Synthesis and characterization of poly(4-mercaptobenzoyl) whiskers from *S*-acetyl-4-mercaptobenzoic acid

Kunio Kimura
TOYOBO Co. Ltd, Research Center, Ohtsu, Shiga 520-02, Japan

and Yuhiko Yamashita*
Faculty of Engineering, Okayama University, Okayama 700, Japan
(Received 5 July 1993; revised 24 December 1993)

Poly(4-mercaptobenzoyl) (PMB) whiskers were obtained from *S*-acetyl-4-mercaptobenzoic acid by high-temperature solution polymerization. The whisker prepared in liquid paraffin at a concentration of 1.0% at 300°C has an almost uniform width of 0.3–0.5 μm and a length of 5–8 μm. These whiskers show radial growth from the centre. The optimal conditions for preparing them are by using liquid paraffin as a solvent and polymerization temperatures of 260–300°C. Electron diffraction reveals that the PMB whiskers show single crystal nature and the polymer chains are aligned along the long axis of the whisker. D.s.c. analysis of the PMB whiskers shows the presence of the reversible solid–solid transition as already reported by Kricheldorf *et al.* The transition temperature and enthalpy of the PMB whiskers are higher and larger than those of PMB crystals with other morphologies. Another endotherm is found at ~420°C, but only when measurement is carried out using a faster heating rate of 100°C min^{-1}. This is deduced to be a solid–liquid crystal transition from the observation of the nematic domain structure in a quenched specimen using an optical microscope. Finally, the formation mechanism of the PMB whiskers is discussed from the polymerization time dependencies of the length, the degree of polymerization and the yield.

(Keywords: poly(4-mercaptobenzoyl); polymer whisker; needle-like polymer crystals)

INTRODUCTION

In recent years there has been a dramatic development in the preparation of chain extended polymer crystals as high-performance materials due to their good mechanical properties. Usually, chain extended crystals are difficult to obtain by conventional processing methods so that special processing techniques such as gel spinning and spinning from liquid crystalline solutions have been developed[1].

There exists another stream of development for chain extended polymeric materials by means of crystallization during polymerization. Needle-like crystals of both flexible and rigid chain polymers, so-called polymer whiskers, have been obtained by solid-state polymerization of monomers and polymerization in solution. Examples of the former polymerization include oxacyclobutanes such as 1,3,5-trioxane[2,3], diolefins undergoing 'four-centre type' photopolymerization[4,5] and monomers with conjugated triple bonds such as substituted diacetylenes[6,7]. However, the first whisker obtained by polymerization in solution was polyoxymethylene[8–10]. This whisker was obtained in a cationic polymerization system of 1,3,5-trioxane and has a width of 1–2 μm and a length of 10–50 μm. It was of practical use on account of its unique morphology and good mechanical properties[11,12].

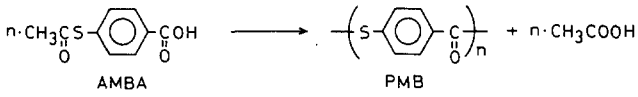
The first trial for obtaining needle-like crystals of a wholly aromatic polymer was reported in 1977[13]. Needle-like crystals of poly(1,4-benzamide) were prepared by solid-state thermal polymerization or solid-state polymerization in a poor solvent containing an acid acceptor of the needle-like crystal of 4-aminobenzoyl chloride. The resultant needle-like crystals were highly crystalline but the polymer chains were oriented crosswise to the long axis of the needle-like crystals. Recently, whiskers of wholly aromatic polyester were obtained in a high-temperature solution polycondensation system by the authors[14–20]. These whiskers were poly(*p*-oxybenzoyl) (POB) and poly(2-oxy-6-naphthoyl) (PON). The width of these whiskers was 1–1.5 μm. The length of the POB whisker was 50–100 μm and that of the PON whisker was 20–30 μm. The polymer chains of both POB and PON are oriented along the long axis of the whiskers. These whiskers showed outstanding thermal stabilities and good mechanical properties. Therefore, it was anticipated that they would be useful as high-performance materials such as polymer reinforcement.

