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Synthesis of Ordered Polyamides by Direct Polycondensation. 5. Ordered Poly(amide–thioether)s

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ABSTRACT: An ordered (–abcd–) poly(amide–thioether) was prepared by poly(addition–direct condensation) of a pair of two nonsymmetric monomers, 4-(acryloyloxy)benzoic acid (XabX) and 4-aminobenzenethiol (YcdY), using the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1). The polymerization was carried out by mixing both monomers in the presence of 1 and TEA in NMP at room temperature, yielding the ordered poly(amide–thioether) with the inherent viscosity of 0.31 dL/g. The authentic ordered poly(amide–thioether) was prepared to verify the structure of ordered poly(amide–thioether). The microstructure of polymers obtained was investigated by means of ^{13}C-NMR spectroscopy, and it has been found that the polymer obtained had the expected ordered structure. Furthermore, the model reactions were studied in detail to demonstrate the feasibility of ordered polymer formation.

Introduction

As part of our research program on the synthesis of condensation polymers by direct polycondensation, our group has recently initiated the synthesis of ordered polyamide by direct polycondensation. In the preceding papers,[1] we reported a successful synthesis of ordered polyamides (head-to-head or tail-to-tail) from a symmetric monomer and a nonsymmetric monomer,[1a,1b] ordered polyamides (head-to-tail) from a symmetric monomer and a nonsymmetric monomer or a pair of two symmetric monomers,[1c] and an ordered polyamide from a pair of two symmetric monomers and a nonsymmetric monomer.[1d]

Our next target will be the synthesis of ordered polyamide (–abcdef–) from three nonsymmetric monomers, XabX, YcdY, and ZefZ, by direct polycondensation. However, the differentiation among the three amino or carboxy groups, that is, the selective acylation, seems to be very difficult at the present stage. Thus, we thought to combine a polycondensation with a polyaddition to prepare ordered polyamides. And we decided to study the preparation of ordered polymers from two nonsymmetric monomers by poly(addition–direct condensation) prior to preparing an ordered polyamide from three nonsymmetric monomers. The facile addition of nucleophiles to the double bonds activated by electron-withdrawing groups is well known, and the Michael-type polyaddition of diamines, dithiols, and carbanions has been extensively studied.[2] In particular, dithiols are the most powerful nucleophiles and this Michael-type addition is generally much faster than the nucleophilic substitution reaction of carboxylic acid derivatives, such as acid anhydrides and active esters with nucleophiles. With the difference in their reactivities, in fact, the selective polyaddition of 4-aminobenzenethiol to maleic anhydride has been reported.[3]

This article describes the successful synthesis of an ordered poly(amide–thioether) from two nonsymmetric monomers, 4-(acryloyloxy)benzoic acid (XabX) and 4-aminobenzenethiol (YcdY) in the presence of the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)-phosphonate (1).

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP) was stirred over powdered calcium hydride overnight, distilled under reduced pressure, and then stored over 4-Å molecular sieves. Phenyl acrylate (2) was prepared by the reaction of acryloyl chloride with phenol in the presence of TEA in THF. 4-Aminobenzenethiol (6) was purified by vacuum distillation. Triethylamine (TEA) and tetrahydrofuran (THF) were purified by the usual method. Other reagents and solvents were obtained commercially and used as received.

The activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1) was prepared according to the reported procedure.[4]

Model Reaction. Phenyl 3-Phenylthiopropanoate (3). Benzenethiol (0.11 mL, 1.0 mmol) was added to a solution of phenyl acrylate (0.148 g, 1.0 mmol) in THF (2 mL) at room temperature. The solution was stirred for 5 min and poured into

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10% aqueous sodium hydrogen carbonate. The solution was extracted with ether. The extract was dried ($MgSO_4$) and evaporated. The residue was subjected to silica gel column chromatography using benzene as eluent to give a colorless liquid. The yield was 0.219 g (85%). IR (NaCl): ν 1760 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ 2.84 (t, 2H, $-CH_2-$), 3.25 (t, 2H, $-SCH_2-$), ^{13}C-NMR ($CDCl_3$): 28.3 ($-CH_2-$), 34.0 ($-SCH_2-$), 169.6 ppm (C=O). Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46. Found: C, 69.56; H, 5.55.

