Study of 2:1 poly(ethylene oxide)—resorcinol molecular complex

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X-ray diffraction, electron microscopic and physico-mechanical studies have been made on the poly(ethylene oxide)–resorcinol system where a molecular complex exists. These studies provide support for the suggested mechanism describing the formation of the 2:1 (monomer:resorcinol) complex, in which resorcinol molecules form hydrogen bonds to the polymer chain. This is accompanied by a close packing of the molecules of two types without any substantial change in the polymer chain conformation.

INTRODUCTION

The occurrence of a molecular complex (MC) in the poly(ethylene oxide)–resorcinol system was found when studying the phase diagrams of a number of binary systems, one component of which was a high molecular weight compound, poly(ethylene oxide) (PEO), and the other from a great variety of low molecular weight organic species[1]. These systems were found to possess the eutectic-type phase diagram. Among the low molecular weight species were those whose molecules could form, in principle, a hydrogen bond with an oxygen atom of the PEO chain, i.e. molecules capable of forming a molecular complex; however, most cases were such that the eutectic-type phase diagram was observed. Sometimes (PEO with α- or β-naphthol) the contact zone remained liquid at temperatures below 0°C. A stable crystalline MC was found to exist in the PEO–resorcinol system only. For all the systems the type of phase diagram was determined by the contact preparation technique[2] with a hot stage attached to the polarizing microscope. The phase diagram of the PEO–resorcinol system was then constructed using a point-by-point method (*Figure 1*).

In the phase diagram of the PEO–resorcinol system the bell-shaped MC occurrence region is separated by two eutectic points from the pure components, the MC melting temperature being about 30°C higher than that for the pure PEO. The centre of the bell corresponds to the stoichiometric 2:1 ratio, i.e. each two monomeric PEO units are bound with one resorcinol molecule.

The formation of the MC is proposed to take place through envelopment of the PEO chain by resorcinol molecules, accompanied by the development of hydrogen bonding according to the scheme in *Figure 2a*. This Figure shows clearly a periodicity along each chain; a period contains two resorcinol molecules and four monomeric PEO units, with two carbon atoms following each O_4 sequence in a special position, i.e. outside the envelope zone. It is obvious that where the envelopment takes place such a clear periodicity should manifest itself in X-ray diffraction patterns.

The scheme suggested to explain the formation of the MC is favoured by the following facts: (1) the PEO samples with varying molecular weights (2000, 6000, 20 000, 40 000 and 2–4 × 10^6) which interact with resorcinol form the same phase diagram with 2:1 ratio in the centre of the MC occurrence region, with the MC melting temperature varying between 86 and 99°C; (2) pure resorcinol sublimes readily but practically no sublimation from the MC melt in air takes place; the excess resorcinol over the stoichiometric 2:1 ratio (e.g. 50 mol % and more) sublimes on stirring of the melted mixture.

The geometrical model analysis (*Figure 2b*) indicates that the formation of hydrogen bonding is in agreement with a close fitting of the resorcinol molecules to the PEO chain in the 'projection into hollow' fashion[3]. In the case of other rigid molecules (α- and β-naphthol, phenol, benzoic acid) such a fitting turns out to be impossible.

The PEO–resorcinol system was studied by X-ray diffraction, electron microscopy and physico-mechanical methods.

