JOURNAL OF MATERIALS SCIENCE 8 (1973) 1495–1504

Polymers with phenylene groups in the main chain: the effect of solvent on the formation of crystalline entities

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The effect of solvents and mixed solvents on the formation of crystalline entities in polycarbonate, polysulphone, polyphenylene oxide and a phenoxy resin has been investigated. It is shown that by the correct choice of solvent or mixed solvent many crystalline entities previously observed in other polymers can be formed. It appears that despite increased difficulty in assuming folded structures these polymers attempt to crystallize in a manner similar to simpler ones.

1. Introduction

Previous work has shown that polycarbonate can readily be induced to crystallize and that polysulphone can be made to produce occasional crystalline entities under similar conditions [1, 2]. Most films produced either by spreading at temperatures above the glass transition or by deposition from solvent are mainly amorphous, these, if under stress, will produce spherulitic structures on treatment with very poor solvents such as acetone and xylene. A possible explanation of the tardiness of these polymers to crystallize from good solvents is the inability of the molecules, owing to chain bulkiness and partially restricted rotation, to assume folded structures in the time between the first formation of a film and its becoming completely dried out. If this was so, then film formation in the presence of a poor solvent of suitable boiling point could lead to the formation of a film which was plasticized by the poor solvent, and remained so, long enough to permit chain folded crystals to form.

A suitable system to encourage crystalline formation was considered to be a dilute solution of polymer in a good solvent diluted with the poor solvent until the polymer was just about to precipitate. Such polymer solutions in mixed solvents were made up and poured into petri dishes, containing microscope slides, and films allowed to form on the slides by relatively slow evaporation to dryness. The films were then examined and compared with those formed from polymer solutions in pure good solvents.

2. Experimental

2.1. Polymeric materials

Good quality commercial material in the form of granules for injection moulding was used (not specially dried).

Polycarbonate (PC)

The polycarbonic ester of 2,2-*bis*(4-hydroxyphenyl)propane. The grade used was Makrolon 3000W.

Polysulphone (PS)

This is the polycondensation product of 2,2,*bis*-(4-hydroxyphenyl)propane with 4,4′ dichlorodiphenyl sulphoxide manufactured by Union Carbide (Grade PL 1700).

Polyphenylene oxide (PPO)

The material used was poly(2,6-dimethyl-1,4-phenylene oxide), grade PL 500 CT 1002, also manufactured by Union Carbide.

Phenoxy-Resin (PR)

The material was a copolymer of bisphenol A with epichlorohydrin manufactured by Union Carbide (grade Bakelite 8060).

2.2. Liquids

The best available laboratory reagents were used in all cases. They were not specially dried.

2.3. Film preparation

Approximately 0.01 g cm^{-3} solutions of polymer were made up in either chloroform or dichloromethane. When solutions of polymer in mixed solvents were required they were prepared as follows: to a known volume of chloroform or dichloromethane solution an equal volume of another liquid was added slowly with stirring either until an equal volume had been added or until the polymer was just about to precipitate, whichever volume was the less. The following solvent systems were used with each polymer: chloroform or dichloromethane, and each of these admixed with acetone, benzene, xylene or carbon tetrachloride. The polymer solutions were then poured into petri dishes containing microscope slides and cover glasses on which the film of polymer deposited as the solvent evaporated. Film formation took between 4 and 14 days depending on temperature, boiling point of the solvent etc. When the films were quite dry the microscope slides and cover glasses were removed and the films on them examined with the microscope using ordinary illumination, polarized light or phase contrast techniques. In this way films were obtained at all stages of the evaporation; in general the morphologies were similar.

2.4. Melting points

Careful observation of the behaviour on heating of all the entities obtained in films, were made and the melting points determined.

3. Results

The results are summarized in Table I.

3.1. Morphology

3.1.1. General

Rapid evaporation of solvent (in a few minutes) always produced completely amorphous film. Slow evaporation (several hours or days) gave films which were in the main amorphous, but in certain cases the following crystal types in varying amounts were observed. Polycarbonate was an exception since it always gave more crystal entities and was often largely crystalline even on rapid evaporation.

Spherulites. These were normally negative – either perfect or more or less deformed – but were only considered as spherulites when a clear Maltese cross was observed. Globular spherulites were seen in some preparations; usually a Maltese cross could be made out but the spherical nature of the crystal entity often rendered it indistinct.

