Nonstoichiometric Synthesis of Poly(4,4′-oxydiphenylene pyromelliteimide) by Reaction-Induced Crystallization of Oligomers

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ABSTRACT: Nonstoichiometric synthesis of poly(4,4′-oxydiphenylene pyromelliteimide) was examined by using reaction-induced crystallization of oligomers during solution polymerization. Polymerizations of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were carried out in Barrel Therm 400 at 330 °C at various molar ratios of PMDA and ODA in feed (χ). Although high molecular weight polymer was usually prepared only under stoichiometric condition by a conventional solution polymerization, it was obtained as the crystals at χ of 0.5−2.0. The polymerization at χ of 0.77 afforded the highest polymer having M_w of 2.81×10^5, which was higher than that prepared by the solution polymerization. The oligomers were precipitated to form the crystals due to the low miscibility into the solvent. The precipitated oligomers were end-capped by excess monomers, but the end-capping groups were eliminated by transimidization reaction when they were registered into the crystals. The transimidization reaction also occurred in the crystals, leading to the increase in molecular weight. Since the nucleophilicity of amino end group was higher, the transimidization reaction proceeded more efficiently with eliminating ODA, and thereby the higher molecular weight polyimides were given in the range of $\chi < 1.0$ than the range of $\chi > 1.0$. The polymerization by the reaction-induced crystallization of oligomers was unsusceptible to the stoichiometry.

Introduction

The stoichiometric ratio between two functional groups is of great importance to produce high molecular weight polymers by a step-growth type polymerization. If the stoichiometry is out of balance, the number-average degree of polymerization (DP_n) follows eq 1 and molecular weight does not increase.[1−3] Hence, the maximum average degree of polymerization (DPn_{max}) possibly corresponds to a complete conversion of the one functional group (i.e., to $p = 1$), and it is then given by eq 2.

$$\mathrm{DPn} = \frac{1 + r}{2r(1 - p) + 1 - r} \tag{1}$$

$$\mathrm{DPn}_{\max} = \frac{1 + r}{1 - r} \tag{2}$$

where r is the ratio of two functional groups and less than unity. p is the extent of reaction.

Equation 2 illustrates clearly the necessity for ensuring exact stoichiometric functional group concentrations to synthesize high molecular weight polymers. It has been reported that the preparation of poly(orthocarbonate)[4] and polythioether[5] was unsusceptible to the stoichiometric conditions due to the large difference on the reactivity of functional groups. Palladium-catalyzed allylic substitution polymerization between bis-allylic monomers and malonate also yielded high molecular weight under nonstoichiometric conditions.[6] The polymerization of *p*-acetoxybenzoic acid in poor solvents afforded crystals of high molecular weight poly(*p*-oxybenzoyl) even though an excess of monofunctional compounds coexisted, generally called end-capping reagents, such as aromatic carboxylic acids or phenyl acetates.[7−9] Nucleation−elongation imine metathesis polymerization afforded high molecular weight poly[(*m*-phenylene ethylene)imine]s under nonstoichiometric conditions.[10] These findings indicate that the heterogeneous polymerization, in which the solution polymerization and the solid-state polymerization are combined by the crystallization of oligomers, should be fairly tolerant of mismatched functional group stoichiometry, like biological systems such as the self-assembling process of proteins,[11] and the nucleation-growth mechanism in heterogeneous polymerization should give a substantial answer to overcome the nonstoichiometric issue.

Aromatic polyimides are characterized by their outstanding thermal and mechanical properties, and they have been attracted as high-performance materials. Their properties strongly depend on many parameters such as chemical structure, molecular weight, molecular orientation, morphology, and so on. The morphology control of various polyimides has been studied by means of the crystallization of oligomers during solution polymerization.[12,13] Lathlike crystals and particles of poly(4,4′-oxydiphenylene pyromelliteimide) (PI-PMDA/ODA) were successfully precipitated during the polymerization of PMDA and ODA in poor solvents.[14] Surprisingly, the obtained polyimides had high molecular weight. In general, the precipitation terminates the polymerization due to the imbalance of the oligomer end groups and the loss of the mobility of the oligomers in the precipitates. It is well-known that the molecular weight of poly(amic acid)s which is a precursor of polyimides is quite sensitive to the molar balance between diamine and dianhydride, and the solution polymerization under strict stoichiometric conditions is usually performed to prepared high molecular weight poly(amic acid)s giving high molecular weight polyimides.[15,16] Previous results for morphology control indicate the possibility of the nonstoichiometric synthesis of polyimides. In this study, the synthesis of PI-PMDA/ODA under nonstoichiometric conditions is examined by using the reaction-induced crystallization of oligomers.

