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Phase behaviour and structure formation in solutions of poly(2,6-dimethyl-1,4-phenylene ether)

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The phase behaviour and the structure formation of solutions of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) in cyclohexanol and decalin have been studied. Interesting structures were formed and the morphologies depended on the rate at which the solutions were cooled. This was caused by the competition between melting–crystallization, vitrification and phase separation. Differential scanning electron microscopy (SEM) was used to study the different morphologies. Porous materials can be used as membranes. Hollow porous PPE fibres were spun.

(Keywords: PPE; phase behaviour; membranes)

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is a crystallizable polymer that is difficult to crystallize from the melt[1]. The narrow temperature gap between the melting point and the glass transition limits the crystallizability very strongly. The presence of low molecular mass substances can, however, promote this supramolecular structure formation and many examples have been reported in the literature[2–8]. These investigations mostly deal with the behaviour of PPE in good solvents. When the solvent quality decreases, the behaviour becomes more complex and liquid–liquid demixing can take place on cooling[4,5,9–11]. It has been shown that liquid–liquid demixing, in combination with crystallization or vitrification, can lead to the formation of interesting porous materials[12–23].

In order to study the possibility of using this technique for the preparation of porous PPE materials, a detailed investigation of the phase behaviour of this polymer in two solvents of different quality, cyclohexanol and decalin, was carried out. Both solvents are poor solvents for polystyrene, a polymer compatible with PPE, but their solvent quality for PPE is not known. The phase behaviour of PPE in these solvents will be studied in order to determine the structures that are formed during the processing of these solutions.

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EXPERIMENTAL

Solutions of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) in cyclohexanol were analysed by differential scanning calorimetry (d.s.c.). PPE solutions of two different molecular masses were used: a low molecular mass of $30 \times 10^3\,g\,mol^{-1}$ (PPE1) and a high molecular mass of $350 \times 10^3\,g\,mol^{-1}$ (PPE2). Cyclohexanol had a purity of 98% (Jansen) and was used without further purification. Samples with polymer concentrations between 0.01 and 1.00 wt% (expressed as polymer mass fraction w_2) were used. It was possible to prepare solutions of low concentration ($w_2 < 0.30$ for PPE1 and $w_2 < 0.2$ for PPE2) by mixing and heating polymer powder and solvent in a glass tube at 150°C. The homogeneous solutions were poured into d.s.c. sample pans. Higher concentrations were prepared by evaporating the solvent from sample pans until the desired concentration was reached. The pans were sealed and homogenized.

Visual observations were performed as follows: solutions ($w_2 < 0.2$) were heated in a glass tube until they became homogeneous and subsequently cooled slowly ($2.5°C\,min^{-1}$) in an oil bath until they became turbid. The temperature at which turbidity sets in is recorded as the cloud point temperature. Morphological observations were carried out with samples cooled at $2.5°C\,min^{-1}$ to room temperature. The solvent was removed by washing the material in isopropanol, the dried samples were broken in liquid nitrogen and the

morphology was analysed by scanning electron microscopy (SEM). The morphologies formed at high cooling rates were analysed by pouring homogeneous solutions (at 150°C) onto a glass plate at room temperature, then the solvent was removed with isopropanol and the morphology was analysed by SEM.

Hollow porous fibres were spun from solutions of PPE2 in cyclohexanol ($w_2 = 0.2$) prepared in a Berstorff ZE 25 co-rotating twin screw extruder. The temperature of mixing was 150°C. The spinneret was designed by KRI TNO in Delft to produce hollow fibres. The fibres were spun in the open air (dry spinning). The solvent was washed out with isopropanol and the fibres were broken in liquid nitrogen and analysed by SEM.

RESULTS

Visual observations

PPE–cyclohexanol mixtures. The influence of the cooling rate on the resulting morphology was investigated. When solutions of PPE1 and PPE2 in cyclohexanol are cooled slowly (2.5°C min^{-1}) from 150°C to room temperature, turbidity develops in a non-uniform way. Nuclei are formed somewhere in the solution and these nuclei continue to grow until the solution as a whole is turbid. This nucleation-controlled development of turbidity cannot be ascribed to liquid–liquid demixing. A cloud point temperature is nevertheless recorded and corresponds with the temperature at which the first nuclei are formed. On heating, this turbidity disappears at temperatures far above its formation temperature on cooling. The observation of this important degree of undercooling is characteristic for a nucleation-controlled phenomenon such as crystallization and certainly not for liquid–liquid demixing.