Sheaf structures were in general commoner than spherulites. The term was also applied to

TABLE I Quality and crystal morphology of polymer films cast from chloroform, dichloromethane, and binary mixed solvents

Solvent	Film quality				Crystal morphology												
	PC	PS	PR	PPO	PC				PS				PR				PPO
$CHCl_3$	G	G	G	B	S												X
$CHCl_3$/acetone	P	G	G	None	S	Sh			S	Sh							
$CHCl_3$/benzene	G	G	G	B	S	Sh	X		S*				S	Sh	X		X
$CHCl_3$/xylene	W	G	F	B		Sh*	X			Sh	X	R	S	Sh	X		X
$CHCl_3/CCl_4$	W	W	F	B		Sh*				Sh			S				X
CH_2Cl_2	F	G	G	B	S						X						X
CH_2Cl_2/acetone	P	F	G	None	Sg						X						
CH_2Cl_2/benzene	F	G	F	W	Sg	Sh*	X		S*		X		S				X
CH_2Cl_2/xylene	W	G	G	B			X		S*		X			Sh		R	
CH_2Cl_2/CCl_4	W	W	W	B-W		Sh		R	S	Sh							X

Film type
G = good tough film (similar to a melt-cast one)
F = fair film, coherent but weaker than G
W = weak film tears easily
P = hardly a film very powdery and collapses readily
B = brittle

Crystal types
S = normal spherulites
Sg = globular spherulites
Sh = sheaf structures
R = oblong crystals (very narrow)
X = very small crystals usually present in aggregates
* = structures incomplete or deformed

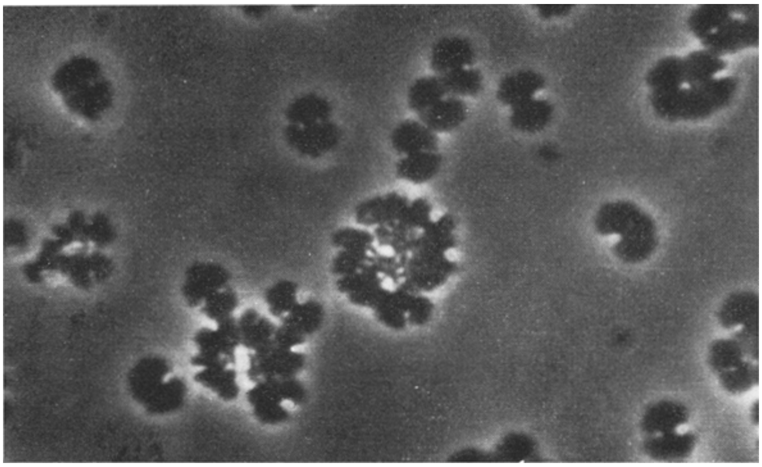

Figure 1 Polycarbonate. Sheaves in film cast from chloroform/acetone solution. Phase contrast (× 1500).

entities which appeared to be more a crystal cross than an obvious sheaf. These structures are presumably the progenitors of spherulites.

Oblongs. A number of oblong crystals was observed. They were not common and appeared to be similar to crystal types already reported [2].

Crystals. A number of crystal entities which could not be definitely assigned to any of the above was also formed. They were circular, lozenge shaped, or cylindrical and usually occurred as an agglomerate although individual entities could be distinguished. They were often ill-formed but could comprise the main form over an area.

The results are summarized in Table I and amplified as necessary in the following paragraphs.

All the films prepared from solutions containing benzene or xylene with the exception of PPO contained sheaf-like structures as illustrated for polysulphone (Fig. 8) but only rarely.

3.1.2. Polycarbonate

Film from chloroform was either largely amorphous with areas containing spherulites and occasional rhombohedral crystals as previously described [1, 2], or 60 to 90% spherulitic. Addition of other liquids in general reduced the area of spherulites and led to the formation of less perfect crystal structures. The most prominent of these were sheaves which showed every possible combination from single to multiple structures where the crystals overlap and interlace so that the sheaving can hardly be detected. With acetone the sheaves were well formed (Fig. 1). Benzene produced larger and less well formed ones (Fig. 2). Xylene (Fig. 3) and carbon tetrachloride (Fig. 4) produced very ill-formed sheaves in large quantities.