Poly(4-mercaptobenzoyl) (PMB) has a straight rigid-rod molecular chain and it is highly crystalline[21]. The molecular structure of PMB is similar to that of POB, that is, the ether oxygen of POB is replaced by sulfur, and hence it is anticipated that PMB whiskers may be prepared during solution polymerization. It was shown that PMB was obtained by high-temperature solution

* To whom correspondence should be addressed

0032-3861/94/15/3311-06

polymerization in an aromatic solvent at high monomer concentration[21]. However, the crystal morphology of PMB crystals has not been reported so far. Thus, it is the purpose of the present work to synthesize PMB whiskers from *S*-acetyl-4-mercaptobenzoic acid (AMBA) by solution polymerization as shown in *Scheme 1* and to describe their crystal morphologies.



Scheme 1 Synthesis of poly(4-mercaptobenzoyl) (PMB)

EXPERIMENTAL

Materials

AMBA was prepared as described in the literature[21–24]. Purity was checked by g.c.-m.s. spectrometry. Liquid paraffin was obtained from Nakarai Tesque Co. Ltd. Therm S 800 (TS 800), a mixture of isomers of diethylbiphenyl, was obtained from Nippon Steel Chemical Co. Ltd. Liquid paraffin and TS 800 were used as polymerization solvents after purification as described in the literature[15].

Measurements

Morphological characterization was performed by SEM and TEM. The instruments used were a Hitachi 530-S and a Hitachi HU-11B, respectively.

Thermal properties were evaluated using d.s.c. and t.g.a. D.s.c. was performed on a Perkin-Elmer DSC-7 with a heating rate of 10 or 100°C min^{-1} in nitrogen. T.g.a. was performed on a Shimazu TG-30 with a 5 mg sample and a heating rate of 10°C min^{-1} in nitrogen or air.

The degree of polymerization (*DP*) was measured by ^{1}H n.m.r. end-group analysis of the acetyl group after hydrolysis of PMB with concentrated sulfuric acid in an n.m.r. tube with a Varian Gemini-200 spectrometer as described in the literature[19,25].

Preparation of PMB crystals

The typical preparation procedure of PMB whiskers is as follows: AMBA (0.865 g) and liquid paraffin (60 ml) were placed in a cylindrical reactor (200 ml) equipped with a thermometer, a stirrer, and gas inlet and outlet tubes. The reaction mixture was heated with stirring under a slow stream of nitrogen. When the monomer had dissolved completely, stirring was stopped. Heating was continued up to 300°C. When the temperature reached 260°C, the reaction solution became turbid and crystals began to precipitate. The temperature was finally maintained at 300°C for 6 h. The reaction mixture was allowed to cool to room temperature and chloroform was added. The polymer crystals were collected by filtration, washed several times with chloroform and acetone, and then dried at 100°C under reduced pressure to a constant weight.

Analysis: calculated for C_7H_4OS polymer: C, 61.74; H, 2.96; S, 23.55%. Found: C, 61.81; H, 3.01; S, 23.10%.

RESULTS AND DISCUSSION

Synthesis

The PMB whiskers were obtained by high-temperature solution polymerization of AMBA in liquid paraffin. The morphological features of crystals prepared under various conditions are summarized in *Table 1*. The PMB whisker prepared in liquid paraffin at 300°C (PMB-2) has a length of 5–8 μm and a width of 0.3–0.5 μm as shown in *Figure 1*. The whiskers show radial growth from the centre.

When the polymerization was carried out in TS 800, crystals did not precipitate even after 6 h. Oligomers precipitated after cooling the polymerization mixture to 25°C and their *DP* was 3.4. This shows that further polycondensation of AMBA does not proceed at a concentration of 1.0 wt% in TS 800 at 200°C. Under the condition of low monomer concentration, the precipitation of oligomers seems to be an important process for further polycondensation[15,16]. In the case of POB, crystals were not obtained at a concentration of 1.0 wt% in diphenyl sulfone which was a good solvent for the oligomers[15]. Also, in the case of PMB/TS 800 (PMB-6 in *Table 1*), a similar consideration may be allowable. If the oligomers of low *DP* do not precipitate because of their good solubility, it is thought that the effective rate of polycondensation decreases with a decrease of the concentration of the end-group and the polycondensation actually stops. The *DP* of the oligomers does not exceed the critical value for the precipitation and therefore a crystal is not formed. Further study is required to clarify the details of this phenomenon.