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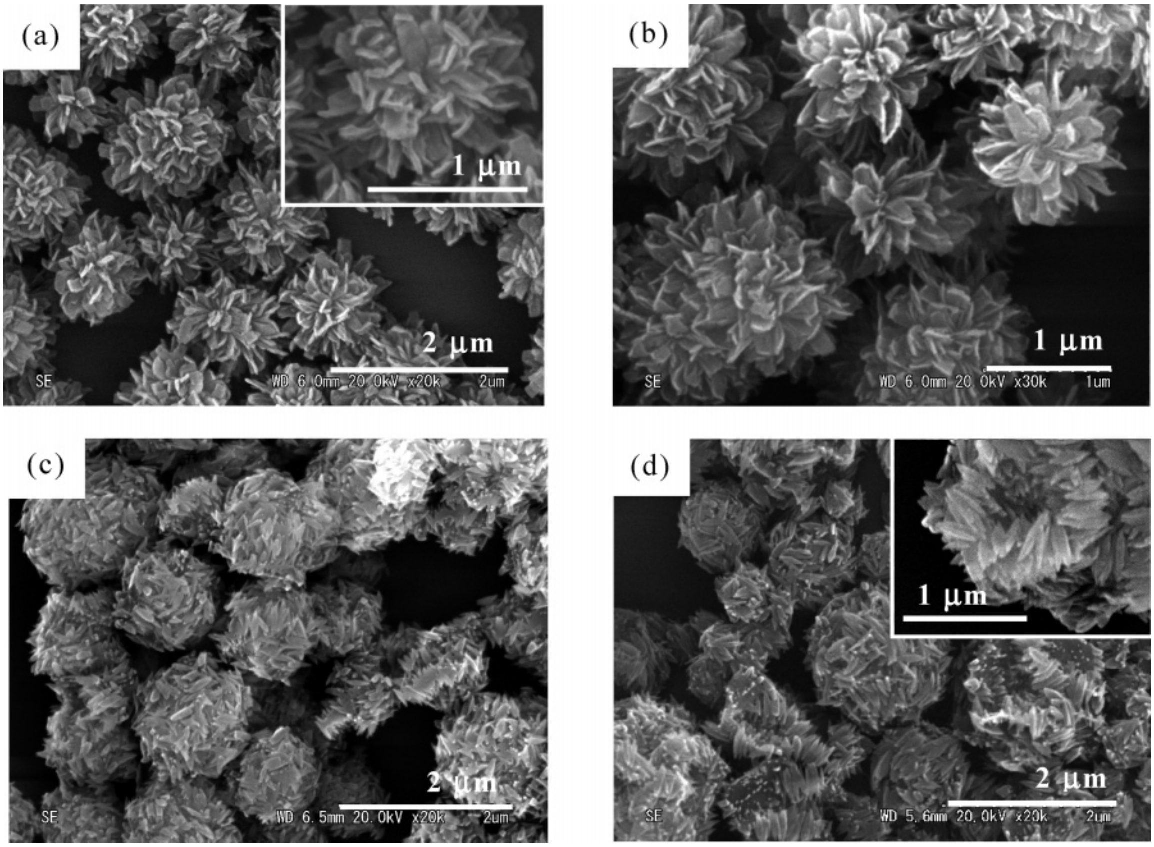


Figure 1. Morphology of the precipitated PI-PMDA/ODA prepared at χ of (a) 1.5, (b) 1.0, (c) 0.77, and (d) 0.5.

Experimental Section

Materials. PMDA was purchased from Aldrich Co. Ltd. and purified by sublimation. ODA was purchased from Tokyo Kasei Co. Ltd. and used as received. Barrel Therm 400 (BT4), which was a mixture of isomers of dibenzyltoluene, was purchased from Matsumura Oil Co. Ltd. and purified by distillation (160−170 °C/0.3 mmHg).

Measurements. The morphology of the products was observed on a Hitachi S-3500N scanning electron microscope. Samples were dried, sputtered with platinum/palladium, and observed at 20 kV. Infrared (IR) spectra were recorded on a JASCO FT/IR-410 spectrometer. Inherent viscosities (η_{inh}) of polyimides were measured in 97% sulfuric acid at a concentration of 0.5 g dL^{-1} and 30 °C. Weight-average molecular weight (M_w) was estimated from the viscosity by using the reported equation $\eta_{\text{inh}} = 2.76 \times 10^{-3} M_w^{0.53}$.[17] WAXS powder patterns were recorded on a Rigaku MiniFlex diffractometer at 30 kV and 15 mA with a scanning rate of 1° min^{-1}. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed on a Bruker Daltonics AutoFLEX MALDI-TOF MS system operating with a 337 nm N_2 laser. Spectra were obtained in the linear positive mode with accelerating potential of 20 kV. Mass was calibrated with angiotensin I (MW 1296.69) and insulin B (MW 3496.96) of a Sequazyme peptide mass standard kit. Samples were prepared by the evaporation-grinding method and then measured in 3-aminoquinoline and dithranol as a matrix doped with potassium trifluoroacetate salt according to the reported procedure.[18] Thermogravimetric analysis was performed on a Perkin-Elmer TGA-7 with a scanning rate of 20 °C min^{-1} in N_2.

