Morphology of solution-cast thin films of wholly aromatic thermoplastic polyimides with various molecular weights

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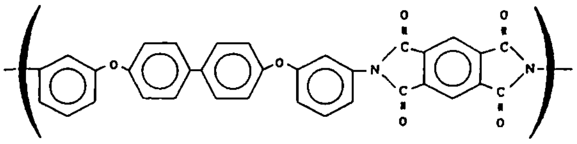
The morphology of solution-cast thin films of wholly aromatic thermoplastic polyimides (TPIs) with various molecular weights ($M_w = 3490$–$85\,800$) was studied using transmission electron microscopy (TEM). Thin TPI films suitable for TEM studies were prepared from 0.3% solution in *p*-chlorophenol/phenol cast onto hot polyphosphoric acid, where the solvent was evaporated. A TPI oligomer of $M_w = 3490$–6500 forms droplet-like structure (D structure) during casting, whereas TPIs with higher molecular weights ($M_w = 23\,900$–$85\,800$) form ellipsoidal and elongated structures. On heating the as-cast film of TPI with $M_w = 3490$, the D structure is converted into a flat, layer structure with extended chains, which gives an electron diffraction pattern of the single-crystal type. On the other hand, long curved crystals with folded chains develop in the D structure of a TPI with molecular weight of 6500. The supermolecular structures of TPIs with higher molecular weights ($M_w = 23\,900$–$85\,800$) are noticeably affected by the molecular orientation in the original structure of the as-cast films. Oriented crystallization occurs in the elongated structure, while lamellar crystals develop in the D structure or ellipsoidal structures.

(Keywords: thermoplastic polyimide; morphology; electron microscopy)

INTRODUCTION

Various kinds of wholly aromatic heat-resistant polymers such as thermoplastic polyimides, aromatic polyethers, poly(aryl ether ketone)s (PAEKs) and poly(ether nitrile)s (PENs) have been developed in the past 10 years. These polymer materials offer outstanding mechanical and thermal properties, along with a high solvent resistance. Numerous research papers on these polymers have been published, most of them focusing on PEAKs[1–6]. In recent years, crystallization behaviour and morphological features of some wholly aromatic thermoplastic polyimides have been studied by some workers[7–11].

In this paper the polymer under consideration is poly[3,3'-(4,4'-dioxyphenyl)diphenylene pyromellitimide], hereafter referred to simply as TPI. This polymer belongs to a new class of wholly aromatic thermoplastic semicrystalline polyimide. The chemical repeat unit of the polymer is:



TPI is a recent development in the search for thermostable polymers in which a good compromise is realized between heat resistance and processability. Crystal structure[12], solution properties[13], thermal behaviour[14], melt-spinning and dynamic mechanical properties[15,16] of TPI have been studied by some workers. We have studied the supermolecular structures and thermal behaviour of TPI[17–19].

In the present investigation, the morphology of solution-cast thin films of TPIs with different molecular weights has been studied using transmission electron microscopy (TEM), differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffractometry (WAXD). It has been found that the supermolecular structure of solution-cast TPI specimens depends remarkably on the molecular chain length and orientation in the original as-cast film.

EXPERIMENTAL

Materials

Seven TPI samples with average molecular weight ranging from 3490 to 85 800 were kindly supplied by Mitsui-Toatsu Co. *Table 1* lists sample number, average molecular weight evaluated by light scattering method and extended chain length.

Transmission electron microscopy

Thin films of TPI suitable for TEM study were prepared according to the procedure of Thomas[20]. First, a 0.1–0.3% solution in *p*-chlorophenol/phenol (10/1) was cast onto polyphosphoric acid at 150°C, where the solvent was evaporated. After the polyphosphoric acid

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was cooled to room temperature, the thin film was picked up by a carbon-coated copper grid, washed with water, dried, heat-treated and shadowed with heavy metal (gold/palladium alloy or gold) in a vacuum evaporator. Electron micrographs and electron diffraction (ED) patterns were obtained at 100 kV using a Nihon-Denshi model 2000FX-II transmission electron microscope. For ED studies, a selected-area aperture of 2.7 μm diameter was used throughout this work.

Wide-angle X-ray diffractometry and differential scanning calorimetry

For WAXD studies, many as-cast films were collected, washed, dried and then packed randomly into a hole of 2 mm diameter and 0.5 mm depth in an aluminium plate. The WAXD studies were carried out with a Rigaku-Denki diffractometer using Ni-filtered Cu Kα radiation. D.s.c. measurements were carried out using a Seiko differential scanning calorimeter (DSC-SSC4000).