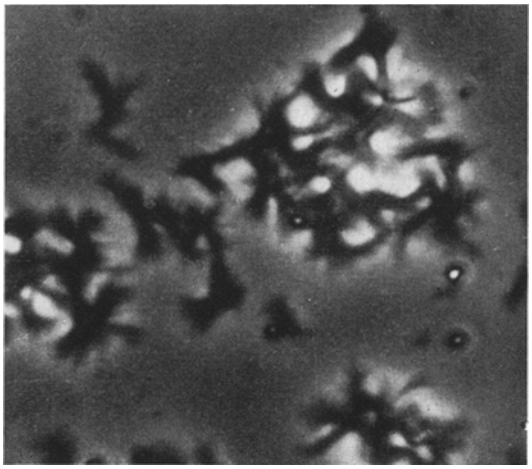

Figure 2 Polycarbonate. Interlaced sheaves in film cast from chloroform/benzene solution. Phase contrast (× 1500).

Dichloromethane gave a film in which spherulites were distributed in patches throughout giving 50% of crystal areas embedded in amorphous material. Within the crystal areas, between 60 and 90% was occupied by negative spherulites (Fig. 5); the rest was amorphous. Very occasionally several areas in the same film contained a number of positive spherulites (Fig. 6) the occurrence of which has not previously

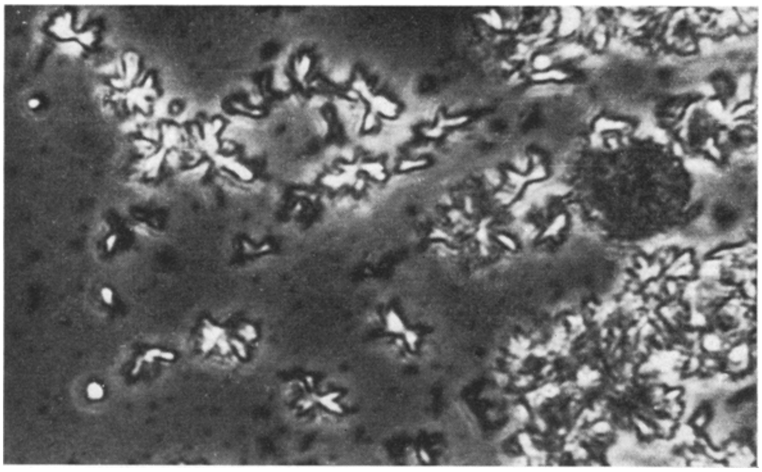

Figure 3 Polycarbonate. Crystalline entities in film cast from chloroform/carbon tetrachloride solution. Phase contrast (× 1500).

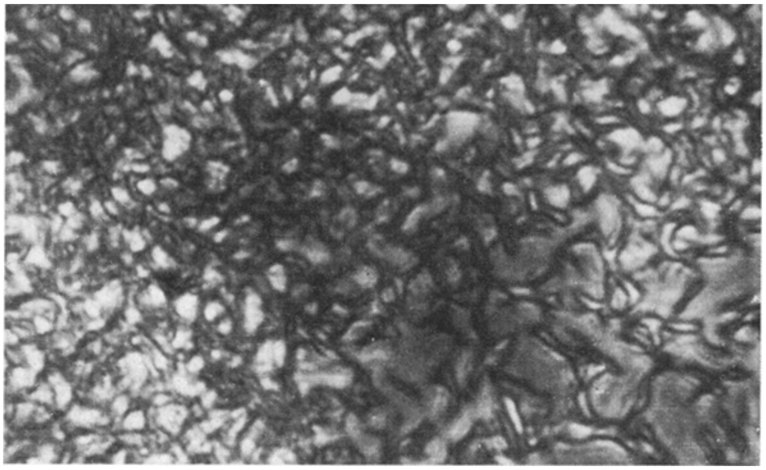

Figure 4 polycarbonate film cast from chloroform/xylene solution. Phase contrast (× 1500).

been reported for this polymer. Ringed spherulites (Fig. 7) and spherulites in which the Maltese cross has a zig-zag configuration only previously reported for polyethylene [3, 4] have also been produced by this technique.

The films from mixed solvents containing dichloromethane were very weak, exceedingly powdery and in most cases could hardly be considered as films since they could only just hold their own weight. All the structures previously described were observed, but generally globular spherulites were by far the commonest.

