Synthesis and characterization of poly(oxy-2,6-naphthalenediylcarbonyl) whiskers from 2-acetoxy-6-naphthoic acid

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The synthesis and characterization of poly(oxy-2,6-naphthalenediylcarbonyl) (PON) whiskers from 2-acetoxy-6-naphthoic acid are described. The important factors in controlling PON crystal morphologies during high-temperature solution polymerization are polarity of solvent, concentration of monomer and stirring. Less-polar solvents like liquid paraffin or Therm S 800, low concentration of monomer and no stirring are desirable for making PON whiskers. The size of the whisker prepared in liquid paraffin is 7–17 μm in length and 0.5–1.0 μm in width. From its electron diffraction patterns, it was found that this whisker exhibits a single-crystal nature and the polymer chains align along the long axis of the whisker. Owing to the close packing of polymer chains in this crystal, the whisker has the highest thermal stability compared with the other fibrillar and slab-like crystals. The formation mechanism of PON whiskers is also investigated in comparison to that of poly(oxy-1,4-benzenediylcarbonyl) whiskers.

(Keywords: poly(oxy-2,6-naphthalenediylcarbonyl); polymer whisker; aromatic polyester; morphology control; needle-like crystals; extended-chain crystals)

INTRODUCTION

Recently, there has been growing interest in wholly aromatic polymers, especially with regard to the production of high-performance materials. In the 1960s it was reported, notably by Kwolek[1], that certain wholly aromatic polyamides such as poly(*p*-phenylene terephthalamide) exhibited anisotropic properties in solution, and this led ultimately to the development of aramid fibre. In 1972, Economy and coworkers[2] patented melt-processable aromatic copolyesters from *p*-hydroxybenzoic acid, 4,4-biphenol and terephthalic acid. These studies accelerated research in the high-performance polymer field, and many kinds of polymers have been reported so far[3].

Generally, wholly aromatic polymers that consist of rigid-rod repeat units possess excellent thermal stability, good mechanical properties and good solvent resistance. But, in many cases, they are not amenable to conventional processing techniques (they show no T_g or T_m, or have low solubilities). In order to overcome such intractability, some chemical modification to reduce their rigidity or special processing techniques are necessary. But these modifications result in the loss of these excellent properties, while reducing their rigidity, and therefore it is hard to educe their essential properties.

Economy and coworkers reported on the synthesis of poly(oxy-1,4-benzenediylcarbonyl) (POB) from 4-acetoxybenzoic acid (ABA) in a heat-exchange medium and the unexpected isolation of single crystals formed during polymerization[4]. Afterwards, we obtained fibrillar crystals of POB using a low concentration of ABA and vigorous stirring[5]. These findings prompted us to investigate the relationship between crystal morphology and the reaction conditions to establish the morphology control method of POB.

In 1987, we found and reported that needle-like POB whiskers, which were single extended-chain crystals, could be formed under certain polymerization conditions[6–8]. This was the first polymer whisker obtained by a polycondensation reaction and showed a new morphological processing route for intractable polymers. That is, intractable polymers can be processed by building monomers into some crystal form one by one while polymerizing. In a series of reports, we have also shown the formation mechanism of POB whiskers[9–11]. Kricheldorf confirmed the formation of POB whiskers and investigated the phase transitions of POB[12]. Our results suggested that this morphology control method could be applicable to other rigid-rod polymers, and we succeeded in obtaining whiskers of poly(oxy-2,6-naphthalenediylcarbonyl) (PON) from 2-acetoxy-6-naphthoic acid (ANA)[6]. This paper will report further results on the synthesis conditions, growth mechanism and thermal properties of PON whiskers.

