Crystalline and amorphous morphologies of an aromatic polyimide formed on precipitation from solution

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The solution-precipitated morphology of a new sulphonated aromatic polyimide, poly(benzophenone tetracarboxylic dianhydride 3,3′-diaminodiphenylsulphone) (BTDA 3, 3′-DDS), has been studied by transmission electron microscopy (t.e.m.) and wide-angle X-ray diffraction (WAXD). First, it has been shown that if held in solution in dimethylacetamide for an extended period, the polymer can crystallize as sheaf-like, multicrystallite aggregates that take on the appearance of axialites at a sufficiently advanced stage of growth. This morphology is very similar to that displayed by other relatively stiff polymers such as poly(ether ether ketone) (PEEK), poly(ether ketone) (PEK), and poly(phenylene sulphide). The generation of this general type of morphology is attributed to the inflexibility of the backbone, which renders folding difficult and hence leads to the production of a thick amorphous region on the lamellar surface, which then limits lateral crystal growth and creates a high density of cilia that cause nucleation of other crystals, leading to the formation of multilayered aggregates. Secondly, if the solvent is evaporated in moist air before crystallization can occur, a phase separation takes place on absorption of water vapour from the atmosphere. In this case the resulting polymer is amorphous and adopts a bead-like morphology on the scale of 300–2000 Å (1 Å = 10^{-10} m).

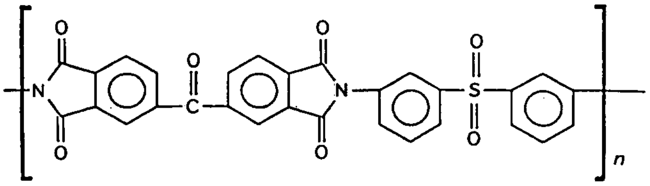
(Keywords: polyimide; morphology; t.e.m.; WAXD; phase separation)

INTRODUCTION

Aromatic polyimides are an emerging family of polymers that are currently attracting technical interest on account of their impressive thermal and, in some cases, mechanical properties. Examples of such polymers already receiving industrial attention are poly(ether imide) (Ultem 1000, General Electric Company), XU 218 (Ciba-Geigy) and PI 2080 (Dow Chemical Co.).

However, it is apparent that despite this technical interest, on a fundamental level the physical properties of these materials are not well documented. It is this that we seek to address here, with particular reference to the issue of crystallization.

In this contribution the polymer under consideration is poly(benzophenone tetracarboxylic dianhydride 3,3′-diaminodiphenylsulphone), hereafter referred to simply as BTDA 3, 3′-DDS. This was prepared by J. E. McGrath of Virginia Polytechnic Institute and has a theoretical molecular weight of approximately 30000 g mol^{-1}. The chemical repeat unit of the molecule is:



From this it is evident that, in common with other aromatic polyimides, the BTDA 3, 3′-DDS molecule is relatively stiff; in this case whatever flexibility does exist is located at the carbonyl and sulphone linkages. This low degree of chain flexibility is considered to account for the high glass transition temperature (T_g) of this polymer (~260°C).

Although it is generally believed that aromatic polyimides are amorphous, recent work has shown that limited crystallization can occur in at least some of these materials when solvents are present[1,2], and indeed in BTDA 3,3′-DDS itself[3]. Clearly the fact that solvent-induced crystallization of these polyimides can occur necessarily means that the usual absence of crystallinity in these materials cannot be a result of an inherent inability of the molecules to form ordered, crystal structures. Rather, the general failure of the polyimides to form crystalline phases is considered to be a result of exceptionally low crystallization rates at normal crystallization temperatures that, again, are probably a result of limited chain mobility. Thus, while it is possible that some of the generic family of aromatic polyimides may have steric factors that preclude crystallization, it is equally likely that many more of this family are inherently crystallizable, but fail to crystallize because of prohibitively slow rates. Hence, on a practical level, under usual circumstances, whether cooled from the melt or cast from solution, aromatic polyimides are amorphous. However, notwithstanding this usual absence of crystallinity, where crystallization can be induced even

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by exceptional treatments, studies of the process and the ensuing morphologies allow access to hitherto unobtainable fundamental information concerning this class of polymer.

The major points in this contribution are two. First, new documentation is presented regarding the morphology of solution-grown crystals of BTDA 3, 3′-DDS, which may provide insight into the crystallization behaviour of aromatic polyimides and, indeed, of inflexible polymers in general. Secondly, the formation of an amorphous bead-like morphology is reported, which develops if BTDA 3, 3′-DDS is precipitated from solution and dried in moist air before the polymer is able to crystallize.

