Macromolecules **2003,** *36,* 1815−1818

Tandem Type Polymerization. Synthesis and Characterization of Ordered Poly(amide−thioether) from 2,6-Dichlorophenyl Methacrylate, 4,4′-Thiobis(benznenethiol), and 4,4′-Oxydianiline

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Received October 5, 2002; Revised Manuscript Received January 9, 2003

ABSTRACT: Ordered poly(amide−thioether) (**17**) was prepared by tandem type polymerization of 2,4-dichlorophenyl acrylate (**11**), 4,4′-thiobis(benznenthiol) (**12**), and 4,4′-oxydianiline (**16**). The polymerization was carried out by mixing all monomers in the presence of catalytic amounts of triethylamine (TEA) and 1-hydroxybenzotriazole (HOBt) in 1-methyl-2-pyrrolidinone (NMP) at 20 °C for 2 h and then 80 °C for 2 days, yielding polymer **17** with a number-average molecular weight (M_n) of 25 000. Authentic ordered poly(amide−thioether) (**18**) was prepared to verify the structure of polymer **17**. The microstructure of polymers obtained was investigated by ^{1}H and ^{13}C NMR spectroscopy, and it has been found the polymer obtained has the expected ordered structure. Furthermore, model reactions were studied in detail to demonstrate the feasibility of ordered polymer formation.

Introduction

The combination of several reactions in single operation, which is called a tandem reaction,[1] is a powerful means to enhance synthetic efficiency and has been widely applied in polymer chemistry. The modification of a polymer after its polymerization in a single operation is a typical example of a tandem type polymerization. For instance, Wagener et al. reported a tandem homogeneous metathesis/heterogeneous hydrogenation procedure, which consists of using a ruthenium complex to first drive homogeneous metathesis of dienes and then to promote heterogeneous hydrogenation.[2] Grubbs et al. also reported that a single ruthenium catalyst mediates three mechanically distinct reactions: the ring-opening metathesis polymerization of 1,5-cyclooctadiene, the atom-transfer radical polymerization of methyl methacrylate, and hydrogenation of the resulting copolymers in a single-step operation.[3] Furthermore, a new synthetic route to polybenzoxazole via tandem Claisen rearrangement was reported by Hiratani et al., where the tandem Claisen rearrangement of polyamide containing isobutenyl bis(aryl ether) moieties gives hydroxyl groups ortho to the amide groups, and then sequential intramolecular cyclization leads to the polybenzoxazole.[4]

The monomer transformation−polymerization is another example of tandem type polymerization. Crivello et al. reported the synthesis of poly(vinyl ether) by a tandem isomerization−cationic polymerization technique using allylic ethers.[5] Swager et al. reported the synthesis of poly(naphthodithiophene)s via tandem cyclization−polymerizations to produce aromatized monomers in situ prior to oxidative polymerization.[6] The step growth polymerization via tandem ene and Diels−Alder reactions was demonstrated by Stadler et al., where the regiochemistry of the Diels−Alder reaction could be controlled by the solvent polarity.[7]

We have been interested in the synthesis of ordered polymers by polycondensation and developed the method of sequence control in one-step polycondensation.[8−10] Tandem reactions will provide us another synthetic route to prepare ordered polymers. Conjugated esters are less reactive than saturated esters in nucleophilic substitution, because the former lose a certain amount of resonance energy when they are converted to addition products. This difference in their reactivity can be used for the synthesis of condensation polymers using tandem reactions. The facile addition of nucleophiles to double bonds activated by electron-withdrawing groups is well-known, and the Michael-type polyaddition of diamines, dithiols, and carbanions has been extensively studied.[11] Thus, we decided to study the preparation of ordered polymers from α,β-unsaturated esters, dithiols, and diamines using a class of tandem reactions where one of the reactions is addition and the other is condensation. The Michael-type polyaddition of dithiols to α,β-unsaturated esters produces saturated esters, whose enhanced reactivity promotes the reaction with diamines to produce ordered poly(amide−thioether)s.

This article describes a successful synthesis of ordered poly(amide−thioether) (**17**) by tandem type polymerization of 2,4-dichlorophenyl acrylate (**11**), 4,4′-thiobis(benzenethiol) (**12**), and 4,4′-oxidianiline (**16**).