Synthesis of PI-PMDA/ODA. Nonstoichiometric Synthesis by Reaction-Induced Crystallization of Oligomers. PMDA (0.11 g, 0.52 mmol) and 10 mL of BT4 were placed into a cylindrical flask equipped with a gas inlet tube, and the reaction mixture was heated to 330 °C with stirring in a N_2 atmosphere. PMDA was entirely dissolved at ca. 240 °C. A solution of ODA (0.10 g, 0.52 mmol) in 10 mL of BT4 was heated at 330 °C, and then this solution was added to the PMDA solution at 330 °C under stirring. The stirring was stopped within 5 s, and then the polymerization was continued for 6 h with no stirring. The solution became turbid immediately due to the precipitation of oligomers. After 6 h, the precipitated PI-PMDA/ODA crystals were filtrated at 330 °C, washed with *n*-hexane and acetone, and then dried at 100 °C for 12 h. The filtrate was poured into *n*-hexane, and the precipitates were collected, which were dissolved in the solution at 330 °C.

Synthesis by Homogeneous Solution Polymerization. PI-PMDA/ODA was prepared from PMDA and ODA by solution polymerizations in *N*,*N*-dimethylacetamide at 15−25 °C and following thermal imidization according to the previous procedure.[15]

Results and Discussion

Polymerizations were carried out at 330 °C for 6 h in BT4 at various molar ratios (χ) of PMDA to ODA in feed (χ = [PMDA]/[ODA]). Polymer concentration was fixed to 1.0%. Pale orange precipitates were obtained under these conditions. Although the morphologies of the precipitates were slightly different on the χ, they exhibited clear crystal habits as shown in Figure 1. The spherical aggregates of the platelike crystals were formed at χ of 1.5 and 1.0, of which the average thickness was ca. 40 nm and the diameter of the spherical aggregates was averagely 1.1 μm. The spherical aggregates of fine needlelike crystals were formed at χ of 0.77 and 0.5, of which the average length and width were 400 and 100 nm, respectively. It has been reported that the chemical structure of oligomer end groups influenced significantly the morphology of the crystals prepared by the reaction-induced phase separation during solution polymerization.[19,20] The oligomers precipitated in poor solvents were low molecular weight, and therefore the crystallization feature of them was closed to monomeric compounds rather than high molecular weight polymers. The characters of the end group such as the bulkiness and polarity change the miscibility,

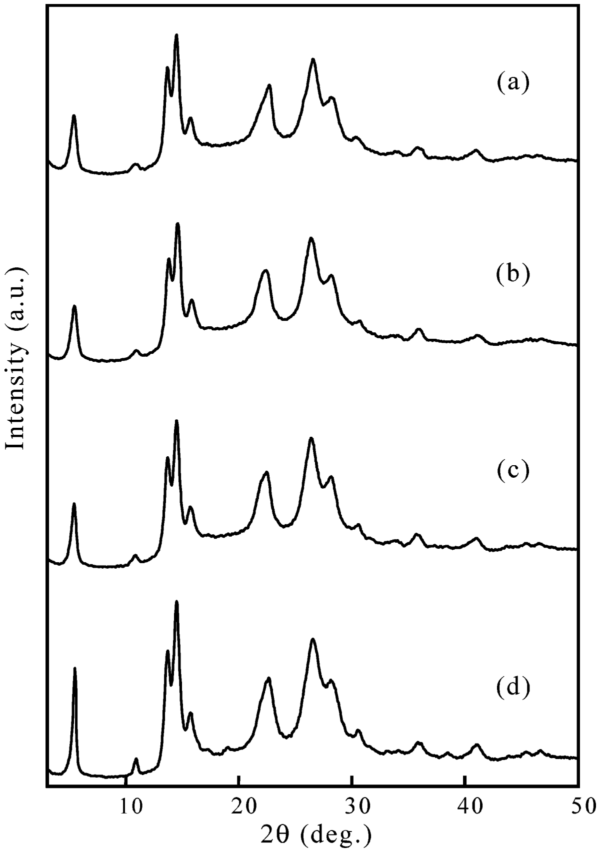


Figure 2. WAXS intensity profiles of the precipitated PI-PMDA/ODA prepared at χ of (a) 1.5, (b) 1.0, (c) 0.77, and (d) 0.5.