Phenyl 3-Anilinopropionate (4). The mixture of phenyl acrylate (0.148 g, 1.0 mmol) and aniline (0.0931 g, 1.0 mmol) was heated at 60 °C for 4 h and poured into water. The product which precipitated was filtered out, washed with water, and dried. The product was purified by silica gel column chromatography using ethyl acetate–*n*-hexane (2:3) as eluent to afford white plates. The yield was 0.214 g (89%). Mp: 82–84 °C. IR (KBr): ν 3400 (N–H), 1750 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ 4.06 (s, 1H, N–H), 2.83 (t, 2H, $-CH_2-$), 3.54 (t, 2H, $-NHCH_2-$). ^{13}C-NMR ($CDCl_3$): 34.0 ($-CH_2-$), 39.3 ($-NHCH_2-$), 170.9 ppm (C=O). Anal. Calcd for ($C_{15}H_{15}NO_2$): C, 74.66; H, 6.27; N, 5.81. Found: C, 74.40; H, 6.14; N, 5.75.

Competitive Reaction of Benzenethiol and Aniline with 2. Compound **2** (0.741 g, 5.0 mmol) was added to a solution of benzenethiol (0.52 mL, 5.0 mmol) and aniline (0.466 g, 5.0 mmol) in THF (10 mL) at room temperature. The solution was stirred for 5 min and poured into 10% aqueous sodium hydrogen carbonate. The solution was extracted with ether. The ether layer was extracted with 1 M hydrochloric acid solution, dried ($MgSO_4$), and evaporated to give pure **3**. The yield was 1.21 g (94%).

***p*-(Acryloyloxy)benzoic Acid (5).** To an ice-cooled solution of *p*-hydroxybenzoic acid (13.8 g, 0.1 mol) in aqueous 5% sodium hydroxide solution (200 mL) was added dropwise acryloyl chloride (10.9 g, 0.12 mol). After being stirred for 1 h, the reaction solution was acidified with 2 M hydrochloric acid solution. The product was precipitated was collected and dried in vacuo. Recrystallization from acetic acid–water afforded white plates. The yield was 9.9 g (51%). Mp: 208 °C dec. IR (KBr): ν 1740 (C=O, ester), 1690 cm^{-1} (COOH). ^{1}H-NMR (DMSO-d_6): δ 13.02 (broad s, 1H, COOH), 6.39–6.64 (dd, 2H, CH_2=, t, 1H, CH_2=C*H*). ^{13}C-NMR (DMSO-d_6): 163.8 (C=O, ester), 166.7 ppm (COOH). Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.20; H, 4.24.

4-(3-(Phenylthio)propionyl)oxy)benzoic Acid (7). The solution of **5** (0.961 g, 5.0 mmol) and benzenethiol (0.52 mL, 5.0 mmol) in NMP (4.0 mL) was stirred at room temperature for 1 h. Then, the solution was poured into 1 M hydrochloric acid solution. The precipitate was filtered out, washed with water, and dried. Recrystallization from chloroform–*n*-hexane yielded white plates. The yield was 1.27 g (84%). Mp: 128–129 °C. IR (KBr): ν 1760 (C=O, ester), 1690 cm^{-1} (COOH). ^{1}H-NMR (DMSO-d_6): δ 2.96 (t, 2H, $-CH_2-$), 3.33 (t, 2H, $-SCH_2-$), 13.02 (broad s, 1H, COO*H*). ^{13}C-NMR (DMSO-d_6): 27.8 ($-CH_2-$), 34.0 ($-SCH_2-$), 166.7 (COOH), 169.8 ppm (C=O, ester). Anal. Calcd for $C_{16}H_{14}O_4S$): C, 63.56; H, 4.67. Found: C, 63.43; H, 4.78.

4-((3-(Phenylthio)propionyl)oxy)benzanilide (8). Activating agent **1** was added to a solution of **7** (0.302 g, 1.0 mmol) and aniline (0.0931 g, 1.0 mmol) in NMP (2 mL) at room temperature. The solution was stirred for 1 h and poured into 10% aqueous sodium hydrogen carbonate. The precipitate was filtered out, washed with water, and dried. Recrystallization from benzene–*n*-hexane afforded white plates. The yield was 0.363 g (96%). Mp 138–139 °C. IR (KBr): ν 3300–3400 (N–H), 1750 (C=O, ester), 1650 cm^{-1} (C=O, amide). ^{1}H-NMR (DMSO-d_6): δ 2.85 (t, 2H), $-CH_2-$), 3.23 (t, 2H, $-SCH_2-$), 10.21 (s, 1H, N–H). ^{13}C-NMR (DMSO-d_6): 27.7 ($-CH_2-$), 33.9 ($-SCH_2-$), 164.8 (C=O, amide), 169.8 ppm (C=O, ester). Anal. Calcd for $C_{22}H_{19}NO_3S$: C, 70.00; H, 5.07; N, 3.71. Found: C, 69.85 H, 5.13; N, 3.80.