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP) was distilled from CaH_2 under reduced pressure and stored over 4-A molecular sieves. *p*-Nitrophenyl acrylate (**1**) and *p*-nitrophenyl methacrylate (**2**) were prepared according to the reported procedure.[12] 4,4′-Thiobis(benzenethiol) (**12**) and 4,4′-oxydianiline (**16**) were recrystallized from toluene/methanol and tetrahydrofuran, respectively. Triethylamine (TEA) was distilled from KOH and stored over KOH. Other reagents and solvents were used as received.

2,4-Dichlorophenyl Acrylate (11). To an ice-cooled solution of 2,4-dichlorophenol (17 g, 100 mmol) and TEA (13.8 mL, 100 mmol) in THF (40 mL) was added dropwise acryloyl chloride (8.5 mL, 105 mmol) at 0 °C. After being stirred for 1 h, TEA·HCl was filtered and the solution was evaporated. The product was purified by distillation at 60−61 °C/1.5 mmHg.

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10.1021/ma025712j CCC: $25.00

The yield was 9.8 g (45%). IR (NaCl): ν 1751 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 6.08 (1H, dd), 6.34 (1H, dd), 6.67 (1H, dd), and 7.13 (1H, d), 7.27 (1H, dd), 7.46 ppm (1H, d). Anal. Calcd for $C_9H_6Cl_2O_2$: C, 49.80%; H, 2.79%; Cl, 32.67%. Found: C, 49.88%; H, 2.94%; Cl, 32.83%.

Model Compounds. *p*-Nitrophenyl 3-Phenylthiopropionate (5). Benzenethiol (**3**) (0.1 mL, 1.0 mmol) was added to a solution of **1′** (0.207 g, 1.0 mmol) and TEA (0.003 mL) in NMP (2 mL) at room temperature. The solution was stirred for 2 h and poured into 3 wt % aqueous sodium hydrogen carbonate (50 mL). The precipitate was filtered, washed with water, and dried. The yield was 0.275 g (91%). The product was purified by silica gel chromatography using ethyl acetate/*n*-hexane (2:3). IR (KBr): ν 1766 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ 2.91 (2H, t), 3.28 (2H, t), 7.30 (5H, m), and 7.43 (2H, m), 8.26 ppm (2H, d). Anal. Calcd for $C_{15}H_{13}NO_4S$: C, 59.39%; H, 4.32%; N, 4.62%; S, 10.57%. Found: C, 59.62%; H, 4.33%; N, 4.69%; S, 10.48%.

Reaction of 11 with 4-Phenoxyaniline. A solution of **11** (0.109 g, 0.5 mmol), 4-phenoxyaniline (0.0926 g, 0.5 mmol), TEA (0.03 mL), 1-hydroxybenztriazole (HOBt) (0.004 g, 5 mol %), and *p*-*tert*-butylanisole (0.016 g 1.0 mmol) as an internal standard in NMP (2 mL) was stirred at 20 °C. The yield of *N*-(4-phenoxyphenyl)acrylamide (**14**) was determined by the integration ratio between phenyl protons (7.47 ppm) of **14** and butyl protons (1.3 ppm) of *p*-*tert*-butylanisole in a ^{1}H NMR spectrum.

Reaction of 2, 4-Dichlorophenyl Acetate with 4-Phenoxyaniline. This reaction was carried out as described above.