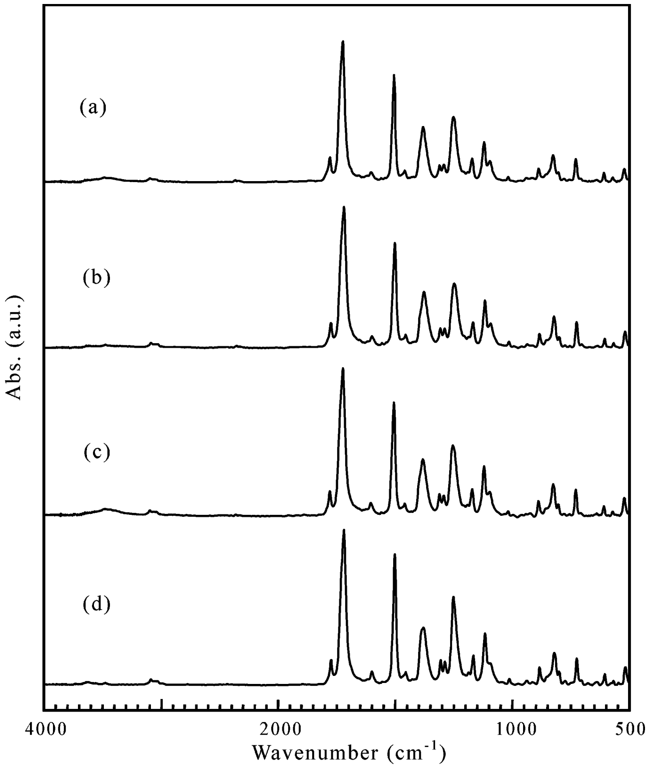


Figure 3. IR spectra of precipitated PI-PMDA/ODA prepared at χ of (a) 1.5, (b) 1.0, (c) 0.77, and (d) 0.5.

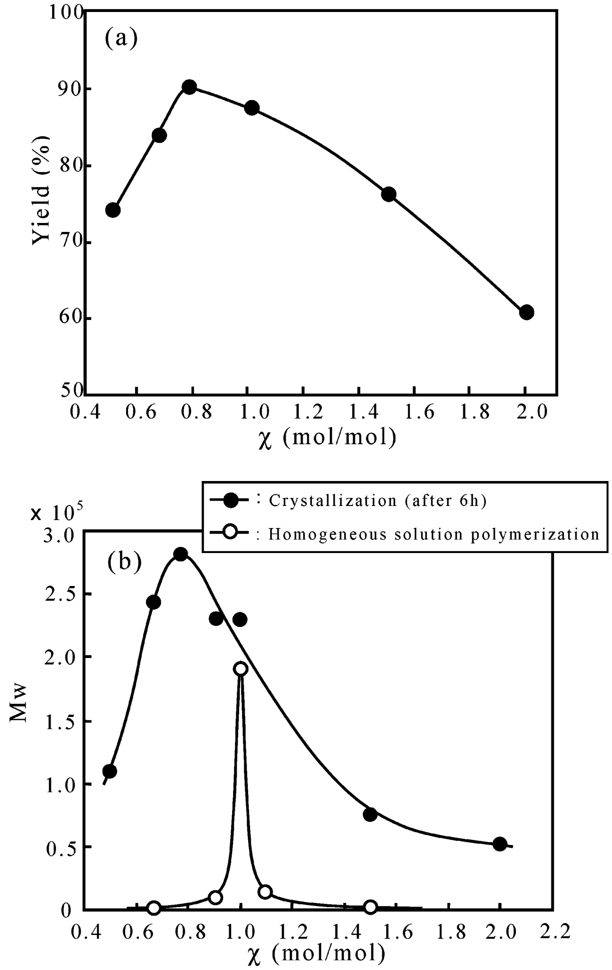


Figure 4. Influences of stoichiometry on (a) yield and (b) M_w of PI-PMDA/ODA prepared by (●) the heterogeneous polymerization via crystallization for 6 h and by (○) the homogeneous solution polymerization and the following thermal imidization.

crystallizability, coagulation ability, and so on, resulting in the change of the morphology of the precipitated crystals. The end groups of the oligomers prepared at $\chi > 1.0$ are mainly anhydride groups and those at $\chi < 1.0$ are amino groups, as discussed later. This difference in the chemical structure of the oligomer end groups might change the morphology of the precipitated crystals. WAXS intensity profiles of these precipitates shown in Figure 2 had no broad halo attributed to amorphous parts, and the sharp reflection peaks were assignable according to the orthogonal unit cell.[21] All these precipitates exhibited quite high crystallinity. IR spectra of the precipitates prepared at various χs are shown in Figure 3. The characteristic bands of imide group such as a symmetric C═O stretching (1720 cm^{-1}), C−N stretching (1380 cm^{-1}), and C−N bending (720 cm^{-1}) appeared, and the bands attributed to amic acid moieties were not detected at all in these spectra. Additionally, the bands of amino and anhydride end groups were not observed. These spectra are identical with that of PI-PMDA/ODA, and these results reveal that high molecular weight polyimides are formed as the precipitates irrespective of χ.

To compare the influence of χ on the molecular weight, PI-PMDA/ODA was synthesized by the conventional homogeneous solution polymerization at various χs and the following thermal imidization according to the previous procedure.[15,16] Results are shown in Figure 4. The weight-average molecular weights (M_w) were calculated from the inherent viscosity measurements. It has been well-known that the molecular weight of polyimide is quite sensitive to the stoichiometric balance between two monomers in the solution polymerization, and the highest molecular weight polyimide was obtained under stoichiometric conditions at χ of 1.0. A slight shift of χ from 1.0 lowered the