Table 1 Molecular weight, chain length and long period of TPI with various molecular weights

Sample number	Molecular weight, M_w	Chain length (nm)	Long period (nm)
TPI-1	3 490	15.9	17.5
TPI-2	6 050	27.6	18.9
TPI-3	6 500	29.7	20.2
TPI-4	23 900	109.1	19.7
TPI-5	35 100	160.3	20.1
TPI-6	55 600	253.8	(Amorphous)
TPI-7	85 800	391.7	(Amorphous)

RESULTS AND DISCUSSION

Characterization of TPI

Table 1 shows sample number, molecular weight and extended chain length of seven TPI samples. TPI-1, TPI-3, TPI-4, TPI-5 and TPI-7 were used in this study. The long period of the same TPI samples crystallized from the melt was evaluated using small-angle X-ray scattering (SAXS). Results are also tabulated in *Table 1*. TPI-6 and TPI-7 did not give a scattering maximum in their SAXS patterns.

I.r. spectroscopic studies were made to determine the poly(amic acid) content in these TPI samples. Only a faint shoulder attributed to C=O of the residual amide groups is revealed at 1670 cm^{-1}, indicating that poly(amic acid) segments are hardly contained in these samples.

Structures of solution-cast films of TPI

We have reported the supermolecular structures of TPIs with various molecular weights crystallized from the melt[18]. TPI oligomers (TPI-1, TPI-2, TPI-3) were crystallized as hedrite, oval structure, as well as

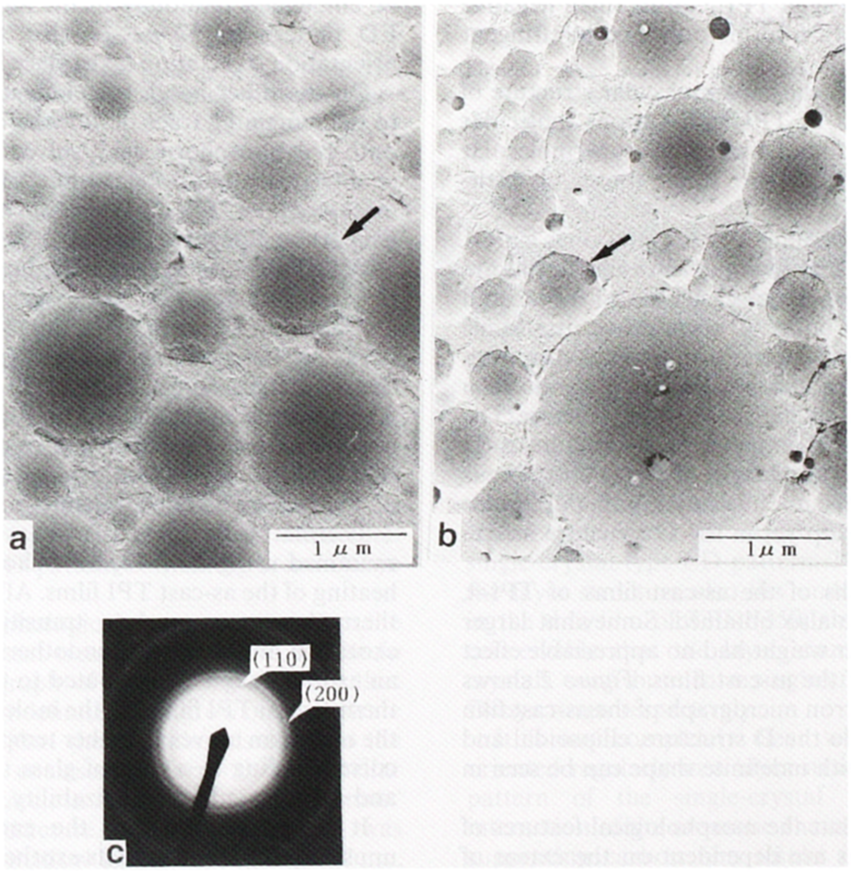

Figure 1 Electron micrographs and an electron diffraction pattern of the as-cast films of TPI with lower molecular weights. (a) Electron micrograph of TPI-1 (M_w=3490). (b) Electron micrograph of TPI-3 (M_w=6050). (c) Electron diffraction pattern of TPI-3. The arrows indicate the droplet-like structure