EXPERIMENTAL

BTDA 3, 3′-DDS powder in the as-received condition was dried in a vacuum oven at approximately 100°C for 2–4 days and then dissolved in *n*, *n*-dimethylacetamide at room temperature to form a 1% (weight per volume) solution. This solution was held at room temperature for various times ranging from a few hours to 3–4 weeks. Solutions were deposited on carbon-coated transmission electron microscopy (t.e.m.) grids and allowed to dry in moist air at ambient temperature. Subsequently the grids were examined in a Jeol 100 CX transmission electron microscope operating at an accelerating voltage of 100 kV. In most cases the grids were obliquely shadowed with gold or platinum–palladium alloy before examination.

In similar fashion specimens were also precipitated from solution in a form suitable for subsequent characterization by wide angle X-ray diffraction (WAXD) by allowing the solution to dry at room temperature in moist air in a dish after holding it in solution for the desired time. After the solvent had evaporated, the precipitates were further dried in a vacuum oven at approximately 50°C overnight. Then the polymer precipitates were mounted in Lindemann tubes and WAXD patterns obtained on film by using an evacuated flat-plate Statton camera operating with Ni-filtered CuKα radiation from a sealed tube generator. Additionally, a WAXD pattern from the as-received powder was obtained.

RESULTS

The WAXD pattern from the as-received powder (*Figure 1*) is dominated by an amorphous halo at approximately 4.3 Å with only a hint of a few weak crystalline reflections, the strongest of which is at 4.78 Å. Hence, in the as-received condition, it is apparent that BTDA 3, 3′-DDS is essentially amorphous with no appreciable crystallinity. This, then, provides a reference point for subsequent investigations.

For the specimens held in solution for an extended period of time (i.e. approximately 3–4 weeks), it was noted that after approximately 10 d the solution became turbid, indicating the formation of microscopic particles or domains. Holding the material for longer increased the degree of turbidity. Electron micrographs (*Figure 2*) of the dried material held in solution for many weeks reveal two distinctive and different morphologies.

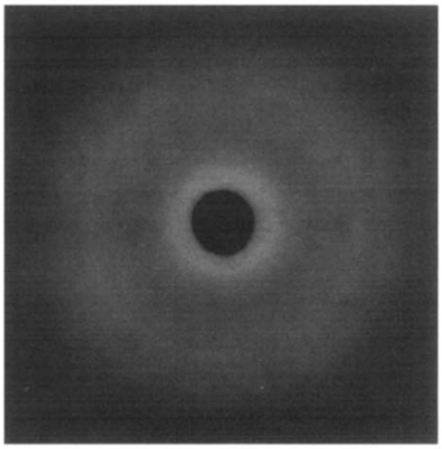

Figure 1 WAXD pattern of as-received powder of BTDA 3, 3′-DDS

(i) Multilayered, jagged-edged, laths that have developed as sheaf-like aggregates and which are clearly crystalline. The length of the sheaves is approximately 5 μm and the width (measured across the centre of the sheaves) is about 0.3 μm (*Figure 2a*).

(ii) Dispersed in places among the laths is a bead-like morphology on the scale of 300 to 1000 Å (see *Figures 2b* and *c*). The lath-like, crystalline morphology will be discussed first, and then the bead-like morphology.

The needle-like morphology of the crystals is apparent from *Figure 2*. Additionally, the multicrystallite nature of the sheaf arms is indicated both by the multilayered nature of the arms at all but the very tips and also by the jagged edges within a monolayer, where monolayers are visible. Of course, the complicating effect of the multilayered nature prevents individual crystallites from being resolved at any place other than the very sheaf ends. However, when measured at these locations, the crystallite widths are found to be approximately 0.01 μm to 0.02 μm (100 to 200 Å).

Some oriented selected-area electron diffraction patterns from sheaves were obtained, but the diffraction was particularly weak. Moreover, since the crystal structure of the polymer has yet to be elucidated, correlation of the diffraction pattern with crystal and molecular orientation is, at best, difficult. Nevertheless, from past precedent the polymer crystals will consist of lamellae with the lamellar thickness commensurate with the lath thickness and the molecular axis normal to the lamellar surface. There is no reason to expect any different behaviour here, and indeed visual inspection of the micrographs suggests a lamellar morphology. In fact the lath morphology observed here is strikingly similar to that found in other systems such as poly(ether ether ketone) (PEEK), poly(ether ketone) (PEK), poly(phenylene sulphide) (PPS) and certain polyamides[4–6]. Indeed, the close parallels with the morphologies of these materials provide a basis for understanding that of BTDA 3, 3′-DDS.

