Solvent effect on the morphology of poly(oxy-1,4-benzenediylcarbonyl) whiskers from *p*-acetoxybenzoic acid

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Poly(oxy-1,4-benzenediylcarbonyl) (POB) whiskers from *p*-acetoxybenzoic acid were prepared in mixtures of liquid paraffin having many branched carbons (LP) and completely linear paraffin (SW). The crystal shapes of the POB whiskers obtained were largely changed by the mixing ratio of LP and SW. When the content of SW in the solvents increased: (i) both the length and the width of the whiskers decreased; (ii) the tip angle of the whiskers increased; and (iii) radial growth of the whiskers increased. The size of the POB whiskers was attributed to both the number and the size of those lamellar crystals with screw dislocations (primary nuclei for whisker growth) which had formed in the early stages of polymerization. In SW, larger numbers of smaller lamellar crystals were formed than in LP, owing to the lower solubility of POB oligomers at 330°C in SW; that is, the higher supersaturated state of the POB oligomers produced a larger number of smaller primary nuclei for whisker growth. Hence, whiskers having smaller lengths and widths were obtained as the content of SW increased. The other characteristic changes in whisker shapes, i.e. tip angles and radial growth, also seemed to be attributable to the degree of supersaturation of the POB oligomers, though further study is required. The thermal properties of the whiskers were evaluated by differential scanning calorimetry and thermogravimetric analysis.

(Keywords: polymer whiskers; aromatic polyester; morphology control)

INTRODUCTION

Wholly aromatic homopolyesters have received much attention as hopeful candidates for new, high-performance materials owing to their excellent mechanical properties and good thermal stabilities. However, owing to their low tractabilities (they show no T_m values and their solubilities in many common organic solvents are low), it is very hard to process them by conventional processing techniques. This is probably the greatest limitation to a broad commercial utilization of these polymers. In order to overcome this problem, copolyesters were developed to suppress the melting points below the decomposition points[1]. Copolymerization of a second or third monomer, however, degraded the inherent properties, especially the mechanical properties.

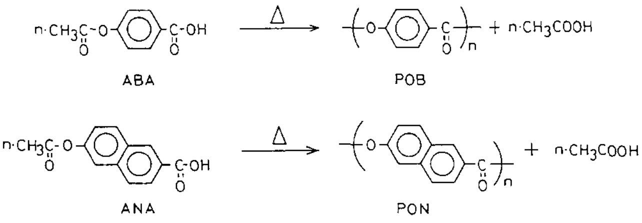
We have been studying the morphology control of polymer crystals during polymerization and have succeeded in obtaining whiskers of poly(oxy-1,4-benzenediylcarbonyl) (POB) and poly(oxy-2,6-naphthalenediylcarbonyl) (PON)[2–8]. They were synthesized by high-temperature polymerization of the acetoxy derivatives of the corresponding hydroxycarboxylic acids in liquid paraffin, as shown in *Scheme 1*. These whiskers were single and extended chain crystals. Therefore, it is possible that they will display outstanding inherent properties and become attractive materials for industrial usage. Our findings signify a new concept in the processing of low-tractability polymers into special crystal shapes during polymerization. In previous studies, we revealed that the important parameters in controlling the crystal morphology during solution polymerization were the nature of the solvent, concentration, and stirring[2,3,8]. Control of the size of the whisker is very important for the industrial application of these whiskers.

Here, we report on the influence of solvents on the morphology of POB whiskers, the solvents being linear and branched paraffins.

EXPERIMENTAL

Materials

p-Acetoxybenzoic acid (ABA) was prepared as described in the literature[3]. Liquid paraffin (LP), purchased from



Scheme 1 Preparation of poly(oxy-1,4-benzenediylcarbonyl) (POB) and poly(oxy-2,6-naphthalenediylcarbonyl) (PON)

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Nakarai Tesque Co. Ltd, was used after purification according to that described in our previous paper[3]. Sasol wax H2 (SW), purchased from Sasol, South African Coal & Gas Co. Ltd, was used after recrystallization from benzene.

Measurements

Morphological characterizations were performed by scanning electron microscopy (SEM) on a Hitachi 530-S.