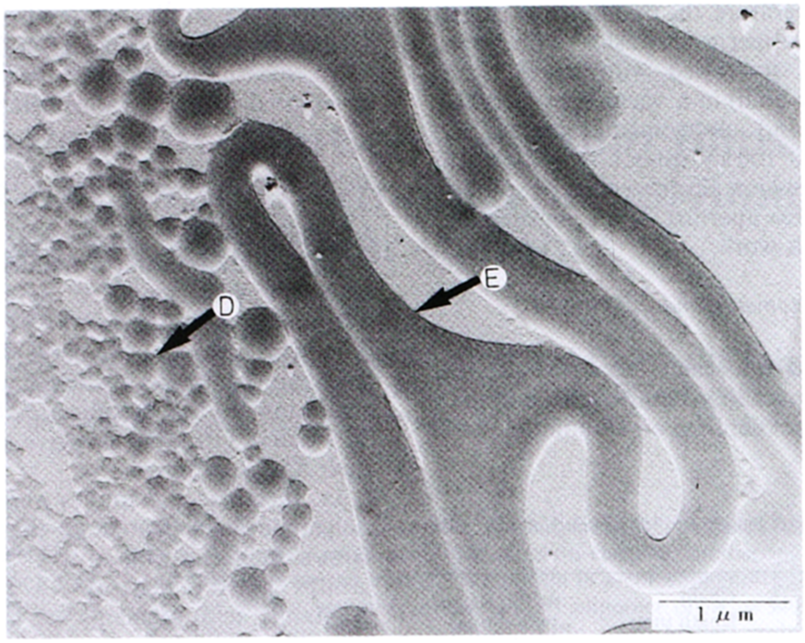

Figure 2 Electron micrograph of the as-cast film of TPI-5 ($M_w = 35\,100$). The arrows [D] and [E] show the droplet-like and elongated structures, respectively

spherulitic structures. It was confirmed by SAXS studies that TPI molecules longer than ca. 20 nm fold back at the crystal surface to form folded-chain crystals. Their supermolecular structures became imperfect with increasing molecular weight; TPI-5 forms small negative spherulites, whereas TPI-6 forms only fine birefringent objects.

This paper deals with the supermolecular structure of solution-cast thin films of TPI with various molecular weights. It has been found that their supermolecular structures are quite different from those of melt-crystallized TPI.

Structure of as-cast TPI films. *Figures 1a* and *1b* are electron micrographs of the as-cast films of TPI-1 and TPI-3, showing that both of them have the same morphological features. Many droplet-like structures with different diameters can be seen in these electron micrographs; arrows show the droplet-like structure. The droplet-like structure will hereafter be referred to as 'D structure'. It seems that the height of the D structure is as high as about 100 nm. Distinct supermolecular structures do not develop yet in the D structure as can be seen in *Figure 1*.

Electron micrographs of the as-cast films of TPI-4, TPI-5 and TPI-7 were also obtained. Somewhat larger differences in molecular weight had no appreciable effect on the morphology of the as-cast films. *Figure 2* shows for an example an electron micrograph of the as-cast film of TPI-5. In addition to the D structure, ellipsoidal and elongated structures with indefinite shape can be seen in *Figure 2*.

It can be assumed that the morphological features of these as-cast TPI films are dependent on the extent of orientation–relaxation during casting. It seems likely that the D structures originate from the droplets of TPI solution formed on hot polyphosphoric acid during casting. The D structure gave an electron diffraction (ED) pattern containing faint (1 1 0) and (2 0 0) reflection rings as shown in *Figure 1c*, indicating that the as-cast TPI films are not amorphous but reveal some crystallinity. It seems reasonable to assume that fine crystallites may be embedded randomly in the amorphous matrix. The ED pattern in *Figure 1c* also suggests that enough orientation–relaxation takes place in these D structures.

On the other hand, the elongated structures are due to the remaining trace of flow of TPI solution when cast onto polyphosphoric acid; solvent is evaporated before enough orientation–relaxation takes place. As will be discussed later, TPI molecules are oriented along the long axis of the elongated structure.

WAXD studies were carried out to elucidate a state of molecular aggregation in the as-cast TPI films. Results are shown in *Figure 3*. Some broad crystalline diffraction peaks are detected together with an amorphous halo in the diffraction angle range of $2\theta = 2–40°$. Even TPI-7, which does not crystallize from the melt, can crystallize to some extent. This result can be explained by assuming that the solvent lowers the glass transition temperature of TPI and reduces chain entanglement.

Thermal behaviours of the as-cast TPI films were examined using d.s.c. *Figure 4* shows d.s.c. scans for the heating of the as-cast TPI films. All samples exhibit three thermal events, a glass transition, a crystallization exotherm and a melting endotherm. The appearance of an exotherm can be attributed to the low crystallinity of these as-cast TPI films. As the molecular weight increases, the exotherm moves to higher temperature and broadens, corresponding to a shift of glass transition temperature and a decrease in crystallizability.

It is noteworthy that the endotherm of TPI-1 is unusually broad, though its exotherm is sharp. The sharp exotherm seems to indicate that TPI molecules with various lengths are once incorporated into the same crystal during crystallization at 210°C. On the other hand, the broad endotherm might be attributed to the