Thus, in accord with analogous studies on this subject[4–6], the crystal laths at the ends of the sheaves are held to be essentially single lamellae. Moving progressively towards the centre of a sheaf, the aggregate takes on a more multilayered nature, with increasing randomization of crystals about the lath direction such that the structure assumes a fibre symmetry, the fibre axis being identified

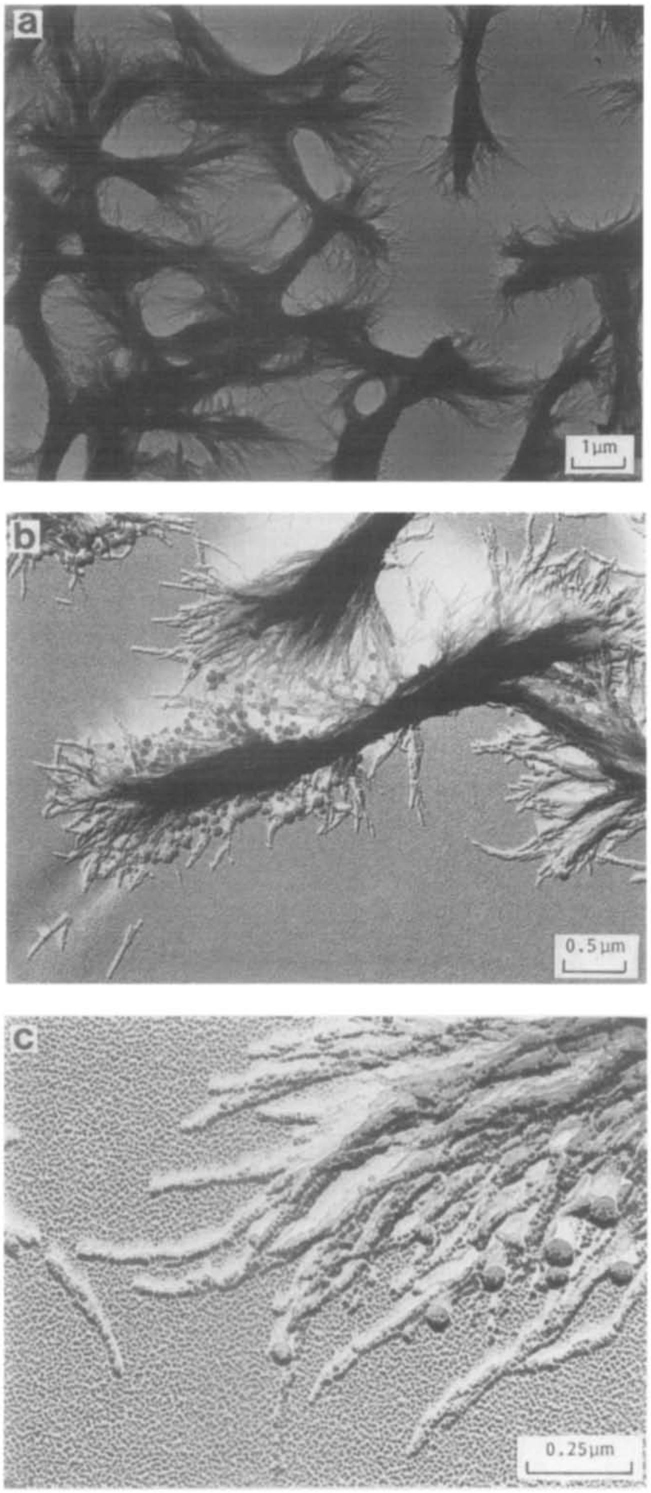

Figure 2 Transmission electron micrographs of BTDA 3, 3′-DDS dried in moist air after holding in a 1% solution in dimethylacetamide for 3–4 weeks: (a) lower magnification; (b) medium magnification; (c) higher magnification. (Au shadowed)

with the lath direction. Of course, at a sufficiently advanced stage of growth, the sheaf-like aggregates take on the appearance of axialites, which, if growth were able to continue further, would presumably evolve into entities of a more spherulitic nature. Examples of axialites in relatively advanced stages of growth are visible in *Figure 2*.

The WAXD pattern of a sedimented precipitate held in solution for $\sim$24–25 d is shown in *Figure 3*. (T.e.m. of this sample also showed a similar two-component morphology in which the laths were the major constituent, with a much smaller bead-like content interspersed (see *Figure 8*).) The WAXD pattern reveals numerous crystalline reflections, the spacings of which are listed in *Table 1*. It is apparent, then, that BTDA 3, 3′-DDS is perfectly capable of crystallizing if held in solution for a sufficiently long period of time.

