

Phosgen-free Synthesis of Oligoureas Having Amino End-groups: Their Application to the Synthesis of Poly(urea-imide)

Beom Jin Kim and Ji Young Chang*

Hyperstructured Organic Materials Research Center and School of Materials Science and Engineering,
Seoul National University, Seoul 151-742, Korea

(Received May 31, 2002; Revised June 14, 2002; Accepted June 18, 2002)

Abstract: The thermal reaction of acetoacetanilide in the presence of aniline or phenol yielded carbanilide in quantitative yields. This reaction was applied to the synthesis of polyurea. Bisacetoacetamides were prepared from diamines and diketene in DMF. They were thermally polymerized in the presence of phenol or a diamine (6FDA) to yield polyureas of low molecular weights. The polymers were soluble in DMSO and NMP. ¹H-NMR analysis showed that they had amino group terminated structures. Poly(urea-imide) was synthesized by the reaction of an oligourea diamine with pyromellitic dianhydride in NMP. The concentration of terminal amino groups was determined by an acid-base titration. The thermal property of poly(urea-imide) was evaluated by thermogravimetric analysis (TGA). Initial decomposition took place at 332-350 °C.

Keywords: Phosgen-free synthesis, Bisacetoacetamide, Oligourea, Poly(urea-imide), End group analysis

Introduction

Polyureas have many practical applications as elastomers, adhesives, and fibers. They are readily formed by a polyaddition reaction between diisocyanates and diamines. Isocyanates are generally prepared in two ways: (1) degradation of carbamoyl intermediates obtained from amines and (2) rearrangement of amides derived from carboxylic acids[1]. In former method, the reaction rates and reaction temperatures are dependent on nature of a living group. In industrial processes, a chloro group has been used as a leaving group[2].

Carbamoyl chloride is obtained by the reaction of an amine and a phosgen. Since phosgen is very toxic, there has been a great interest on the phosgen-free synthesis of isocyanates. Recently, we found that an acetoacetamide could be used as a precursor for an isocyanate[3]. At moderate temperatures, the C-C bond of an acetoacetamide cleaved to yield an isocyanate, an acetyl groups acting as a leaving group. The self-addition reaction of acetoacetamides was also observed due to their 1,3-dicarbonyl structures. In this work, we prepared linear oligoureas having amino end groups by the thermal polymerization of bisacetoacetamides in the presence of phenol or a diamine. These oligourea diamines were expected to use for the synthesis of urea copolymers by the reaction with bifunctional comonomers.

Experimental

Materials

1,4-Phenyldiamine, 4,4'-oxydianiline, 4,4'-(hexafluoroisopropylene)dianiline, diketene, aniline, acetic anhydride, pyromellitic dianhydride, and phenol were purchased from

Aldrich Chemical Co., and used without further purification. Zeolite was purchased from ACROS chemical Co. The composition of zeolite is a ratio of SiO₂/Al₂O₃=1000. The solvents were purified by standard procedures[4].

Measurement

The infrared spectra were recorded by using a Midac FT-IR spectrophotometer. The UV-Vis. spectra were obtained with a Hewlett-Packard HP8452A spectrometer. The ¹H-NMR spectra were recorded by using a Jeol JNM-LA300 spectrometer. Gel permeation chromatography (GPC) was carried out with a Viscotek Model 250 equipped with a M410 refractive index detector and PL Gel Mix-B and 5 μ Mix-D columns at room temperature. Elemental analysis was performed by a CE Instrument EA1110 analyzer. Thermogravimetric analysis (TGA) was carried out under N₂ by using a TA instruments TGA 2050 at a heating rate of 10 °C/min. The potentiometric titration was performed by a Dongwoo Medical Systems DP-880M pH/ION meter with a combined electrode.

Synthesis of Bisacetoacetamide 4

This compound was prepared according to our previous report[3]. Diketene (7.17 ml, 93 mmol) in DMF (12 ml) was added to a solution of 1,4-phenylene diamine (5.05 g, 46 mmol) in DMF (12 ml). The solution was stirred at 80 °C for 2 h. The product was isolated by precipitation of the reaction mixture into diethyl ether. Further purification was done by recrystallization from acetone (78 % yield).

Synthesis of Bisacetoacetamide 5

Diketene (1.92 ml, 25 mmol) in DMF (5 ml) was added to a solution of 4,4'-oxydianiline (2.5 g, 12.5 mmol) in DMF (5 ml). The solution was stirred at 80 °C for 2 h. The product was isolated by precipitation of the reaction mixture into

*Corresponding author: jychang@gong.snu.ac.kr

Table 1. Model reaction conditions and results^{a)}

Reactants	Mole ratio	Yield (%)	
		Carbanilide	3
1	-	45	40
1/phenol	1/4	100	-
1/aniline	1/4	100	-
1/o-toluic acid	10/1	49	34

^{a)}The reaction was carried out in DMF at 160°C for 6 h. The concentration of **1** in DMF was 1 mol/l.

diethyl ether. Further purification was done by recrystallization from acetone (80 % yield).