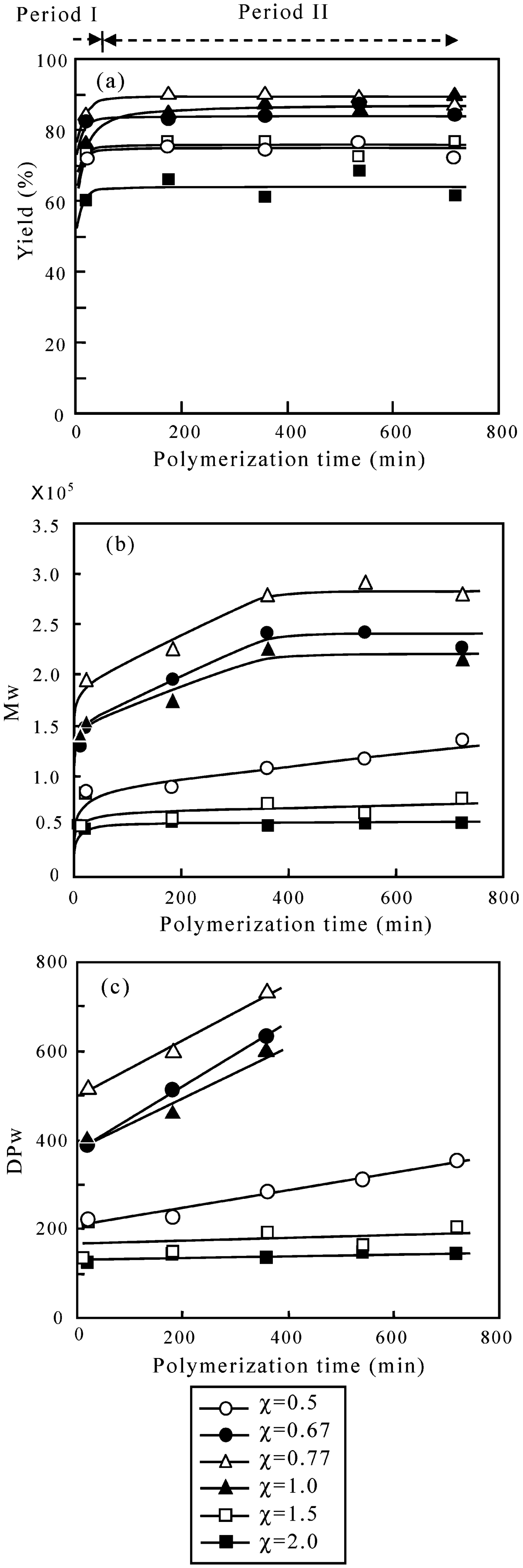


Figure 5. Plots of (a) yield, (b) M_w, and (c) DPw of precipitated PI-PMDA/ODA prepared at various χs as a function of polymerization time.