When a solution of polymer mass fraction 0.20 is cooled in this way and cyclohexanol is eliminated by washing with isopropanol, a morphology like the one represented in *Figure 1* is observed. An agglomerate of spherical particles, apparently composed of densely packed lamellae, can be seen.

When homogeneous solutions are cooled fast, the system turns opaque almost instantaneously and becomes hard when the polymer concentration exceeds a weight fraction of 0.10. A completely different structure is observed (see *Figure 2*). Porous structures are formed, very similar to those obtained with the system atactic poly(methyl methacrylate)/butanol[24]. For concentrations $w_2 = 0.15$ and 0.20 the structure is very open. At higher concentration ($w_2 = 0.30$), a closed cellular foam is obtained. The use of a high molecular mass sample does not influence the overall shape of the morphology (compare *Figure 2b* and *d*). In order to study the nature of the phase transition that causes these two different morphologies to be formed, d.s.c. experiments were performed.

PPE–decalin mixtures. When solutions of PPE in decalin are cooled slowly turbidity also develops in a non-uniform way. Fast cooling, however, does not produce porous structures. In this system apparently no liquid–liquid phase separation occurs but only a nucleation-controlled phenomenon, like crystallization.

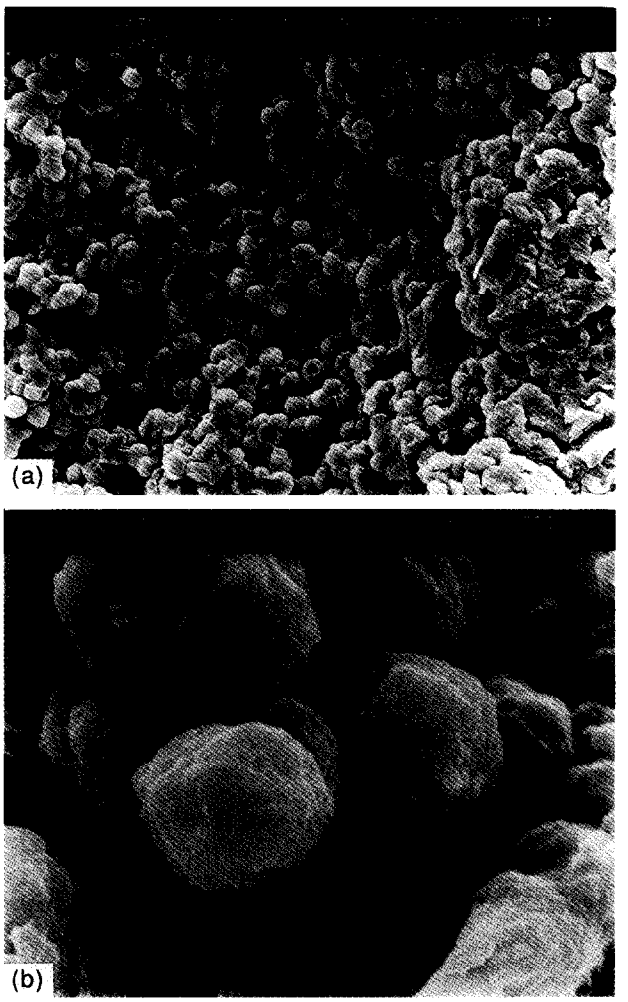

Figure 1 Morphology obtained with a solution of PPE2 in cyclohexanol ($w_2 = 0.20$), cooled at 2.5°C min^{-1}, (a) and (b): different magnifications

Calorimetric investigations

PPE–cyclohexanol mixtures. Cooling a solution of PPE1 with $w_2 < 0.70$ and PPE2 with $w_2 < 0.60$ at a low cooling rate (<2.0°C min^{-1}) results in the formation of a crystalline phases, as can be deduced from the appearance of an exotherm in the d.s.c. curve (see *Figure 3*, curve (a)). When these solutions are heated in the d.s.c. at 10°C min^{-1}, a melting endotherm, caused by the melting of the crystalline structure, is observed. A typical d.s.c. scan is shown in *Figure 3*, curve (b). These observations are consistent with the optical observations.