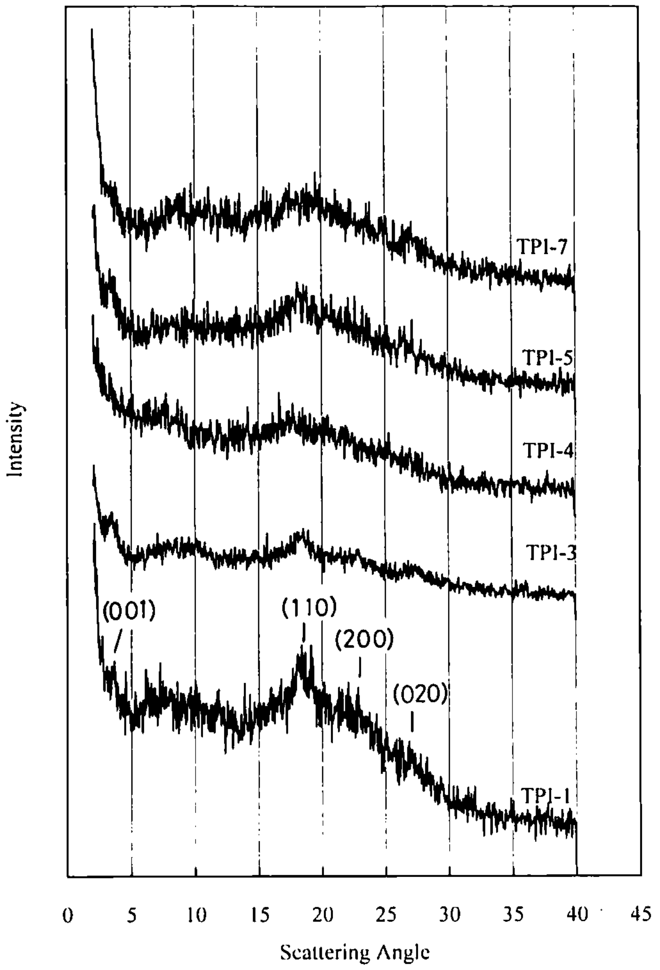

Figure 3 Wide-angle X-ray diffraction patterns of the as-cast TPIs with various molecular weights. The scattering angles for some crystallographic planes are shown

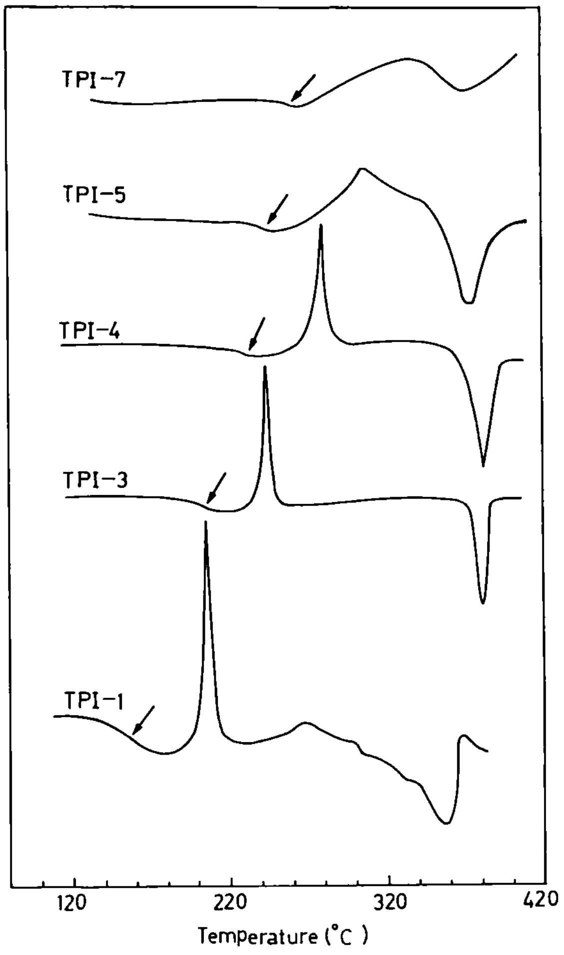

Figure 4 D.s.c. scans for the heating of the as-cast TPI films

melting of extended-chain crystals with different thicknesses. It can be suggested that fractional crystallization–melting occurs during heating at 300–370°C.

Development of supermolecular structures of TPIs during heat treatment. The development of supermolecular structure in the as-cast TPI films during heat treatment has been studied. The TPI film heat-treated at *T* (°C) will hereafter be abbreviated as TPI(*T*). On heating the as-cast film of TPI-1 at 300°C, small crystals developed randomly in the original D structure. TPI-1(300) gave an ED pattern containing some Debye rings.

A pronounced morphological change occurs when the as-cast TPI films are heat-treated up to 350°C. *Figure 5a* is an electron micrograph of TPI-1(350), showing that lamellar crystals with indefinite shape grow on a substrate layer. It seems likely that the crystals arising from the original D structure coalesce to form these lamellar structures; the dotted circle in *Figure 5a* shows a 'remnant' of the original D structure. Lamellar thickness was determined from the shadow length to be about 17 nm, whereas the average chain length of TPI-1 is 15.9 nm, indicating that the lamellar crystals contain extended chains.

The ED pattern included in *Figure 5a* was obtained from a central region of 2.7 μm diameter. The ED pattern contains both a ($h\,k\,0$) reciprocal lattice pattern as well as some faint Debye rings; the former ED pattern will hereafter be referred to as a single-crystal-type ED pattern, since it is similar to the one given by solution-grown single crystals.