Thermal properties were evaluated using differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.); the instruments used were a Perkin–Elmer DSC 7 and a Shimadzu TGA-30, respectively. D.s.c. was performed at a heating rate of 100°C min^{-1} in nitrogen. T.g.a. was performed on a 5 mg sample at a heating rate of 10°C min^{-1} in nitrogen or air.

The chemical structures of the solvents were analysed by ^{13}C n.m.r. at 120°C on a Varian FT-80A.

Preparation of poly(oxy-1,4-benzenediylcarbonyl) whiskers

A typical preparation procedure for POB whiskers is described in the following. Other crystals were also obtained in a similar manner.

Into a 200 ml cylindrical reactor equipped with a thermometer, a stirrer, and gas inlet and outlet tubes were added 0.90 g of ABA and 60 g of SW. 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 whiskers were formed. The reaction was continued at 330°C for 6 h under a slow stream of nitrogen. The reaction mixture was allowed to cool to room temperature and then benzene was added. The whiskers were collected by filtration after being washed in hot benzene several times, and they were then dried at 100°C under reduced pressure to constant weight.

RESULTS AND DISCUSSION

Chemical structure of paraffin

Two kinds of paraffin were used as solvents in this work: one was a liquid at room temperature (LP) and the other was a solid (SW) with a melting temperature of around 110°C. The chemical structures of these paraffins were analysed by ^{13}C n.m.r. The distributions of primary, secondary and tertiary carbons, assigned according to previous studies[9–12], are tabulated in *Table 1*. From these results, it can be seen that SW is a totally linear paraffin containing no branches. On the other hand, LP has many branches i.e. 15.2% of the carbons are tertiary.

Morphology of whiskers

The POB whiskers prepared in LP (POB-1) and SW (POB-4) are shown in *Figures 1* and *2*, respectively. The features of the whiskers are quite different depending on the solvents used. The conspicuous differences in their crystal shapes are: (i) both the length and width of POB-4 are smaller, the length and width being, respectively, a tenth and half that of POB-1; (ii) the tips of POB-1 are very sharp but those of POB-4 are completely flat; and (iii) POB-1 shows single, needle-like crystals but POB-4 shows radial growth from the centre. In order to clarify that these differences are attributable to the solvent effect, we observed the shapes of crystals prepared in various mixtures of LP and SW. The results are summarized in *Figures 3* and *4* and *Table 2*. The crystal shape was largely changed with the mixing ratio of the two solvents. As the content of SW in the solvent increased, both the length L and width W of the whiskers decreased. The tip angle θ of the whiskers became broader and the trunk ratio l/L (see *Figure 5*), which is proportional to the tip angle, became higher as the content of SW increased. Furthermore, the yield of POB-4 was quite low compared with the others. The solubility test of ABA in these paraffins at 330°C showed that the maximum solubility of ABA in LP was over 15 wt%, but in SW it was only 1.5 wt%. Because of this low solubility, sublimation of ABA from the SW solution occurred more vigorously during polymerization compared with the LP solution, and this sublimation diminished the yield of the whiskers.

Table 1 Chemical structures of paraffins, analysed by ^{13}C n.m.r.

Paraffin	M_n	Distribution of carbon atoms (number): Primary	Secondary	Tertiary	Molar ratio of tertiary carbons (%)
LP	928	12	44	10	15.2
SW	759	2	52	0	0

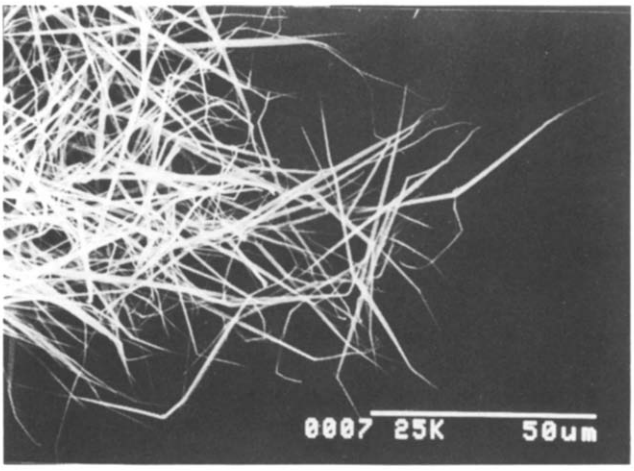

Figure 1 Scanning electron micrograph of POB whiskers prepared in LP (POB-1)