This crystallization can be suppressed by quenching the sample to room temperature. When these samples are heated in the d.s.c., a glass transition followed by crystallization is observed (*Figure 3*, curve (c)). This T_g occurs at a temperature that is much higher than would be expected from a normal T_g–solvent concentration relationship. This calorimetric observation also illustrates the high rate of crystallization of PPE in the presence of a solvent. The sample crystallizes close to its T_g (compare *Figure 3*, curve (a) and curve (c)). Melting of the crystalline phase takes place at a higher temperature and this has to be expected as crystallization on cooling sets in at much higher temperatures.

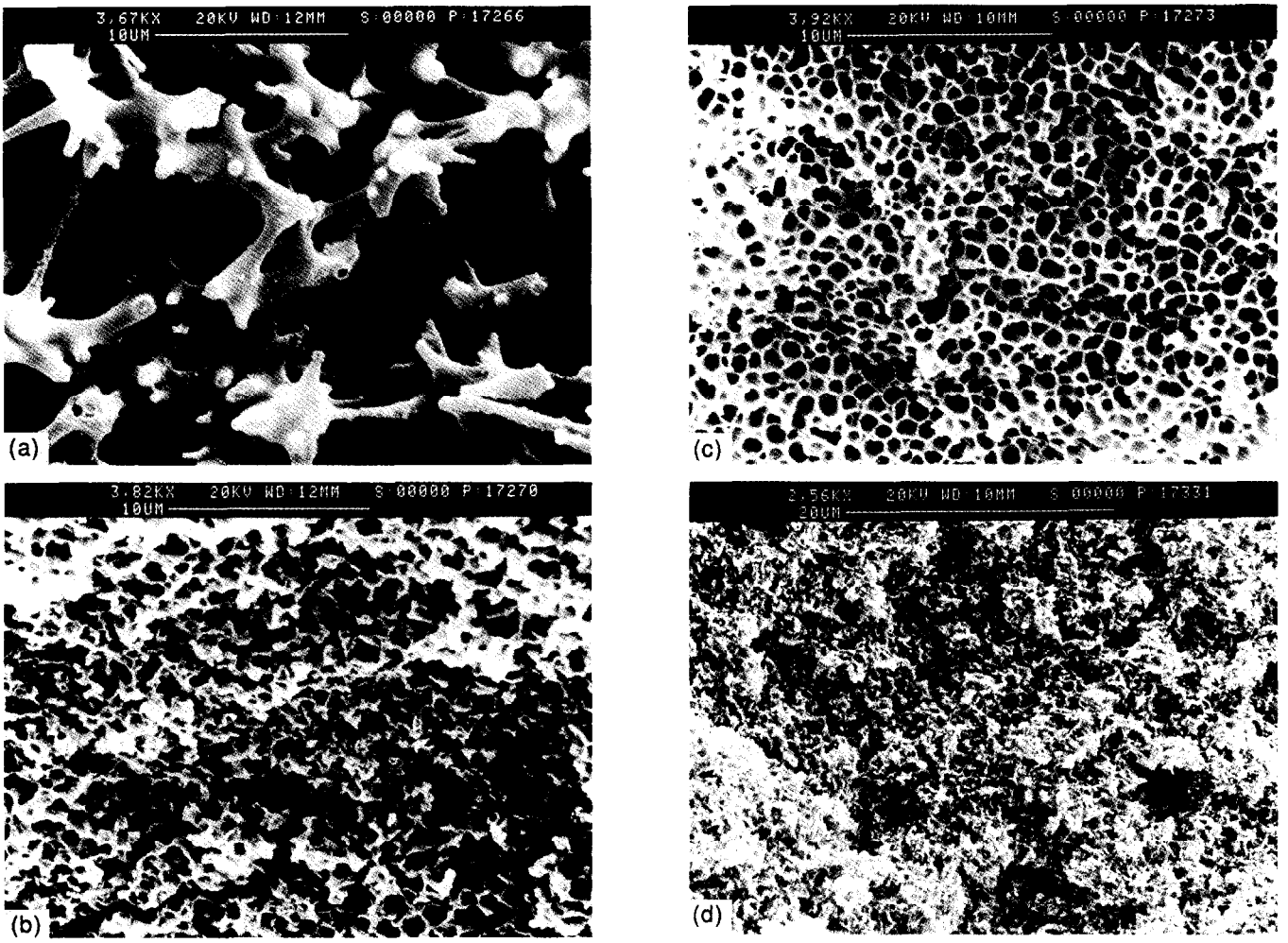

Figure 2 Morphology obtained with solutions of PPE in cyclohexanol cooled at a high rate and different w_2: PPE1 = (a) 0.15, (b) 0.20 and (c) 0.30; (d) PPE2 = 0.20

