Size Control of Poly(2-oxy-6-naphthoyl) Whiskers by the Addition of Oligomers During Polymerization

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ABSTRACT: The method of controlling the size of a poly(2-oxy-6-naphthoyl) (PON) whisker was examined with a focus on lengthening the whisker. PON whiskers were prepared by the polymerization of 2-acetoxy-6-naphthoic acid in liquid paraffin at 330°C. The whiskers were very symmetrical. and both tips were very sharp. Growth of the whiskers along the length took place by which oligomer lamellae piled up along the long axis of the needlelike crystals with spiral growth. During steady growth until 8 min, the tip angle of the whiskers was constant at 80°. However, it became significantly sharper (22°) at 30 min, and later the trunk part of the whiskers stopped increasing. To depress the sharpening of the tips and to extend the steady-growth period for longer whiskers, oligomers were added to the polymerization system after 8 min, just before the tip angle became sharper, to keep the concentration of the oligomers in the polymerization system constant. The addition of the oligomers extended the steady-growth period, and the length increased from 12.5 to 17.3 μm. Although the width of the whiskers increased very slightly with the addition of the oligomers, the axial ratio of the whiskers increased from 19.4 to 24.7. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1320–1327, 2003

Key words: polyesters; morphology; crystallization; oligomers

INTRODUCTION

Poly(2-oxy-6-naphthoyl) (PON) is a hopeful candidate for high-performance materials characterized by a unique combination of thermal and mechanical properties and by a remarkable chemical resistance. However, PON shows neither meltability nor solubility because of its rigid-rod structure, and its intractability is a serious problem in industrial use. To overcome the intractability, many trials have been performed from the viewpoint of structural modifications, and numerous thermotropic polyesters containing 2-oxy-6-naphthoyl as one of the components have been developed so far.[1] Although these thermotropic polyesters exhibit a good balance between properties and processability, the structural modifications sacrifice the essential properties of PON. We have been studying the morphology control of PON with the crystallization of oligomers during solution polymerization and have succeeded in preparing PON whiskers by the polymerization of 2-acetoxy-6-naphthoic acid (ANA) in liquid paraffin (LPF) at high temperatures.[2,3] PON whiskers have also been prepared in an aromatic solvent.[4] These whiskers are extended-chain single crystals, and the chain molecules are oriented to the long axis of the whiskers. From morphological observations of the whiskers during polymerization in LPF, it has been revealed that the formation mechanism of the PON whiskers contains the following steps: (1) the resulting oligomers in solution polymerization are precipitated in the form of lamellae from solution, (2) the lamellae pile up along the long axis of the needlelike crystals with spiral growth, and (3) the whiskers are accomplished with an increase in the degree of polymerization by the postpolymerization in the interlamellar regions.[3,5]

The PON whiskers prepared in LPF at 330°C and 1.0 w/v (based on the polymer weight) were 12.5 μm long on average and 0.6 μm wide on average, as shown in Figure 1. When PON whiskers are used as high-performance materials, such as reinforcements, the method of controlling the size is very important because the aspect ratio affects its performance. The length control method of poly(*p*-oxybenzoyl) (POB) whiskers was previously studied from various angles, such as the addition of oligomers, the addition of nuclei, and the solvent effect.[6–8] Of these, the addition of oligomers was the most favorable method for tuning the size of the POB whiskers. The key points for the addition of oligomers are the timing of the addition and the amount of added oligomers, which should be determined on the basis of the growth features of the whiskers. This method has not been applied to other whiskers so far. In this study, the de-

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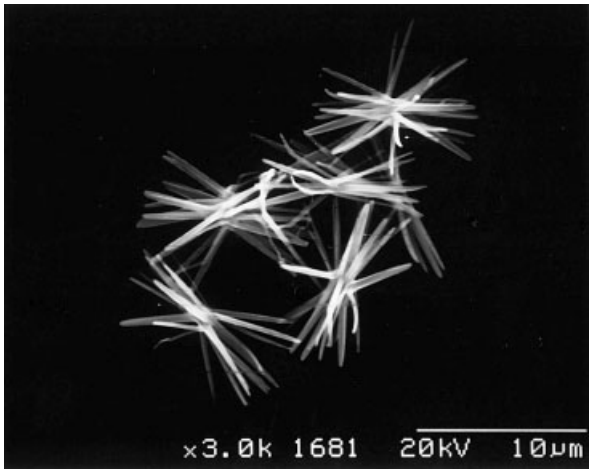


Figure 1 PON whiskers prepared from ANA at 330°C in LPF for 6 h.

tailed growth features of PON whiskers were examined, and the addition of oligomers was applied to lengthen the PON whiskers.