Figure 5b is another electron micrograph and a corresponding ED pattern of TPI-1(350), showing rather homogeneous layer structure; lamellar crystals are not discernible. It is interesting to note that D structures are transformed into the layer structure, which give a single-crystal-type ED pattern. This result suggests that the layer structure also lies under the lamellar crystals in the thin film of TPI-1(350) shown in *Figure 5a*. It is conceivable that the layer structure and the lamellar crystals contribute to a single-crystal-type pattern and Debye rings, respectively.

It is not completely clear why TPI molecules are oriented regularly in a layer structure that gives an ED pattern of the single-crystal type. Presumably an interaction of the aromatic chain ends of TPI-1 with the supporting carbon film results in the molecules being normal to the plane of the carbon film. It should be pointed out that the ED pattern of the single-crystal type could not be obtained when TPI-1 film was cooled rapidly from 350°C to room temperature. We suggest

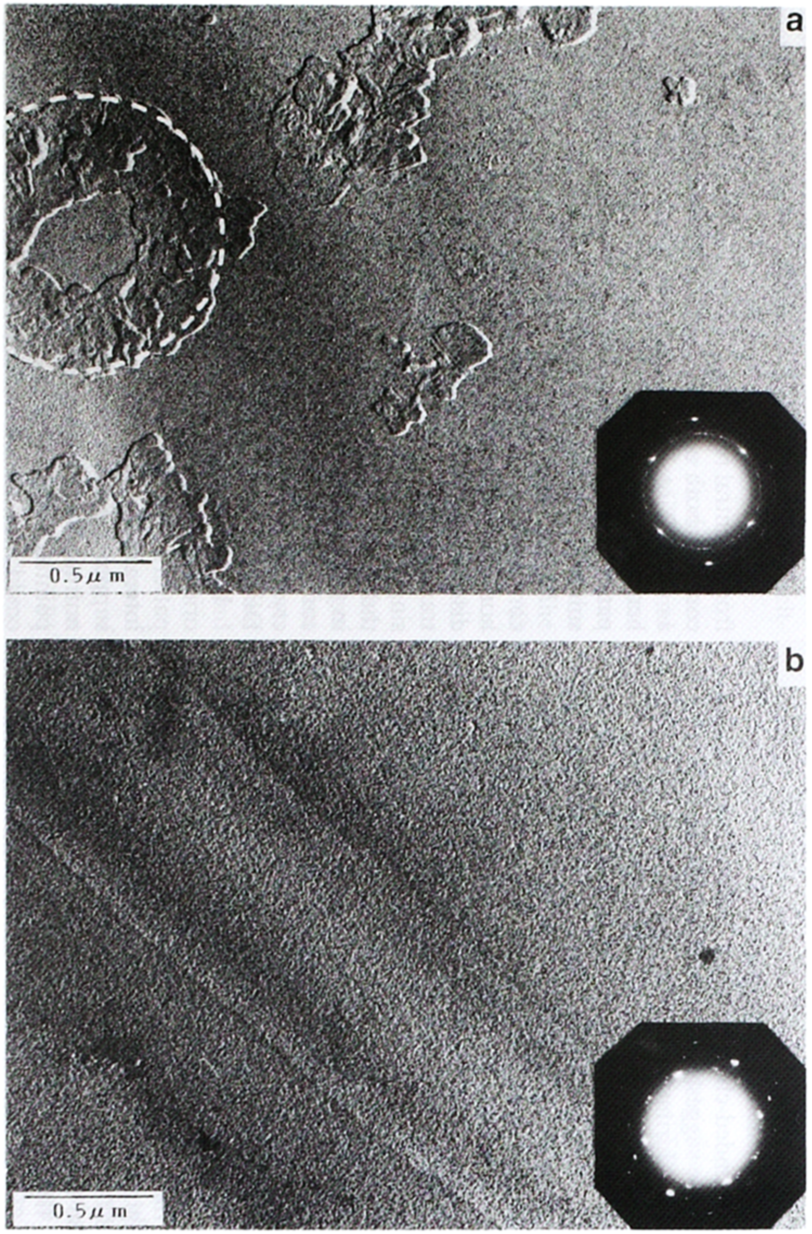

Figure 5 Electron micrographs and corresponding electron difrraction patterns of TPI-1 ($M_w = 3490$) heat-treated at 350°C. The dotted circle in (a) shows a 'remnant' of the original droplet-like structure