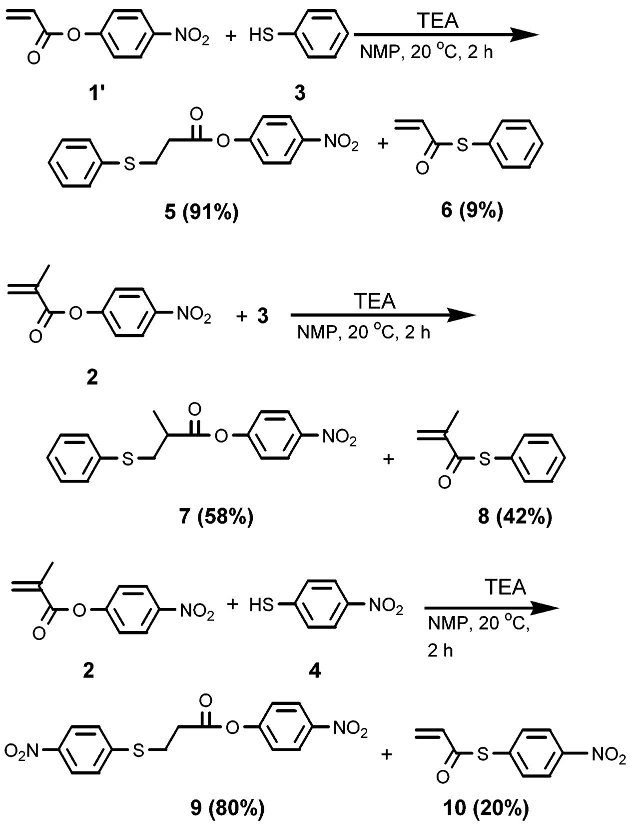
3,3′-[4,4′-Thiobis(phenylenethio)]bis(2,4-dichlorophenyl propionate) (13). A solution of **11** (0.434 g, 2.0 mmol), **12** (0.251 g, 1.0 mmol), and TEA (0.003 mL) in NMP (2.0 mL) was stirred at room temperature for 1 h and poured into 3 wt % aqueous sodium hydrogen carbonate (50 mL). The solution was extracted with dichloromethane. The extract was dried over $MgSO_4$ and evaporated. The residue was subjected to silica gel column chromatography using dichloromethane as an eluent to give a yellow liquid. The yield was 0.64 g (94%). IR (NaCl): ν 1778 cm^{-1}(C=O). ^{1}H NMR ($CDCl_3$): δ 2.92 (4H, t), 3.27 (4H, t), 7.05 (2H, d), 7.29 (10H, m), and 7.43 ppm (2H, d). Anal. Calcd for $C_{30}H_{22}Cl_4O_4S_3$: C, 52.64%; H, 3.24%; S, 14.05%; Cl, 20.72%. Found: C, 52.54%; H, 3.16%; S, 14.41%; Cl, 20.90%.

Synthesis of Ordered Poly(amide−thioether) (17). Compound **11** (0.217 g, 1.0 mmol), **12** (0.125 g, 0.5 mmol), and **16** (0.1 g, 0.5 mmol) were dissolved in NMP (1.4 mL). To this solution was added TEA (0.003 mL) and HOBt (0.008 g, 0.05 mmol). The solution was stirred at room temperature for 2 h and then at 80 °C for 2 days. The resulting viscous solution was poured into methanol (50 mL). The polymer was filtered off and dried at 80 °C in vacuo for 24 h. The yield was 0.27 g (97%). Number- and weight-average molecular weights (M_n and M_w) were 25 000 and 44 000, respectively. IR (KBr): ν 3135 (aromatic C−H), 2927 (aliphatic C−H), 1658 (C=O), 1218 cm^{-1} (C−O−C), 813 (C−S−C). ^{1}H NMR ($CDCl_3$): δ 2.64 (4H, t), 3.23 (4H, t), 6.90 (4H, d), 7.30 (8H, dd), and 7.53 ppm (4H, d). ^{13}C NMR ($CDCl_3$): δ 29.20, 36.97, 119.49, 121.86, 130.19, 132.28, 133.02, 135.47, 136.74, 153.56, 169.65 ppm. Anal. Calcd for ($C_{30}H_{26}N_2O_3S_3$): C, 64.49%; H, 4.60%; N, 5.01%; S, 17.22%. Found: C, 64.45%; H, 5.07%; N, 5.17%; S, 17.00%.

Authentic Ordered Poly(amide−thioether) (18). Compound **13** was prepared from **11** and **12** as described above. The solution of **13** (0.54 g, 0.5 mmol) and **16** (0.1 g, 0.5 mmol) was dissolved in NMP (1.4 mL) was stirred 80 °C for 2 days. The polymer was isolated as described above. The yield was 0.273 g (98%). The M_n and M_w were 19 000 and 36 000, respectively. Anal. Calcd for ($C_{30}H_{26}N_2O_3S_3$): C, 64.49%; H, 4.60%; N, 5.01%; S, 17.22%. Found: C, 63.77%; H, 4.80%; N, 5.09%; S, 16.93%.

Measurement. The infrared spectra were recorded on a Horiba FT-210 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. Thermal analyses were performed on a Seiko thermal analyzer at a heating rate of 10 and 5 °C/min for thermogravimetry (TG) and differential scanning calorimetry (DSC) under nitrogen, respectively. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using Tosoh HLC-8120GPC equipped with consecutive TSK gel columns GMH_{HR}-M and GMH_{HR}-L at 40 °C in DMF containing 0.01 mol/L LiBr. Wide-angle X-ray measurements were performed using Rigaku-Denki RU-200 BH with Ni-filtered Cu Kα radiation.