EXPERIMENTAL

Materials

2-Hydroxy-6-naphthoic acid was a gift from Ueno Seiyaku Co., Ltd., (Osaka, Japan) and was used after recrystallization from water. ANA was synthesized from 2-hydroxy-6-naphthoic acid according to a previously published procedure.[3] The melting point of ANA was 224°C (lit. 224°C). LPF was purchased from Nacalai Tesque Co., Ltd. (Kyoto, Japan) and was purified by vacuum distillation (220–240°C at 0.1 mmHg).

Polymerization method

ANA (0.81 g) and 60 mL of LPF were placed in a polymerization reactor equipped with a thermometer, a mechanical stirrer, and gas inlet and outlet tubes. This reaction mixture was heated up to 330°Cunder a slow stream of nitrogen. The solution was stirred until ANA was completely dissolved, and then stirring was stopped. In another reactor, 1.35 g of ANA and 10 mL of LPF were placed and heated to 250°C under a slow stream of nitrogen. The solution was stirred for 1 min after the monomer was dissolved completely. This solution (2.03 or 4.54 mL) was added to the polymerization system 8 or 30 min after the crystallization occurred. The reaction was continued at 330°C for 6 h. The resulting crystals were collected by the filtration of the crystal suspension at 330°C, washed several times with *n*-hexane and acetone, and then dried in a vacuum oven at 50°C overnight. The filtrate was cooled to room temperature, and precipitated oligomers were collected with a centrifuge machine, washed several times with *n*-hexane, and dried at 50°C in a vacuum oven overnight.

Measurements

Morphological observations were performed by scanning electron microscopy with a Hitachi S-2150 (Hitachi Ltd., Tokyo, Japan).

The concentration of the oligomers in the polymerization solution was described as the 2-oxy-6-naphthoyl unit and was estimated with the following equation, in which the number-average degree of polymerization (DP_n) was calculated by acetyl end-group analysis according to a previously published procedure:[9]

$$\text{Concentration of oligomers (mol L}^{-1}) = \frac{\text{Oligomer weight}}{\text{DP}_n \times 170.2 + 60} \times \text{DP}_n \times \frac{1000}{60}$$

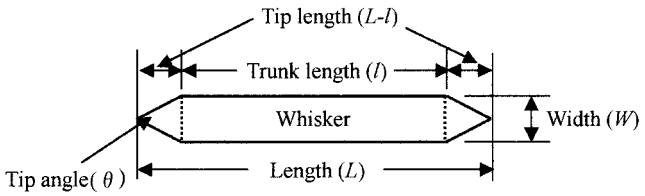
For the comparison of the growth rates in the spiral surface and in the lateral side, the average shape parameters of the whiskers were estimated from the morphological observations during the course of polymerization. The PON whiskers exhibited hexagonal cross sections, and the volume of the whiskers was calculated with the following equation from the obtained shape parameters:

$$\text{Volume of whiskers } (\mu\text{m}^3) = (\sqrt{3}/8)W^2(L + 2l)$$

where W is the average width of the whiskers, L is the average length of the whiskers, and l is the average trunk length of the whiskers as illustrated:

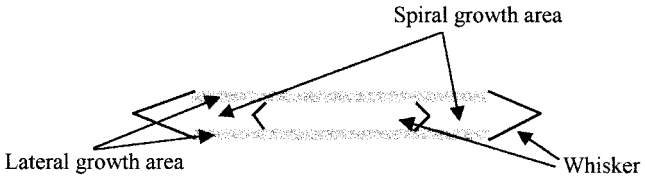
$$l = L - \frac{W}{\tan(\theta/2)}$$

W and L were determined by the average of over 60 observation values. l was calculated from L, W, and θ with the following equation:



The increased volumes with the spiral growth and with the lateral growth per growth surface area were calculated according to the illustrated drawing in the following diagram, which defines the spiral growth

and lateral growth surface areas used for the calculation of crystallized oligomers:



RESULTS AND DISCUSSION

Growth feature of PON whiskers during solution polymerization

The formation mechanism of PON whiskers in LPF has already been proposed (i.e., a spiral growth mechanism), as well as that of POB whiskers. To determine how to lengthen PON whiskers, we investigated the growth features further. The increase in the whisker length is caused by the oligomer lamellae that pile up along the long axis of the needlelike crystals with spiral growth. That is, the secondary nucleation in the spiral step is easier than that in the lateral side surface. It is obvious that if oligomers are consecutively provided to the spiral step, the whisker length is forever increased. However, it is unavoidable that the resulting oligomers during polymerization decrease with the polymerization time in a batch system. The shape change is followed during the course of polymerization to clarify the influence of the remaining oligomer concentration on the whisker growth. Figure 2 shows the PON whiskers obtained at 330°C for 8 and 30 min. The length of the whiskers increased and the tip angle decreased with time. The polymerization time dependencies of the length, width, tip angle, trunk length, and tip length of the PON whiskers are shown in Figure 3. Figure 3(a) shows that the length of the whiskers increased rapidly from the beginning to 5 min and then slowed down around 10 min. Then, it speeded up again from 15 to 30 min. The width of the whiskers increased slightly from the beginning. Figure 3(b) shows that the tip angle of the whiskers was constant at 80° up to 8 min but became gradually sharper to 22° from 8 to 30 min. The polymerization time dependencies of the trunk length and tip length shown in Figure 3(c) indicate that the trunk length increased up to 15 min with a constant tip length and then became constant after 15 min with the tip length increasing. From these results, it can be understood that the increase in the length up to 15 min was due to the increase in the trunk length and that after 15 min was due to the sharpening of the tips. The oligomer concentration that remained in the polymerization solution was estimated as shown in Figure 3(d). The sharpening of the tips happened at a lower concentration of oligomers in the polymerization solution. It is well known that the growth rate in a step at a small