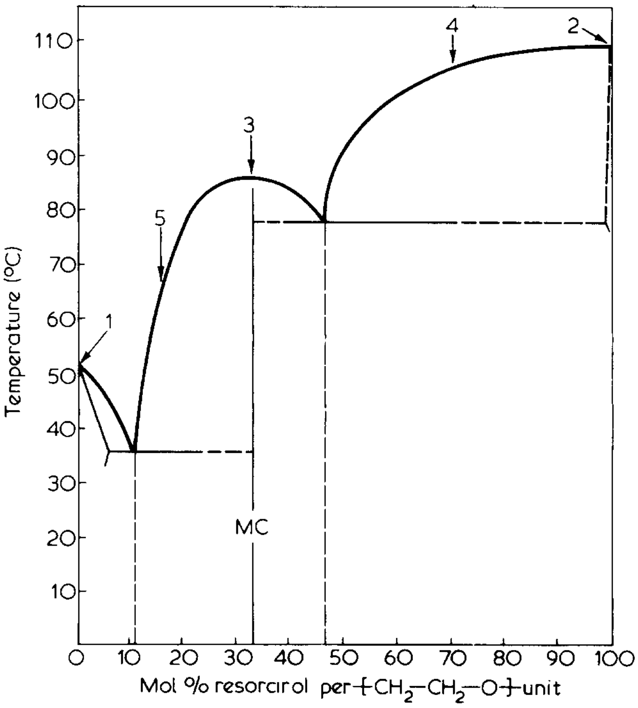

Figure 1 The phase diagram of the PEO–resorcinol system (in mol % per one [$-CH_2-CH_2-O-$] unit)

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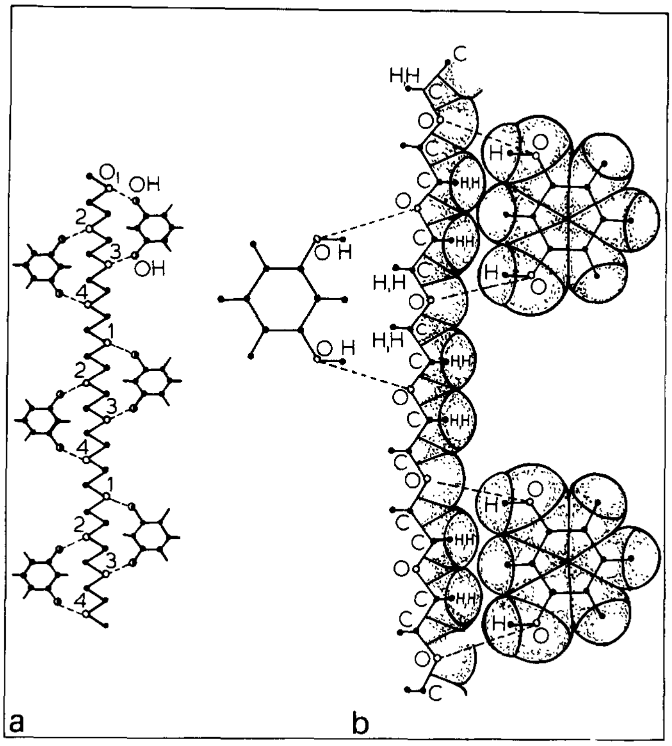

Figure 2 (a) The scheme of the MC formation through the development of hydrogen bonding between the PEO chain and resorcinol molecules. (b) 'Envelopment' model, the right part is drawn with intermolecular radii; the PEO molecule conformation – planar zigzag

EXPERIMENTAL

X-fay diffraction measurements

The oriented MC film was obtained by mixing resorcinol with high molecular weight PEO only (molecular weight = 2–4 x 10^6). The mixture of a specified concentration, thoroughly stirred, was pressed under conditions which largely excluded air at 120°C (the resorcinol melting temperature being 111°C) and a pressure of 50 atm; then the mixture together with the apparatus was allowed to cool slowly. The MC film thus obtained was stretched manually.

Figure 3a shows a fibre X-ray diffraction pattern from the MC, the plane of the stretched sample being parallel to the film plane. The vertical direction of stretching is shown by an arrow. For comparison, *Figure 3b* shows the X-ray diffraction pattern from a pure PEO sample prepared by a similar method (pressing at 80°C). It can be seen that the MC gives a more complicated diffraction pattern as compared with PEO. There were measured d_{hkl} for 49 reflections. The presence of meridian 001 reflections suggests that the c^*-axis of the reciprocal lattice does not coincide with the c-axis of the unit cell of the MC crystal, directed along the stretching axis, i.e. the MC crystal symmetry cannot be higher than monoclinic. The X-ray pattern of a fixed sample taken on a cylindrical film possessed reflections with 1 = 2, 3, 4, i.e. there were no special absences in this direction.

Electron microscopy study

The numbered arrows in *Figure 1* show the points of the phase diagram which were studied by using scanning and transmission electron microscopes. Use was made of the following three polymer types: PEO-2000, PEO-40 000 and PEO-2–4 x 10^6. Samples were prepared either by slow cooling the melt or by pressing at 50 atm at a temperature 10–15°C above the liquidus line for the corresponding composition.