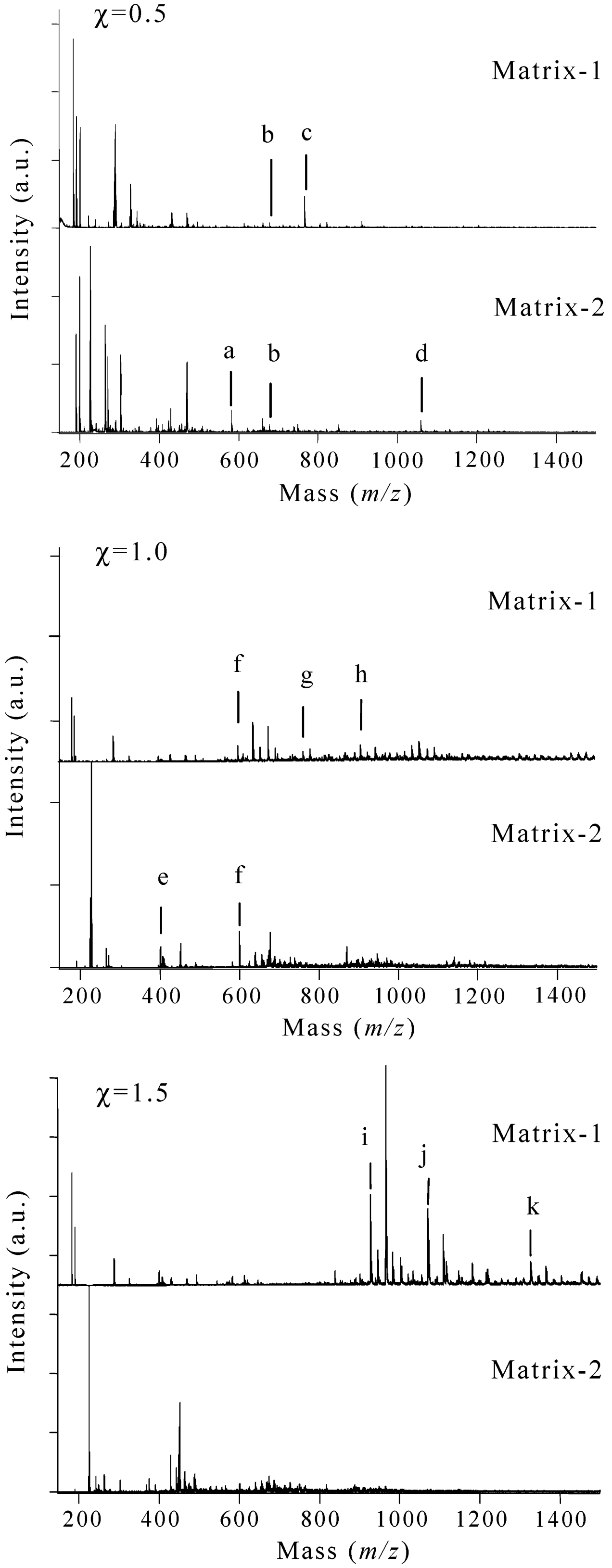


Figure 6. MALDI-TOF mass spectra of oligomers collected from solution at the initial stage of polymerization on a condition of χ = 0.5, 1.0, and 1.5. 3-Aminoquinoline (matrix 1) and dithranol (matrix 2) were used as matrices.

molecular weight drastically. On the contrary, the polymerizations with the crystallization of oligomers afforded the high molecular weight polyimides under the wide range of χ as also shown in Figure 4. The χ of 0.77 which was 30 mol % ODA

Table 1. Values of α at Various χs

χ	molar ratio in feed PMDA/ODA	α (× 10^{-2} min^{-1})
0.5	1.0/2.0	20.0
0.67	1.0/1.5	72.0
0.77	1.0/1.3	63.9
1.0	1.0/1.0	57.6
1.5	1.5/1.0	2.8
2.0	2.0/1.0	1.8

excess afforded the highest polyimide having M_w of 2.81×10^5, and the change in M_w was gentle on the value of χ. Even at χ of 0.5 and 2.0, which are 2 times excess of ODA and PMDA, polyimides had M_w of 1.09×10^5 and 5.20×10^4, respectively.

This polymerization system is unsusceptible to χ as expected. Interestingly, M_w is larger in the range of $\chi < 1.0$ than in the range of $\chi > 1.0$. With respect to the yield as also shown in Figure 4, the polymerization at χ of 0.77 gave the highest yield of 90.3%, and they became lower far from χ of 0.77 as well as the molecular weight. Here, the yield of the precipitated crystals was calculated on the basis of the polymer weight as follows:

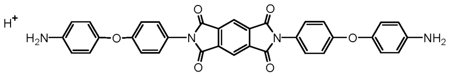
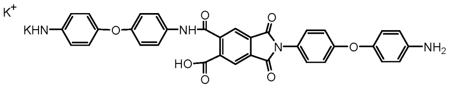
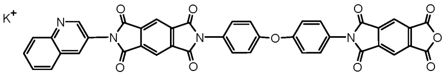
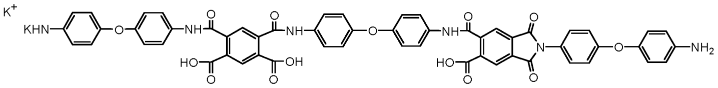
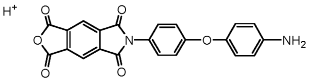
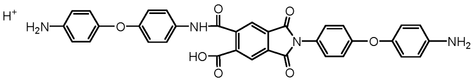
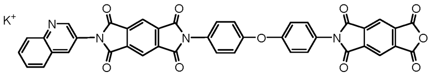
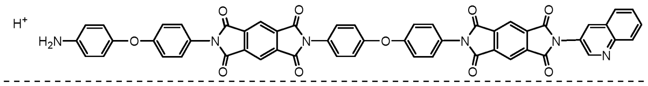
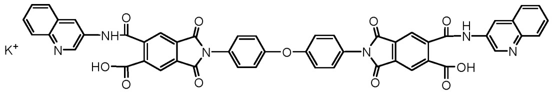
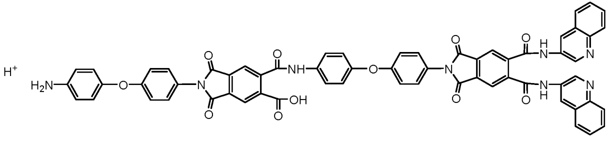
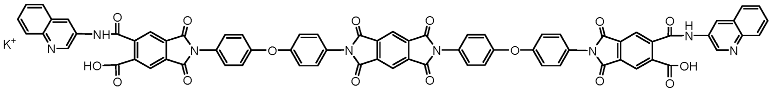
$$\text{yield (\%)} = \frac{\text{obtained crystal weight (g)}}{\text{calculated polymer weight (g)}} \times 100$$

where $\chi \geq 1.0$: calculated polymer weight = the number of moles of ODA × molecular weight of the repeating unit. $\chi < 1.0$: calculated polymer weight = χ × the number of moles of ODA × molecular weight of the repeating unit.