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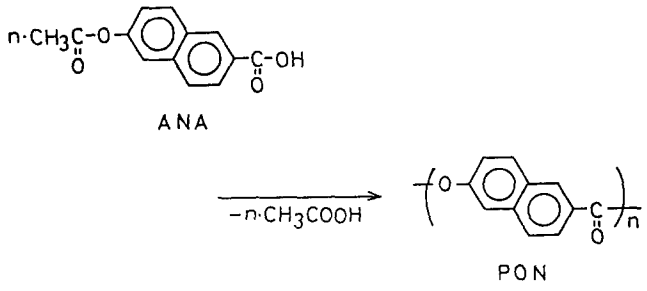


EXPERIMENTAL

Materials

2-Acetoxy-6-naphthoic acid (ANA) was prepared as described in the literature[13]. Liquid paraffin (LP), Therm S 800 (TS 800), benzophenone (BP), 4-chlorobenzophenone (CBP) and diphenylsulphone (DPS) were used as polymerization solvents after purification as described in our previous paper[7].

Measurements

Morphological characterization was performed by scanning electron microscopy, transmission electron microscopy and wide-angle X-ray diffraction. The instruments used were a Hitachi 530-S, a Hitachi HU-11B and a Rigaku 2028.

Thermal properties were evaluated by using differential scanning calorimetry (d.s.c.) and thermal gravimetric analysis (t.g.a.). The instruments used were a Rigaku R-DSC and a Shimadzu DT-30. D.s.c. was performed at a heating rate of 10°C min^{-1} in nitrogen. T.g.a. was performed with a 5 mg sample at a heating rate of 10°C min^{-1} in air.

The density of the crystals was measured by the flotation method using n-butyl bromide and carbon tetrachloride at 25°C.

The chemical structure was checked by infra-red spectroscopy, using a Hitachi 270-30.

Preparation of poly(oxy-2,6-naphthalenediylcarbonyl) crystals

The typical preparation procedure of PON whiskers was as described below. Other crystals were also obtained in a similar manner. To a 200 ml cylindrical reactor equipped with a thermometer, a stirrer and gas inlet and outlet tubes were added 0.82 g of ANA and 60 ml of LP. This reaction mixture was heated with stirring until the monomer dissolved completely. Then stirring was stopped and heating was continued up to 330°C and maintained at this temperature. In a couple of minutes, the reaction solution became turbid and the reaction was continued at 330°C for 6 h under a slow stream of nitrogen. The reaction mixture was allowed to cool at room temperature and chloroform was added. Polymer crystals were collected by filtration, washed several times with chloroform and acetone, and dried at 100°C under reduced pressure to constant weight. The i.r. spectrum of PON whiskers obtained is shown in *Figure 1*.

Analysis calculated for $C_{11}H_8O_2$ polymer: C, 77.64; H, 3.55. Found: C, 78.87; H, 3.77.

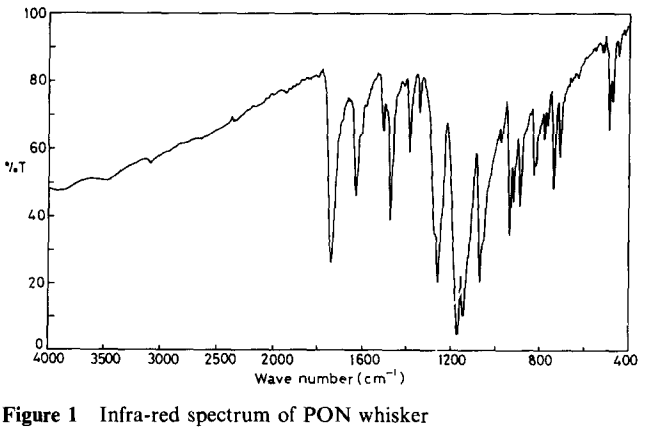


Figure 1 Infra-red spectrum of PON whisker

RESULTS AND DISCUSSION

Synthesis

The PON whiskers, shown in *Figures 2* and *3*, are obtained by high-temperature solution polycondensation from ANA. Economy *et al.* reported the high-temperature solution polycondensation of PON previously[14]. The crystals that they obtained were uniform, well oriented and slab-like, but not needle-like. A comparison of the morphology of crystals prepared under various conditions is summarized in *Table 1*.