Turning now to the material precipitated shortly after dissolution, it was found that soon after the solvent was exposed to moist air, the solution became turbid. However, if the solvent was evaporated in dry air (i.e. in a desiccator) optically clear, transparent films formed, suggesting that the development of opacity in this case was associated with the absorption of water from the air. When moist air-dried specimens were examined by t.e.m., a strikingly different morphology from the foregoing was apparent (*Figure 4*). In this instance there was a complete absence of laths; instead only the spherical, bead-like morphology that had formed very much the minor component in the previous specimen is seen. However, in this case the beads appear to be larger than before, the size estimated to be 500 to 2000 Å.

Assuming values of 1800 Å for bead diameter, of $30\,000\ \mathrm{g\,mol^{-1}}$ for molecular weight and approximating the density to $1.4\ \mathrm{g\,cm^{-3}}$ (a typical value for aromatic polyimides), such a bead would contain of the order of 80000 molecules. In places, the beads are physically linked, forming an interconnected net. At other places beads appear to have dried on the grid, with neighbouring surfaces in contact, giving them a facetted appearance. Where three beads have dried together, the extended lines of contact meet at approximately 120°. Elsewhere, where isolated beads also display facets, these are likely, again, to be the product of previous contact with other beads during the drying process.

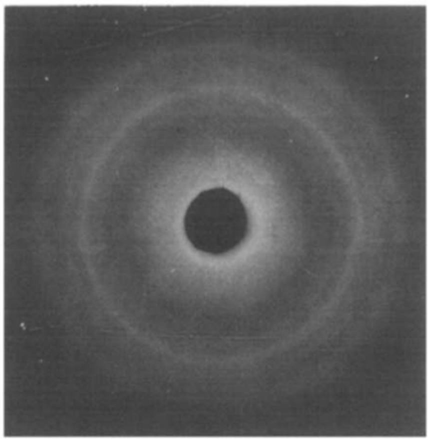

Figure 3 WAXD pattern of crystalline dried precipitate of BTDA 3, 3′-DDS after holding in solution for 24–25 d

Table 1 Spacings and relative intensities of main reflections in BTDA 3, 3′-DDS crystals

d spacing (Å)	Relative intensity
5.59	Weak
4.84	Strong
4.36	Weak
3.83	Medium

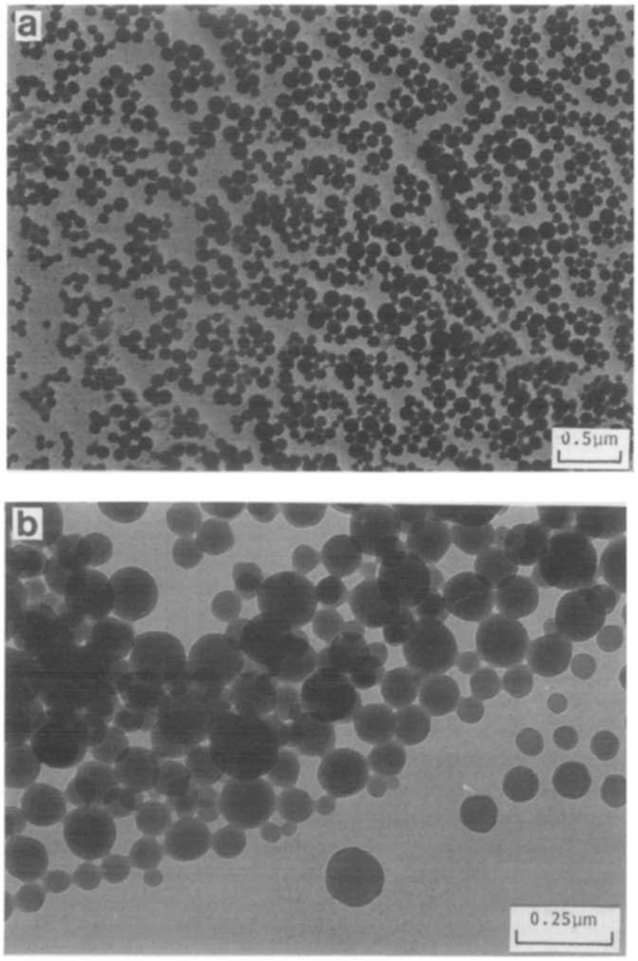

Figure 4 Transmission electron micrographs of BTDA 3, 3′-DDS dried in moist air after holding in a 1% solution for approximately 16 h: (a) medium magnification; (b) higher magnification. (Unshadowed)

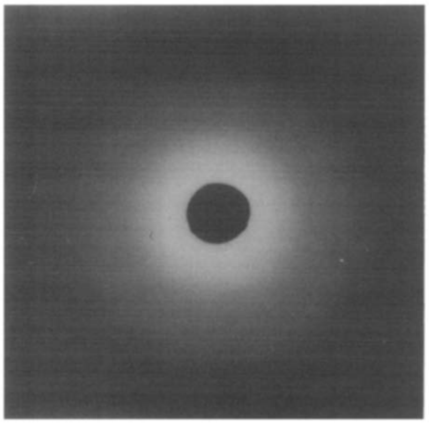

Figure 5 WAXD pattern of amorphous dried precipitate of BTDA 3, 3′-DDS after holding in solution for approximately 18 h