¹H-NMR(DMSO-d₆, 300 MHz): δ 10.1 (s, NH, 2H), 7.55, 6.95 (dd, phenyl proton, 8H), 3.52 (s, COCH₂CO, 4H), 2.20 (s, COCH₃, 6H). IR (KBr, cm⁻¹): 3282, 3144, 3085, 2927, 1716, 1654, 1556, 1164. Anal Calcd for C₂₀H₂₀N₂O₅: C, 66.21; H, 5.47; N, 7.60. Found: C, 65.98; H, 5.51; N, 7.51.

Model Reaction

Typical procedure is as follows. Acetoacetanilide (5.4 g, 30.6 mmol) and phenol (11.5 g, 122.6 mmol) were dissolved in DMF (30 ml). The solution was stirred for 6 h at 160°C. Yields of carbanilide **2** and compound **3** were determined by ¹H-NMR spectroscopy in DMSO-d₆. The reaction conditions and results are summarized in Table 1.

Synthesis of Oligoureas

The polymerization conditions and results are summarized

Table 2. Polymerization conditions and results^{a)}

Polymer	Monomer	Catalyst (g)	Temp (°C)	Time (h)	$M_n^{b)}$	$M_w^{b)}$	Yield (%)
6a	4/6FDA		210	18	1230	1550	26
6b	4/6FDA	phenol (0.56)	160	18	730	1160	32
6c	4/6FDA	Zeolite (0.50)	200	12	480	670	31
6d ^{c)}	4	Phenol (0.56)	160	18	520	-	55
7a	5	Phenol (0.56)	210	18	1380	1480	58
7b	5	Phenol (0.56)	210	18	720	860	49
7c ^{c)}	5/6FDA	Phenol (0.56)	160	18	920	-	28
7d	5/6FDA	Zeolite (0.50)	160	12	1720	2580	31
7e	5/6FDA	Zeolite (0.50)	160	12	2060	3810	34

^{a)}The polymerization was carried out in NMP (12 ml). The concentration of a bisacetoacetamide in NMP was 0.12 mol/l.

^{b)}Molecular weights were obtained by gel permeation chromatography in THF versus PS standards.

^{c)}Number average molecular weight was calculated based on the ¹H-NMR peak area after acetylation of amino groups with acetic anhydride in NMP.

in Table 2. Typical procedure for the synthesis of polymer **6c** is as follows. A two-necked flask equipped with a reflux condenser was charged under nitrogen with bisacetoacetamide **4** (0.41 g, 1.5 mmol), 4,4'-(hexafluoroisopropylidene)dianiline (0.5 g, 1.5 mmol), zeolite (0.5 g), and 12 ml of NMP. After stirring at 200°C for 12 h, the reaction mixture was cooled to room temperature. The catalyst was removed by filtration and washed with NMP. The filtrate was poured into a vigorously stirred distilled water (200 ml). The precipitated polymer was isolated by filtration and purified by reprecipitating the polymer solution in dimethyl sulfoxide into diethyl ether.

Potentiometric Titration

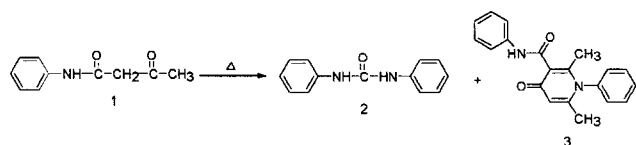
A known amount of an oligourea (0.1 g) was added to 30 ml of a DMF/glacial acetic acid mixture [2/1(v/v)]. The sample was stirred for 30 min. A certain volume of HBr (0.01 N) was added to the sample. The potential of the solution was measured by using a pH meter.

Synthesis of Poly(urea-imide) (9)

To a solution of oligourea **7e** (1 g, [-NH₂] = 0.019 mol/l) in NMP (30 ml), pyromellitic dianhydride (0.06 g, 0.28 mmol) was added at room temperature. The solution was stirred for 4 h at the same temperature. The solution was cast on a glass plate. The plate was heated at 80°C for 4 h and then at 250°C for 4 h.