Concerning the solvents, needle-like PON whiskers were obtained only in LP and TS 800, which is an aromatic heat-exchange medium. The sizes of PON

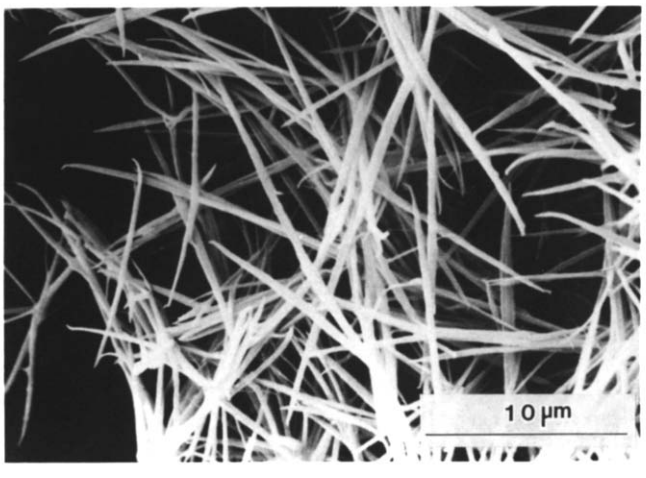


Figure 2 Scanning electron micrograph of PON whiskers prepared in LP (PON-1)

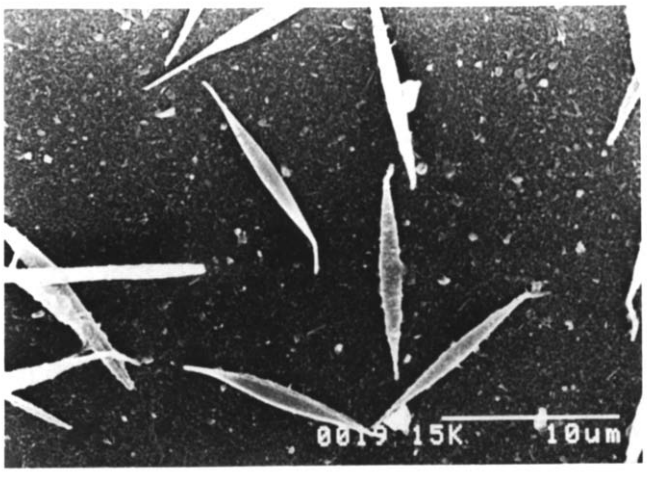


Figure 3 Scanning electron micrograph of PON crystals prepared in TS 800 (PON-2)

Table 1 Comparison of PON crystal morphology from ANA

Polymer no.	Solvent[a]	Conc. (%)[b]	Polymerization temp. (°C)/time (h)	Stirring	Crystal morphology
PON-1	LP	1.0	330°C/6 h	No	Whisker
PON-2	TS 800	1.0	330°C/6 h	No	Whisker
PON-3	BP	1.0	320°C/6 h	No	Fibril
PON-4	DPS	1.0	330°C/6 h	No	Fibril
PON-5	CBP	1.0	330°C/6 h	No	Slab
PON-6[c]	Therminol-66	3.0	220°C/1 h, 240°C/1 h, 350°C/12 h	Yes	Slab

[a] Solvents: LP, liquid paraffin; BP, benzophenone; DPS, diphenylsulphone; CBP, 4-chlorobenzophenone; TS 800, Therm S 800, aromatic heat-exchange medium of Nippon Steel Chemical Co. Ltd; Therminol-66, aromatic heat-exchange medium of Monsanto Co. Ltd
[b] Conc. (%) = [theoretical polymer yield (g)/solvent volume (ml)] × 100
[c] Data from ref. 14

Table 2 The sizes of PON and POB whiskers

Polymer no.	Size (μm)		Axial ratio, *L/D*
	Length, *L*	Width, *D*	
PON-1	10–17	0.5	20–34
PON-2	7–15	1.0	7–15
POB	30–70	1.0	30–70