Concerning the polymerization temperatures, the PMB whiskers were obtained in the range of 260–300°C in liquid paraffin. The crystals prepared in liquid paraffin at 330°C (PMB-1) were a bundle of coloured needle crystals (*Figure 2*). PMB is relatively thermally unstable and

Table 1 Polymerization conditions and morphological features of the PMB crystals

Polymer no.	Solvent[a]	Conc.[b] (%)	Polymerization temp.(°C)/time(h)	Yield (%)	Crystal morphology
PMB-1	LP	1.0	330/6	50.0	Fibrillated
PMB-2	LP	1.0	300/6	61.6	Needle-like
PMB-3	LP	1.0	280/6	61.7	Needle-like
PMB-4	LP	1.0	260/6	50.0	Needle-like
PMB-5	LP	5.0	300/6	72.9	Fibrillated
PMB-6	TS 800	1.0	300/6	–[c]	–

[a] Solvent: LP, liquid paraffin; TS 800, Therm S 800
[b] Conc. (%) = [theoretical polymer yield (g)/solvent volume (ml)] × 100
[c] Crystal was not obtained

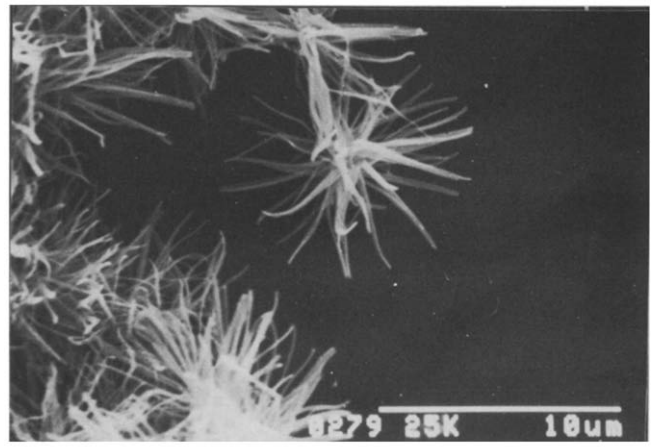


Figure 1 Scanning electron micrograph of the PMB whiskers prepared at a concentration of 1.0 wt% in liquid paraffin at 300°C (PMB-2)

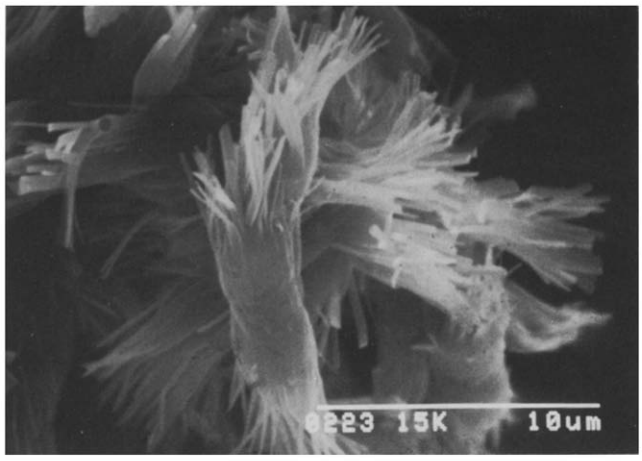


Figure 2 Scanning electron micrograph of the PMB crystals prepared at a concentration of 1.0 wt% in liquid paraffin at 330°C (PMB-1)