***S*-Phenyl 4-Acetoxythiobenzoate (9).** Activating agent **1** (0.460 g, 1.2 mmol) was added to a solution of *p*-acetoxybenzoic acid (0.180 g, 1.0 mmol), benzenethiol (0.11 mL, 1.0 mmol), and TEA (0.34 mL, 2.4 mmol) in NMP (2 mL) at room temperature. The solution was stirred at room temperature for 2 h and then poured into 10% aqueous sodium hydrogen carbonate solution. The precipitate was filtered out and dried. Recrystallization from *n*-hexane afforded white plates. The yield was 0.264 g (96%). Mp: 83–85 °C (lit.[5] mp 84–85 °C). IR (KBr): ν 1760 (C=O, thioester), 1670 cm^{-1} (C=O, ketone). ^{1}H-NMR (DMSO-d_6): δ 2.40 (s, 3H, CH_3CO-). ^{13}C-NMR (DMSO-d_6): 168.7 (CH_3C=O), 188.1 ppm (C=O, thioester).

Authentic Ordered Poly(amide–thioether) 11. 4-[(3-((4-Aminophenyl)thio)propionyl)oxy]benzoic acid (10). A solution of **5** (0.385 g, 2.0 mmol) and **6** (0.250 g, 2.0 mmol) in NMP (4 mL) was stirred at room temperature for 1 h and poured into water (100 mL). The product was filtered out and dried. Recrystallization from chloroform–*n*-hexane gave white plates. The yield was 0.521 g (82%). IR (KBr): ν 1690 (COOH), 1750 cm^{-1} (C=O, ester). ^{1}H-NMR (DMSO-d_6): δ 2.82 (t, 2H, $-CH_2-$), 3.04 (t, 2H, $-SCH_2-$). ^{13}C-NMR (DMSO-d_6): 31.1 ($-CH_2$), 34.2 ($-SCH_2-$), 166.7 (COOH), 169.9 ppm (C=O, ester). Anal. Calcd for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.42. Found: C, 60.48; H, 4.80; N, 4.49.

To a solution of **10** (0.317 g, 1.0 mmol) in NMP (1.3 mL) was added activating agent **1** (0.460 g, 1.2 mmol) and TEA (0.17 mL, 1.2 mmol) at room temperature. The solution was stirred for 24 h and poured into methanol (200 mL). After thorough washing with methanol and drying, the polymer weighed 0.299 g (100%). The inherent viscosity of the polymer in NMP was 0.56 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr): ν 3300–3400 (N–H), 1760 (C=O, ester), 1650 cm^{-1} (C=O, amide). ^{13}C-NMR (NMP): 34.3 ($-SCH_2-$), 164.8 (C=O, amide), 169.8 ppm (C=O, ester). Anal. Calcd for $(C_{16}H_{13}NO_3S)_n$: C, 64.19; H, 4.38; N, 4.68. Found: C, 64.02; H, 4.58; N, 4.73.

Poly(amide–thioester) 12 from *p*-Aminobenzenethiol (6) and 5. Compound **6** (0.125 g, 1.0 mmol) was dissolved in NMP (0.5 mL). To this solution was added successively a solution of **5** (0.192 g, 1.0 mmol) in NMP (0.8 mL), activating agent **1**, and TEA (0.17 mL, 1.2 mmol). The solution was stirred at room temperature for 24 h and poured into methanol. The polymer was isolated described above. The yield was 0.293 g (98%). The inherent viscosity of the polymer in NMP was 0.31 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr): ν 3300–3400 (N–H), 1760 (C=O, ester), 1650 cm^{-1} (C=O, amide). ^{13}C-NMR (NMP): 34.3 ($-SCH_2-$), 164.8 (C=O, amide), 169.6 ppm (C=O, ester). Anal. Calcd for $(C_{16}H_{13}NO_3S)_n$: C, 64.19; H, 4.38; N, 4.68. Found: C, 64.06; H, 4.56; N, 4.94.