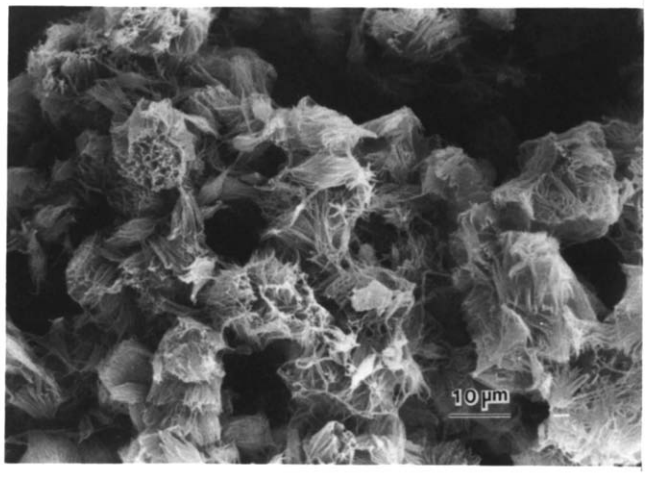


Figure 4 Scanning electron micrograph of PON crystals prepared in BP (PON-3)

whiskers were strongly related to the properties of the solvents, summarized in *Table 2*. The whiskers prepared in LP (PON-1) had ca. 10–17 μm length and ca. 0.5 μm width, and the whiskers prepared in TS 800 (PON-2) had ca. 7–15 μm length and ca. 1.0 μm width. TS 800 made the length shorter, the width wider and eventually decreased the axial ratio. In BP and DPS, fibrillar crystals that were uniform and well oriented were obtained, but each fibril did not separate, as shown in *Figures 4* and *5*. In CBP, slab-like crystals were obtained as shown in *Figure 6*. These results indicated that the polarity of the solvent seemed to correlate qualitatively with the crystal morphology, i.e. a less-polar solvent was preferable to obtain a PON whisker having higher axial ratio. These facts could be explained as follows. The ANA is found to react initially in the homogeneous state and then the reaction continues in the heterogeneous state once precipitation has occurred. This precipitation in the early stage of polymerization is due to the formation of primary crystal nuclei by oligomers that dominate the final crystal habits. The precipitation, which was defined as when the

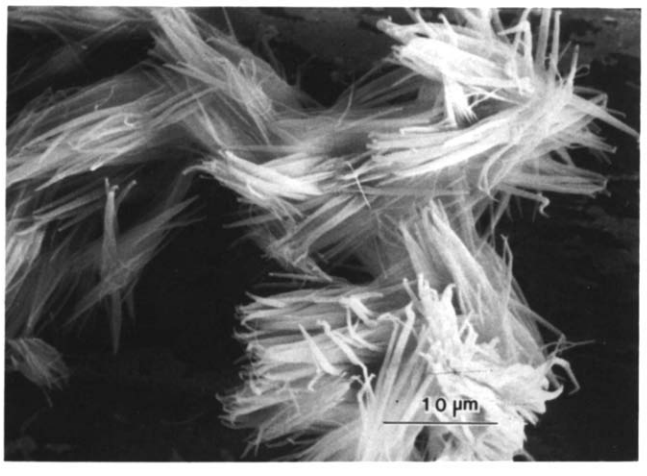


Figure 5 Scanning electron micrograph of PON crystals prepared in DPS (PON-4)

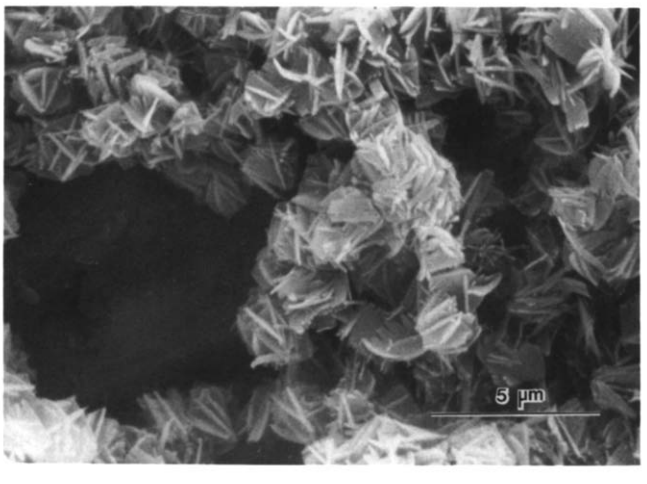


Figure 6 Scanning electron micrograph of PON crystals prepared in CBP (PON-5)