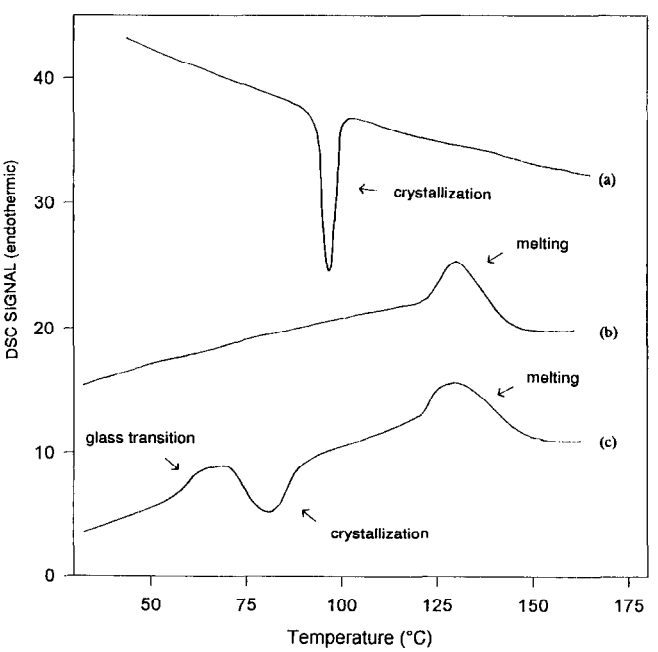

Figure 3 (a) D.s.c. cooling exotherm at a cooling rate of 5°C min^{-1}; (b) d.s.c. heating endotherm after cooling at a rate < 20°C min^{-1}; heating rate = 10°C min^{-1}; (c) d.s.c. heating endotherm after cooling at a rate >20°C min^{-1}, heating rate = 10°C min^{-1}; PPE in cyclohexanol ($w_2 = 0.20$)

No crystallization exotherm can be observed at $w_2 > 0.70$ for PPE1 and $w_2 > 0.60$ for PPE2 and only a glass transition is observed upon cooling. When the sample is heated a small melting endotherm is observed. The formation of the corresponding crystalline phase cannot be detected by d.s.c.

The heating and cooling rates used in these dynamic experiments have a pronounced effect on the melting and crystallization behaviour. *Figure 4* shows the influence of heating and cooling rates on the melting and crystallization temperatures of a solution of PPE2 ($w_2 = 0.30$) in cyclohexanol. The melting temperature decreases with decreasing heating rate and extrapolates to 142°C at zero scanning rate. For cooling, the opposite is found and increases to a crystallization temperature of 115°C at zero cooling rate. When the cooling rate is too high (40°C min^{-1}) crystallization no longer takes place and a glass transition is measured.

Figure 5 shows the important influence of the concentration on the melting enthalpy for PPE1 and PPE2. The enthalpy is calculated per gram of polymer. The enthalpies increase with decreasing polymer concentration.

PPE–decalin mixtures. Solutions of PPE1 in decalin show an endotherm upon heating and an exotherm

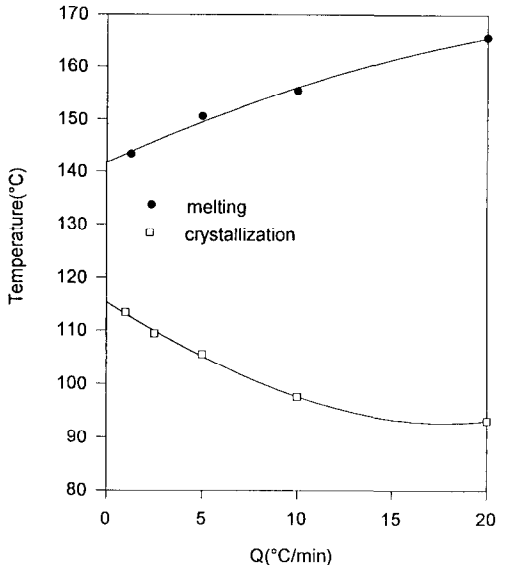

Figure 4 Influence of heating and cooling rate (Q, °C min^{-1}) on the melting and crystallization temperature of PPE2 in cyclohexanol ($w_2 = 0.30$)