Scheme 1



Results and Discussion

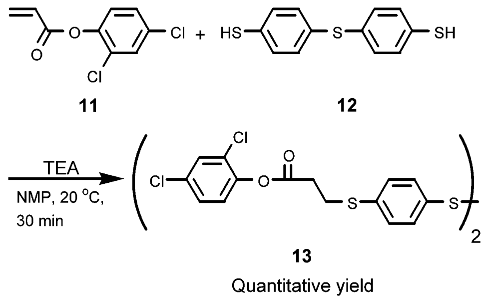
Design of α,β-Unsaturated Esters. The choice of α,β-unsaturated esters is most important in the preparation of an ordered poly(amide−thioether) by tandem consecutive reactions, the Michael addition, and aminolysis. First, *p*-nitrophenyl acrylate (**1**) and *p*-nitrophenyl methacrylate (**2**) were selected as α,β-unsaturated esters, where acrylate and active ester units are responsible for the Michael addition and aminolysis, respectively.

Addition reactions of **1** or **2** with benzenethiol (**3**) or *p*-nitrobenzenethiol (**4**) were carried out in the presence of catalytic amounts of TEA in NMP at 20 °C. The reaction was monitored by taking the NMR spectrum of a drop from the reaction mixture at different times (Scheme 1). Compounds **1** and **2** disappeared in 2 h.

The molar ratio of an adduct, *p*-nitrophenyl 3-phenylthiopropanoate (**5**), and a substitution product, *S*-*p*-phenyl propenethioate (**6**), was 91:9 in the reaction of **1** with **3**. On the other hand, **2** reacted slowly with **3** and gave *p*-nitrophenyl 3-phenylthio-2-methylpropenoate (**7**) (58 mol %) and *S*-*p*-phenyl 2-methylpropanethioate (**8**) (42 mol %). The use of **4** in the model reaction gave better yield of the addition product **9** in 80 mol %, but the formation of S-*p*-nitrophenyl 2-methylpropenethioate (**10**) was still observed.

To suppress the substitution reaction, a less reactive ester than *p*-nitrophenyl ester, 2,4-dichlorophenyl acrylate (**11**), was prepared from acryloyl chloride and 2,4-dichlorophenol. The reaction of **11** with 4,4′-thiobis-

Scheme 2



Scheme 3

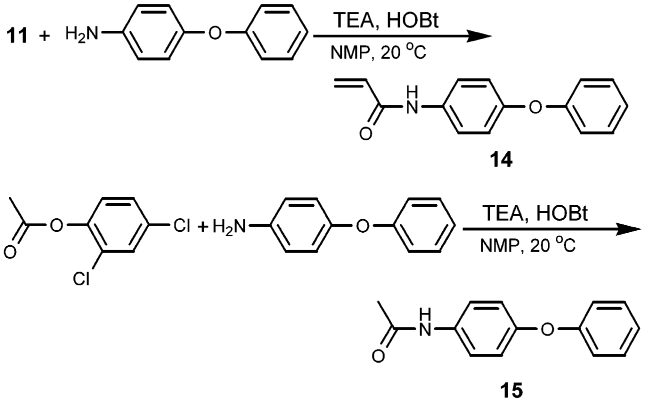


Table 1. Reaction of Monomer 11 and 2,4-Dichlorophenyl Acetate with 4-Phenoxyaniline

run	temp (°C)	time (h)	yield (%) 14	yield (%) 15
1	20	1	8	16
2	20	18	18	80
3	60	0.5	10	55
4	80	0.5	27	77
5	80	2	40	99

[a] Reaction was carried out with 1.0 mmol of each compound in the solvent at room temperature for 4 h. [b] Determined by ^{1}H NMR spectroscopy.

(benznenthiol) (**12**) was performed in the presence of catalytic amounts of TEA in NMP at 20 °C. The desired addition product, 3,3′-[4,4′-thiobis(phenylenethio)]bis-(2,4-dichlorophenyl propionate) (**13**), was obtained in quantitative yield in 30 min. Furthermore, no substitution product was observed (Scheme 2).