reaction solution became turbid, occurred within 1 min in LP after the temperature reached 330°C, 6 min in TS 800, 42 min in BP, 58 min in DPS and 7 min in CBP. The order of these precipitation times corresponds to the order of the polarity of solvents, but does not correspond for the case of CBP:

Order of precipitation time
early ⟷ *late*
LP < TS 800 < BP, DPS
low ⟷ *high*
Order of polarity of solvent

It is reasonable to suppose that the polymerization rates are nearly equal in all solvents or the rates in polar solvents are higher in the homogeneous state. Under these situations, the degrees of polymerization (*DP*) of oligomers precipitated are lower when the reaction is carried out in LP or TS 800 in comparison with the other solvents.

The difference of the *DP* of precipitated oligomers might have an influence on the crystal habits of the primary nuclei and ultimately final crystal morphologies. The details of this will be discussed with the growth mechanism of whiskers in a later section. What occurred in CBP might be different from the others. This is not understood clearly and is under investigation.

Furthermore, concentration and stirring are also very important factors in controlling the crystal morphologies. At a high concentration (over 5%), whiskers were not obtained, but uniform, well oriented, slab-like crystals were formed. Stirring influenced the crystal morphologies drastically as well. With vigorous stirring, unseparated fibrillar crystals were formed. In other words, lower concentration and slow or no stirring are desirable for making whiskers.

From these results, it can be concluded that the most important factors in controlling the PON crystal morphologies from ANA are the polarity of the solvent, concentration and stirring. PON whiskers can be obtained in less-polar solvents at a low concentration and under 'no stirring' conditions. This conclusion is very similar to that for POB whiskers.

Characterization of PON whiskers

Examination of PON-1 whiskers using an electron microscope showed needle-like morphologies very similar to POB whiskers (see *Figures 2* and *7*). Both tips of this whisker were very sharp and the surface was very smooth. The X-ray diffraction pattern in *Figure 8* showed no amorphous peak and an extremely high degree of crystallinity. In order to determine the unit cell, the electron diffraction technique was used, and a diffraction pattern of PON-1 whisker is shown in *Figure 9*. This diffraction pattern did not show the true fibre pattern of cylindrical symmetry. This is due to the single-crystal nature of these whiskers. The meridian of this pattern corresponds to the long axis of the whisker. The fibre identity period was 16.81 Å, corresponding to two chemical residues. The unit-cell parameters are shown in *Table 3*. The observed densities of PON whiskers summarized in *Table 4* are in excellent agreement with

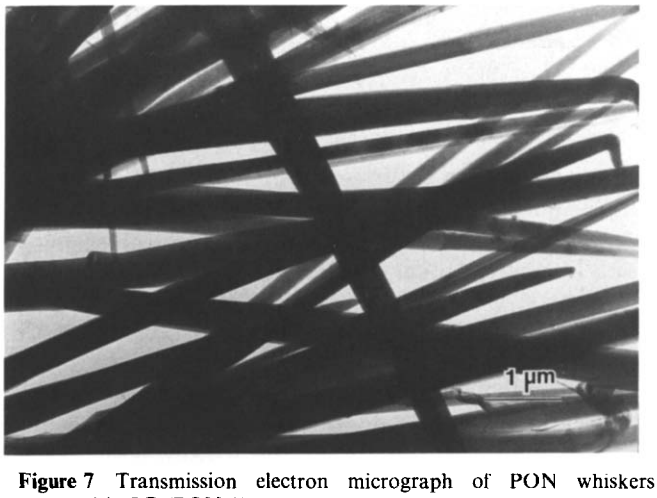


Figure 7 Transmission electron micrograph of PON whiskers prepared in LP (PON-1)