Measurements. The infrared spectra were recorded on a Hitachi I-5020-FT-IR spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out by using a Cannon-Fenske viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000 TG-DTA 200 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry.

Results and Discussion

According to the theoretical aspects of systems involving the synthesis of ordered polymer from two nonsymmetric monomers, XabX and YcdY,[6] the relevant elementary reactions and the relative reactivities of functional groups of both monomers for this polymerization can be shown as follows:

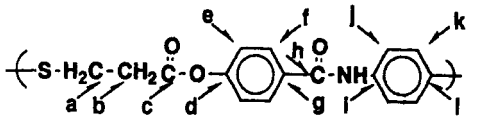
$$-aX + Yc- \xrightarrow{k_{ac}} -ac- + XY \qquad r_1 = k_{ad}/k_{ac},\ 0 \le r_1 \le 1$$

$$-aX + Yd- \xrightarrow{k_{ad}} -ad- + XY \qquad r_2 = k_{bc}/k_{ac},\ 0 \le r_2 \le 1$$

$$-bX + Yc- \xrightarrow{k_{bc}} -bc- + XY \qquad r_3 = k_{bd}/K_{ac},\ 0 \le r_3 \le 1$$

$$-bX + Yd- \xrightarrow{k_{bd}} -bd- + XY$$

In order to obtain one (–bacd–) of the ordered polymers the relative reactivity ratios r_1 and r_2 should be both smaller than unity (less than 0.01). In this case regardless of the synthetic procedure whether XabX adds to YcdY or YcdY



	a	b	c	h
1)	33.9	27.7	169.8	164.8
found	34.4	29.5	169.6	164.8
	d	e	f	g
calcd.	154.3	121.5	127.7	130.3
found	153.3	121.4	130.9	130.9
	i	j	k	l
calcd.	134.6	120.6	126.5	134.0
found	138.8	120.8	129.2	132.7

1) on the basis of assignments for model compounds 4,8,9.

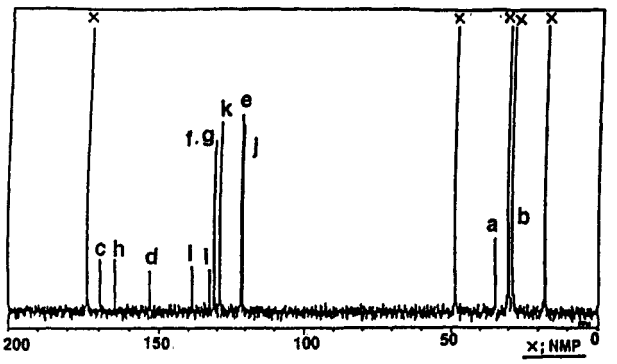
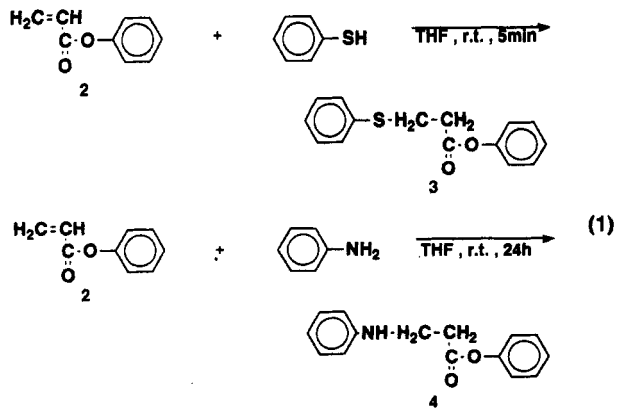


Figure 1. ^{13}C-NMR spectra of polymers 11 and 12 in NMP at 25 °C.

adds to XabX, the first intermediate is XbacdY, which will later polymerize stoichiometrically to the fully ordered polymer.

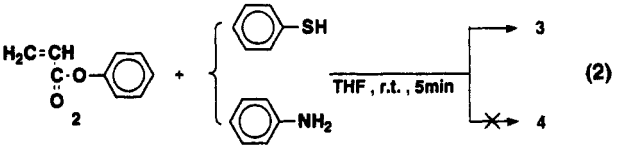
In the previous papers,[7] we reported the polymer synthesis by the Michael-type polyaddition of bisacrylamides and divinyl sulfones with aromatic diamines and dithiols. These investigations revealed that the polyaddition reaction of aromatic diamines proceeded in the presence of acid catalyst in *m*-cresol, and aprotic polar solvents, such as hexamethylphosphoramide and NMP, were the best mediums for the polyaddition of dithiols.