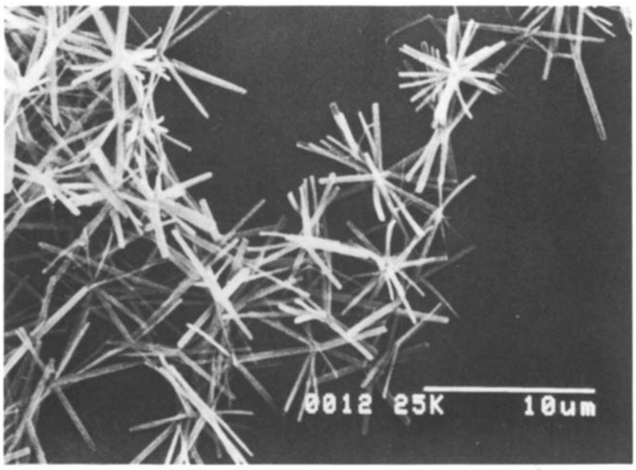

Figure 2 Scanning electron micrograph of POB whiskers prepared in SW (POB-4)

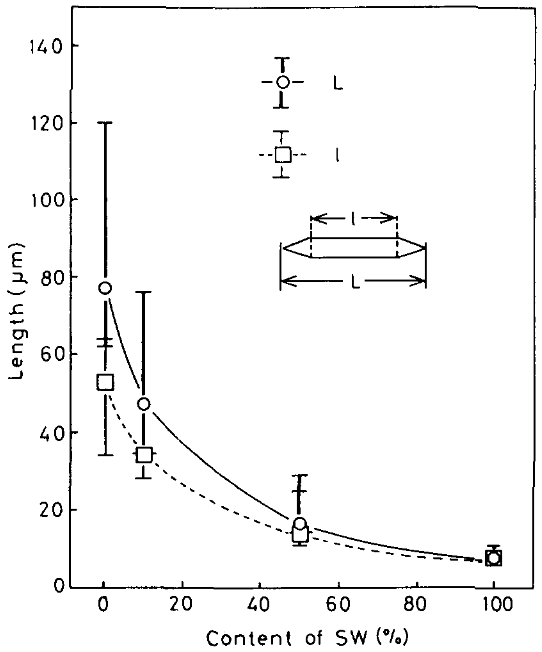

Figure 3 Length *L* and trunk length *l* of whiskers plotted as functions of content of SW in the solvent

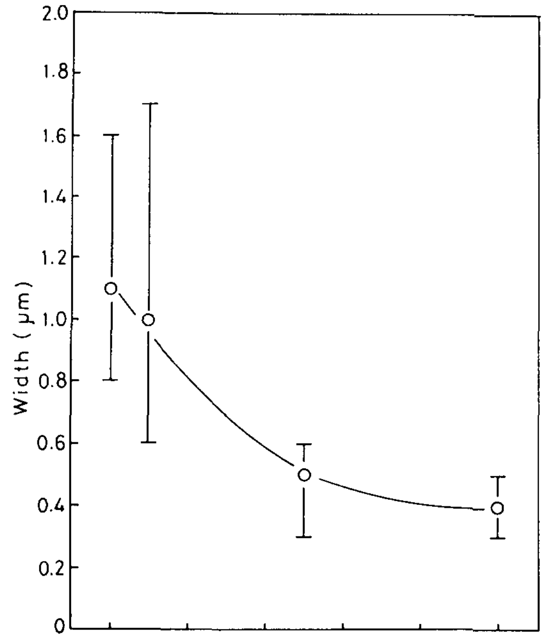

Figure 4 Width *W* of whiskers plotted as a function of content of SW in the solvent

We have already suggested that the size of the whiskers is determined by both the number and the size of those lamellar crystals with screw dislocations formed in the early stages of polymerization. The number of lamellar crystals *N* contributing to whisker growth can be experimentally estimated from the yield of polymer and the average weight of whiskers obtained (equation (1)). Here, it is shown that these whiskers have hexagonal cross-sections, as described in a previous paper[6]

$$N=\frac{\varepsilon M}{(\sqrt{3}/8)W^{2}(L+21)\rho} \qquad (1)$$

where ε is the yield (%), M is the molar mass of the POB repeating unit, W is the average width of the whiskers, L is the average length of the whiskers, l is the average trunk length of the whiskers and ρ is the density of the POB whisker (1.54×10^{-12} g μm^{-3}).