Carbon–platinum replicas were prepared on the surface of fractures obtained from samples frozen in liquid nitrogen. Owing to the fact that pure resorcinol sublimes readily the frozen sample fractures for points 2 and 4 were obtained by employing a special device designed for the vacuum apparatus VUP-1[4], the replica being made on the fracture surface at –190°C. Replicas were washed out in distilled water (at 90°C for 2–3 days) or in alcohol (for a day). The replicas were observed in a transmission electron microscope EMV-100L at magnifications 1000–10 000x, in some cases a scanning electron microscope SEM-501 (Philips, Holland) being used. While using the scanning microscope, gold was deposited onto the sample surface.

Thermomechanical measurements

In order to reveal the changes in molecular mobility, occurring on heating the samples, use was made of the thermomechanical integral method consisting in measure-

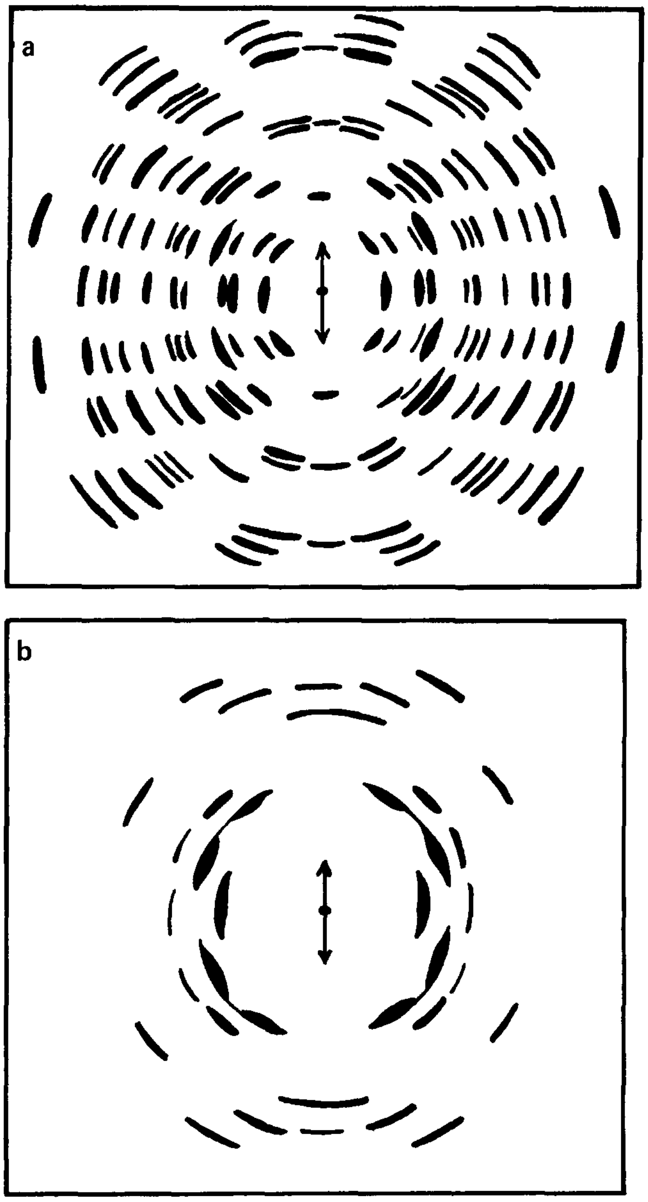

Figure 3 Fibre X-ray diffraction patterns from (a) the PEO–resorcinol molecular complex; (b) pure PEO–2–4 x 10^6

Figure 4 Micrograph of PEO with molecular weight 40 000. Magnification 25 000x

ments of sample deformation as a function of temperature under a constant load[5]. Also the usual procedures were used for thermogravimetric and calorimetric analyses[6].

