Synthesis of Poly(amide-quinazolinedione)s

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ABSTRACT: Some aromatic bisurethanes containing amide linkage were synthesized from *p*-phenoxycarbonylaminobenzoyl chloride and aromatic diamines. Polyamides containing quinazolinedione rings in the main chain were obtained by either heating a mixture of bisurethane and aromatic bis-*o*-amino ester in pyridine or directly in solid state at elevated temperatures. The model reaction for the formation of quinazolinedione was carried out in pyridine. The formation of quinazolinedione ring in the polymer was investigated by infrared spectroscopy and thermal analysis. The poly(amide-quinazolinediones) were reasonably thermal stable.

KEY WORDS Bisurethanes / Aromatic Bis-*o*-amino Ester / Quinazolinedione / Solution Polymerization / Solid-State Polycondensation /

It has been previously reported that the respective reactivities of the isocyanate and acid chloride of aliphatic or aromatic isocyanatocarboxylic acid chlorides toward nucleophilic reagents such as amines, alcohols, and water are highly different.¹ In the continued investigation of the reactions of these highly reactive compounds, the reaction of *p*-isocyanatobenzoyl chloride and phenol was undertaken. It was found that phenol reacted preferentially with the isocyanate group of this compound with addition of a small amount of di-*n*-butyltin dilaurate as catalyst to give *p*-phenoxycarbonylaminobenzoyl chloride (I). In an attempt to use this addition product to prepare ordered polymers, (I) was first reacted with aromatic diamines to prepare bisurethanes containing an amide linkage. Urethanes, especially those derived from phenol, have been used as generators for the isocyanates. In our laboratory, high molecular weight polypeptides were synthesized from the urethanes of α -aminoacids.² Recently, polyureas containing a benzimidazole ring were synthesized by solid-state polycondensation from aromatic bisurethanes having a preformed benzimidazole ring and aromatic diamines.³ In the continued investigation of the polycondensation of bisurethanes, we found that quinazolinedione could be easily obtained from a urethane and an aromatic *o*-amino ester by refluxing them in a pyridine solution. By using this reaction, the

polymers containing amide linkages and a quinazolinedione ring in the main chain could be produced from aromatic bisurethanes and aromatic bis-*o*-amino esters. In this paper, we wish to report the synthesis of poly(amide-quinazolinediones) by the pyridine solution and solid-state polycondensation.

RESULTS AND DISCUSSION

Synthesis of Bisurethanes

With addition of a small amount of di-*n*-butyltin dilaurate as catalyst, *p*-isocyanatobenzoyl chloride reacted with 1 mol of phenol preferentially at the isocyanate group to give *p*-phenoxy-

Figure 1. Infrared spectra: a, *p*-isocyanatobenzoyl chloride (without diluent); b, *p*-phenoxycarbonylaminobenzoyl chloride (in nujol); c, *p*-phenoxycarbonylaminobenzanilide (KBr disk).

carbonylaminobenzoyl chloride (I), which was characterized by the infrared spectrum and by its derivative with aniline. Figure 1b indicated the absorption at 2275 cm^{-1} due to the isocyanate group of *p*-isocyanatobenzoyl chloride which disappeared completely when it was reacted with

phenol for 24 hr. Aromatic bisurethanes containing an amide linkage were obtained by reacting (I) with aromatic diamines in aprotic organic solvents such as *N*-methylpyrrolidone and dimethylacetamide. The yields and the physical properties

of the bisurethanes are summarized in Table I. These bisurethanes had no melting points and they dissociated into the isocyanate compounds and phenol at temperatures between 210°C and 330°C as indicated in DTA and TGA curves. Figure 2 shows an example of DTA and TGA curves of bisurethane IIA-1. The infrared spectra of bisurethane IIA-3 and the isocyanate compound obtained when heated it up to 258°C were shown in Figure 3. By the heat treatment, a new absorption at 2275 cm^{-1} due to the isocyanate group appeared along with the disappearance of the absorption of the urethane at

Figure 2. DTA and TGA curves of bisurethane IIA-1; heating rate, $5^\circ\text{C}/\text{min}$ in air.