To investigate the difference of reactivity between conjugated esters and saturated esters, the reaction of **11** and 2,4-dichlorophenyl acetate with 4-phenoxyaniline was carried out in NMP in the presence of 1-hydroxybenzotriazole (HOBt) that is an extremely efficient catalyst in the aminolysis of active 4-nitrophenyl and trichlorophenyl esters (Scheme 3).[13]

The yields of *N*-(4-phenoxyphenyl)acrylamide (**14**) and *N*-(4-phenoxyphenyl)acetamide (**15**) were determined by the integration ratios between phenyl protons of **14** (7.47 ppm) and those of **15** (7.55 ppm) with butyl protons (1.3 ppm) of *p*-*tert*-butylanisole as an internal standard in ^{1}H NMR spectra. The results summarized in Table 1 indicated that 2,4-dichlorophenyl acetate is about 5 times more reactive than **11** at 60 °C in 30 min. The Michael addition converts unsaturated esters to saturated esters, leading to a facial aminolysis.

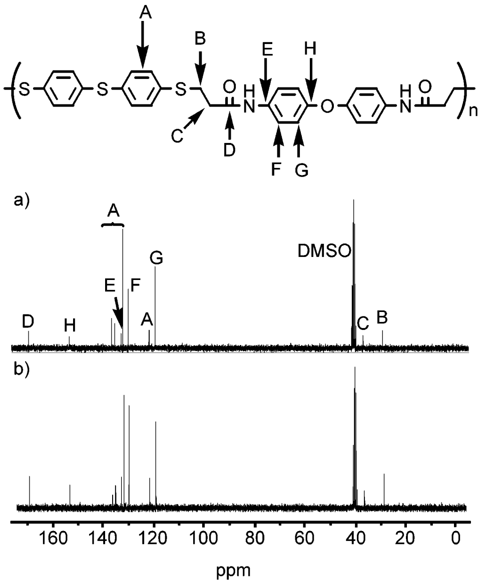
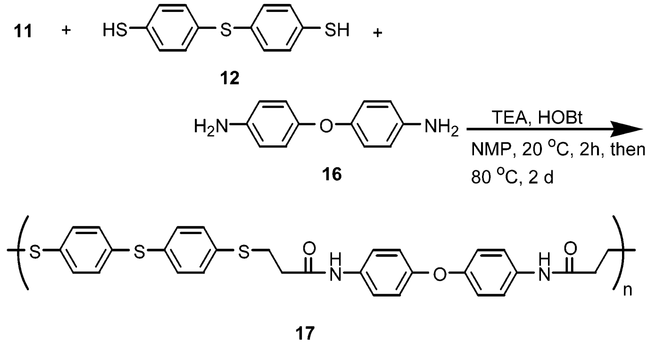
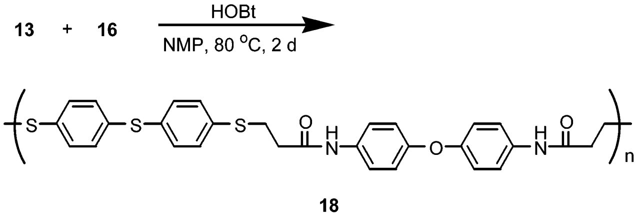


Figure 1. ^{13}C NMR spectra of (a) polymer **17** and (b) polymer **18** in DMSO-d_6 at 60 °C.

Scheme 4



Scheme 5



Polymer Synthesis. Synthesis of Ordered Poly(amide−thioether) by Tandem Polymerization. On the basis of these model reactions, we decided to use following three monomers, **11**, **12**, and 4,4′-oxydianiline (**16**) for the preparation of ordered poly(amide−thioether) (**17**). The polymerization was carried out by using a direct procedure (Scheme 4).

The solution of **11**, **12**, and 1**6** in the presence of TEA and HOBt in NMP was stirred at 20 °C for 2 h and then 80 °C for 2 days. The polymerization involves the following two steps: (i) the Michael addition of **12** to **11**, i.e., generation of the diester with the enhanced reactivity, (ii) condensation of the diester with the diamine. The polymerization proceeded in homogeneous solution and gave polymer with a number-average molecular weight of 25 000 (relative to polystyrene standards by GPC in DMF).

Synthesis of Authentic Ordered Poly(amide−thioether). Authentic ordered polymer (**18**) was synthesized for the characterization of the structure of ordered polymer **17** obtained by tandem polymerization. Authentic polymer **18** was prepared as shown in Scheme 5.