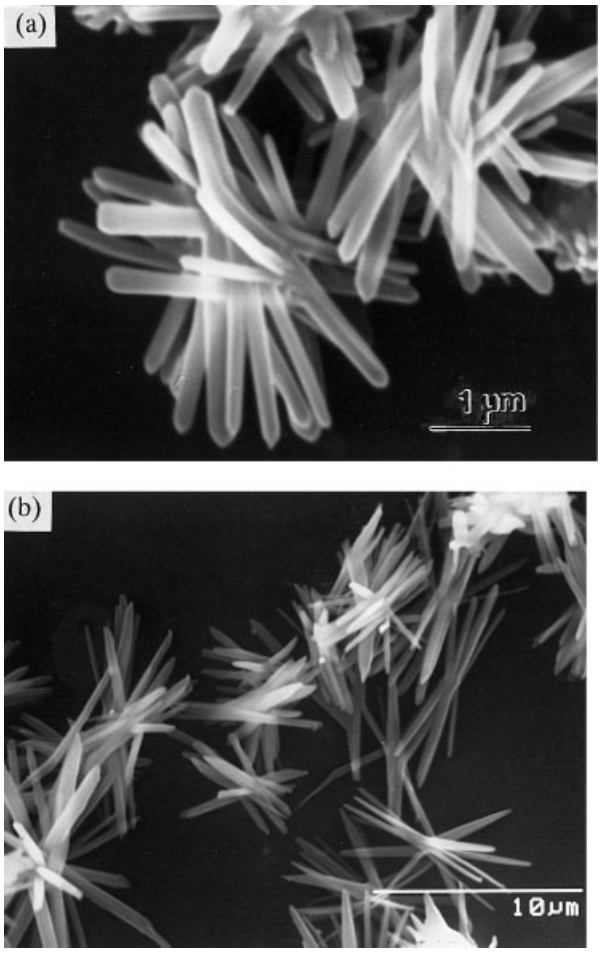


Figure 2 PON whiskers prepared at 330°C in LPF for (a) 8 and (b) 30 min.

radius of curvature decreases because of the increase in the strain energy, and so the spiral appears to rotate with a uniform angular velocity under a steady state.[9,10] The steady-growth period of the whiskers could keep the tip angle of 80° during the early stage of polymerization. The growth rate was determined by nucleation. It is not clearly understood why the sharpening of the tip angle occurred when the degree of supersaturation of the oligomers became lower, but it can be speculated at present as follows. The supply rate of crystallizable oligomers to the step area decreased with the polymerization time. Then, the growth rate was determined by the number of crystallizable oligomers that could reach the step. The growth rate inside and outside the spiral became similar, and then the faster angular velocity at a smaller radius of curvature caused the sharpening of the tip angle. In any case, the sharpening of the tips occurred with the lower oligomer concentration. The supply of the oligomers from outside necessitated keeping the critical degree of supersaturation and continuous steady growth, and this had to lengthen the whiskers.