WAXD from a sedimented precipitate of a similar sample showed only a very slight hint of one crystalline reflection (visible only upon very careful inspection of the negative) (*Figure 5*). Thus it is clear that the beads were amorphous and probably the crystalline reflection originated from sheaves also present in the WAXD sample that were not detected by t.e.m. Furthermore, there is no reason to suspect that there is any fundamental difference between the beads produced after a short holding time in solution and those produced after a longer holding time. It is therefore concluded that in the previous WAXD pattern (*Figure 3*), the laths alone gave rise to the crystalline reflections while the beads contained solely the amorphous phase.

In cases where the holding time in solution was intermediate between that of the two cases discussed above, a morphology consisting of both laths and beads was observed. Moreover, both the proportion of laths to beads and the level of development of the laths increased with holding time (*Figures 6–8*).

For a holding time of about 10 d the morphology consisted almost entirely of beads, with a few laths in the very early stages of development (*Figure 6*). At this stage the laths appeared to be single-layered, about 0.7 μm in length, 0.04 μm in width, and had not yet adopted the sheaf-like structure manifested at a later stage of growth. It is noted that this holding time, which seemed to correlate approximately with the first appearance of a significant crystal population, also approximately coincided with the development of turbidity in the solution. For a longer holding time of 14 d, the population of laths relative to beads increased further

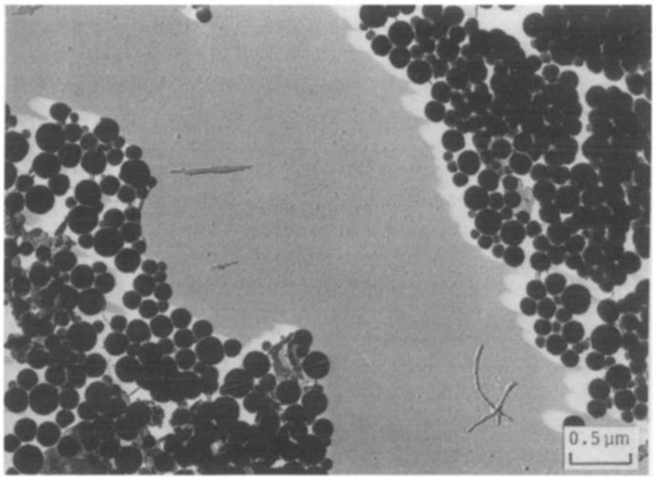

Figure 6 Transmission electron micrograph of BTDA 3, 3′-DDS dried in moist air after holding in a 1% solution in dimethylacetamide for 10 d. (Pt–Pd shadowed)

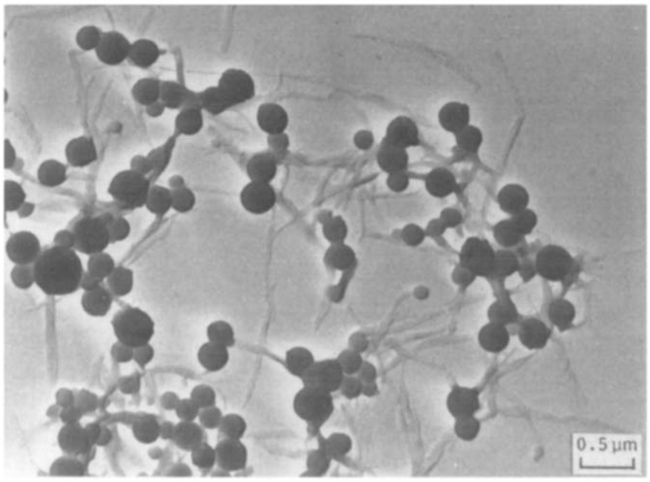

Figure 7 Transmission electron micrograph of BTDA 3, 3′-DDS dried in moist air after holding in a 1% solution in dimethylacetamide for 14 d. (Pt–Pd shadowed)

Figure 8 Transmission electron micrograph of BTDA 3, 3′-DDS dried in moist air after holding in a 1% solution in dimethylacetamide for 24 d. (Pt–Pd shadowed)

(*Figure 7*). The laths lengthened considerably, to approximately 1 μm, but had not yet developed a significant multilayered structure, which thereby allowed measurement of the width of a single layer at the middle of a lath, a dimension of approximately 0.05 μm.