Before the synthesis of the ordered polymer, the following model compound work was performed to determine if the model compounds were formed in quantitative yields to constitute an ordered polymer forming reaction. The addition reactions of phenyl acrylate (2) with benzenethiol and aniline were carried out in THF at room temperature to clarify the difference in their reactivities (eq 1). The reaction of benzenethiol was



(1)

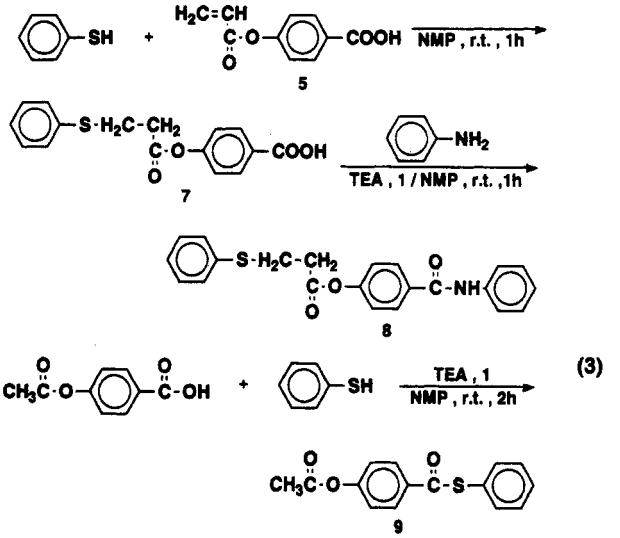
completed in 5 min and yielded adduct 3. On the other hand, aniline reacted very slowly and gave only a 10% yield of adduct 4 after 24 h under the same conditions. Furthermore, the competitive reaction between benzenethiol and aniline with 2 was carried out in THF at room temperature for 5 min (eq 2). The selective addition



(2)

reaction of benzenethiol was observed, and the desired product, phenyl 3-phenylthiopropanoate (3), was obtained in quantitative yield.

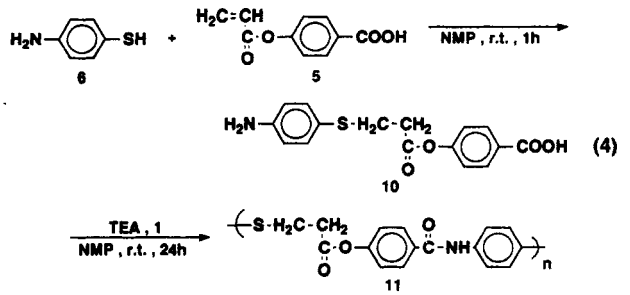
On the basis of these model reactions and availability of reagents, we decided to use the two nonsymmetric monomers, *p*-(acryloyloxy)benzoic acid (5) and *p*-aminobenzenethiol (6). The model compounds depicted in eq 3 were prepared in order to clarify the structure of



(3)

polymer obtained. The Michael addition of benzenethiol to 5 gave 4-((3-(phenylthio)propionyl)oxy)benzoic acid (7), which was converted to 4-((3-(phenylthio)propionyl)-oxy)benzanilide (8) by treatment with aniline in the presence of 1. Phenyl 3-anilinopropionate (4) was prepared by the reaction of 2 with aniline at 60 °C. *S*-Phenyl 4-acetoxythiobenzoate (9) was also synthesized from *p*-acetoxybenzoic acid and benzenethiol.

Polymer Synthesis. Synthesis of Ordered Poly(amide–thioether) 11. The authentic ordered poly(amide–thioether) 11 was prepared by direct polycondensation of 4-[(3-((4-aminophenyl)thio)propionyl)oxy]-benzoic acid (10), which was obtained from 5 and 6 (eq 4). The polycondensation proceeded smoothly, giving polymer 11 with an inherent viscosity of 0.56 dL/g.