Results and Discussion

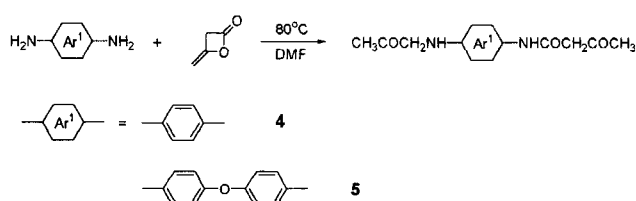
In the previous study, we found that the thermal reaction of



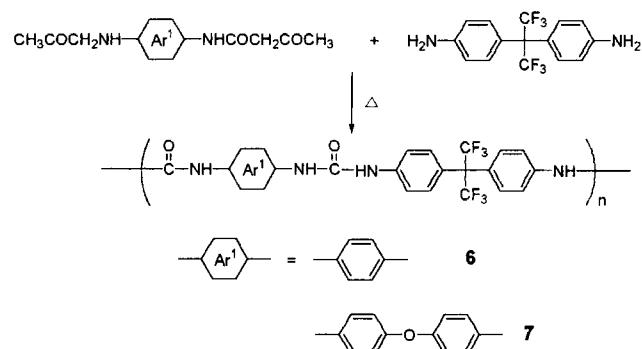
Scheme 1. Model reaction.

acetoacetanilide produced two major compounds (Scheme 1) [3]. When acetoacetanilide was heated in a flask equipped with a cold trap, acetone was trapped at 150 °C. Two compounds isolated from the reaction mixtures were carbanilide **2** and the condensation product **3** of two acetoacetanilide molecules, losing two H₂O molecules. Based on these results, it was concluded that an isocyanate was formed as an intermediate during the reaction. We further studied on the thermal reaction of acetoacetanilide in the presence of aniline, phenol, or zeolite. The ratio of two products varied according to the reaction conditions. The reaction results are summarized in Table 1. When acetoacetanilide was heated at 160 °C for 5 h under nitrogen without other reactants, carbanilide **2** and condensation product **3** were obtained in 45 % and 40 % yields, respectively. The same reaction was carried out in the presence of an acid catalyst. Interestingly the reaction with phenol yielded the urea exclusively, while the reaction in the presence of *o*-toluic acid as a catalyst yielded both carbanilide **2** and condensation product **3**. One possible explanation for this result is that phenol functioned as a nucleophile rather than a catalyst, forming a carbamate first and eventually producing an isocyanate. Recently, Sartori and coworkers reported that the reaction of acetoacetanilide with amines in the presence of acid catalysts produced ureas in high yields[5,6]. We also observed the similar results. The thermal reaction of acetoacetanilide in the presence of aniline at 160 °C produced carbanilide **2** in a quantitative yield. Aniline likely reacted with acetoacetanilide, acting as a nucleophile, or with an isocyanato intermediate formed by thermal degradation of acetoacetanilide.

The high yield of the urea from the reaction of acetoacetanilide in the presence of aniline prompted us to investigate the step reaction between a bisacetoacetamide having α , ω -acetoacetamide groups and a diamine, which could yield a polymer. Bisacetoacetamides were prepared



Scheme 2. Synthesis of bisacetoacetamides.



Scheme 3. Synthesis of oligoureas by copolymerization.

according to Scheme 2[7,8]. Bisacetoacetamide **5** was prepared from 4,4'-oxydianiline and 2 mol of diketene in DMF. The chemical structure of bisacetoacetamide **5** was confirmed by means of IR, ¹H-NMR spectroscopy, and elemental analysis. The IR spectrum exhibited the characteristic absorption band at 1716 cm⁻¹ for the carbonyl stretching vibration. In the ¹H-NMR spectrum in DMSO-d₆, the peak for amide proton appeared at 10.1 ppm. Bisacetoacetamide **4** was prepared in the same manner. In TGA analysis, the loss in weight corresponding to elimination of acetone was observed at 180 °C.

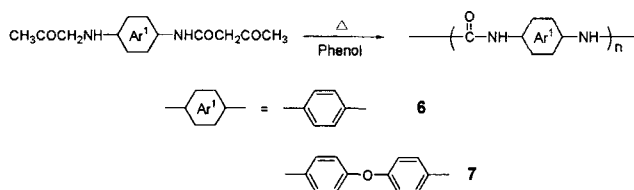
A bisacetoacetamide was reacted with a diamine (6FDA) as shown in Scheme 3. The copolymerization conditions and results are summarized in Table 2. Polymer **6a** was prepared from **4** and 6FDA in NMP at 210 °C. The obtained polymers were soluble in THF, DMSO, and NMP. In the IR spectrum, absorption band at 1717 cm⁻¹ due to the carbonyl stretching vibration of diketone groups disappeared and a new absorption band at 1653 cm⁻¹ appeared, which implies the formation of urea group. In the ¹H-NMR spectrum in DMSO-d₆, the peaks for benzene ring and amide protons appeared at 6.86-7.41 and 8.6 ppm, respectively. No peaks corresponding to acetylonyl groups appeared, indicating that the resulting oligomer had an amino group terminated structure. This was attributable to that terminal acetoacetamide groups, if any, were degraded to amino groups under the reaction