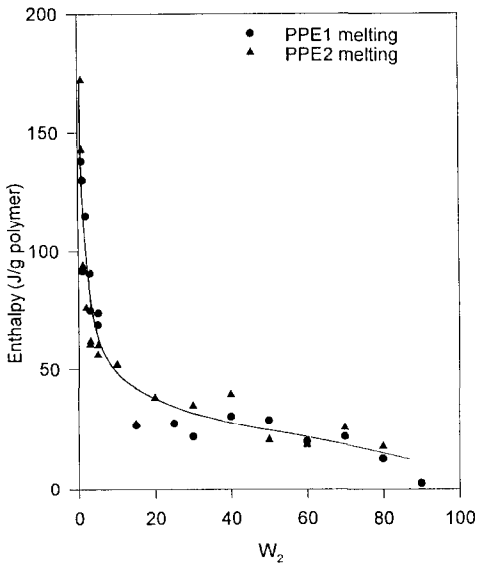

Figure 5 Influence of the concentration on melting enthalpy for PPE1- and PPE2-cyclohexanol solutions

upon cooling. At higher concentrations ($w_2 > 0.70$) the solutions no longer crystallize but only show a glass transition upon cooling. No glass transition is observed for solutions with $w_2 < 0.70$. The influence of the concentration on the melting enthalpy is shown in *Figure 6*. In this case the enthalpy is relatively independent of concentration.

Construction of the phase diagrams

Temperature–concentration diagrams were constructed by plotting the melting point of the polymer as a function of w_2. The temperature at the end of the melting endotherm has to be taken as the melting point for a system composed of two constituents: a polymer with a molecular mass distribution and a solvent. The crystallization temperature is also reported in these phase diagrams. This temperature corresponds to the temperature at the onset of the crystallization exotherm.

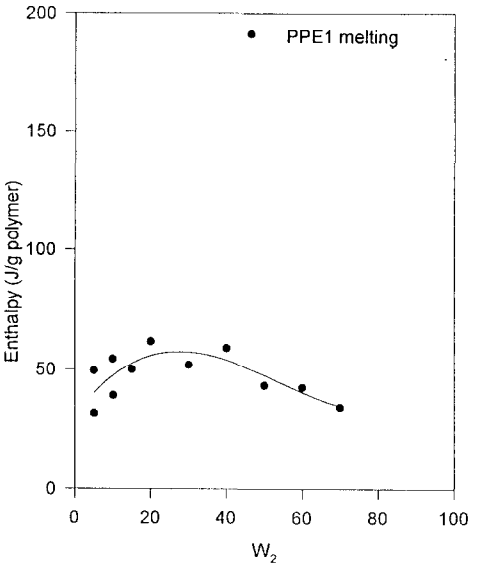

Figure 6 Influence of the concentration on melting enthalpy for PPE1–decalin solutions

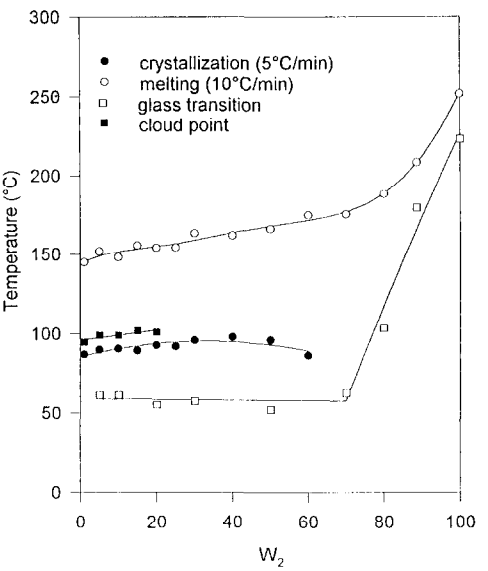

Figure 7 Temperature–concentration diagram of PPE1 in cyclohexanol

The concentration dependence of the glass transition is also included. The T_g values at low concentration are only obtained with quenched samples. The cloud point temperature is also reported in these phase diagrams. No corrections were made for the dynamic character of the experiments and the non-equilibrium nature of the experimental data.