(4)

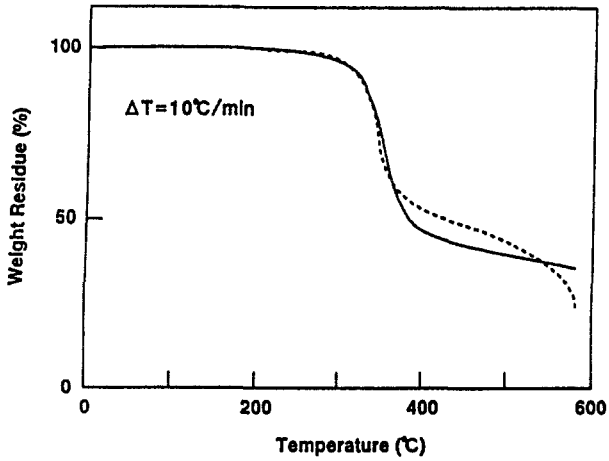
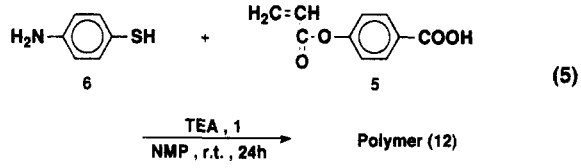


Figure 2. TG traces of polymer **12** in nitrogen (—) and in air (- - -).

Synthesis of Ordered Poly(amide–thioether) 12. The ordered polymer is obtained when the monomers are mixed very rapidly.[6] Therefore, the synthesis of ordered polymer **12** was carried out by mixing two monomers in the presence of activating agent **1** and TEA in NMP at room temperature. This polymerization formed polymer **12** with an inherent viscosity of 0.31 dL/g (eq 5).

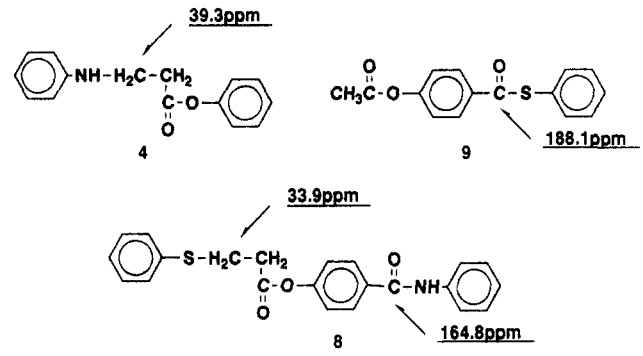


(5)

Characterization. The IR spectra of the poly(amide–thioether)s **11** and **12** were consistent with those of model compounds and known analogues. These polymers prepared showed characteristic N–H, amide I, and amide II bands in the range 3300–3400, 1650–1660, and 1530–1540 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

The most conclusive spectral evidence for the prepared polymer structures and especially that for the ordered poly(addition–condensation) was provided by ^{13}C-NMR spectroscopy. ^{13}C-NMR chemical shifts of methylene and carbonyl carbons for model compounds are as follows.

The ^{13}C-NMR spectra of authentic ordered polymer **11** and polymer **12** prepared by direct polycondensation are presented in Figure 1. The signals of carbon nuclei in methylene and amide carbonyl groups for polyamide **11** appeared at 34.3 and 164.8 ppm. These peaks were assigned, as shown in the inset Figure 1, on the basis of assignments for model compounds. No methylene adjacent amino group and ester peaks derived from random structures were observed. Furthermore, the spectrum of authentic ordered polymer **11** is identical to that of polymer **12**. These findings clearly indicate that poly(addition–direct condensation) of **5** and **6** produced the desired ordered (–abcd–) poly(amide–thioether) **12**.



Polymers **11** and **12** were white solids, soluble in sulfuric acid, methanesulfonic acid, and NMP at room temperature and DMSO and DMF on heating.

The thermal stability of the polymer was examined by thermogravimetry (TG). Typical traces for polymer **12** both in nitrogen and in air are shown in Figure 2. The polymer showed a 10% weight loss in air and in nitrogen at 325 and 330 °C, respectively.

In summary, we have demonstrated that the synthesis of an ordered (–abcd–) poly(amide–thioether) can be achieved by the combination of polyaddition and direct polycondensation of two nonsymmetric monomers **5** and **6** using activating agent **1**. This synthetic method for ordered (–abcd–) polymers would be successfully applied to the synthesis of ordered polymer (–abcdef) from three nonsymmetric monomers, XabX, YcdY, and ZefZ.

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