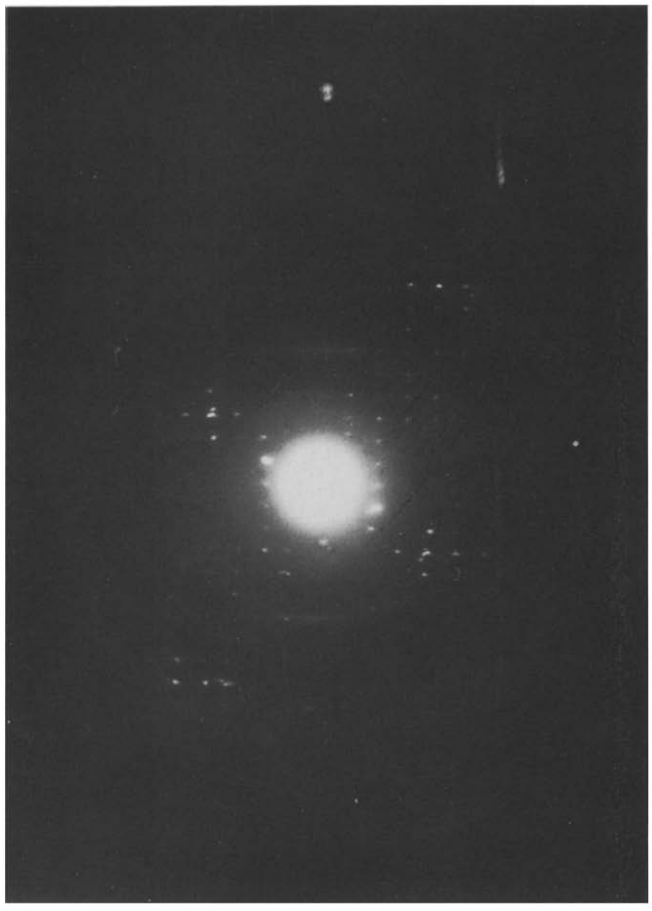


Figure 3 Electron diffraction pattern of the PMB whiskers (PMB-2)

thermal decomposition begins at ~330°C even under nitrogen. A higher temperature (>300°C) is undesirable for preparing PMB whiskers as thermal decomposition might prevent ideal crystallization during polymerization.

Characterization of PMB whiskers

An electron diffraction pattern of PMB whiskers is shown in *Figure 3*. The diffraction pattern consists of sharp spots of lower- to higher-order reflections. This is due to the single crystal nature of the whiskers. The meridian of this pattern corresponds to the long axis of the crystal, and therefore it is concluded that polymer chains are aligned along the long axis of the whisker. The fibre identity period is 1.33 nm, corresponding to two chemical residues. A detailed observation of this electron diffraction pattern shows diffuse streaks around 004 and 006 reflections. These streaks may be due to the nematic-like disorder in the chain direction.

Thermal properties of PMB crystals

It has been reported that the PMB crystal has a reversible first-order transition with an endotherm at ~366°C on a heating scan and an exotherm at ~328°C on a cooling scan from d.s.c. analysis[21]. This transition is a solid–solid transition differing from the melting process and it was closely analogous to that of POB crystals. It was revealed by WAXS measurements with synchrotron radiation that this solid–solid transition was regarded as a transition to a pseudohexagonal packing of chains by rotation of the 1,4-phenylene rings[21].

D.s.c. analysis of the PMB crystals obtained here confirmed the presence of a reversible solid–solid transition when the measurements were performed up to 400°C using a rate of 20°C min^{-1}. The solid–solid transition temperatures (T_t) and their enthalpies (ΔH_t) measured on the heating scans are given in *Table 2*. The T_t and ΔH_t of the PMB whiskers (PMB-2, -3 and -4) are higher and larger than the others, and this suggests the closer packing of polymer chains in the whiskers than in the crystals with other morphologies. The existence of a higher transition temperature where significant flow may occur should be predictable from the results of POB crystals[26–28] but it has not been reported previously. Here, a higher transition than T_t might be masked by the thermal decomposition of PMB during the heating process. D.s.c. experiments were carried out with a faster heating rate of 100°C min^{-1} to avoid thermal decomposition. It was found that an endotherm was detected at ~420°C as shown in *Figure 4*. An optical micrograph with crossed polarizers (*Figure 5*) was obtained from the specimen which was molten at 450°C in the absence of externally applied shear and then quenched rapidly to room temperature to avoid a change in texture by thermal

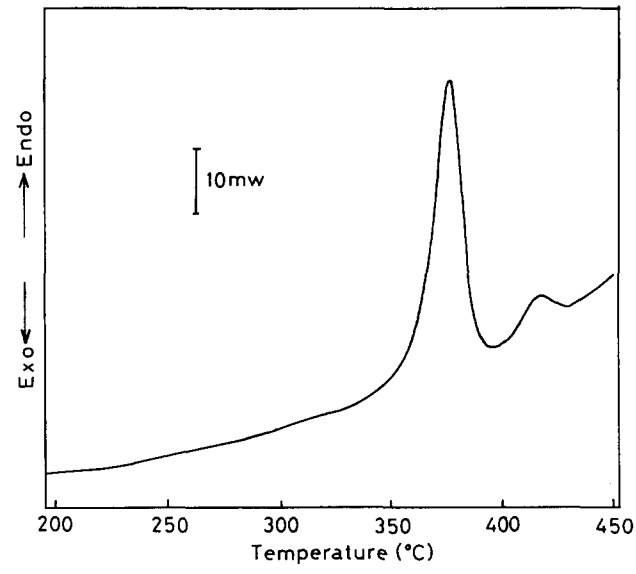


Figure 4 Typical d.s.c. profile of the PMB crystals measured with a scanning rate of 100°C min^{-1} under 450°C