PPE–cyclohexanol mixtures. The phase diagram of PPE–cyclohexanol mixtures is represented in *Figure 7* for the low molecular mass and in *Figure 8* for the high molecular mass. The diagrams are very similar. The melting temperature (measured at 10°C min^{-1}) decreases with increasing solvent concentration and levels off at a concentration w_2 of about 0.40. The crystallization temperature (measured at 5°C min^{-1}) does not change much with increasing solvent concentration. This temperature cannot be reported for mixtures with a concentration w_2 above 0.60 as they do not show a crystallization endotherm on cooling. A melting

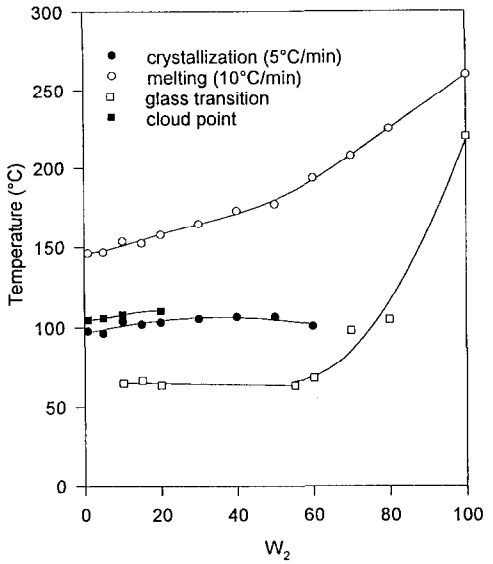

Figure 8 Temperature–concentration diagram of PPE2 in cyclohexanol

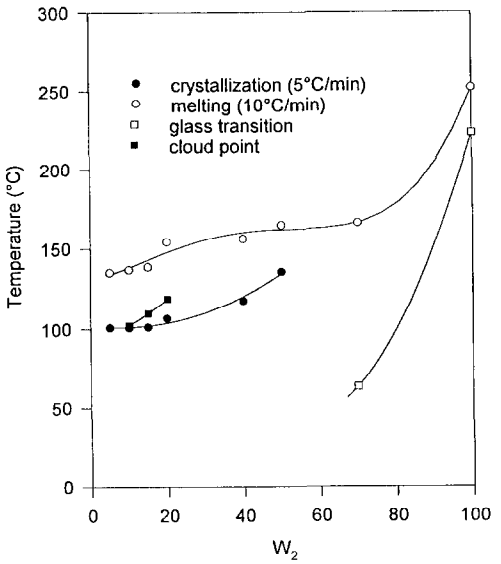

Figure 9 Temperature–concentration diagram of PPE1 in decalin

point can be reported up to high polymer concentrations. The glass transition temperature also decreases with increasing solvent concentration and becomes constant for w_2 below 0.60 for the high molecular mass and 0.70 for the low molecular mass. This constant part of the T_g–concentration line is only measured for quenched samples. The cloud point temperature is situated just above the crystallization temperature.

PPE–decalin mixtures. Figure 9 shows the temperature–concentration diagram of solutions of PPE1 in decalin. The melting temperature also increases with increasing concentration, and the crystallization temperature stays relatively constant. The glass transition temperature decreases with decreasing concentration.

DISCUSSION

The phase behaviour of the system PPE–cyclohexanol is complex and different thermal transitions interfere. The behaviour differs from what is observed with most other polymers. The temperature domains in which crystallization and vitrification normally take place are generally far apart on the temperature scale. Crystallization usually proceeds at much higher temperatures than the glass transition. The difference becomes even more pronounced when solvents are added[22]. Consequently, liquid–liquid demixing only interferes with crystallization[12,23,25]. Interference of T_g with liquid–liquid demixing only takes place if the sample does not crystallize.

Because of the small difference between glass transition and the melting point of PPE, both crystallization and glass transition can interfere with liquid–liquid demixing. Therefore the three transitions take place in the same temperature region in the system PPE–cyclohexanol and the behaviour is strongly influenced by the experimental conditions. Slow cooling of moderately concentrated solutions results in a fast crystallization of the polymer. The concentration dependence of the melting point is characteristic for the melting of a polymer in a poor solvent and corresponds to what can be expected from theoretical considerations[26]. At polymer concentrations above 0.60 or 0.70, depending on the molecular mass, no crystallization can be observed any more and the sample vitrifies upon cooling. The T_g–w_2 relationship has the expected shape.