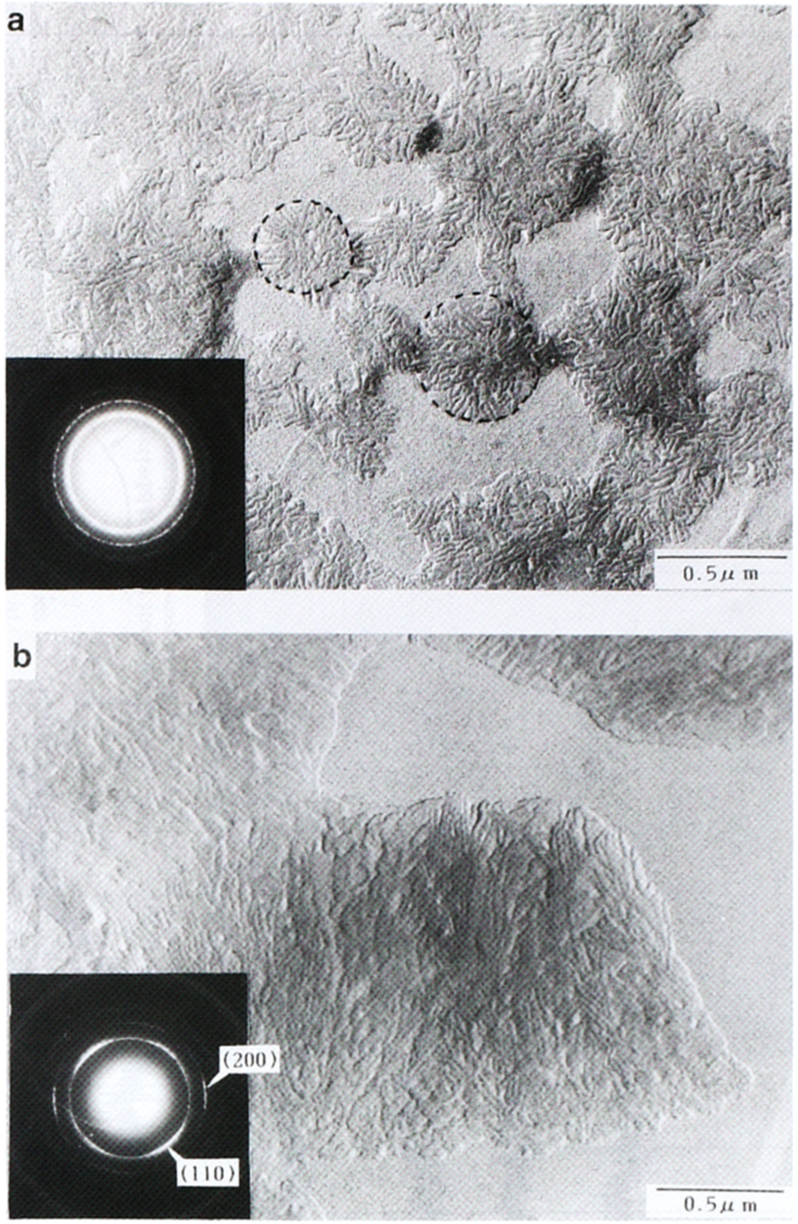

Figure 6 Electron micrographs and corresponding electron diffraction patterns of TPI-3 ($M_w = 6500$) heat-treated at 350°C. The dotted circles in (a) show 'remnants' of the original droplet-like structure

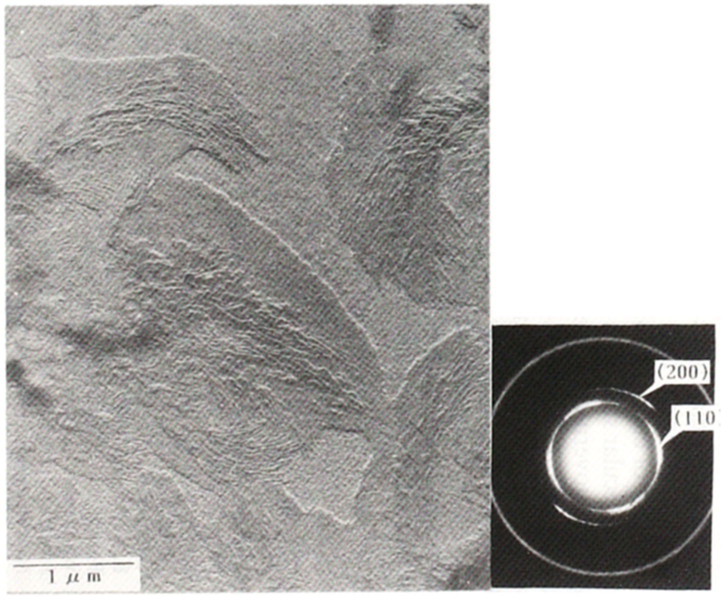

Figure 7 An electron micrograph and a corresponding diffraction pattern of TPI-4 (M_w = 23 900) heat-treated at 350°C