Table 2 Thermal properties of the PMB crystals

Polymer no.	D.s.c.[a] T_t (°C)	ΔH_t (kJ mol^{-1})	ΔS_t (J K^{-1} mol^{-1})	T_n (°C)	ΔH_n (kJ mol^{-1})	ΔS_n (J K^{-1} mol^{-1})	T.g.a.[b] (°C) Air	Nitrogen
PMB-1	358.0	9.08	14.39	424.2	0.25	0.35	387	395
PMB-2	365.3	9.46	14.82	416.4	0.89	1.28	385	404
PMB-3	364.6	10.00	15.68	421.2	0.50	0.73	383	396
PMB-4	362.9	9.14	14.37	414.0	1.00	1.46	382	389
PMB-5	339.2, 355.2	3.32, 7.28	5.42, 11.59	398.9	0.25	0.37	373	374

[a] T_t, solid–solid transition temperature measured on the heating scan at a heating rate of 20°C min^{-1}; T_n, solid–liquid crystal transition temperature measured on the heating scan at a heating rate of 100°C min^{-1}
[b] Temperature at which 5% weight loss was recorded in t.g.a. curves

decomposition. This micrograph shows the presence of nematic-like domain structures and therefore this higher temperature modification may be called a liquid crystal phase. An exothermic peak corresponding to this higher transition could not be detected on the cooling scan due to probable decomposition of the sample. The higher transition temperatures (T_n) and their enthalpies (ΔH_n) are also given in *Table 2*. The T_n of the PMB whiskers is higher than PMB-5 but lower than PMB-1. The ΔH_n of the PMB whiskers, however, is much larger than the others. The larger value of ΔH_n of the PMB whiskers is ascribed to the closer packing of polymer chains.

The thermal stabilities of the PMB crystals from t.g.a. measurements are also summarized in *Table 2*. It was found that the thermal decomposition of the PMB crystals began at ~310°C in air and 330°C in nitrogen. The PMB-2 whiskers have the best thermal stability compared to the other morphological crystal forms.

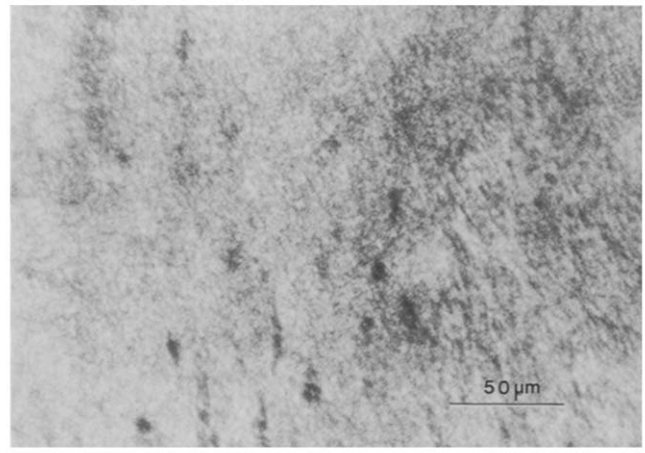


Figure 5 Optical micrograph with crossed polarizers of a PMB specimen quenched to 25°C from the melt phase at 450°C

Growth mechanism of PMB whiskers

In order to understand the growth mechanism of the PMB whiskers, the change in crystal morphology was examined with polymerization time at 300°C in liquid paraffin. The crystals were collected by vacuum filtration at 300°C to avoid any influence of the crystallization of oligomers onto the surface of crystals during cooling. The transmission electron micrograph of incipient crystals prepared for 3 min at 300°C is shown in *Figure 6*. As can be seen, many fibrillar crystals (1.0–1.5 μm long and 0.1–0.3 μm wide) grow radially. These incipient crystals have smooth surfaces. The lamellar structure piling up along the long axis of the needle crystals as observed in the incipient crystals of the POB whiskers[16] was not observed.