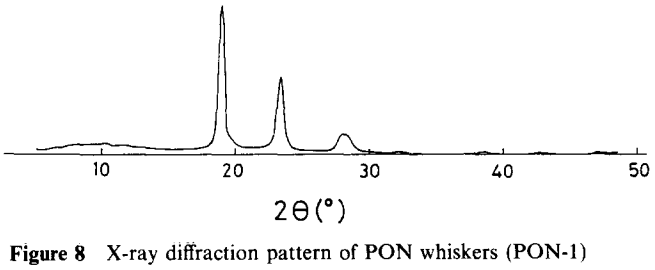
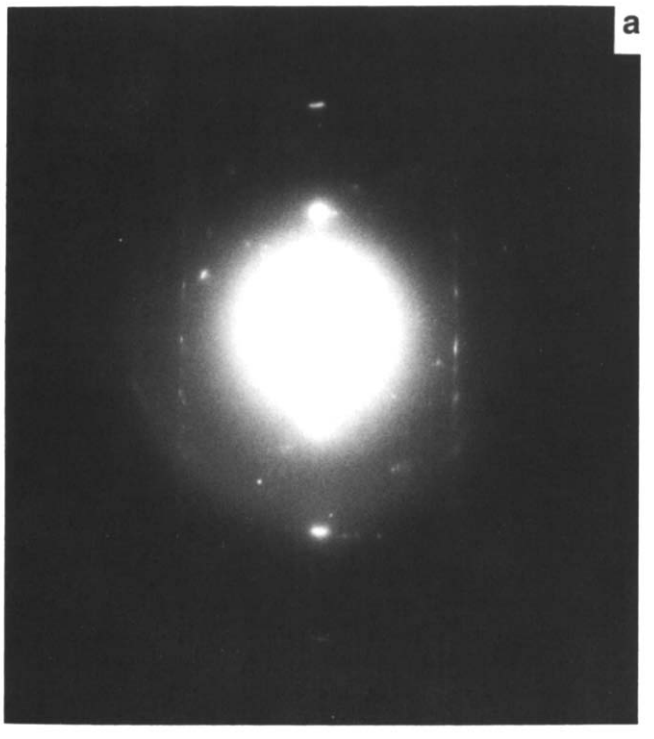


Figure 8 X-ray diffraction pattern of PON whiskers (PON-1)



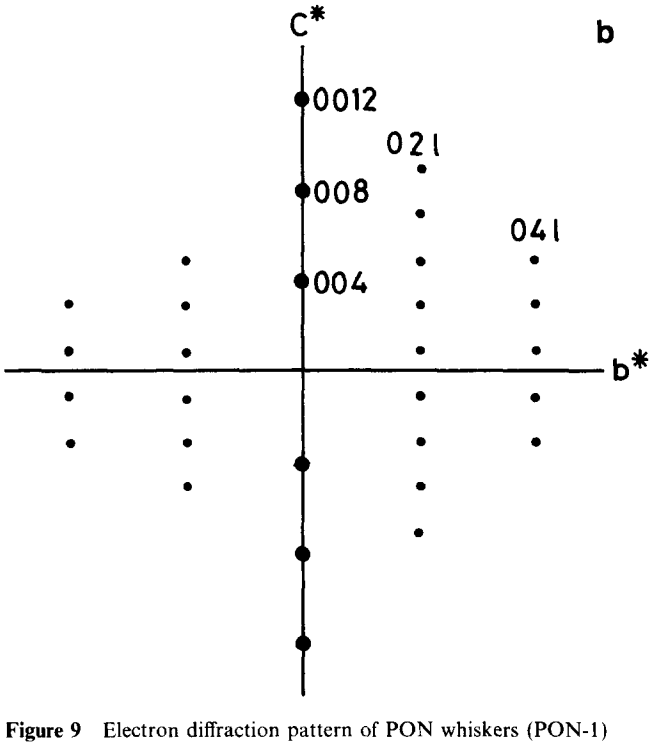


Figure 9 Electron diffraction pattern of PON whiskers (PON-1)