3.1.3. Polysulphone

Except in one case this polymer gave mainly amorphous films (98%) in all conditions but usually the films contained a few of the entities already described. Film from the solution diluted with benzene showed a few instances of shrinkage patterns such as have already been reported for PC [5, 6].

The polysulphone film prepared from dichloromethane/carbon tetrachloride was unique in showing an approximately even distribution (10 to 25% of the surface area) of spherulites and sheaf structures (Fig. 8). The sheaf structures in this preparation often appeared to nucleate at crazes or crack lines, as also did crystal growths corresponding to line nucleation well known in polyethylene [7, 8] and similar

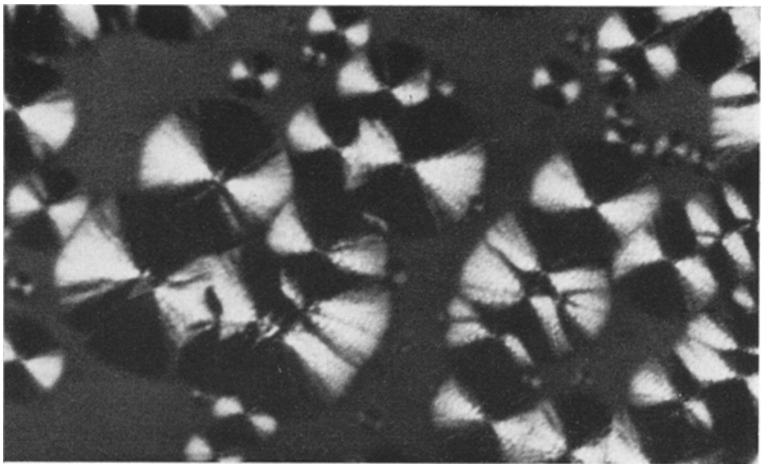

Figure 5 Negative polycarbonate spherulites in film cast from dichloromethane. Crossed polaroids plus tint plate (× 700).

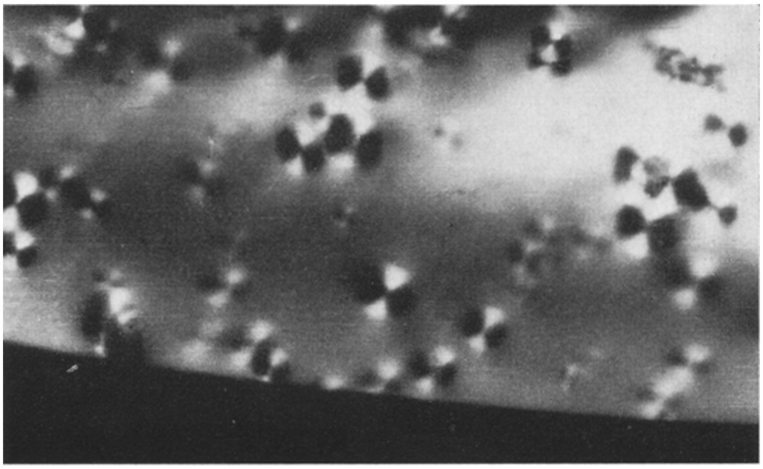

Figure 6 Positive polycarbonate spherulites in film cast from dichloromethane. Crossed polaroids plus tint plate (× 350).

polymers (Fig. 9).

3.1.4. Phenoxy resin

Films of PR, even those which contained some crystalline entities, were very largely (95%) amorphous except for small areas in which the crystals occupied up to 20% of the surface; these areas were often adjacent to the edges of the surfaces, on which the films were cast.