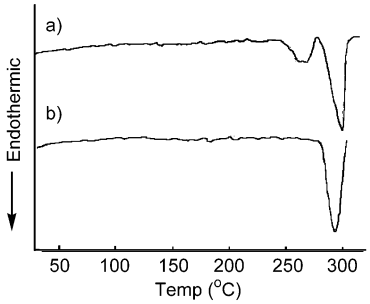


Figure 2. DSC profiles of (a) as-made polymer **17** and (b) polymer **17** after annealing at 270 °C for 1 h.

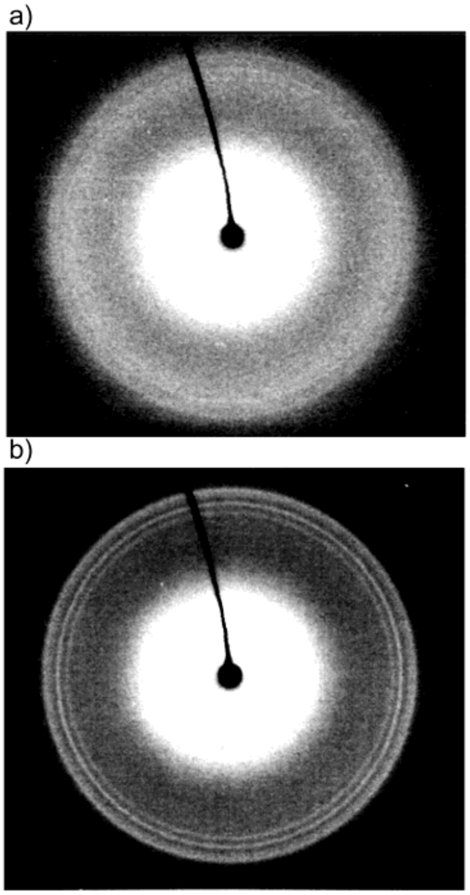


Figure 3. X-ray diffraction of (a) as-made polymer **17** and (b) polymer **17** after annealing at 270 °C for 1 h.

Compound **13** was prepared from **11** and **12**, and then the solution polycondensation of **13** with **16** was carried out in the presence of HOBt in NMP, giving poly(amide−thioether) **18** with a number-average molecular weight of 20 000.

Polymer Characterization. All the polymers showed characteristic NH, amide I, amide II, and thioether bands in the ranges 3274, 1658, 1542, and 1218 cm^{-1}, respectively. Elementary analysis also supported the formation of the expected polymers.

The microstructure of the polymers determined by ^{1}H and ^{13}C NMR spectroscopy. All peaks in the ^{1}H NMR spectra of authentic polymer **17** and polymer **18** were well assigned, and the spectra of polymers **17** and **18** were identical.

The ^{13}C NMR spectra of polymers **17** and **18** with the assignment of each resonance are presented in Figure 1. The spectrum of polymer **18** is identical to that of polymer **17**. These findings clearly indicate that direct poly(addition−condensation) of **11**, **12**, and **16** produced the desired ordered poly(amide−thioether) **17**.

Polymers **17** and **18** were white solids, soluble in sulfuric acid, methanesulfonic acid, and NMP at room temperature. A transparent film was cast from a solution of polymer **17** in NMP.

The thermal stability of polymer **17** was examined by thermogravimetry (TG). The polymer showed a 10% weight loss at 350 °C. The DSC trace of the first-heating process for polymer **17** illustrated in Figure 2 showed a bimodal endothermic peak appeared at 265 and 297 °C. When as-synthesized polymer was annealing at 270 °C for 1 h, the sample exhibited a unimodal trace, and the endothermic peak became comparatively sharp. It suggested that the recrystallization took place during the annealing process. Thus, the lower endothermic peak could be assigned to submelting due to the thin and thermodynamically unstable crystallinities.

WAXD diffraction patterns of as-made and annealed polymers are illustrated in Figure 3. Well-defined sharp rings were observed on the annealing treatment polymer. It was another evidence for recrystallization. These results agreed with those of DSC.

Conclusions

We have demonstrated that the synthesis of ordered poly(amide−thioether) can be achieved by tandem polymerization of **11**, **12**, and **16** in the presence of TEA and HOBt in NMP. Thus, tandem reaction proves highly suitable to the preparation of ordered polymers. We are currently extending tandem reaction to the synthesis of other condensation polymers.

Acknowledgment. We acknowledge the help from Dr. Masatoshi Tokita (Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology) with the WAXD measurement. This study was financially supported by the New Energy and Industrial Technology Development Organization (NEDO) for the project on Technology for Nanomaterials.

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MA025712J