Table 3 Unit-cell dimensions for PON whiskers

Crystal system	Orthorhombic
Lattice constants	$a = 7.96$ Å
	$b = 5.82$ Å
	c = (fibre axis) = 16.81 Å
Number of chains in a unit cell	Two (four repeat units)
Density calcd.	1.45 g cm^{-3}

Table 4 The density and thermal properties of PON crystals

		D.s.c.			T.g.a
Polymer no.	Density (g cm^{-3})	T_t (°C)[a]	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T_5 (°C)[b]
PON-1	1.45	343.5/327.0	3.46	5.61	506
PON-2	1.44	343.5/327.0	3.38	5.48	498
PON-3	1.42	–[c]	–	–	482
PON-4	1.43	–	–	–	489
PON-5	1.45	319.5/–[d]	–	–	443

[a] Transition temperature, the temperature on heating/on cooling
[b] Temperature at which 5% weight loss was recorded in air in t.g.a. curves
[c] Transition was not detected
[d] Transition peak was very weak and the peak on cooling scan was not detected

the theoretical density. The densities of other crystals are lower except for PON-5. These results are sufficient to regard these whiskers as single extended-chain crystals.

Growth mechanism of PON whiskers

The crystal sizes of PON whiskers are different from those of POB whiskers, but the quite similar characteristics indicate a very close similarity in these two formation processes. We proposed a growth mechanism of POB whiskers in the previous work[9–11], schematically illustrated in *Figure 10*. This growth mechanism contains the following steps: (1) Oligomers of low *DP* are formed in the homogeneous state, and, as soon as the *DP* exceeds a critical value, oligomeric materials crystallize in the form of lamellae from the solution. A screw dislocation is formed in the precipitated lamellae and subsequent crystallization occurs at the slip plane rather than the usual growth plane, because of the advantage of secondary nucleation for crystal growth. Then needle-like crystals are formed with spiral growth. It should be clarified with further examination whether the Burgers vector is of the magnitude of the fibre identity period or of the size of lamellar thickness. (2) The *DP* increases by transesterification in the interlamellar regions, and reorganization of crystals occurs.

In order to examine whether PON whiskers are formed via the same mechanism as POB whiskers, the morphology of a PON crystal obtained in the early stage of polymerization was observed. The transmission electron micrograph of an incipient crystal is shown in *Figure 11*. In this micrograph, the lamellar structure piling up along the long axis of the needle crystal was observed clearly. Both tips of this crystal were sharp and the 'shish' as in 'shish-kebab' fibrous crystals did not exist. On the other hand, the eventual whiskers did not have any lamellar structures but a smooth surface (see *Figure 7*). These facts are strong evidence that the mechanism of formation of PON whiskers is quite similar to that of POB whiskers.