RESULTS AND DISCUSSION

X-ray diffraction measurements

The X-ray diffraction pattern given in *Figure 3a* presents a monoclinic unit cell, a = 16.05 Å, b = 14.25 Å, c = 9.84 Å, β = 112°, space group $P2_1/a$, Z = 4. This implies that four MC chains pass through the plane *ab*; each chain contains four PEO units and two resorcinol molecules. The density, d_{calc} = 1.261 g cm^{-3}, found from these data somewhat exceeds the values measured pycnometrically for various MC samples: 1.244 g cm^{-3} for a pressed MC film with PEO-40 000, 1.236 g cm^{-3} for a drop of solidified MC melt with the same PEO-40 000 and 1.241 g cm^{-3} for the stretched MC film with PEO-2–4 x 10^6. The disagreement between the measured and calculated densities suggests that the MC, like any crystalline polymer, contains intercrystalline amorphous regions.

It is known that in the structure of pure PEO (a = 8.16 Å, b = 12.99 Å, c (the fibril axis) = 19.30 Å, β = 126.5°) the PEO molecule represents a 7_2 helix, i.e. the c-axis = 19.30 Å is matched with seven chain units describing two helix turns[7]. Consequently, the length of each unit is 2.76 Å, whereas in a planar zigzag it equals 3.5 Å.

In the MC structure the c-axis = 9.84 Å is matched with four PEO units, i.e. the length of each chain is equal to 2.46 Å. Hence it can be said that the formation of the MC has little effect on the PEO chain conformation: only insignificant contraction of the chain units due to hydrogen bonding takes place. Using the planar zigzag model, one can draw 'space-filled molecules' (*Figure 2b*) and then twist the two-component chain thus obtained into a helix; the resorcinol molecules will follow each other along the chain without any voids, i.e. a close packing of the ends of the resorcinol molecules will also occur. Incremental calculation[8,9] of the volume of such a complex molecule yields a fairly high molecular packing coefficient for the crystal, k = 0.73, (ignoring the approach of the groups due to hydrogen bonding).

Electron microscopy study

Figure 4 shows the electron micrographs of PEO-40 000 and observations on other molecular weights also reveal lamellar structures with thickness varying between 150 Å (PEO-2000) to 180 Å (PEO-40 000 and PEO 2–4 x 10^6). It is evident that the lamellae grow in various directions; with increasing molecular weight the number of crystallization centres seems to increase, and the length of the lamellae tends to shorten because of a faster collision with the other lamellae. For PEO-2000 and even for PEO-40 000 the growth of lamellae in the form of screw dislocations is not rare. The structure of PEO-40 000 (in a transmission microscope, magnification 1000x) represents plates composed of a great number of lamellae (*Figure 5*); similar plates were observed in the scanning microscope. The results of microscopic studies demonstrate that increasing molecular weight of PEO does not affect the plate-like structure although their size is smaller.

The structure of resorcinol (point 2 of the phase diagram) differs sharply from that of PEO (*Figure 6*): in the former rectangular-shaped crystals with the thickness up to 2–3 μm can be observed. The crystal faces are characterized by separate globular particles whose number grows drastically as the sample preparation temperature increases from −190°C to +20°C. The formation of globular particles is likely to occur as a result of resorcinol sublimation. The other micrographs, not presented here, show, along with large crystals, small well-faced resorcinol crystals.

Figure 7 shows the electron micrographs of the MC samples (point 3 of the phase diagram). It is seen here that the MC, like PEO, has a lamellar structure. The single-

Figure 5 Micrographs of the PEO-40 000 plates in a transmission electron microscope, magnification 15 000x

Figure 6 Micrograph of the resorcinol crystals, magnification 15 000x

Figure 7 Micrograph of the MC with REO-40 000 in a transmission electron microscope, magnification 25 000x

phase nature of the system with no resorcinol crystals is clearly observed. The preparation of MC samples with PEO-2–4 x 10^6 by pressing at a temperature over T_M and a pressure of 50 atm with subsequent slow cooling results in the formation, along with lamellar structures, of spherulites. This confirms a well-known concept of the effect of polymer production conditions on their supramolecular structure[10].

The structure of the system corresponding to point 4 of the phase diagram is shown in *Figure 8*. A two-phase nature of the system is distinct here; along with resorcinol crystals there are regions of a lamellar structure, which correspond to MC, as follows from the phase diagram; the interfaces between the resorcinol crystals and the MC lamellae are clearly defined.

Figure 9 shows the micrograph of the system corresponding to point 5 of the phase diagram, i.e. representing a mixture of the PEO and MC. The apparent single-phase nature of the micrograph is explained by a similar lamellar structure of both PEO and MC. It is important that at such a component ratio no resorcinol crystals appear, the whole of the resorcinol existing in the MC only.