Table I. Bisurethanes

$\text{C}_6\text{H}_5-\text{OCONH}-\text{C}_6\text{H}_4-\text{CONH}-\text{R}-\text{NHCO}-\text{C}_6\text{H}_4-\text{NHCOO}-\text{C}_6\text{H}_5 \quad (II)$						
Expt no	-R-	Yield, %	Dissociating temp, ^b $^\circ\text{C}$	Elemental analysis. Found (Calcd)		
				C	H	N
—	C_6H_5 ^a	80	—	72.22 (72.28)	4.94 4.85	8.61 8.43
IIA-1	$-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-$	88	222–331	72.80 (72.49)	4.52 4.56	8.31 8.46
IIA-2	$-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-$	87	212–308	72.72 (72.60)	4.72 4.73	8.12 8.28
IIA-3	$-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-$	82	210–295	70.89 (70.80)	4.87 4.42	8.02 8.25
IIA-4	$-\text{C}_6\text{H}_4-$	83	215–325	69.61 (69.23)	4.47 4.61	9.55 9.46

^a $\text{C}_6\text{H}_5-\text{OCONH}-\text{C}_6\text{H}_4-\text{CONH}-\text{C}_6\text{H}_4$ mp $218\text{--}219^\circ\text{C}$.

^b The temperatures at which bisurethanes dissociated into isocyanates and phenol were measured by DTA and TGA (heating rate, $5^\circ\text{C}/\text{min}$, in air).

Figure 3. Infrared spectra: a, bisurethane IIA-3 (KBr disk); b, its isocyanate derivative obtained when heated IIA-3 up to the temperature of 258°C (in nujol).

1740 cm⁻¹, but the absorption of the amide at 1650 cm⁻¹ showed almost no change.

Reaction of Urethane with Anthranilic Acid Methyl Ester

In order to see if quinazolinedione could be formed between urethane and aromatic *o*-amino ester, a model reaction was carried out in pyridine. Phenyl *N*-phenylcarbamate reacted with anthranilic acid methyl ester at the refluxing temperature of pyridine for 5 hr to give 3-phenyl-2,4-(1H, 3H)-quinazolinedione (IV) in 69% yield. The reaction mechanism

was thought to be that phenyl *N*-phenylcarbamate first dissociated into phenyl isocyanate and phenol and then the isocyanate reacted with anthranilic acid methyl ester to give an urea derivative (III) followed by the ring-closing reaction to produce the compound (IV). The urea-forming reaction from urethane and amine has been demonstrated to proceed through dissociation of urethane followed by addition to the amine.⁴ In order to check the ring-closing reaction, the urea derivative (III) prepared from phenyl isocyanate and anthranilic acid methyl ester was used for the above reaction. As expected, (IV) was obtained from (III) in 85% yield when the reaction was carried out under a reflux of pyridine for 5 hr. This result will support the above consideration.

Solution Polymerization in Pyridine

From the result of the above reaction, the polymerization was carried out in pyridine for various aromatic bisurethanes and aromatic bis-*o*-amino esters to give polymers having quinazolinedione rings in the polymer main chain as described in eq 4.

Table II. Preparation of poly(amide-quinazolidiones) from bisurethanes and bis-*o*-amino esters

Bis- <i>o</i> -amino esters	Bisurethanes —R—	Expt no.	Solution polymerization		Solid-state polymerization	
			Yield, ^b %	η_{inh}^a dl/g	Yield, %	η_{inh}^a dl/g
		VIA-1	84 87 ^c	0.12 0.11	88	0.19
		VIA-2	70	0.12	85	0.16
		VIA-3	69 62 ^c	0.14 0.20	89	0.20
		VIA-4	86	0.12	89	0.18
		VIA-5	92	0.10	88	0.52
		VIA-6	65	0.23	84	0.39
		VIA-7	66	0.19	86	0.30
		VIA-8	85	0.13	89	0.56
		VIA-9	97	0.10	96	0.21
		VIA-10	73	0.23	89	0.17
		VIA-11	80	0.22	85	0.20
		VIA-12	100	0.14	100	0.16

^a Measured at a concentration of 0.5 g/100 ml in concentrated sulfuric acid at 30°C.^b In pyridine, 120°C, 12 hr.^c In dimethylacetamide/pyridine, 2 : 1 (v/v), 120°C, 12 hr.