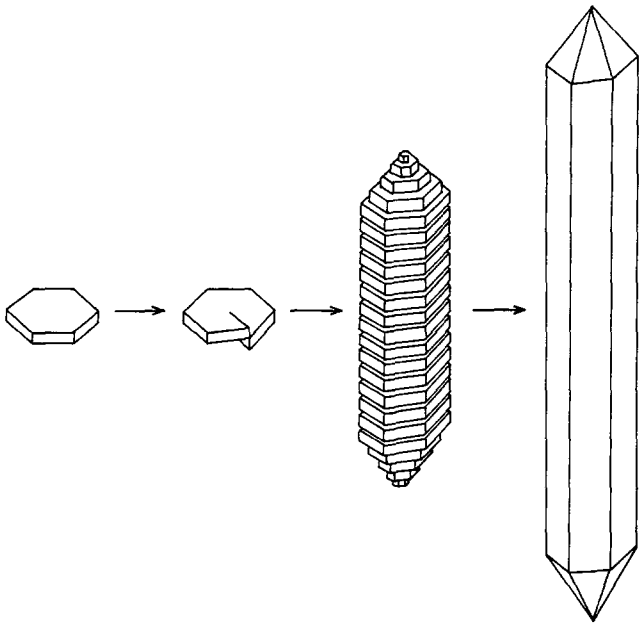


Figure 10 Schematic drawing of formation mechanism of POB whiskers

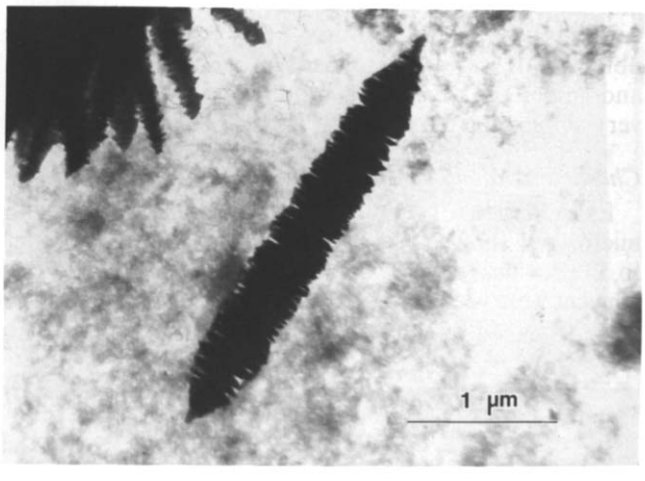


Figure 11 Transmission electron micrograph of an incipient crystal obtained in LP at 330°C for 3 min

From this mechanism, the influence of the solvent properties on the crystal habits, which are fibrillar and slab-like crystals, can be speculated more clearly. The oligomers of higher *DP* that are produced in a polar solvent form thicker primary nuclei. Because of this thickness, it is difficult for a screw dislocation to form in the thicker lamellae, and the lamellae grow preferentially in the lateral direction. Fibrillation occurs even in crystals that develop from the thicker and wider nuclei, because of the extended-chain packing along the same direction.

Thermal properties

Thermal properties of PON crystals were tabulated in *Table 4*. The PON whiskers displayed much better thermal stability than the other crystals on the basis of t.g.a. The temperature of 5% weight loss of PON whiskers prepared in LP was 506°C, which was the highest in PON crystals. But for PON-5, the temperature of 5% weight loss correlates very well with the density of the crystal, i.e. the crystal in which the polymer chains pack more densely shows higher thermal stability.

D.s.c. analysis confirmed the presence of a reversible transition (see *Table 4*). The transition temperatures of PON whiskers were 343.5°C on the heating scan and 327.0°C on the cooling scan. The other crystals did not show these transitions distinctly. Economy[14] also reported the same kind of transition for slab-like PON crystals at 338°C at a heating rate of 40°C min^{-1}. These higher transition temperatures of PON whiskers than for slab-like crystals are due to the closer packing of polymer chains in the crystals. The transition temperature of PON whiskers is slightly lower than that of POB whiskers (around 325–360°C) but basically both may be described as a plastic crystal transition or a highly ordered smectic, which is identical with the interpretation for the POB crystals[15–18].

CONCLUSIONS

Whiskers of poly(oxy-2,6-naphthalenediylcarbonyl) (PON) were obtained from 2-acetoxy-6-naphthoic acid (ANA) by high-temperature solution polycondensation. The sizes of these whiskers were ca. 7–17 μm in length and ca. 0.5–1.0 μm in width. The most important factors in controlling the crystal morphology during polymerization are the polarity of the solvent, concentration and stirring. In terms of these factors, less-polar solvent, such as liquid paraffin or Therm S 800, lower concentration and no stirring are desirable for making whiskers. From the structural analysis, these whiskers could be regarded as extended-chain single crystals. This PON whisker represents the second whisker for polycondensation polymers after the poly(oxy-1,4-benzenediylcarbonyl) (POB) whiskers.

From morphological observations, it was concluded that a PON whisker was formed with a spiral growth of lamellae and post-polymerization occurred in the interlamellar region, which was the same mechanism as for a POB whisker.

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