Faster cooling leads to liquid–liquid (L–L) demixing. This is reflected in the concentration dependence of T_g. This transition temperature is invariant for $w_2 < 0.60$ in the case of PPE2, and slightly increases with decreasing polymer concentration for $w_2 < 0.70$ when PPE1 is used. A concentration dependence of T_g in a L–L demixing domain was explained by the influence of the molecular mass distribution[24]. These data show that the average value of this molecular mass must also be taken into consideration. A variant T_g is obtained with a low average molecular mass, while an invariant T_g is observed with a higher average value. This specific concentration dependence of T_g, together with the resulting morphology, are the only experimental facts that support the occurrence of L–L demixing at high cooling rates. Opalescence measurements cannot be used as they have to be performed at low scanning rates. Under these conditions, crystallization will set in and L–L demixing will not take place. The absence of L–L demixing in this case is supported by the absence of a T_g signal at around 70°C.

The occurrence of a demixing domain in the vicinity of the crystallization temperature of PPE also has a pronounced influence on the crystallization of the polymer. Crystallization takes place at a much higher rate than in the melt. Exothermic signals are observed in the d.s.c. at scanning rates $< 20°C\,min^{-1}$, and this cannot be realized with the pure polymer. This influence can be observed even at low scanning rates, when crystallization precedes and prevents L–L demixing. The close vicinity of the demixing domain will induce concentration fluctuations in the solution and these fluctuations will trigger the crystallization by lowering the nucleation energy barrier[27].

From these observations one can infer the existence of a metastable liquid–liquid demixing domain, situated below the crystallization–melting transition. This is represented schematically in *Figure 10*. Fast cooling of

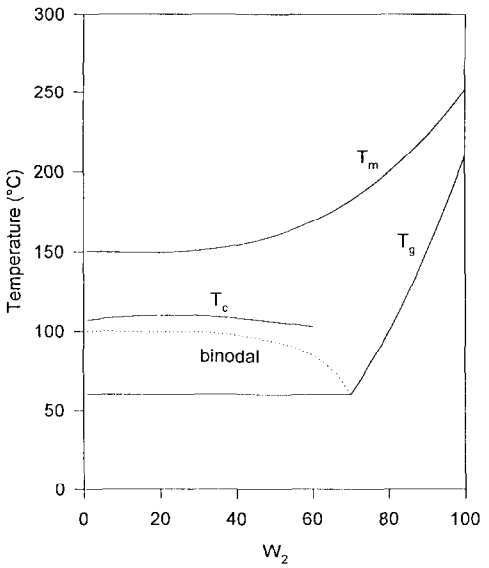

Figure 10 Schematic representation of the temperature–concentration diagram of PPE in cyclohexanol

the solutions will therefore suppress the nucleation-controlled crystallization and bring the solution into the metastable demixing region. Liquid–liquid demixing will take place and this demixing is faster than crystallization so that it will precede crystallization. If the sample is quickly cooled to room temperature, crystallization will be completely suppressed and an amorphous, glassy, demixed system will be obtained. An important consequence is the constancy of T_g in the concentration region of demixing or its slight increase with overall polymer concentration. Demixing is expected to be followed by crystallization at intermediate cooling rates. This vicinity of L–L demixing also has an influence on the overall crystallinity of PPE. The melting enthalpy of the crystalline polymer at low polymer concentrations increases by a factor of 5 for the high molecular mass sample and 10 for the low molecular mass sample. No explanation was found up to now for this peculiar behaviour.

Confirmation of the influence of demixing on crystallization was found in the behaviour of the system PPE–decalin. Only melting and crystallization are observed to take place and the glass transition shows its monotonous decrease with increasing solvent content. The melting enthalpy can be considered constant, within experimental error. The different concentration dependence indicates the different mechanism of crystallization for a system in which no liquid–liquid demixing takes place.

HOLLOW FIBRE MEMBRANES

Demixing induced by a cooling of a polymer solution cannot only be used to produce porous membrane-like structures. Processing of these solutions by extrusion allows the formation of porous fibres[24]. In this paper the thermal quenching technique was used to produce hollow porous PPE fibres as an alternative to the conventional route where a polymer, solvent and non-solvent mixture is contacted with a non-solvent in order to induce phase separation[28].