After a holding time of 24 d the morphology consisted almost entirely of laths with a few very small beads in evidence (*Figure 8*). At this point the laths were very definitely multilayered and had become appreciably sheaf-like in appearance.

In summary, two different distinct morphologies can be produced when BTDA 3, 3′-DDS is precipitated from solution. If given sufficient time, the polymer can crystallize. However, if forced to precipitate in moist air before crystallization can occur, a quite separate, amorphous, bead-like morphology develops. Although BTDA 3, 3′-DDS requires an extraordinarily long time to crystallize, its crystals display no unusual or unique features, and the observed morphology has many precedents in the literature[4–6], as does the bead-like structure[7–12].

DISCUSSION

Crystallization

Although BTDA 3, 3′-DDS can crystallize from solution, this only occurs at exceptionally slow rates, approximately three weeks being the required time period under our experimental conditions for nearly full crystallization. The very slow rates of crystallization of aromatic polyimides have been commented on before by other authors[13], and we consider it a consequence of the limited molecular mobility imposed by the aromatic and cyclic groups contained within the chain backbone.

BTDA 3, 3′-DDS crystals bear an extraordinarily close resemblance to those of the polyaryls, PEEK, PEK and PPS. This similarity suggests that there are factors common to the crystallization of these polymers that lead to the development of a common morphology. There is, of course, a close chemical similarity between the polyaryls themselves. However, the chemical similarities between the polyaryls and BTDA 3, 3′-DDS are less obvious, which suggests that it is necessary to look elsewhere for the underlying cause of this morphology. The crucial factor, we believe, is that on a purely physical level all of these polymers consist of relatively inflexible molecules in which chain folding is difficult and sharp folding, in particular, impossible. Thus folding, where it occurs, necessarily must be over many repeat units, which quickly leads to the formation of a thick, amorphous lamellar surface region.

The morphological consequences of such a situation have been considered and documented in an earlier recent work[14]. In this paper, in which the morphology of chain-extended crystals of PEK-based oligomers was compared with that of chain-folded crystals of PEK polymer, a dramatic morphological transition from large, regular lozenges of the oligomers to multilayered microcrystallite aggregates of the polymer was observed, despite the existence of a crystal structure common to both oligomers and polymers. This led to the conclusion that it was the presence of folds and, more particularly, the type of folding in the folded crystal, that was responsible for the generation of the multilayered sheafs of microcrystallites in the polymer. We believe that the same factors are significant in the present system.

Explicitly, where molecules are incapable of forming tight folds, a disordered lamellar surface region must inevitably develop. Additionally, if one ignores the effects of chain ends terminating in one or the other of the phases, every chain leaving the crystal phase of the core must enter the amorphous phase of the surface region. The consequences of such a situation have long been recognized in the subject of polymer morphology, namely, that due to the density discrepancy between crystal and amorphous phases, the specific volume of the surface region will exceed that of the core. Such a problem is avoided where tight folding allows molecules exiting the lattice to turn back on themselves, as, for example, in linear polyethylene. However, if the molecular architecture renders this impossible, the surface region will ‘bulge’ out over the crystal core. Simultaneously this will create interfacial stresses at the crystal–amorphous interface, however diffuse it may be. Of course, these effects will be cumulative with increasing lateral size and hence will place a severe limit on the extent of lateral growth beyond which the volumetric mismatch can no longer be accommodated. In turn this leads to a morphology consisting of microcrystallites, as is observed for both BTDA 3, 3′-DDS and the polyaryls.

It will be recalled that a feature of the morphology of all these polymers is that the microcrystallites adopt a needle-like appearance in which there appears to be a limit to lateral growth in the direction normal to the needle axis. That there should be a limit predominantly in one direction is probably a consequence of anisotropy of the disordered surface region and also anisotropy in the strength of the crystal, although these are factors on which we cannot comment further at present.

Of course, as well as forming loose folds, it is also possible that chains leaving the crystal core may not fold at all, but rather form cilia that can enter or nucleate crystals above and below the plane of the parent crystal. Repetition of exactly the same events in the new daughter crystals, which are subject to the same size constraints as their parent crystal, will very quickly lead to the generation of multilayered aggregates of very small microcrystallites, as is observed with BTDA 3, 3′-DDS and the polyaryls.