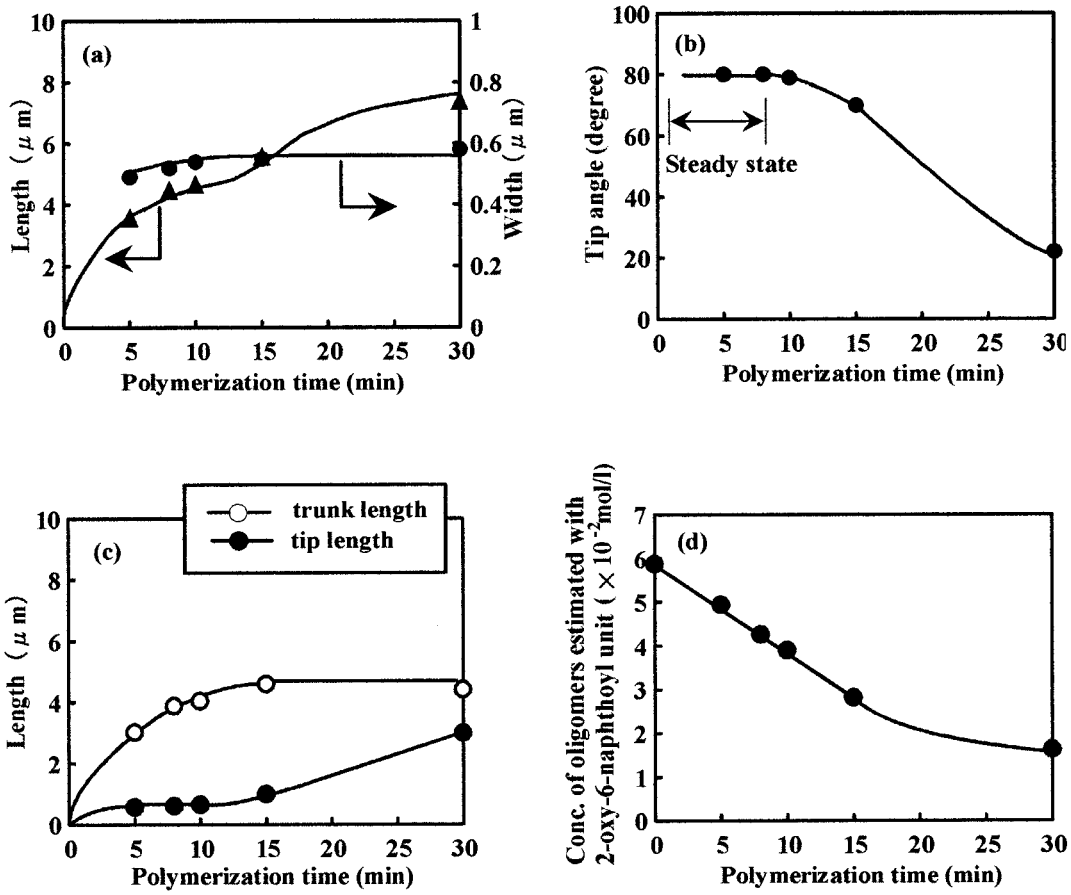


Figure 3 Polymerization time dependencies of (a) the length and width of PON whiskers, (b) the tip angle of PON whiskers, (c) the trunk length and tip length of PON whiskers, and (d) the concentration of oligomers dissolved in solution estimated as the concentration of 2-oxy-6-naphthoyl units.

Preparation of longer whiskers by the addition of oligomers

Addition of oligomers during steady growth

The consumed oligomers with the crystallization were supplied to the polymerization solution from another reactor to lengthen the whiskers. The oligomer solution was prepared to be added to the polymerization system as follows. The highest possible monomer concentration and the highest possible temperature of the oligomer solution were necessary to avoid a temperature drop of the polymerization system when the solution was added. The highest monomer concentration of 10 w/v was chosen on the basis of the solubility of ANA in LPF. The highest temperature needed to keep the oligomer solution homogeneous was desired at which the polymerization did not proceed so rapidly at a 10 w/v concentration that it depressed the nucleation up to at least 30 min. A temperature of 250°C was tentatively applied. The oligomer solution was added into the polymerization system after 8 min just before the tip angle became sharper to compensate for the decreased concentration of oligomers. The results are summarized in Table I. The length of the whiskers increased from 12.5 to 17.3 μm with the addition. The polymerization time dependencies of the length, width, tip angle, and number of whiskers on the addition are shown in Figure 4. It is clear that the length of the whiskers increased with the addition of oligomers, the beginning time of the sharpening of the tip angle became late, and the steady-growth period was extended. The number of whiskers calculated with the experimentally obtained shape parameters, the yield, and the density of 1.45 g cm^{-1} did not change with the addition of the oligomer solution. The width of the whiskers increased very slightly. The whiskers grew more preferentially with the spiral growth rather than with the lateral side growth. This growth feature led to an increase in the axial ratio from 19.4 to 24.7 with the addition of oligomers. It was concluded that the increase in the whisker length was possible with a consecutive supply of oligomers corresponding to the consumption quantity by the crystal growth. The quantity of crystallized oligomers per growth surface area was examined in the spiral and lateral sides with the polymerization time. Table II proves quantitatively that the quantity of the crystal-

TABLE I
Morphological Features of PON Whiskers Obtained by the Addition of Oligomer Solution

Addition time[a] (min)	Amount of oligomer solution added[b] (mL)	Yield (%)	Size of whisker (μm)		Axial ratio	Tip angle (°)	Number of whiskers in 60 mL $\times 10^{-10}$
			Length	Width			
—	0	59.8	12.5	0.64	19.5	10	11.8
8	2.03	60.5	17.5	0.70	24.7	10	10.9
30	4.54	57.7	10.7	0.90	11.9	10	17.5

[a] Polymerizations were carried out in LPF at 330°C for 6 h.
[b] After crystallization occurred.
[c] Each amount of 0.59 mol L^{-1} oligomer solution on the basis of 2-oxy-6-naphthoyl unit was added into the polymerization solution.

lized oligomers in spiral growth was much greater than that in lateral side growth.