A solution of $w_2 = 0.20$ PPE2 in cyclohexanol was used to spin hollow porous fibres. PPE is dissolved in cyclohexanol using a co-rotating twin screw extruder at 150°C. After temperature quenching the fibre is washed out in isopropanol, dried, broken in liquid nitrogen and analysed by SEM. The result is shown in *Figure 11*. The fibre has a uniform structure across the wall although it is completely closed. The shape of the wall is rather irregular and this probably is an effect of shrinkage or a flow irregularity.

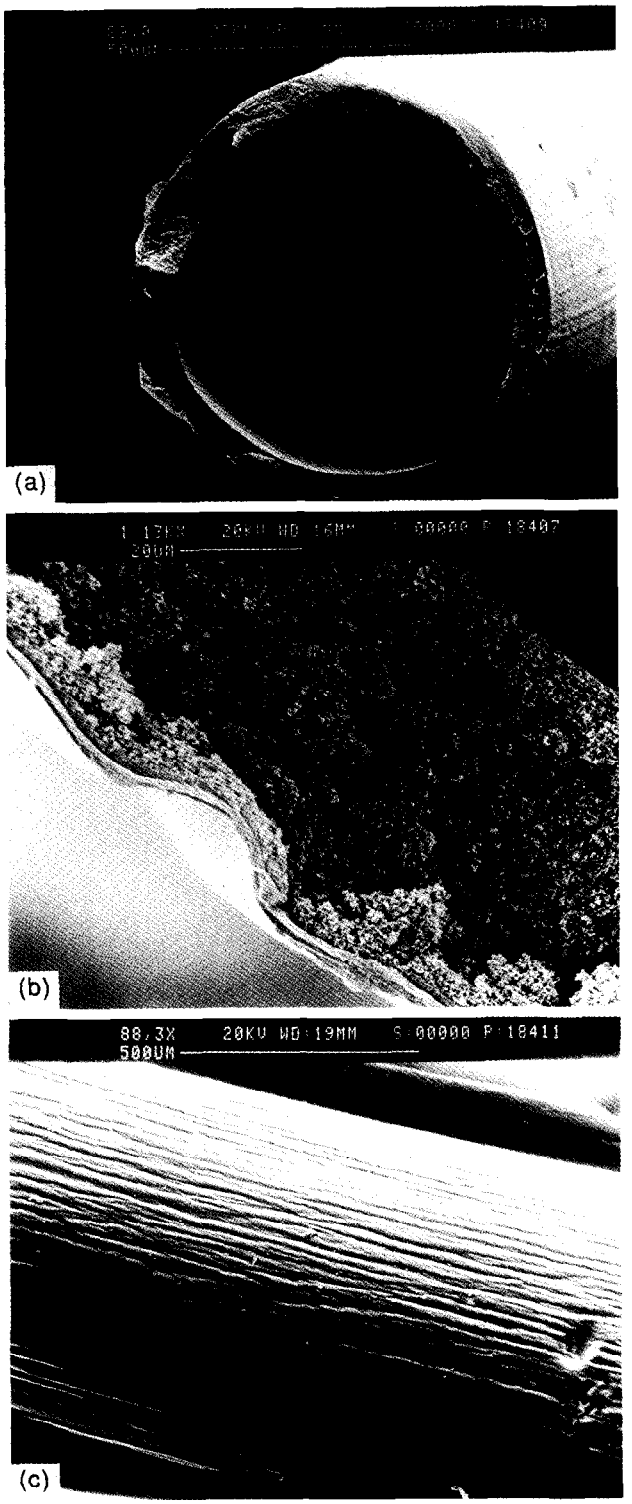

Figure 11 Hollow porous fibre made of a PPE2–cyclohexanol solution ($w_2 = 0.20$). (a) Cross-section; (b) detail of the cross-section; (c) outer skin of the fibre

CONCLUSIONS

Solutions of PPE in cyclohexanol are able to crystallize as well as phase separate, depending on the rate at which they are cooled. Cooling at a low rate ($>20°C\,min^{-1}$) makes the solution crystallize. Cooling at a high rate makes the solution separate into two phases, resulting in a porous material. This can be used to produce membranes. Hollow fibres were spun with this solution and this resulted in the formation of hollow porous fibres with a dense outer skin.

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