Limitations of space prevent a full exposition of the principles presented in reference 14, so the reader is directed there for a full discussion. However, the ideas contained in the earlier work and summarized here quite possibly have wider applicability than to simply the specific cases covered in these works. Indeed, wherever folding is rendered difficult by molecular architecture, branching or high entanglement density, there will be consequent morphological effects along the lines presented in these papers. For example, even the archetypal flexible polymer, polyethylene, exhibits similar morphologies under conditions of significant branch content[15]. It is generally considered that the branches tend to be excluded from the crystalline core; such exclusion will also lead to the creation of a thick fold region that, again, will limit the lateral size of the crystals, as described previously. Of course, for crystallization from the melt, the substantially higher level of entanglements will also inhibit the formation of sharp folds in any polymer, and this will impede lateral crystal growth. Finally, from our solution work it is clear that the multilayered sheaves eventually take on the appearance of axialites (*Figure 2*), which may be regarded as precursors to spherulites. The origin of spherulites in polymeric material has long been debated. We believe that the principles outlined here and in reference 14 that we believe lead to sheaf development in solution-grown crystals may also be relevant to the crystallization of spherulites from the melt. Furthermore, we suggest that this may shed light on the long-discussed problem of the origin of spherulites.

Amorphous bead-like morphology

Having considered the crystallization and crystal morphology of BTDA 3, 3′-DDS, let us now turn our attention to the situation when the solvent is removed in moist air before polymer crystallization can occur. Under such circumstances a point is eventually reached when the solution becomes turbid. From the WAXD pattern (*Figure 5*), it is known that this onset of turbidity is not associated with crystallization; rather, we take this to be indicative of the formation of two amorphous phases, i.e. phase separation. Furthermore, it seems clear that the beads that are finally observed by t.e.m. are the dried-down domains of one of the phases, and that the phase separation and consequent development of the beads are associated with the presence of the water. The final bead-like morphology has great similarities to those reported in the context of the preparation of reverse-osmosis membranes consisting of aggregates of spheres[7–11]. Such membranes are commonly prepared by leaching a solvent from a polymer solution with a non-solvent. We propose that exactly the same phenomenon is occurring in our system, where water, as it becomes absorbed by dimethylacetamide, is the non-solvent. Such a situation can be described by a ternary phase diagram[16–18] (*Figure 9*). The dotted pathway schematically represents the situation where water is first absorbed by the solvent and is then lost with the solvent as both evaporate in the drying process at constant temperature. As the dotted pathway moves across the solid phase boundary, the system moves from a one-phase region to a two-phase region, and hence, in morphological terms, it moves from a one-phase solution to a suspension consisting of polymer-rich beads in a solvent-rich matrix. As the drying process continues, the ratio of polymer-rich phase to solvent-rich phase increases and, eventually, when all the liquid has evaporated, all that remains are beads of amorphous polymer, as observed by t.e.m.

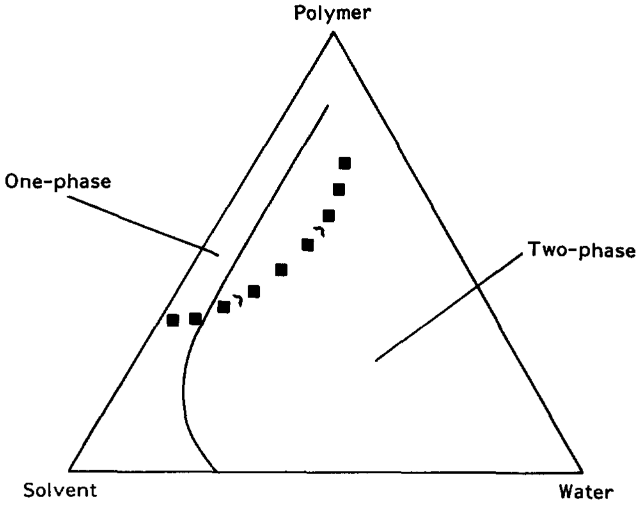

Figure 9 Schematic isothermal ternary phase diagram of polymer–solvent–water showing pathway (broken line) as water is first absorbed and then as both solvent and water evaporate. This type of phase diagram description is after work by Strathmann and co-workers[16–18]

Of course, in addition to phase-separation effects alone, there is also the complicating effect of the plasticizing effect of the solvent on the glass transition. At high solvent content T_g is well below room temperature; for decreasing solvent content this temperature rises, finally reaching a value of ~260°C for pure BTDA 3, 3′-DDS. Obviously at some stage during solvent and water evaporation from the beads, T_g will increase above ambient and the beads will vitrify, eventually reaching the glassy state.

Of course for the specimens that display both crystals and beads in the final morphology, crystallization has simply been arrested by absorption of water, evaporation of the solvent and consequent phase separation. The polymer still in solution at that time then phase separates and precipitates out in the form of amorphous beads, leading to the observed mixed morphologies.