Addition of oligomers after tip-angle sharpening

To determine the influence of the addition time of oligomers on the whisker growth features, we added oligomers to the polymerization system at 30 min, which was out of the steady-growth period. The average length and width of the whiskers prepared for 6 h were 10.7 and 0.90 μm, respectively. The average length became shorter and the width became larger with the addition of oligomers at 30 min. The number of whiskers was 1.5 times larger than that prepared without any addition, and this means that 33% of the whiskers were newly generated. The morphological observations of the incipient crystals prepared for 5 min after the addition (Fig. 5) show that a number of new whiskers were generated, the sizes of which were quite different. The polymerization time dependencies

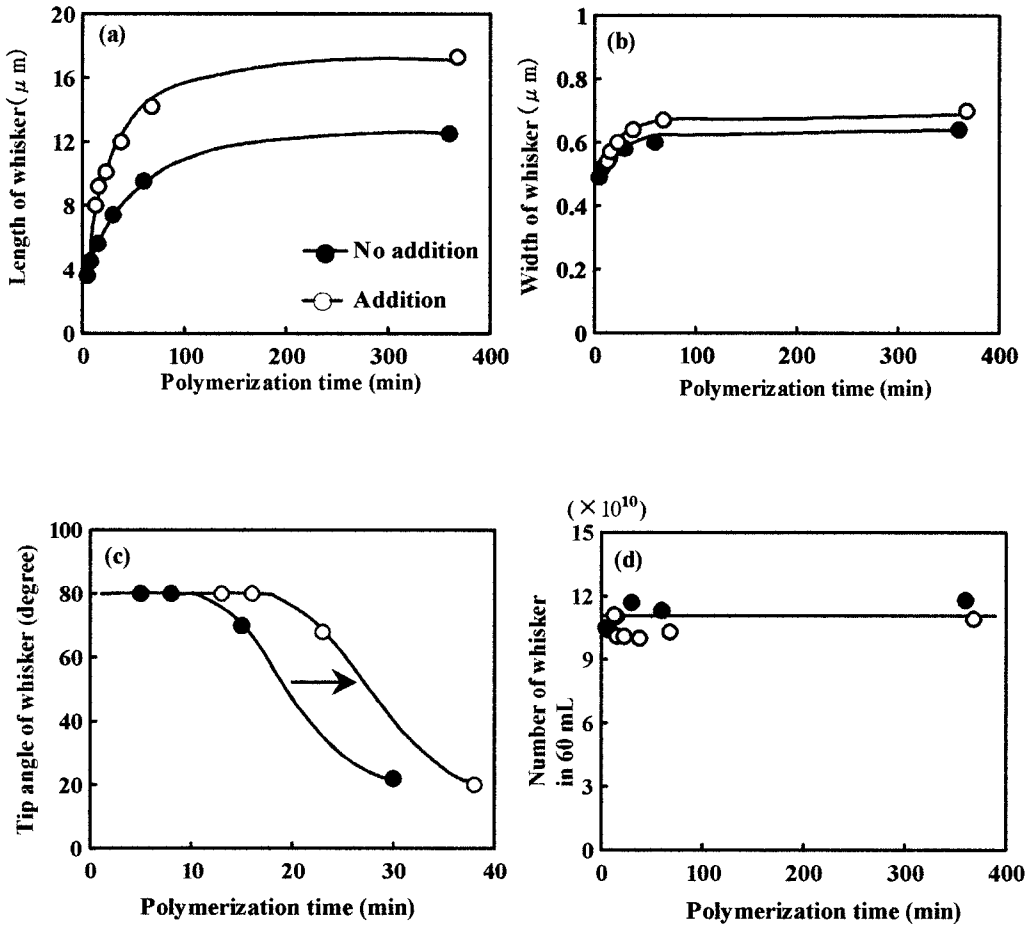


Figure 4 Polymerization time dependencies of (a) the length, (b) tip angle, (c) number, and (d) width of PON whiskers prepared by the addition of oligomers at 8 min.