The main morphological features were observed in film cast from admixtures of benzene or xylene with chloroform or dichloromethane, which all contained spherulites, sheaves, oblong crystals and axialites, those in the films from solution containing chloroform being more prolific and better formed. Spherulites in film cast from chloroform/benzene were small, smooth and particularly well formed; the typical structure is shown under polarized light with crossed polars (Fig. 10a) but with phase contrast (Fig. 10b) reveals an outer non-birefringent ring in which material is being ordered into the spherulite structure: only the centre smooth portion shows birefringence and a Maltese cross under polarized light with crossed polars. Axialites (Fig. 11) in films were not common but were most frequent in those cast from dichloromethane/benzene. Sheaves (Fig. 12) were the main crystals in films cast from xylene containing solution and often appeared as

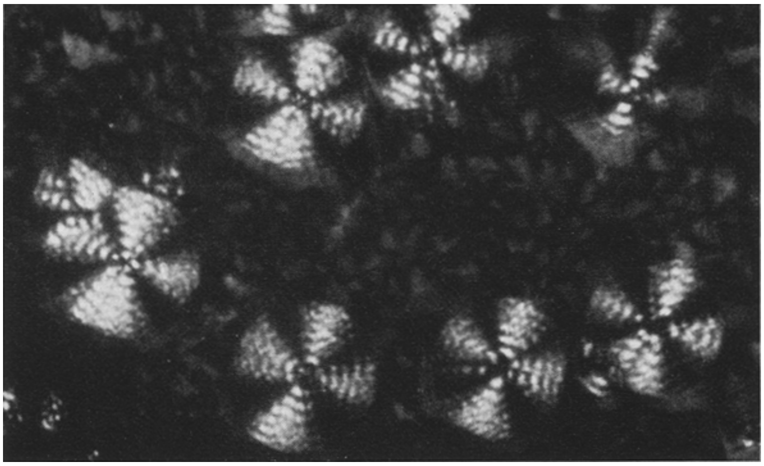

Figure 7 Ringed spherulites of polycarbonate in film cast from dichloromethane. Phase contrast (× 350).

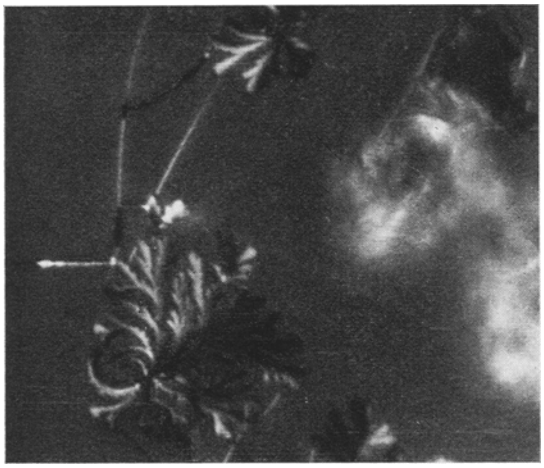

Figure 8 Sheaving structures in polysulphone film cast from dichloromethane/carbon tetrachloride. Crossed polaroids plus tint plate (× 700).

crosses composed of oblong crystals (Fig. 13); these latter developed the Maltese crosses and appeared to be forming into spherulites.

3.1.5. Polyphenylene oxide

In all cases exceedingly brittle films resulted from solvent casting from a chloroform containing solution. The presence of dichloromethane resulted in films that were less brittle and occasionally showed some flexibility. The films were mainly amorphous but contained some areas of crystal agglomerates. Addition of acetone to the PPO solutions caused immediate precipitation of an amorphous powder. The presence of xylene appeared to favour crystallinity and a very few spherulite-like structures were observed within the agglomerates in these conditions.

3.2. Melting points

In general the melting behaviour of the various crystal entities depended on their morphology rather than the solvent mixture from which the film had been cast.

3.2.1. Polycarbonate

Amorphous PC becomes fluid at approximately 222°C and this is relatively easy to detect.

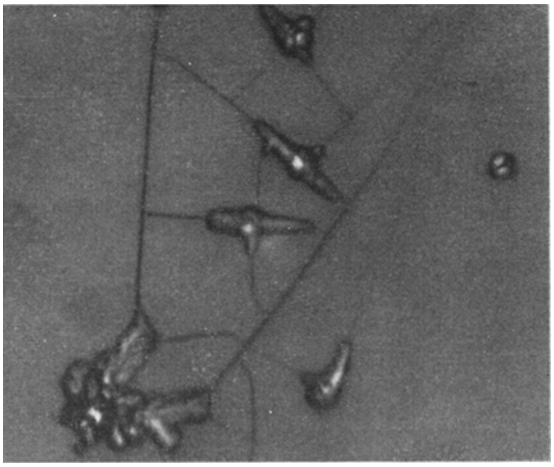

Figure 9 Line nucleation at cracks or crazes in polysulphone film cast from dichloromethane/carbon tetrachloride solution. Crossed polaroids plus tint plate (× 350).