Table 3. Molecular weight data for oligoureas

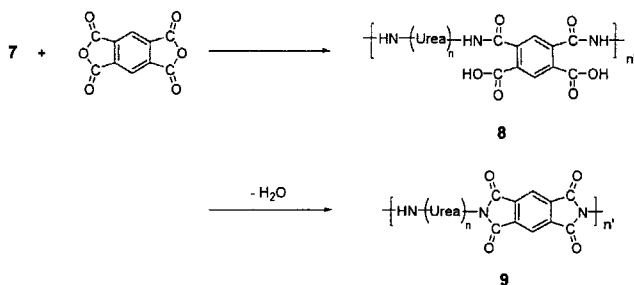
Polymer	End group analysis	Gel permeation chromatography (GPC)	
	<i>M_n</i>	<i>M_n</i>	<i>M_w</i>
6a	920 ^{a)}	1230	1550
7d	1510 ^{a)}	1720	2580
7e	3640 ^{b)}	2060	3810

^{a)}After acetylation of amino groups with acetic anhydride in NMP, number average molecular weights were calculated based on the ¹H-NMR peak area.

^{b)}Number average molecular weight was calculated by using a potentiometric titration method.



Scheme 4. Synthesis of oligoureas by homopolymerization in the presence of phenol.



Scheme 5. Synthesis of polyurea-imide.

conditions. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymer were determined to be 1230 and 1550 by GPC in THF, respectively.

The polymerization was also carried out in the presence of acidic catalysts. Polymer **6b** and **7c** were obtained by the reaction of **4** and **5** with a diamine, **6FDA** in the presence of phenol. Although the model reaction of acetoacetanilide in the presence of phenol yielded a urea in a quantitative yield, the polymerization gave an oligomer in a low yield. The reaction **4** and **5** with **6FDA** in the presence of a zeolite at 200 °C and 160 °C, respectively, also gave the polymers of low molecular weights. The polymers were soluble in DMSO and NMP. Low molecular weights of the polymers are ascribed to the imbalance of molar ratio of the reactants, probably originated from self-degradation of bisacetoacetamide compounds to yield amines. Actually, the unreacted **6FDA** monomer was found in the reaction mixture after polymerization. In the $^1\text{H-NMR}$ spectra of the mixture, the peaks for all acetyl groups of **4** or **5** disappeared, but the peak for $-\text{NH}_2$ of **6FDA** still showed up.

As observed in the model reaction of acetoacetanilide, an acetoacetamide group is thermally degraded to an amino group. Accordingly, thermal reaction of bisacetoacetamides could yield polyureas, where newly formed amino groups reacted with remaining acetoacetamide groups. The homopolymerization of **4** or **5** in the presence of phenol is shown in Scheme 4. Polymer **6d**, **7a**, and **7b** were obtained by the reaction of **4** or **5** in the presence of phenol at 160 °C and 210 °C. These reactions gave the polymers of low molecular weights. Polymers **7a** and **7b** were soluble in THF, DMSO, and NMP. Polymer **6d** was soluble in DMSO

and NMP, but insoluble in THF, because it had a rigid structure.

Poly(urea-imide) (**9**) was synthesized by polymerization of the oligourea (**7e**) with pyromellitic dianhydride in NMP (Scheme 5). The concentration of terminal amino groups was determined by an acid-base titration. Potentiometric titration is a method to identify the direct amount of amino groups. Since an aromatic amine was weak base, nonaqueous titration was carried out in DMF/glacial acetic acid[9]. The number average molecular weight estimated based on the titration results was 3640, higher than that obtained by GPC (Table 3). The polymerization was carried out in NMP by using equimolar of **7e** and pyromellitic dianhydride, forming poly(urea-amic acid) (**8**). The poly(urea-imide) was finally obtained by thermal imidization of the resulting poly(urea-amic acid) at 250 °C for 4 h. In the IR spectrum of poly(urea-imide), absorption bands at 1720, 1774, 1376, and 726 cm^{-1} from imide groups appeared. The absorption bands at 3434 and 1650 cm^{-1} indicated the presence of urea groups. The thermal property of poly(urea-imide) was evaluated by thermogravimetric analysis (TGA). Initial decomposition took place at 332–350 °C, showing high thermal stability.

Conclusions

In the model reaction of acetoacetanilide with aniline or phenol, carbanilide was obtained in high yields. This reaction was applied to the synthesis of a polyurea. Bisacetoacetamides were prepared by the reaction of diamines with diketene. They were reacted with diamines or thermally polymerized to yield linear polyureas of low molecular weights. The NMR analysis showed that the polymers had terminal amino groups. The concentration of amino end groups could be determined by the potentiometric titration. We expect that these oligourea diamines can be used for the preparation of various urea copolymers.

Acknowledgements

This work was supported by Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center at Seoul National University.

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