The results are plotted in *Figure 6*. *N* increases as the content of SW in the solvent increases and *N* in SW is quite large compared with *N* in LP. For the purpose of understanding this phenomenon, we also observed the shapes of the whiskers obtained after 3 min at 330°C in LP (POB-5) and SW (POB-6). The results are summarized in *Table 3* and the distributions of both the length and the width of the crystals are shown in *Figure 7*. It is evident that many more nuclei for whisker growth with smaller width were formed in SW than in LP. The narrow distributions of both the length and the width show that lamellar crystals with dislocations serve as nuclei for whisker growth. The numbers of whiskers after 3 min at 330°C were in good agreement with those estimated from the final whiskers. This good agreement implies that there is no time lapse in the formation of primary nuclei for whisker growth.

These results are explicable on the basis of the following mechanism of formation for POB whiskers[5–7]: (i) POB oligomers precipitate out from the homogeneous solution and crystallize in the form of lamellae; (ii) screw

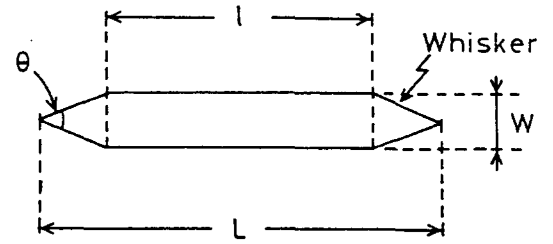

Figure 5 Description of the parameters relating to whisker size and shape

Table 2 Sizes of POB whiskers from ABA in paraffin

Polymer	Solvent^a LP/SW (weight ratio)	Yield (%)	Size of whisker^b (μm) Length L	Trunk length l	Width W	Trunk ratio l/L (%)	Tip angle θ (°)
POB-1	100/0	79	78	41	1.1	53	4
POB-2	90/10	79	47	34	1.0	72	9
POB-3	50/50	73	17	14	0.5	82	19
POB-4	0/100	27	8	8	0.4	100	180

^{a}Solvent weight ratio: LP (liquid paraffin)/SW (Sasol wax)

^{b}Length *L*, trunk length *l*, width *W* and tip angle θ are described in *Figure 5*

Table 3 Shapes of incipient crystals and calculated numbers of primary nuclei for whisker growth

			Average size of crystals (μm)				
Polymer	Solvent	Yield (%)	Length L	Trunk length l	Width W	Tip angle θ (°)	Number of primary nuclei[a] 10^{12} N (mol^{-1})
POB-5	LP	1.5	3.00	2.29	0.60	80	1.2
POB-6	SW	2.8	1.32	0.99	0.28	80	24.7

[a] Number of primary nuclei calculated from equation (1)

Table 4 Thermal transitions of POB whiskers

	Low-temperature transition			High-temperature transition		
Polymer	T_t[a] (°C)	ΔH[b] (kJ mol^{-1})	ΔS[c] (J K^{-1} mol^{-1})	T_t (°C)	ΔH (kJ mol^{-1})	ΔS (J K mol^{-1})
POB-1	374.4	6.82	10.53	454.4	0.63	0.87
POB-2	378.0	6.97	10.71	457.2	0.37	0.51
POB-3	371.7	6.28	10.53	451.7	0.53	0.72
POB-4	369.6	6.79	10.57	450.4	0.67	0.92

[a] Transition temperature on a heating scan at a rate of 100°C min^{-1}
[b] For the oxybenzoyl unit
[c] For the oxybenzoyl unit