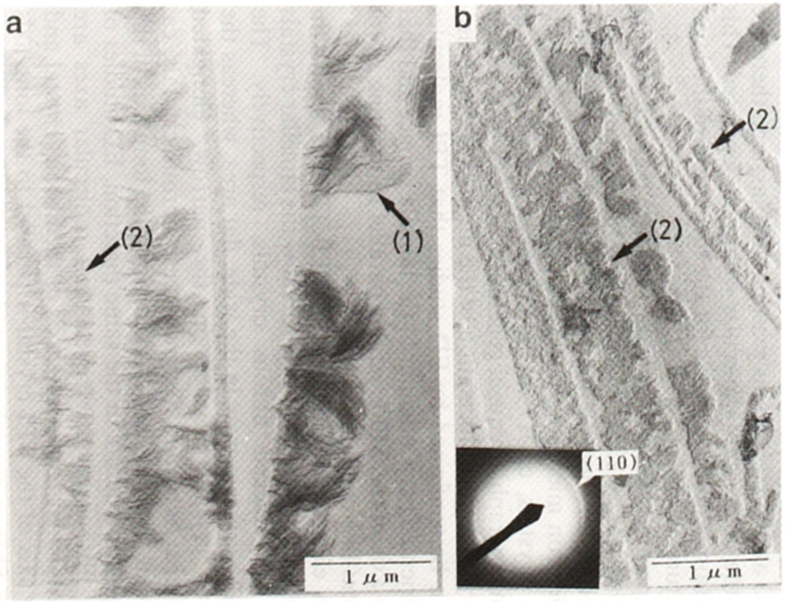

Figure 8 Electron micrographs and an electron diffraction pattern of TPI-5 (M_w = 55 100) heat-treated at 350°C. The arrows show the stacked lamellar structure

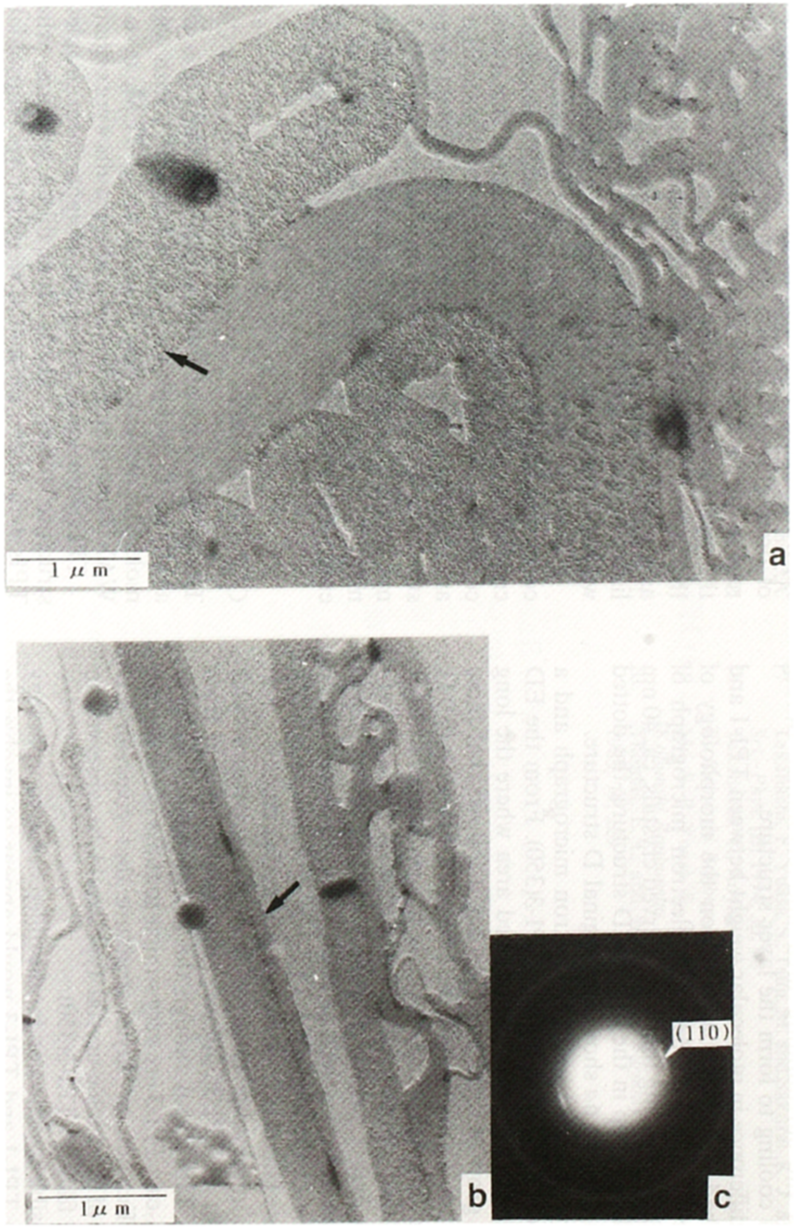

Figure 9 Electron micrographs and an electron diffraction pattern of TPI-7 (M_w = 85 800) heat-treated at 350°C. The electron diffraction pattern (c) corresponds to the electron micrograph (b). The arrows indicate the stacked lamellar structure

that molten TPI molecules diffuse from the D structure towards the surrounding area and crystallize during gradual cooling to form the layer structure.