Thermo-mechanical measurements

Thermo-mechanical curves (*Figure 10*) were obtained for three samples of pure PEO-2000, 40 000 and 2–4 x 10^6 (curves 1, 2 and 3) and three samples of the MC containing PEO of the same molecular weights (curves 4, 5 and 6 respectively). As can be seen from *Figure 10*, all the samples exhibit the transition from the solid crystalline to the viscous-flow state, without exhibiting the rubbery state even for the high molecular weight PEO. Curves 4, 5 and 6 characterizing the properties of the MC are shifted by 25–27°C relative to those for the pure PEO with the corresponding molecular weight. It is likely that the observed increase in the melting temperature can be attributed to a higher stiffness of the polymer chain. Such an explanation agrees with the 'envelopment' model suggested for the formation of the MC.

Calorimetric measurements conducted with the aid of a differential scanning microcalorimeter DSM-2 at a heating rate of 12.5 deg/min have made it possible to find the melting temperature and heat of fusion (Q): for PEO-2–4 x 10^6 $T_M = 62°C, Q = 44$ cal/g; for the MC (based on the same PEO) $T_M = 90°C, Q = 23$ cal/g. Note a lower value of the MC heat of fusion. As the MC is formed at the PEO/

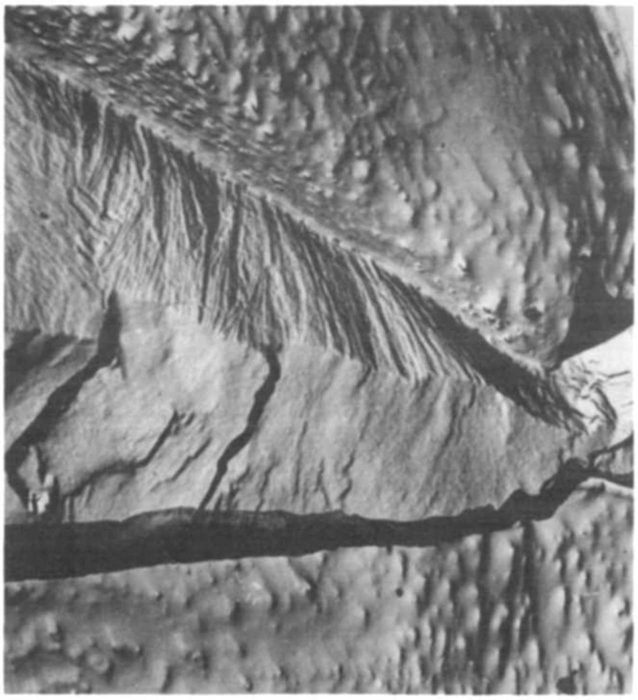

Figure 8 Micrograph of the mixture composed of the MC (with PEO-40 000) and resorcinol (point 4 of the phase diagram), magnification 20 000x

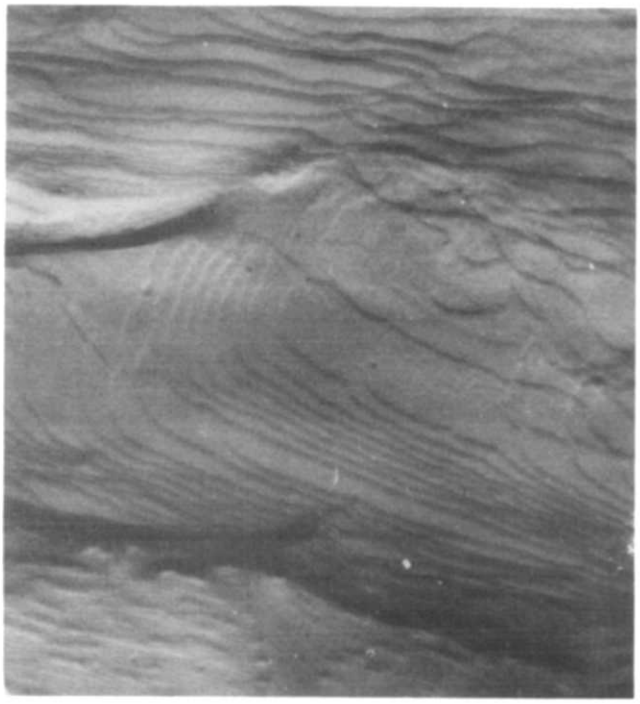

Figure 9 Micrograph of the mixture composed of the MC and PEO-40 000 (point 5 of the phase diagram), magnification 25 000x