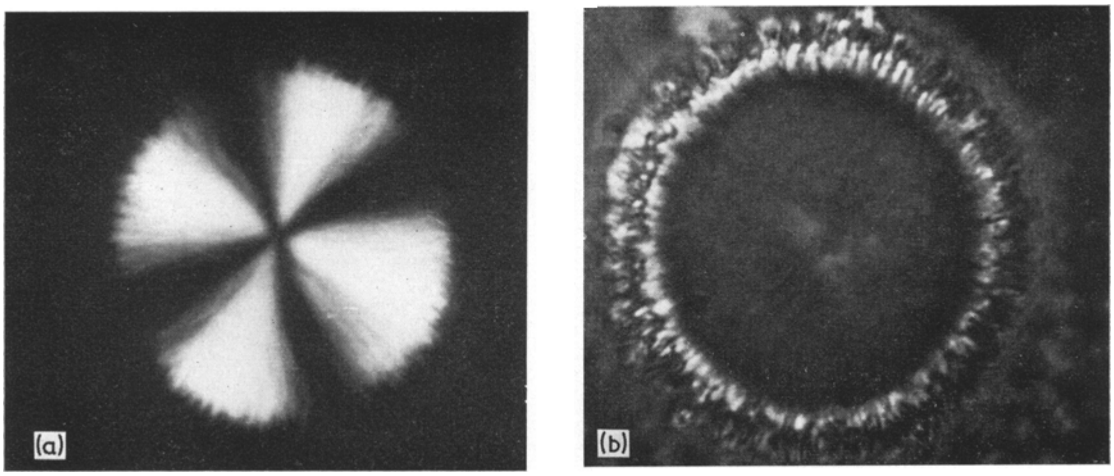

Figure 10 Phenoxy-Resin spherulite in film cast from chloroform/benzene solution. (a) Crossed polaroids; (b) Phase contrast (× 1500).

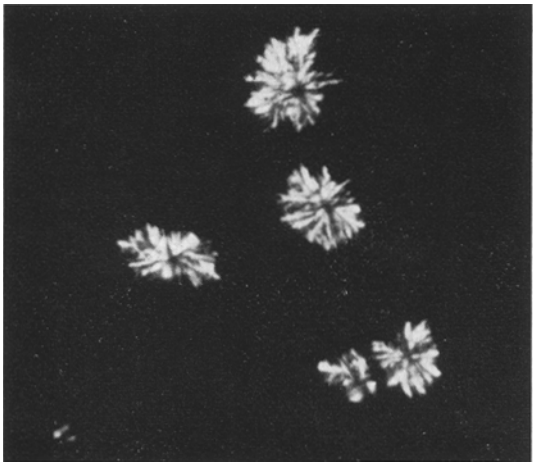

Figure 11 Axialite structures in phenoxy Resin film cast from dichloromethane/benzene solution. Crossed polaroids (× 350).

Spherulites varied in melting point and fell roughly into three classes: large well formed spherulites (ca. 10 μm diameter) melting at 240 to 255°C approximately, those of intermediate size (4 to 5 μm) melting in the range 232 to 235°C and small spherulites about 1 μm in diameter which had a melting range of 226 to 232°C. Sheaving structures melting at about the same temperature as the small spherulites and oblong crystals between 250 and 260 °C. The melting points seemed independent of the solvent from which the film was cast and all crystal entities melted at higher temperatures than the amorphous material, with one exception. The film cast from xylene melted at 220°C but the small spherulites therein melted at 195°C.

3.2.2. Polysulphone

The determination of the melting point of this material is very difficult. It begins to soften at as low a temperature as 195°C and ceases to support its own weight in the region 225 to 235°C, but a flat supported film may show no apparent visual change at temperatures below 300°C. However, strain birefringence is also lost in the 225 to 235°C region and this is taken to be the melting range.

Spherulites again could be roughly classified into three groups, large stable ones which only melted in the range 300 to 350°C or above. The melting temperature of an individual being fairly sharp; medium spherulites melting in the range 270 to 280°C and very small spherulites which had a melting range of 238 to 248°C. Oblong crystals melted fairly sharply but some had much higher melting points than others; the total melting range was 225 to 340°C. Agglomerates of crystal material were very stable and usually did not melt below 350°C, or only partially.