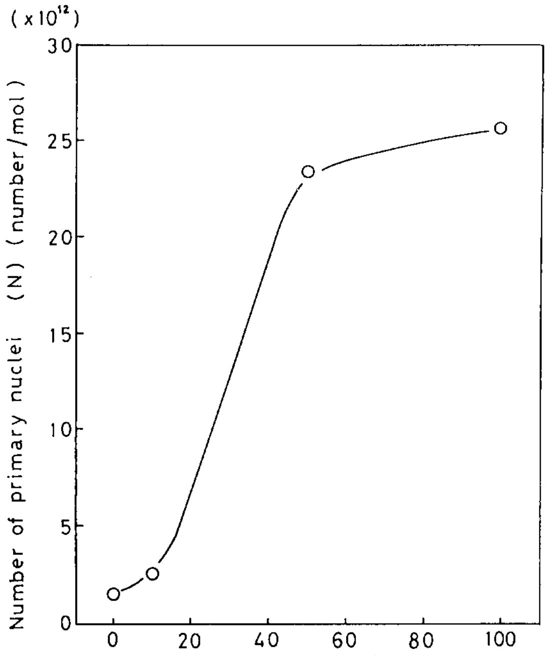

Figure 6 Number of primary nuclei for whisker growth N plotted as a function of content of SW in the solvent

dislocations occur in the lamellae (primary nuclei for whisker growth) and needle-like crystals are formed with spiral growth; and (iii) the molar mass increases by transesterification in the interlamellar region and reorganization of crystals occurs. The formation of lamellar crystals, which correspond to primary nuclei for whisker growth, determines the crystal shape of the eventual whiskers. As described earlier, owing to the lower solubility of POB oligomers in SW, many more primary nuclei for whisker growth are formed in the early stages of polymerization in the SW solution; that is, the lamellar crystals are precipitated from a sufficiently highly

Table 5 Thermal stabilities of POB whiskers

	Temperature of 5 wt% loss (°C)	
Polymer	Nitrogen	Air
POB-1	510	501
POB-2	508	495
POB-3	498	483
POB-4	493	465

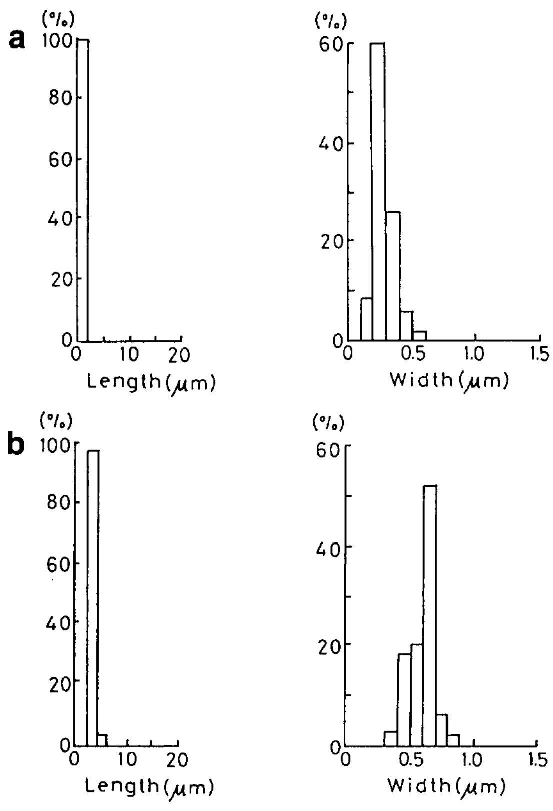

Figure 7 Distributions of the length and the width of the whiskers prepared in 3 min at 330°C in (a) SW and (b) LP

