by complexation. The sodium iodide complex, for example, melts at 205°C.

The order—disorder transformations have only been observed in sodium iodide and ammonium thiocyanate complexes so far. Figure 1a shows a differential thermal analysis (d.t.a.) tracing for the sodium iodide/ PEO 600 000 complex. In this case, the critical temperature, T_λ, occurs at 100°C. For a sample of the ammonium thiocyanate/PEO 6000 complex, T_λ was observed at 69°C before final melting at 76.5°C (Figure 1b). However, as in alloy systems, the critical temperature is lower at compositions other than those giving maximum long range order. Thus, a sodium ion complex having 80% iodide anions and 20% thiocyanate anions formed mixed-ion crystals with T_λ at 77.5°C and the final melting temperature at 187°C. In a second ammonium thiocyanate complex, T_λ was observed at 61°C. The lower value for this sample may have been the result of a small departure from the precise stoichio-

metric composition or to the different thermal treatment received by this sample.

The disordered state of the crystal lattice in the temperature range between T_λ and the melting temperature is reflected in the low entropies of fusion of the complexes. The entropy changes involved in the transformations are estimated from the d.t.a. peak areas following calibration of the instrument with suitable compounds having known heats of fusion and melting temperatures which extend over the temperature range of interest. This procedure gave a value of 5.6 cals/ deg (mol of repeating unit) for the entropy of fusion of uncomplexed poly-(ethylene oxide), in good agreement with literature values[4]. The stoichiometry of the complexes suggests that their entropies of fusion should be somewhat greater than four times this figure for melting of 1 mol of ordered complex. The values for various samples of the complexes estimated from the d.t.a. peaks are generally low in comparison with this expectation; they range between 12 and 27 cal/deg mol. However, the total entropy changes for the order—disorder and melting transformations are estimated to be 35 and 63 cal/deg mol for samples of ammonium thiocyanate and sodium iodide complexes, respectively.

Disordered crystalline lattices are of considerable interest in relation to their influence on polymer morphology. Bassett[5] has suggested that extended chain lamellae simply reflect low entropies of fusion in accord with the following established relation commonly applied to folded chain lamellae of lesser thickness:

$$l = 2\sigma_e/\Delta S_f \Delta T + \delta l$$

where l is the lamellar thickness; σ_e is the fold surface free energy; ΔS_f is the entropy of fusion; ΔT is the supercooling at the crystallization tempera-

ture and δl is a small length. The well known examples of polymers which form extended chain crystals, polytetrafluoroethylene and polyethylene crystallized at high pressures, are known to have disordered crystalline lattices at temperatures close to the melting temperature. Bassett has shown that the polyethylene lattice transforms from an orthorhombic to a disordered hexagonal structure under the high pressure conditions at which chain extension occurs.

A study of the morphology of the poly(ethylene oxide) complexes is in progress. In a preliminary inspection[1] by scanning electron microscopy, the

fracture surface of a sample of the sodium iodide complex which had been slowly cooled from the melt was compared with a similarly treated sample of the uncomplexed polymer. This showed that discrete lamellar structures several thousand angstrom units in thickness were present in the complexed polymer which could not be observed in the uncomplexed polymer. Further work is required to establish whether these structures represent individual extended chain lamellae and so to determine whether the cooperative process which gives rise to the order—disorder transformation is involved in a morphological change.

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Conversion of dielectric to viscoelastic data

In a recent communication[1] it has been shown that it is possible to relate the viscoelastic loss angle with the equilibrium real and imaginary parts of the complex dielectric permittivity in the α-transition zone of some amorphous polymers, by means a formula obtained from a main result of Di-Marzio and Bishop[2]:

$$\frac{\epsilon^*(w) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + KG^*(\omega)} \quad (1a)$$

with

$$K = \frac{4\pi R^3}{kT} \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \quad (1b)$$

where $\epsilon^* = \epsilon' - j\epsilon''$ is the complex dielectric permittivity, G^* the dynamic shear modulus, R the radius of the rotating group, k the Boltzmann constant and T the absolute temperature.

These results have been obtained by generalizing Debye's theory to the case where the friction coefficient, $\zeta(\omega)$, is a function of the frequency.

From equations (1) we can obtain:

$$\tan \delta_{\text{visc}}$$

$$= - \frac{(\epsilon_0 - \epsilon_\infty)\epsilon''}{(\epsilon_0 - \epsilon')(\epsilon' - \epsilon_\infty) - \epsilon''2} \quad (2)$$

which depends only on dielectric parameters. The viscoelastic tan δ

values for some polymers [poly(vinyl acetate)(PVAc) and poly(ethyl methacrylate)(PEMA)] calculated from this equation agree with the direct experimental data, as shown in *Figure 1*. In some cases it is necessary to apply the time—temperature superposition method and in others (curve C in *Figure 1*) a shoulder appears, possibly due to the fact that at high temperatures two mechanisms of relaxation are superimposed: one is due to the glass—rubber transition (α) and the other is due to the first of the secondary transitions (β) in the glass zone. Finally, in another case (curve B), the value of the tan δ peak is not the same in all the cases that we compare, but this is not a critical question because of the difficulties of measuring the tan δ exactly at the top of the transition.

We have checked some empirical equation for the α-transition and show how to reduce the dielectric data represented with a Havriliak and Negami arc[3] to the viscoelastic data by means of equation (2). This arc equation is:

$$\epsilon^* = \epsilon_\infty$$

$$+ \frac{\epsilon_0 - \epsilon_\infty}{(1 + (j\omega\tau_0)^{1-\alpha})^\beta} \quad (3)$$

When we subtitute the real and ima-

ginary parts of this equation into equation (2) we obtain, after some rearrangements:

$$\tan \delta_{\text{visc}} = \frac{r^{\beta/2} \sin \beta\theta}{r^{\beta/2} \cos \beta\theta - 1} \quad (4)$$

where

$$r = \left[1 + (\omega\tau_0)^{1-\alpha} \sin \frac{\pi}{2}\alpha \right]^2$$

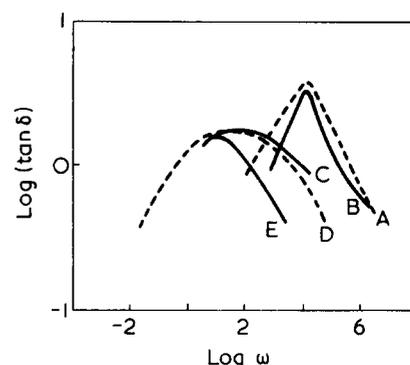$$+ \left[(\omega\tau_0)^{1-\alpha} \cos \frac{\pi}{2}\alpha \right]^2$$

Figure 1 Loss tangent for PVAc and PEMA: A, PVAc (mechanical)[6] 75°C; B, PVAc (mechanical from dielectric)[7] 75°C; C, PEMA (mechanical from dielectric)[8] 100°C; D, PEMA (mechanical)[11] 100°C; E, PEMA (mechanical at 1 Hz for to eliminate the β peak)[9] 100°C