Polymerization time dependencies of the length and the yield of the PMB whiskers are shown in *Figure 7*. The yield increases rapidly in the early stage of polymerization accompanying the increase in the length of the PMB whiskers. This shows the high reactivity of the mercapto group in the transesterification reaction. It is also clear that the needle crystals are not formed by fibrillation of a large crystal but formed by independent growth through polymerization.

The change of the *DP* of the PMB whiskers with polymerization time is shown in *Figure 8*. The *DP* increases rapidly with yield up to 30 min and then it increases gradually after the yield levels off. This implies that polymerization proceeds with crystal growth and post polymerization also occurs in the crystal regions after crystal growth ceases.

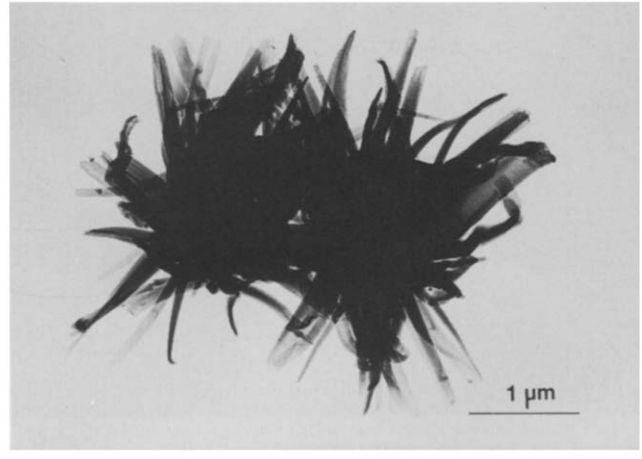


Figure 6 Transmission electron micrograph of the incipient PMB crystals obtained in liquid paraffin at 300°C for 3 min

The solid–solid transition temperature (T_t) and the enthalpy (ΔH_t) of the PMB whiskers are plotted against the polymerization time in *Figure 9*. While both T_t and ΔH_t increase within 5 min, they are almost constant after 5 min through the polymerization. The change of an endothermic peak measured on the heating scan with the polymerization time is shown in *Figure 10*. An

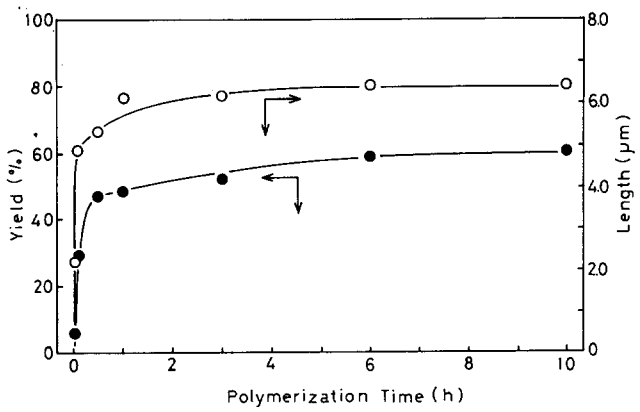


Figure 7 Time dependencies of the length (○) and the yield (●) of the PMB whiskers