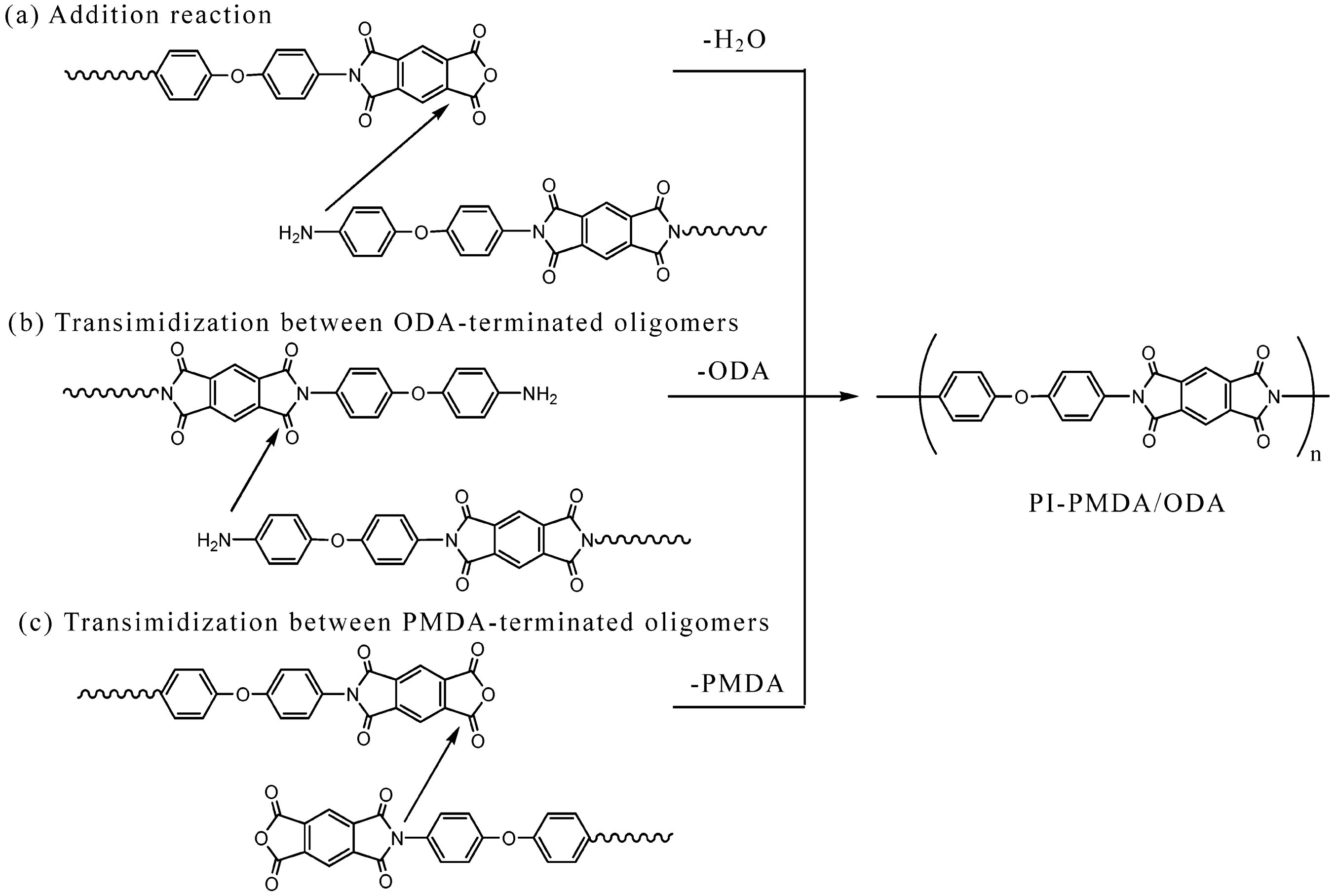
The oligomers are formed in the solution, and their molecular weight increases with time. When the molecular weight of oligomers exceeds a critical value, the oligomers are in the supersaturated state and then phase-separated to form the crystals. Although the oligomers are precipitated even under nonstoichiometric conditions because the critical molecular weight for the precipitation is quite low as discussed later, the nonstoichiometry tends to terminate the formation of oligomers, bringing about the lower yields.

In order to clarify the polymerization mechanism under nonstoichiometric conditions, the changes in the yield and the molecular weight of the precipitated crystals were examined in the course of polymerization at various χs. These plots are shown in Figure 5. The increases in both the yield and the molecular weight can be divided into two periods. The yield

Table 2. Structural Assignments of Peaks in the MALDI-TOF Mass Spectra Reported in Figure 6

peak no.	χ	mass (m/z)			structure
		measured		calculated	
		matrix-1	matrix-2		
a	0.5	-	582.6	583.6	
b		677.0	677.0	677.8	
c		765.2	-	765.7	
d		-	1059.0	1058.0	
e	1.0	-	401.4	401.3	
f		601.4	600.2	601.6	
g		765.1	-	765.7	
h		909.6	-	909.8	
I	1.5	926.8	-	927.9	
j		1070.8	-	1072.0	
k		1328.6	-	1328.2	