TABLE II
Quantity of Crystallized Oligomers in Spiral and Lateral Sides in the Polymerization System with the Addition of Oligomer

Addition time (min)	Time[a] (min)	Crystallized oligomers in spiral growth per growth surface area (concentration 1) (mol/μm^2)[b]	Crystallized oligomers in lateral growth per growth surface area (concentration 2) (mol/μm^2)[b]	Concentration 1/ concentration 2
8[c]	5	7.8×10^{-15}	0.01×10^{-15}	780.0
	8	11.7×10^{-15}	0.02×10^{-15}	585.0
	15	15.0×10^{-15}	0.04×10^{-15}	375.0
30[d]	5	0.81×10^{-15}	0.02×10^{-15}	40.5
	8	1.01×10^{-15}	0.04×10^{-15}	25.3
	15	1.29×10^{-15}	0.11×10^{-15}	11.7

[a] Time after the addition of oligomer.
[b] Described as the concentration of the 2-oxy-6-naphthoyl unit.
[c] 2.03 mL of 0.59 mol L^{-1} oligomer solution was added into the polymerization system 8 min after crystallization occurred.
[d] 4.54 mL of 0.59 mol L^{-1} oligomer solution was added into the polymerization system 30 min after crystallization occurred.

of the length and tip angle of the whiskers are shown in Figure 6. Two kinds of whiskers of different sizes clearly existed, which corresponded to already existing whiskers (old whiskers) and newly created whiskers (new whiskers), respectively. The tip angle of the new whiskers was constant at 75° up to 8 min after an addition, and then it started sharpening. The tip angle of the old whiskers was recovered from 22 to 75°, but it did not return to 80°. This is clearer from the changes in the distribution diagrams of the lengths given in Figure 7. The length of the whiskers prepared by the addition at 8 min increased with a unimodal distribution over the course of polymerization. On the contrary, a distribution at a smaller length newly appeared at 5 min after the addition at 30 min, and the length of the whiskers exhibited a bimodal distribution at the early stage of polymerization. Then, it finally became a unimodal distribution because of averaging. The increase in the number of the whiskers and the bimodality of the distribution were obvious evidence for the formation of new whiskers; that is, nucleation occurred simultaneously with the whisker growth. The length and width seemed to increase linearly with the polymerization time during the early

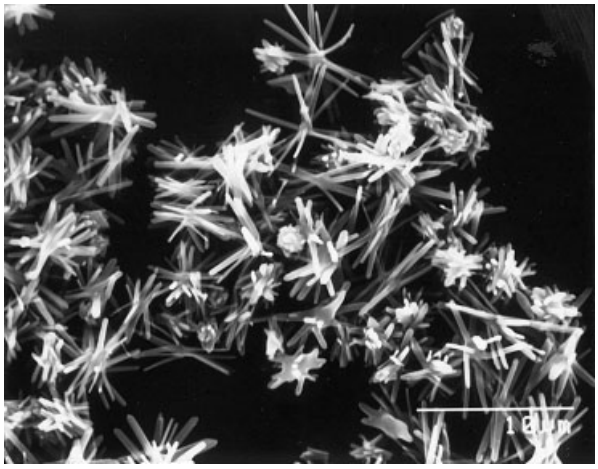


Figure 5 PON whiskers prepared for 5 min after the addition of oligomers at 30 min.

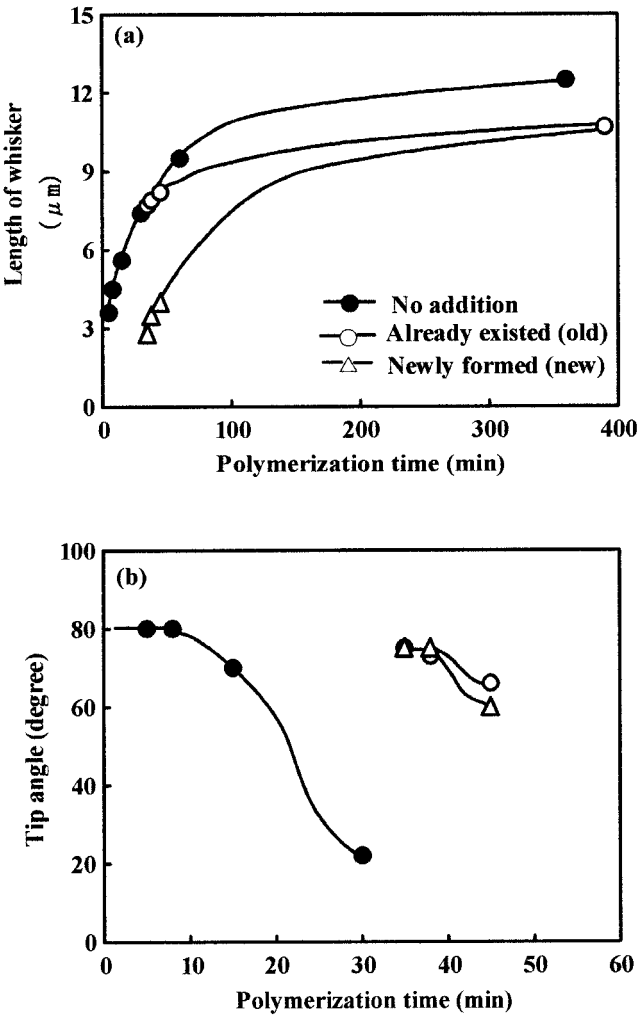


Figure 6 Polymerization time dependencies of (a) the length and (b) tip angle of PON whiskers prepared by the addition of oligomers at 30 min.