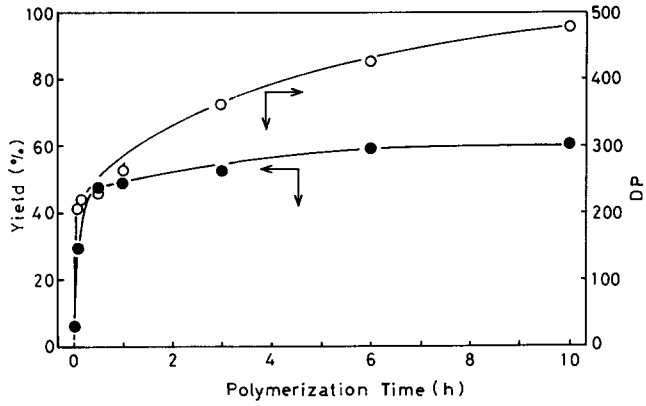


Figure 8 Time dependencies of the *DP* (○) and the yield (●) of the PMB whiskers

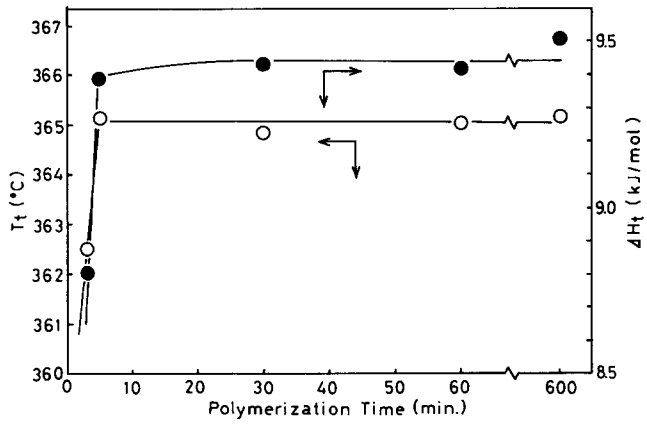


Figure 9 Time dependencies of transition temperature (T_t) (○) and enthalpy (ΔH_t) (●) of the PMB whiskers obtained in liquid paraffin at 300°C

endothermic peak of the crystals polymerized for 3 min is broader with a discernible shoulder on the lower temperature side of the main peak. This shoulder peak disappears after further polymerization for 5 min. The peak of the crystals polymerized for 5 min is as sharp as that of the crystals polymerized for 600 min. A previous study using POB whiskers revealed that the temperature and the enthalpy of the solid–solid transition were closely related to the density of the POB crystals and the crystal having higher density exhibited a higher transition

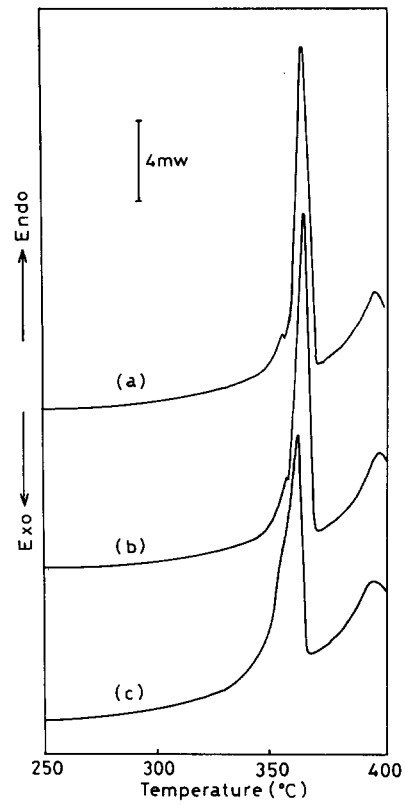


Figure 10 Change of the endothermic peak of the PMB whiskers obtained in liquid paraffin at 300°C for (a) 600 min, (b) 5 min and (c) 3 min

temperature and larger enthalpy[15]. In other words, a higher transition temperature and larger enthalpy indicate a denser packing of polymer chains in the crystal. From the similarity of the nature of the solid–solid transition between POB and PMB, the change of this transition behaviour of the PMB whiskers suggests that reorganization of the polymer chains accompanies polymerization as soon as the oligomers crystallize from the solution, and densely packed polymer crystals are formed rapidly.

From these experimental results the growth of the PMB whiskers can be speculated. The oligomers of low *DP* are formed in a homogeneous solution, and the oligomers are crystallized in the form of needle crystals as soon as the *DP* exceeds a critical value. In a detailed observation of the incipient crystals, the needle crystals are found to be extended chain fibrillar crystals. At present, it cannot be concluded whether the formation of such needle crystals is due to spiral growth like the POB whiskers. This point is now under investigation.

CONCLUSIONS

The PMB whiskers were obtained from AMBA by high-temperature solution polymerization. The PMB whisker prepared in liquid paraffin at 300°C for 6 h has a length of 5–8 μm and a width of 0.3–0.5 μm. These whiskers show radial growth from the centre. The important factors in obtaining PMB whiskers during polymerization are the type of solvent used and the polymerization temperature. Liquid paraffin is the only solvent to provide the PMB whiskers and the optimum polymerization temperature is in the range of 260–300°C.

Electron diffraction reveals that the PMB whiskers

show a single crystal nature and the polymer chains are aligned along the long axis of the whisker.

D.s.c. analysis of the PMB whiskers shows the presence of a reversible solid–solid transition at ~360°C as reported by Kricheldorf *et al.* and a solid–liquid crystal transition at ~420°C. The temperatures and the enthalpies of these transitions of the PMB whiskers are relatively higher and larger than the crystals with other morphologies and this fact suggests the closer packing of polymer chains in the whiskers.