The difference in molecular weight between TPI-1 and TPI-3 had a remarkable effect on the morphology of their crystals. *Figure 6a* is an electron micrograph of TPI-3(350), showing that long, curved crystals, ca. 40 nm in width, develop in the original D structure; the dotted circles in *Figure 6a* show the original D structure.

Figure 6b shows another electron micrograph and a corresponding ED pattern of TPI-3(350). From the ED pattern obtained from the selected area where the long crystals grow in the same direction, it follows that these crystals are formed whose surface coincides with (0 0 1), whose *c* unit-cell axis (*c* axis) is perpendicular to their surface, and whose preferred direction of rapid growth is the *b* axis. Lamellar thickness of these crystals was estimated from the electron micrograph to be ca. 18 nm, while the chain length of TPI-3 is 29.7 nm, indicating that these lamellar crystals contain folded chains.

It is interesting to note that the supermolecular structures of TPI-3(350) are appreciably different from those of TPI-1(350), though the morphological features of the as-cast TPI-3 are very similar to those of the as-cast TPI-1. Further, no layer structure that gives an ED pattern of the single-crystal type could be observed in the thin films of TPI-3(350).

A possible explanation for the difference in morphology between TPI-1 and TPI-3 would appear to involve the effect of chain folding along the *b*-axis; TPI-1 forms extended-chain crystals whereas TPI-3 forms folded-chain crystals. Presumably chain folding along the *b* axis in the lamellar crystals of TPI-3 leads to the development of the crystal habit (1 0 0).

Further, a difference in thermal behaviours relates to the morphological difference between TPI-1 and TPI-3; partial melting does not occur in the as-cast films of TPI-3 at 350°C. It seems reasonable to assume therefore that the diffusion of molecules would be depressed. This situation is not favourable for the formation of the layer structure.

Supermolecular structures of TPIs with higher molecular weights ($M_w = 23\,900–85\,800$) are dependent on the structures of the original as-cast films. *Figure 7a* shows an electron micrograph of TPI-4(350). 'Leaf-like', multi-layer crystals, ca. 17 nm in thickness, are observed in the micrograph. Frequent generation of screw dislocations contributes to the formation of the multi-layer structure. It can be confirmed by ED studies that TPI molecules are oriented perpendicular to the lamella surface and that the *b* axis of the TPI crystal is parallel to the long rib of the leaf-like crystals.

An electron micrograph of TPI-5(350) is shown in *Figure 8*. The arrows (1) and (2) show the lamellar crystals and the stacked fibrous crystals, respectively. The lamellar crystals grow in the wide, flat area, whereas the fibrous crystals develop in the narrow, elongated structure. As *Figure 8* shows, these fibrous crystals, ca. 20 nm in thickness, are stacked along the long axis of the elongated structure in the same direction. ED studies of these fibrous crystals reveal that molecular axes are perpendicular to the long axis of the fibrous crystal and the *b* axis of the TPI crystal is parallel to the long axis of the fibrous crystal; oriented crystallization occurs in the elongated structure[17].

These observations demonstrate that the type of supermolecular structure is governed by the extent of orientation–relaxation in the as-cast film. It seems reasonable to assume that enough relaxation leads to the development of lamellar crystal. As is expected, the orientation–relaxation during casting becomes difficult as molecular weight increases. In fact, oriented crystallization only occurs in the as-cast film with the molecular weight higher than 35 100 when heat-treated at 350°C.

Figure 9 shows an electron micrograph and a corresponding ED pattern of TPI-7(350). Small, fibrous crystals develop in the original elongated structures. The corresponding ED pattern indicates that molecular axes are oriented along the long axis of the original elongated structure. As reported in our previous paper, TPI-7 does not crystallize from the melt because of chain entanglement[18]. It can be assumed that the density of chain entanglement is reduced in the solution-cast TPI-7 film.

CONCLUSIONS

The morphology of solution-cast thin films of a wholly aromatic thermoplastic polyimide (TPI) with various molecular weights was studied using TEM, d.s.c. and WAXD techniques. The following results were obtained.

TPIs with lower molecular weights form droplet-like structure during casting from dilute solution, whereas TPIs with higher molecular weights form ellipsoidal and elongated structures with indefinite shape. It can be assumed that the morphological features of the as-cast TPI films are dependent on the extent of orientation–relaxation during casting.

On heating the as-cast films of TPI-1, the D structure of TPI-1 is converted into lamellar crystals and layer structure with extended chains. The layer structure gave a single-crystal-type ED pattern. On the other hand, long, curved crystals with folded chains develop in the D structure of TPI-3. The morphological difference between TPI-1 and TPI-3 may be explained by assuming that the chain folding along the *b* axis contributes to the development of crystal habit of TPI-3.

Supermolecular structures of TPIs with higher molecular weights are governed by the molecular orientation in the original structure of the as-cast films. Stacked, lamellar crystals develop in the original elongated structure during heat treatment, suggesting that oriented crystallization occurs in the elongated structure. On the other hand, wide, lamellar crystals develop in the original D structure or ellipsoidal structures where enough relaxation takes place.

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