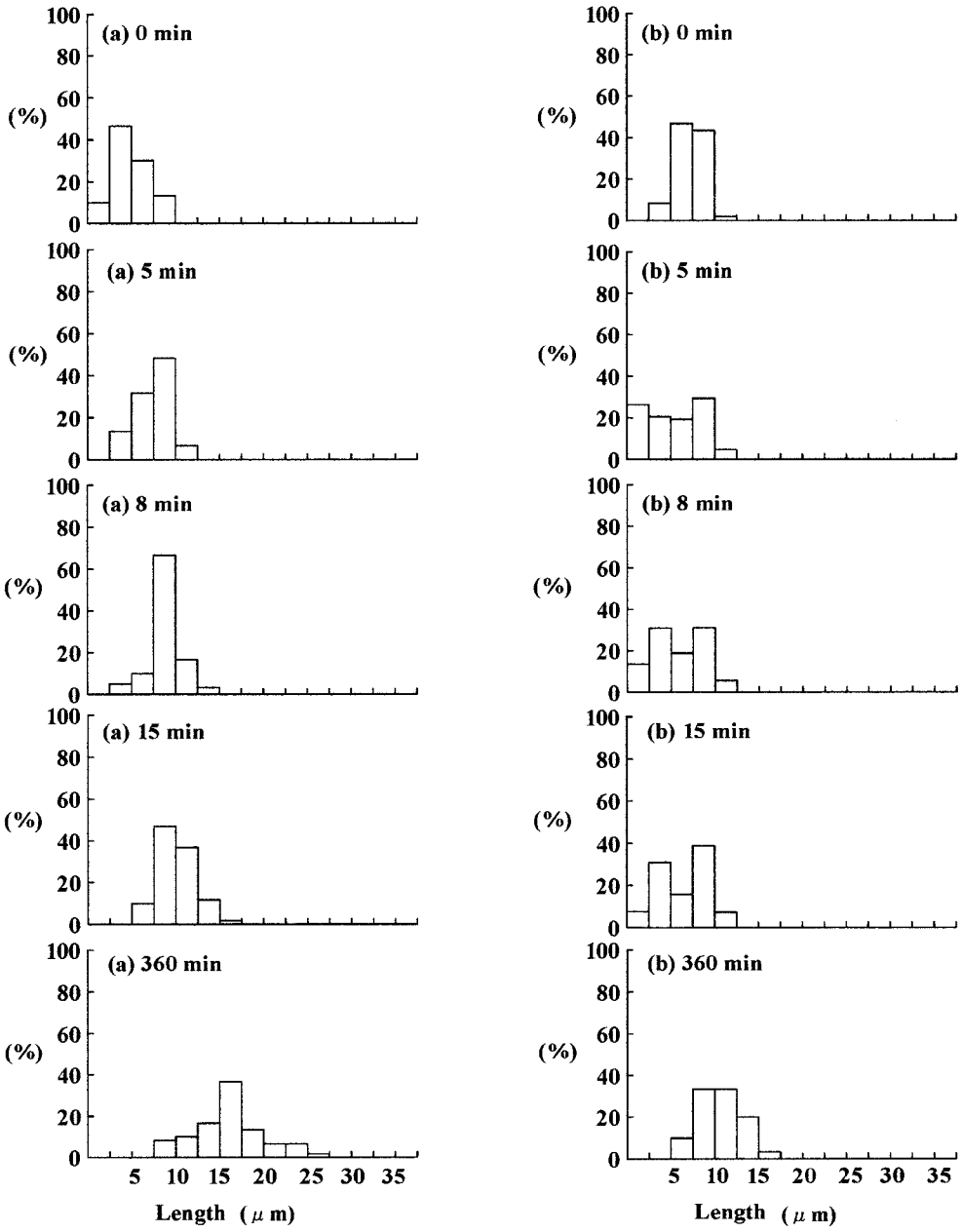


Figure 7 Distribution diagrams of the lengths of PON whiskers prepared by the addition of oligomers at (a) 8 and (b) 30 min. The time in the diagrams describes the polymerization time after the addition of oligomers.

stage of polymerization, and the apparent rates were estimated as shown in Figure 8. The apparent rates of the length and width after the addition at 8 min were almost the same as those before the addition. Concerning the addition at 30 min, the increments of the length of the old whiskers and new whiskers became 3.0 and 1.3 times smaller, respectively, than that before the addition, and this was attributed to the increase in the number of whiskers. Additionally, the increments of the width of the whiskers became 2.6 and 4.4 times larger, respectively, despite the increase in the number of the whiskers. These growth features can be understood as follows. The addition of the oligomers enhanced the degree of supersaturation of the oligomers in the solution. The precipitated oligomers were preferentially used for the crystallization at the spiral surface because of the advantage of surface energy. However, the sharpening of the tips had already occurred when the oligomers were added, and this phenomenon might have resulted in the lowering of the crystallization rate at the spiral surface. The apparent rate of the width became naturally larger because the difference in the advantage of the surface energy for crystallization between the spiral surface and lateral surface became smaller. If the precipitation rate of the oligomers was higher than the consumption rate of the