The growth mechanism of the PMB whiskers can be speculated by the results of the polymerization time dependencies of the length, the *DP* and the yield. The oligomers of low *DP* are formed in a homogeneous solution, and the oligomers are crystallized in the form of needle crystals as soon as the *DP* exceeds a critical value. The change of the solid–solid transition behaviour of the resulting whiskers with time suggests that the polymerization of oligomers and the reorganization of polymer chains in crystals occur as soon as the oligomers crystallize from the solution, and densely packed polymer crystals are formed immediately. Further post polymerization follows in the crystals and the *DP* increases after crystal growth ceases.

ACKNOWLEDGEMENT

The authors thank Dr A. Kaji of TOYOBO Research Center for useful discussions about the ^{1}H n.m.r. measurements for the determination of the *DP* by end-group analysis.

REFERENCES

1 Ward, I. W. 'Developments in Oriented Polymers-2', Elsevier Applied Science, London, 1987
2 Andrew, E. H. and Martin, G. E. *J. Mater. Sci.* 1973, **8**, 1315
3 Patell, Y. R. and Schultz, J. M. *J. Macromol. Sci. Phys.* 1973, **B7**, 445
4 Iguchi, M., Nakanishi, H. and Hasegawa, M. *J. Polym. Sci. A1* 1968, **6**, 1055
5 Nakanishi, H., Suzuki, Y., Suzuki, F. and Hasegawa, M. *J. Polym. Sci. A1* 1969, **7**, 753
6 Wegner, G. *Makromol. Chem.* 1972, **154**, 35
7 Bloor, D., Koski, L., Stevens, G. C., Preston, F. H. and Ando, D. J. *J. Mater. Sci.* 1975, **10**, 1678
8 Iguchi, M. *Br. Polym. J.* 1973, **5**, 195
9 Iguchi, M., Murase, I. and Watanabe, K. *Br. Polym. J.* 1974, **6**, 61
10 Iguchi, M. and Murase, I. *Makromol. Chem.* 1975, **176**, 2113
11 Iguchi, M., Suehiro, T., Watanabe, T., Nishi, Y. and Uryu, M. *J. Mater. Sci.* 1982, **17**, 1632
12 Shimomura, M., Maeda, Y. and Tanabe, Y. *J. Mater. Sci.* 1989, **24**, 2245
13 Morgan, P. W. *Macromolecules* 1977, **10**, 1381
14 Endo, S., Kimura, K., Ohta, T. and Kato, Y. *US Pat. 4673724*, 1987
15 Kato, Y., Endo, S., Kimura, K., Yamashita, Y., Tsugita, H. and Monobe, K. *Koubunshi Ronbunshu* 1987, **44**, 35
16 Yamashita, Y., Kato, Y., Endo, S., Kimura, K., Tsugita, H. and Monobe, K. *Koubunshi Ronbunshu* 1987, **44**, 41
17 Yamashita, Y., Kato, Y., Endo, S. and Kimura, K. *Makromol. Chem. Rapid Commun.* 1988, **9**, 687
18 Kato, Y., Yamashita, Y., Kimura, K., Endo, S. and Kajisaki, K. *Koubunshi Ronbunshu* 1990, **45**, 973
19 Kato, Y., Yamashita, Y., Kimura, K., Endo, S. and Ohta, T. *Koubunshi Ronbunshu* 1990, **47**, 583
20 Kimura, K., Endo, S., Kato, Y. and Yamashita, Y. *Polymer* 1993, **34**, 1054
21 Kricheldorf, H. R. and Conradi, A. *Macromolecules* 1989, **22**, 14
22 Allen, C. F. and McKay, D. D. *Org. Synth.* 1932, **12**, 76
23 Compaigne, E. and Meyer, W. W. *J. Org. Chem.* 1962, **27**, 2835
24 Bordwell, F. G. and Bontan, P. J. *J. Am. Chem. Soc.* 1956, **78**, 854
25 Kaji, A. and Murano, M. *Polym. Prepr. Jpn* 1986, **35**, 837
26 Economy, J., Vollsen, W., Viney, C., Geiss, R., Siemens, R. and Karis, T. *Macromolecules* 1988, **21**, 2777
27 Muhlebach, A., Lyeria, L. and Economy, J. *Macromolecules* 1989, **22**, 3741
28 Kimura, K., Endo, S., Kato, Y. and Yamashita, Y. *Polymer* 1994, **35**, 123