The results were listed in Table II. However, almost all of the bisurethanes used and the resultant polymers were not soluble in this solvent. The polymerization was therefore carried out in an heterogeneous state. Because of reaction condition, the molecular weight of the polymers was low as shown in Table II. An attempt to increase the molecular weight of the polymer by using a polar organic solvent such as dimethylacetamide which dissolves bisurethanes at elevated temperature did not yield polymer. The polymerization was next carried out in a mixture of

pyridine and dimethylacetamide. The monomers were completely dissolved in this system. However, when the polymerization started, the polymer precipitated out of solution immediately. The viscosity of the resulted polymer, as shown in Table II, had the same value as in the case where pyridine was used as a polymerization solvent.

As described in the section on the model reaction, a quinazolidinedione ring was easily formed from urethane and aromatic *o*-amino ester in pyridine; however, in the case of the polymer

Figure 4. TGA curves: ----, polymer VIA-1 obtained by the solution polymerization in pyridine; - · - ·, the same polymer after heat treatment; —, polymer VIA-1 obtained by the solid-state polymerization; heating rate, 5°C/min in nitrogen atmosphere.

formation, the quinazolinedione rings in the main chain were not completely formed. The polymer obtained in pyridine gave a two-step weight loss at around 210°C and over 360°C in its TGA curve as shown in Figure 4. On the other hand, when the polymer was treated at 200–300°C, the TGA curve of the heat treated polymer showed only a single weight loss over 360°C.

The infrared spectra of the polymer also gave different figures before and after heat treatment. The absorption around 1700 cm^{-1} which corresponded to the ester group in the spectrum of the polymer obtained in pyridine disappeared completely after heat treatment (as shown in Figure 5.). The noncompletion of the ring-closing reaction in the polymer might be attributed to limitations in the polymer reaction

Figure 5. Infrared spectra of polymer VIA-1 obtained by the solution polymerization in pyridine: a, before heat treatment; b, after heat treatment.

itself or due to the heterogeneous state of the polymerization process. To complete the formation of the quinazolinediones, the polymers resulting from the pyridine solution had to be heated in the solid state at elevated temperatures from 200°C to 300°C for 4 hr.

Solid-State Polycondensation

As described in the above section, the polyamides containing quinazolinedione rings could be produced in pyridine solution. However, in order to obtain the expected polymers, the polycondensation had to be carried out in two steps, first in pyridine and then in solid state at elevated temperatures. From this result, we decided to carry out the polycondensation in the solid state from the beginning. This examination was also supported by the fact that bisurethane gave the isocyanate compound when it was heated at a high temperature.

By heating a well-mixed equimolar mixture of the bisurethane and bis-*o*-amino ester, first at atmospheric pressure and then at reduced pressure, from 210 to 300°C for several hours under a nitrogen atmosphere, poly(amide-quinazolinediones) were obtained. Although one component of the reaction mixture, bis-*o*-amino ester melted below 215°C as shown in DSC curve in Figure 6, the polymerization proceeded apparently in the solid state. The results are also summarized in Table II.

In comparison with the result obtained from the solution polymerization in pyridine, the molecular weight of the polymers obtained in the solid-state process increased to some extent.

The infrared spectrum of the polymer VIA-7 was shown in Figure 7a. The carbonyl absorption

Figure 6. DSC curve of a mixture of bisurethane IIA-3 and 5,5'-methylenedianthranilic acid methyl ester; heating rate, 10°C/min in nitrogen atmosphere.

Figure 7. Infrared spectra: a, polymer VIA-7 obtained by the solid-state polymerization (KBr disk); b, product from an equimolar mixture of bisurethane IIA-3 and 5,5'-methylenedianthranilic acid methyl ester when heated them in nitrogen atmosphere at the heating rate of 10°C/min up to the temperature of 255°C (in nujol).

bands appeared at 1730 and 1660 cm^{-1} , which were assigned to the 4-carbonyl and 2-carbonyl groups of quinazolinedione, respectively.⁵ The absorption of the amide group seemed to overlap with that of the 2-carbonyl group of quinazolinedione to form a broad band and no ester group absorption at around 1700 cm^{-1} was observed. These indicated the polymer contained the amide linkages and quinazolinedione rings in the main chain.