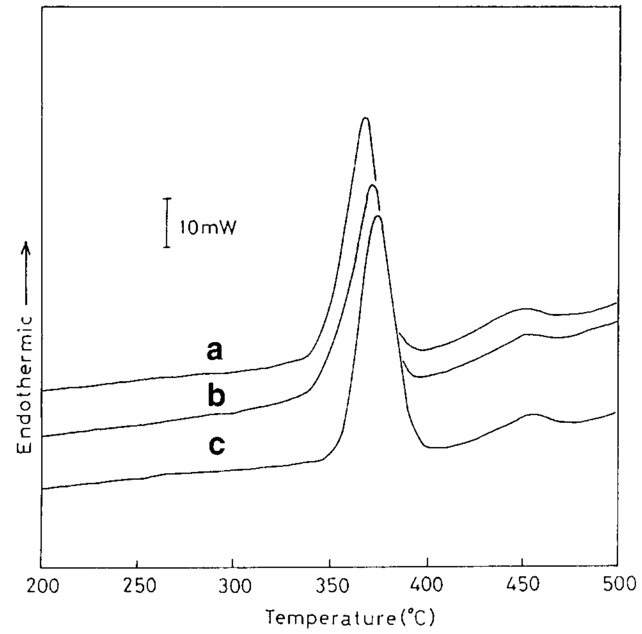

Figure 8 D.s.c. profiles of (a) POB-1, (b) POB-3 and (c) POB-4 on a heating scan at a rate of 100°C min^{-1}

supersaturated solution to give a large number of crystals with small diameter. The sublimation of ABA proceeds concurrently with the polymerization, and therefore the concentration of ABA decreases. Hence, the large number of primary nuclei and the decrease in ABA concentration by sublimation cause the whiskers to be small in SW. Both the solubility of POB oligomers and the decrease in ABA concentration by sublimation are strongly related to the content of SW in the solvent, and it is clear that the size of whisker obtained decreases as the content of SW increases.

The nature of the change in tip angle with varying SW content in the solvent is not clear. The tendency towards radial growth with increased SW content is ascribed to rapid nucleation from a highly supersaturated solution. Further study is required to elucidate the nature of the radial growth and the change in tip angle.

Thermal properties

The thermal properties of POB whiskers were estimated by d.s.c. and t.g.a.

D.s.c. analysis confirmed the presence of two reversible transitions at around 370°C and 450°C on a heating scan, as shown in *Figure 8*. In order to avoid the influence of thermal decomposition, d.s.c. was performed at the extremely high heating rate of 100°C min^{-1}. The transition temperatures T_t, enthalpies ΔH and entropies ΔS for the first heating scan are tabulated in *Table 4*. Both transition temperatures of POB-4 were the lowest and the 100% SW content in the solvent is thought to be the cause of this. It is known that the POB crystal has two reversible thermal transitions. These transitions at 370°C and 450°C are regarded as a plastic crystal or a highly ordered smectic phase transition and a phase transition to a nematic mesophase, respectively[13,14]. In our previous reports, it was clear that these transition temperatures were strongly related to the densities of the POB whiskers, i.e. the packing densities of the polymer chains[3]. On the basis of our previous studies, the low transition temperatures of POB-4 are due to loose packing of the polymer chains in the crystals. It is thought that the packing of the polymer chains in the crystals becomes looser as the content of SW in the solvent becomes higher. This explanation rests on the poor efficiency of the transesterification in the interlamellar region.

The thermal stabilities, as analysed by t.g.a., are summarized in *Table 5*. These whiskers exhibited excellent thermal stabilities. The temperature of 5 wt% loss decreased monotonously in both nitrogen and air as the content of SW increased. This relationship between thermal stability and SW content is substantially identical with the relationship between transition temperature and SW content described above. This identity indicates that the crystals in which the polymer chains pack more densely show the higher thermal stability.

CONCLUSION

POB whiskers were prepared in mixtures of LP and SW at 330°C. The conspicuous changes in cyrstal shape with increasing SW content in the solvent were: (i) both the length and the width of the whisker decreased; (ii) the tip angle of the whisker increased; and (iii) radial growth of the whisker increased. These characteristic changes in size can be attributed to the solubility of POB oligomers in the solvent. Because of the low solubility of POB oligomers in SW, many more primary nuclei for whisker growth are formed in the early stages of polymerization in SW than in LP; that is, the nucleation from a sufficiently highly supersaturated state produces a large number of nuclei with small diameter. The sublimation of ABA proceeds concurrently with the polymerization, and therefore the concentration of ABA decreases over time. Hence, the large number of primary nuclei and the decrease in ABA concentration by sublimation cause the whiskers to be small in SW. The results of observing the incipient whiskers obtained in 3 min at 330°C in SW and LP bore out this conclusion. The change in the tip angle and the increasing tendency towards radial growth with increasing SW content in the solvent seem to be attributable to the high degree of supersaturation, though further study is required.

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