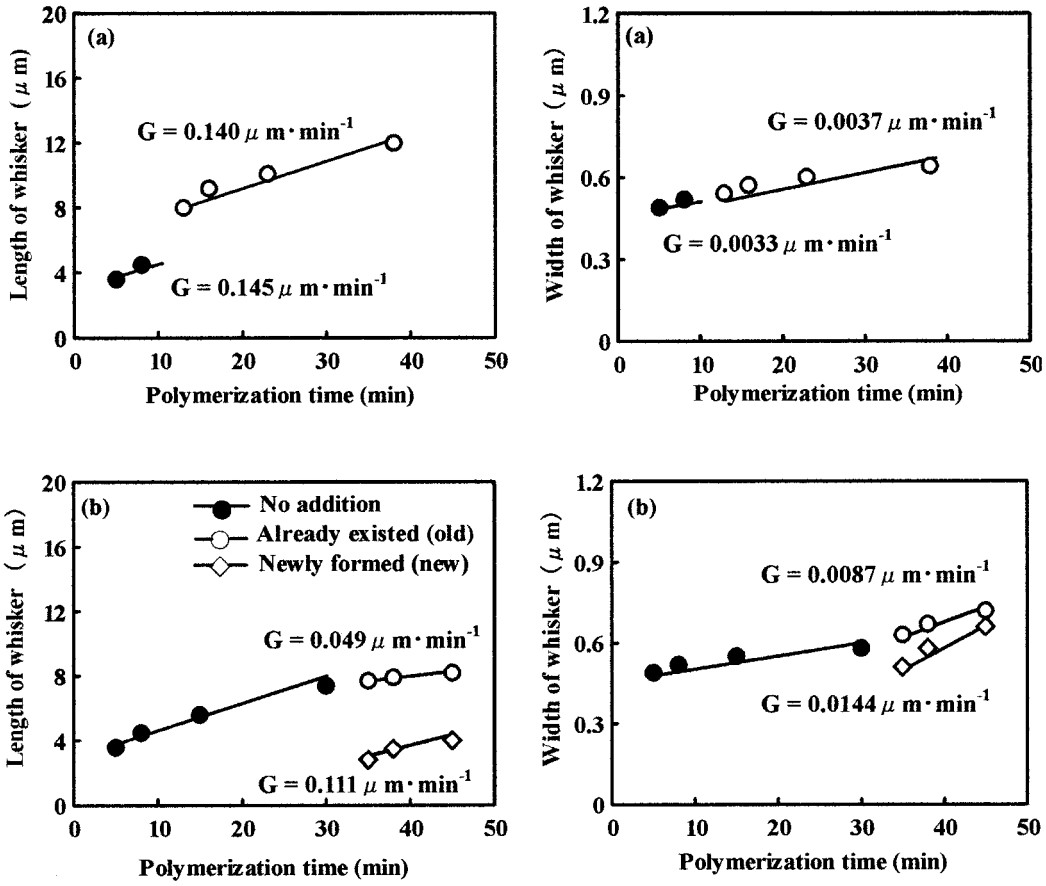


Figure 8 Initial increase in the length and width of PON whiskers prepared by the addition of oligomers at (a) 8 and (b) 30 min after the beginning of crystallization.

oligomers by crystallization, the excess of oligomers that could not participate in the crystal growth generated new crystals. Table II proves that the quantity of the crystallized oligomers in the spiral growth per growth surface area was also larger than that in the lateral side growth. In a comparison of the results for the addition at 8 min, spiral growth was still more favorable than lateral side growth, but the quantities of the crystallized oligomers for both became closer.

CONCLUSIONS

From observations of morphological changes during polymerization, we found that the tip angle of PON whiskers was constant at 80° up to 8 min but became significantly sharper (22°) at 30 min. The increase in the length up to 15 min was due to the increase in the trunk length, and that after 15 min was due to the sharpening of the tips. The sharpening of the tips must have been caused by the decrease in the degree of supersaturation of the oligomers during polymerization. The addition of the oligomers after 8 min just before the sharpening of the tip angle to compensate for the decreased concentration of the oligomers extended the steady-growth period and increased the length. The width of the whiskers increased very slightly with the addition of the oligomers. The whiskers grew preferentially with the spiral growth rather than with the lateral side growth. The addition of the oligomers during the steady-growth period was favorable for PON whiskers growing continuously with the spiral growth.

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