On a practical level this phenomenon opens up the possibility of producing BTDA 3, 3′-DDS and perhaps other aromatic polyimides in the form of a porous mat consisting of amorphous beads of the scale of ~300–2000 Å, or as a latex, or indeed as a foam, in which the polymer forms the matrix phase. This suggests a potential use for such a material as, for example, a microfilter or as a reverse-osmosis membrane in which the beads of the surface monolayer are fused together, as described in references 7–9. Doubtless a full exploration of the phase diagram and of experimental conditions would enable the particle size and final morphology to be controlled to far greater precision than presently possible. Although this is beyond the scope of the present work, we feel that such an investigation may be of significant practical interest.

CONCLUSIONS

In summary, it has been shown that the aromatic polyimide BTDA 3, 3′-DDS can be prepared in either crystalline or amorphous form from solution. The crystalline morphology is that of multilayered, lath-like polycrystalline sheaves that, at an advanced stage of growth, develop into axialites. It is considered that the generation of this type of morphology, which is also exhibited by other polymers, is a consequence of the inflexibility of the BTDA 3, 3′-DDS molecule, which is unable to fold easily. This has two effects: (i) a thick, amorphous, lamellar surface region develops such that there is a density discrepancy between the crystal core and the amorphous surface region (this has the consequence of limiting the extent of lateral growth of the crystallite); (ii) cilia are encouraged to enter or nucleate other crystals rather than fold so that multilayers develop. Such a scheme may also shed light on the question of spherulitic crystallization, although much remains to be done on this topic.

We have also shown that if, by the absorption of water, the polymer is forced to precipitate from solution before crystallization can occur, a phase separation occurs that leads to the creation of an amorphous bead-like morphology of the scale of ~300–2000 Å. Such a structure may have potential practical use as, for example, in microfilters or reverse-osmosis membranes. Mixed morphologies consisting of both crystals and beads can be prepared by evaporation of solvent in moist air during the crystallization process. Any uncrystallized polymer then simply precipitates out as amorphous beads, thereby allowing crystal growth to be arrested at any desired stage. Hence, crystals can be examined at all stages of development, from small single-layered needles to complex axialites.

ACKNOWLEDGEMENT

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REFERENCES

1 Wang, J., DiBenedetto, A. T., Johnson, J. F., Huang, S. J. and Cercena, J. L. *Polymer* 1989, **30**, 718

2 Pratt, J. R., St. Clair, T. L., Gerber, M. K. and Gautreaux, C. R. in 'Polyimides: Materials, Chemistry and Characterization', Elsevier Science Publishers, Amsterdam, 1989, p. 193

3 Hou, T. H., Bai, J. M. and St. Clair, T. L. in 'Polyimides: Materials, Chemistry and Characterization', Elsevier Science Publishers, Amsterdam, 1989, p. 169

4 Waddon, A. J., Hill, M. J., Keller, A. and Blundell, D. J. *J. Mater. Sci.* 1987, **22**, 1773

5 Lovinger, A. J. and Davis, D. D. *Macromolecules* 1986, **19**, 1861

6 Keller, A. *J. Polym. Sci.* 1959, **36**, 361

7 Panar, M., Hoehn, H. H. and Hebert, R. R. *Macromolecules* 1973, **6**, 777

8 Alegranti, C. W., Pye, D. G., Hoehn, H. H. and Panar, M. *J. Appl. Polym. Sci.* 1975, **19**, 1475

9 Hoehn, H. H. in 'Materials Science of Synthetic Membranes', ACS Symp. Ser. 269, American Chemical Society, Washington, DC, 1985, p. 81

10 Kamide, K. and Manabe, S. I. in 'Materials Science of Synthetic Membranes', ACS Symp. Ser. 269, American Chemical Society, Washington, DC, 1985, p. 197

11 Hiatt, W. C., Vitzthum, G. H., Wagener, K. B., Gerlach, K. and Josefiak, C. in 'Materials Science of Synthetic Membranes', ACS Symp. Ser. 269, American Chemical Society, Washington, DC, 1985, p. 229

12 Waddon, A. J., Brookes, L. C., Heyderman, L. J. and Hill, M. J. *Polym. Commun.* 1990, **31**, 5

13 Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V. and Laius, L. A. 'Polyimides: Thermally Stable Polymers', Consultants Bureau, Plenum Publishing Corporation, New York, 1987, p. 165

14 Waddon, A. J., Keller, A. and Blundell, D. J. *Polymer* 1992, **33**, 27

15 Holdsworth, P. J. and Keller, A. *J. Polym. Sci., Polym. Lett. Edn* 1967, **5**, 605

16 Strathmann, H., Kock, K., Amar, P. and Baker, R. W. *Desalination* 1975, **16**, 179

17 Strathmann, H. and Kock, K. *Desalination* 1977, **21**, 241

18 Strathmann, H. in 'Materials Science of Synthetic Membranes', ACS Symp. Ser. 269, American Chemical Society, Washington, DC, 1985, p. 165