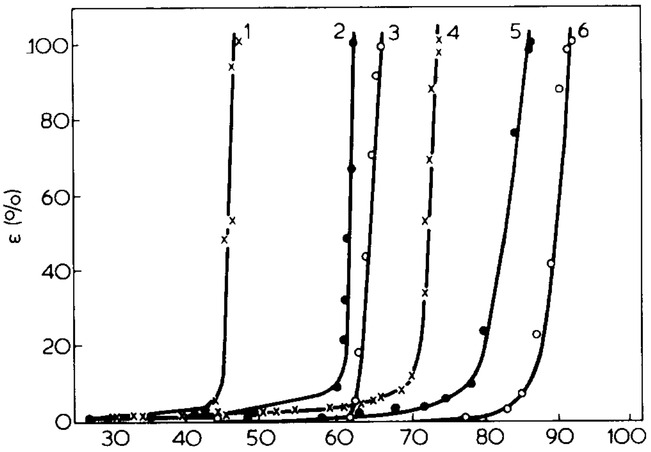

Figure 10 Thermomechanical curves for the PEO with various molecular weights (1, 2000; 2, 40 000; 3, 2–4 10^6) and MC (4, 5, 6) based on PEO with the same molecular weights respectively

resorcinol weight ratio 45/55%, then, by expressing the heat of fusion of pure PEO per 1 g of the MC, we obtain the value 44 x 0.45 = 20 cal/g which is close to that for the MC. It is known that on melting crystalline polymers the major factor responsible for the consumption of thermal energy is the change in macromolecule conformation rather than breakdown of intermolecular van der Waals bonds. Therefore the results obtained may lead to the conclusion that resorcinol produces little effect on the PEO molecule conformation in the formation of the complex.

Thermogravimetric analysis of the MC based on a high molecular weight PEO which was performed by using an apparatus UVDT-1-500 at 1 x 10^{-1} mmHg and a heating rate of 5 deg/min indicates (*Figure 11*) that at a temperature over 40°C the sublimation of resorcinol occurs and is complete at 120°C. It should be noted that at the MC melting temperature (90°C) the sample has lost as little as 20% of resorcinol which seems to point to the presence of hydrogen bonding between the molecules of PEO and resorcinol.

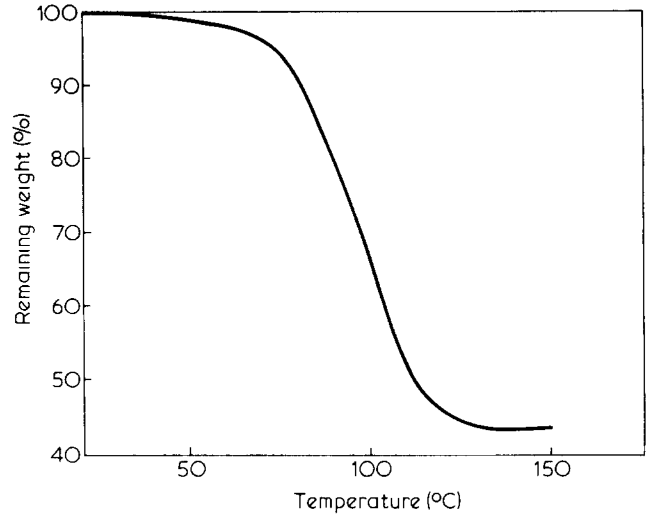

Figure 11 Thermogravimetric curve at 1 x 10^{-1} mmHg at a heating rate of 5 deg/min

CONCLUSION

A comprehensive study of the processes of formation, structure and properties of the 2:1 poly(ethylene oxide)–resorcinol complex has provided support for the mechanism by which resorcinol molecules 'envelope' PEO molecules. In this case the formation of hydrogen bonding is accompanied by a close packing of the molecules of two types without any substantial change in the polymer chain conformation.

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