Scheme 1. Solid-State Polymerization Mechanism of Polyimide via Reaction-Induced Crystallization of Oligomers



increased rapidly up to 1 h (period I) and then became constant afterward (period II). The molecular weight also increased rapidly during period I with the increaser of the yield, and then it increased gradually in period II. The gradual increase in the molecular weight indicates the occurrence of the solid-state polymerization. The polymerization proceeds with forming the crystals by the consecutive supply of the oligomers from the solution in period I, leading to the rapid increase in the molecular weight with the yield, and then it proceeds as the solid-state polymerization in the precipitated crystals in period II. M_w was converted to the weight-average degree of polymerization (DPw), and DPws were plotted as a function of time as also shown in Figure 5. In period II, DPws increase linearly with the time, and the polymerizations in the crystals apparently obey the second-order kinetics even under nonstoichiometric conditions. Since the initial concentration of the end groups could not be determined, the slopes of the linear relation (α) were estimated to compare the apparent rate of the solid-state polymerization instead of rate constants. The values of α are presented in Table 1. They are much larger at $\chi \leq 1.0$ than $\chi > 1.0$. The oligomers dissolved in the solution at 330 °C were collected from the solution just after the precipitation, and they were analyzed by MALDI-TOF MS spectroscopy according to the previous study.[18] The spectra and assignable structures are presented in Figure 6 and Table 2. The dissolved oligomers were the mixtures of the one and two repeating unit oligomers and one to two adducts of monomers including imide and amic acid moiety. This is due to the low miscibility to BT4. Though the oligomers having both amino and anhydride end groups are detected at χ of 1.0, the oligomers having amino end groups are mainly observed at χ of 0.5, and those having anhydride end groups are observed at χ of 1.5. These results strongly imply that the oligomers are naturally end-capped by the excess monomers, and the end groups are nonstoichiometric. These results reveal that the polymerization proceeds by not only the addition reaction between amino end groups and anhydride end groups of the oligomers but also the transimidization reaction, as depicted in Scheme 1. The transimidization reaction between amino end groups with the elimination of ODA occur mainly in the crystals prepared at $\chi < 1.0$ due to the high nucleophilicity of amino group,[22−24] and therefore the molecular weight increases continuously. In contrast to this, the transimidization reaction between anhydride end groups occurs slightly due to the low nucleophilicity of imide group, and the molecular weight does not increase efficiently in the crystals prepared at $\chi > 1.0$. ODA and PMDA eliminated from the crystals by the transimidization reaction move back to the solution, and the stoichiometry in the solution became imbalanced more largely under nonstoichiometric feed, resulting also in the lower yield. The highest molecular polyimide was obtained at the χ of 0.77, which was 30 mol % ODA excess, as aforesaid. The reaction rate of the addition reaction between the amino end groups and the anhydride end groups of the oligomers is the highest, and that of the transimidization reaction between amino end groups is the second highest. The transimidization reaction between the anhydride end groups was less reactive. When the oligomers were prepared at χ of 0.77, the concentration of the amino end groups was slightly higher than that of the anhydride end groups. This end group situation made the contribution of both the addition reaction and the transimidization reaction between amino end groups larger and that of the transimidization reaction between the anhydride end groups smaller. This balance of end groups might lead to the formation of the highest molecular polyimide at χ of 0.77.

Table 3. Thermal Stability of Precipitated Obtained at Various χs[a]

χ	temp (°C) onset	temp (°C) 10 wt % loss	char yield at 700 °C (wt %)
0.5	630	637	57
0.67	630	638	54
0.77	632	641	63
1.0	622	631	56
1.5	622	628	62
2.0	624	629	62

[a] Evaluated on a Perkin-Elmer TGA-7 with a scanning rate of 20 °C min^{-1} in N_2.

The chemical structure of the end groups often influences thermal stability of the polymers.[25−27] Thermal stability of the polyimide precipitates obtained under nonstoichiometric conditions was evaluated by TGA in a nitrogen atmosphere. The results are presented in Table 3. The onset and 10 wt % loss temperatures were in the range of 622−630 and 628−641 °C, respectively. The char yields at 700 °C were 54−63%. Although the polyimides prepared at $\chi < 0.77$ exhibited slightly higher thermal stability, all polyimides were quite thermally stable.

Conclusion

Although the conventional synthesis by the homogeneous solution polymerization of PMDA and ODA was very sensitive to χ and high molecular weight polymer was obtained only under stoichiometric conditions, the polymerization by using the reaction-induced crystallization of oligomers was unsusceptible to χ. High molecular weight polymers were obtained as the crystals under nonstoichiometric conditions, and χ of 0.77 yielded the highest M_w of 2.81×10^5. The crystallization of oligomers was induced by the progress in the reaction, and the oligomers were precipitated to form the crystal. The oligomers end-capped by excess monomers were precipitated. The end-capping groups were eliminated by the transimidization reaction when the oligomers were crystallized, leading to the increase in the molecular weight. High molecular weight polyimides were formed by the following solid-state polymerization in the crystals. Since the nucleophilicity of amino end group is higher, the transimidization reaction proceeded more efficiently with eliminating ODA. Therefore, the higher molecular weight polymers were given in the range of $\chi < 1.0$ than the range of $\chi > 1.0$. Heterogeneous polymerization combining the oligomerization in a solution, crystallization, and solid-state polymerization provides the high molecular weight polyimides even under nonstoichiometric conditions.

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