3.2.3. Phenoxy resin

There is marked softening and at 115°C the material will not support its own weight and collapses but is definitely not molten at this stage. The best approximation to a melting point is 140 to 150°C. Some sheaves melted as low as 150 to 155°C (from acetone solvents) but mostly they melted at about 160 to 170°C. Spherulites

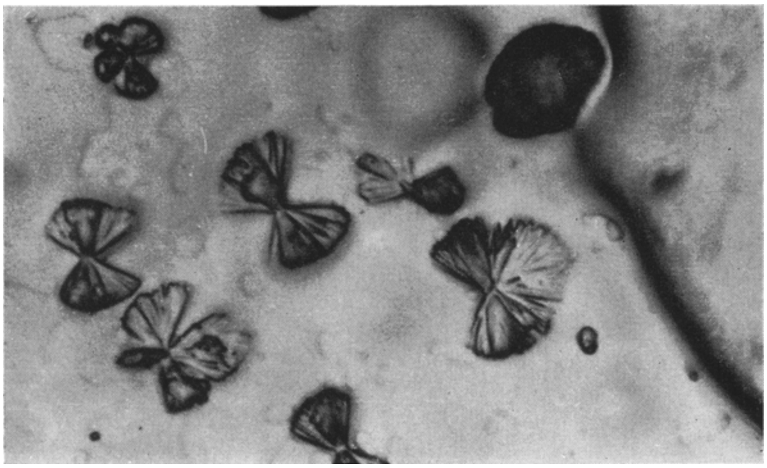

Figure 12 Crystalline sheaves of phenoxy Resin in film cast from dichloromethane/xylene solution. Ordinary light, green filter (× 700).

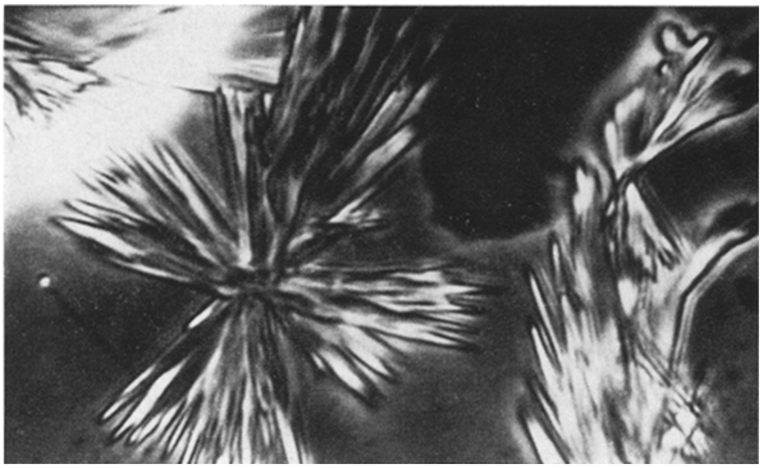

Figure 13 Non-sheaving spherulitic structure in phenoxy Resin film cast from dichloromethane/xylene solution. Phase contrast (× 1500).

again could be classified as to size; the smallest mostly melted in the range 160 to 174° C except in the case of those from chloroform/benzene which melted sharply at 145° C; the medium size ones melted at 175 to 188° C and the large ones usually fairly sharply at 190 to 195° C although a few (from choroform/xylene) did not completely vanish until 225° C. Agglomerates of crystal material melted fairly sharply at 184 to 185° C whilst oblong crystals had melting points in the 170 to 180° C range.

3.2.4. Polyphenylene oxide

On melting all crystal agglomerates behaved similarly; above 180° C they vanished progressively as the temperature approached the glass transition [9] at 225° C (ca.). All signs of crystallinity had usually disappeared by 215° C. Agglomerates in films cast from solvent mixtures containing carbon tetrachloride, however, persisted in part until the temperature of 260° C just below the melting point [9] of 267° C. The melting point was very difficult to determine as visually only very small changes were apparent. Fairly rapid decomposition occurred above this temperature.

4. Discussion

4.1. Film quality

There seems to be no general effect in the quality of film produced by addition of poor or non-solvent to the solution of polymer. For PC addition of non-solvent appears to weaken the film, and the presence of dichloromethane results in less satisfactory film. None of the PPO films produced could be considered satisfactory. For PS and PR only carbon tetrachloride produces obviously weaker film except in the presence of chloroform. However, since perfectly sound completely amorphous films are produced from strong solutions (8 to 10%) in either chloroform or dichloromethane by rapid evaporation of solvent (films produced in less than 30 min) it is probable that rate of formation rather than any other parameter is the controlling factor in quality.

4.2. The effect of solvent on morphology

The present experiments were designed to produce crystalline entities in PS and PPO. PC was included as a check on the effect of mixed solvents on the ability of a similar polymer to crystallize and PR to indicate the effect of increasing the length of straight chain linkage between phenylene groups.

With PC some crystalline material was produced in all cases. The presence of either benzene or xylene in the solvent solution gave rise to many crystal entities in both PS and PR whilst the dichloromethane/carbon tetrachloride mixture was the most successful in producing crystal structures in PS. PPO gave very poor evidence of any crystalline entities under any of the conditions used.

Consideration of the boiling points of the various liquids leads to the expectation that on evaporation the mixed solvent would become richer in the higher boiling component and film formation could take place from an almost pure solution in this liquid, particularly in the binary mixtures with dichloromethane. There is not, however, any clear relationship between boiling points of any of the liquids and the crystal morphology. Neither is there any correlation of morphology with the solubility parameter.

Other work [10] has shown that approximately 50% by volume of acetone or carbon tetrachloride in either chloroform or dichloromethane give theta solvents for PC and the same liquid systems but in different proportions are theta solvents for PS. Combinations of chloroform or dichloromethane with benzene or zylene do not appear to give theta solvents for either polymer. The poor polycarbonate films found in the presence of acetone or carbon tetrachloride may be due therefore to the configuration in which the molecules are thrown out of solution. In the other polymers, good films are formed from these mixed solvents because they are precipitated as film before a theta mixture of the liquids is reached.

Recent publications [11, 12] indicate that in such systems as are considered here there is polymer-liquid as well as liquid-liquid interacting and that the whole system can be quite complex. Crystallization in such cases appears to be preceded by a separation into two liquid phases, a polymer-rich phase and a phase containing relatively little polymer. Such phase separations have recently been observed [10] in comparatively strong solutions of PC and PS. This suggests that the main factors in the production of crystal entities are the various interaction parameters in the systems from which polymer is precipitated. The addition of non-solvent to PC solution seems to slow down or inhibit spherulite formation; this could arise from interactions in the system interfering with the normal ejection of impurities from the crystal face [13]. The possibility that in some systems polymer-solvent or polymer non-solvent complexes are formed which lock molecules in a favourable or unfavourable position for subsequent crystallization should not be overlooked. Such a system has been reported for PPO-dichloromethane [14], and a complex with chloroform may also be formed. It is to the initial formation of these complexes that the failure to form substantial crystals of PPO in the present work is attributed. PPO forms several other solvent complexes [15, 16] and salt-polymer complexes of a similar nature have also been reported [17-21].

Whatever the effect of interactions in the systems, the production of crystal entities in solvent cast film is a markedly time-dependent phenomenon. Working with strong (8 to 10%) solutions, all the polymers produce purely amorphous films on rapid evaporation ($\frac{1}{2}$ to 1 h), but on slow evaporation (2 days and longer) many crystal entities are produced [10].

4.3. Melting points

With the exception of PPO, all crystal entities had melting points above that of the amorphous polymer, some considerably so, which would indicate that they are not composed of markedly low molecular weight material. However, since spherulites could be divided into three groups of low, medium and high melting point there has probably been some separation by molecular weight. PPO forms at the best, low molecular weight, micro-crystalline or para-crystalline agglomerates. No doubt the tendency of this polymer to form solvent complexes, which can be sufficiently stable to form spherulites, limits the chance of pure polymer crystals growing under the conditions of the present experiments.

5. Conclusions

The process of crystal formation in glassy polymers is a complex process and seems to depend on interaction parameters. There is, however, a marked dependence on time of solution evaporation. More work is required particularly with strong solutions and on the interaction parameters of these. It is possible that the correct choice of mixed solvents will enable fully crystal films of polysulphone and polyphenylene oxide to be produced and thus open the way to fibre production from these polymers.

Acknowledgement

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Received 26 September 1972 and accepted 1 June 1973.