As mentioned in the previous section, the formation of quinazolinedione was preceded by the reaction of the isocyanate dissociated from urethane and *o*-amino ester to form a urea intermediate in situ. By taking into consideration the fact that the reaction at solid state is slow in comparison with that in solution (because of the limited mobility of the reaction components), we attempted to check the above-mentioned reaction mechanism in the solid state by stopping the polymerization process halfway to detect the expected intermediate poly(amide-urea) (V). However, as shown in Figure 7b, the infrared spectrum of the product was that of a mixture of poly(amide-urea) and poly(amide-quinazolinedione). The mechanism of the solid-state polycondensation might therefore be thought to proceed by slow dissociation of the bisurethane into the isocyanate compound and phenol followed by the rapid addition reaction of the

generated isocyanate and bis-*o*-amino ester and the ring-closing reaction. If the addition was slower than the dissociation, an exothermic peak due to the addition reaction was expected to appear in the DSC curve. However, as shown in Figure 6, no exothermic peak was observed in DSC curve of a mixture of bisurethane and bis-*o*-amino ester. This observation would therefore support the above assumptive mechanism.

Physical Properties of Polymers

The resultant poly(amide-quinazolinediones) were soluble in dimethylacetamide, hexamethylphosphoramide and concentrated sulfuric acid and partially soluble in dimethylformamide, dimethylsulfoxide and *N*-methylpyrrolidone but insoluble in pyridine and *m*-cresol.

The thermogravimetric analysis showed the polymers were stable in nitrogen atmosphere up to about 360°C (Table III) and beyond this

Table III. Elemental analysis and thermal analysis data of poly(amide-quinazolinediones) obtained from the solid-state polycondensation

Expt no.	Elemental analysis. Found (Calcd)			Initial decomposition temp, ^a °C
	C	H	N	
VIA-1	71.08 (70.89)	4.59 3.69	11.12 11.83)	363
VIA-2	71.81 (71.30)	4.83 3.87	11.43 11.61)	361
VIA-3	70.10 (69.40)	4.49 3.58	12.77 11.56)	349
VIA-4	68.24 (68.14)	4.50 3.49	12.82 13.24)	343
VIA-5	71.55 (71.30)	4.65 3.87	11.29 11.61)	337
VIA-6	71.71 (71.53)	4.81 4.09	11.33 11.38)	355
VIA-7	70.25 (69.80)	4.52 3.78	11.31 11.35)	367
VIA-8	69.22 (68.50)	4.16 3.70	12.24 12.95)	373
VIA-9	68.67 (68.14)	4.06 3.49	12.94 13.24)	353
VIA-10	69.49 (68.50)	4.28 3.70	12.25 12.95)	357
VIA-11	66.56 (66.50)	3.81 3.38	12.61 12.92)	370
VIA-12	65.13 (64.51)	4.12 3.25	14.71 15.05)	360

^a The initial decomposition temperatures were measured by TGA; heating rate, 5°C/min, in nitrogen atmosphere.

temperature, they gradually decomposed.

EXPERIMENTAL

Pyridine was purified by distillation over potassium hydroxide.

Anthranilic acid methyl ester and diamines were commercially available.

Phenyl *N*-phenylcarbamate, mp 127°C (lit.,⁶ mp 126°C) and *N*-(phenylcarbamoyl)anthranilic acid methyl ester (III), mp 144–145°C (lit.,⁷ mp 144–145°C) were synthesized from phenyl isocyanate and phenol and anthranilic acid methyl ester, respectively, with addition of a small amount of triethylamine as catalyst.

4,4'-Diaminobiphenyl-3,3'-dicarboxylic acid methyl ester, mp 212°C (lit.,⁸ mp 213–214°C) and 5,5'-methylenedianthranilic acid methyl ester, mp 147–148°C (lit.,⁹ mp 147°C) were prepared by esterifying their corresponding acids with methanol in the presence of concentrated sulfuric acid as catalyst.

p-Diaminoterephthalic acid ethyl ester was prepared by the method of H. Liebermann from ethyl succinate, mp 168–169°C (lit.,¹⁰ mp 168°C).

Bisurethanes

A typical example of preparation of bisurethane IIA-3 is as follows: To a solution of 4.12 g (0.0227 mol) of *p*-isocyanatobenzoyl chloride and 0.30 g of di-*n*-butyltin dilaurate in 100 ml of ether, a solution of 2.27 g (0.0244 mol) of phenol in 30 ml of ether was added dropwise over a period of 30 min at 0–5°C with stirring. After 24 hr at room temperature, ether was evaporated and 80 ml of dimethylacetamide was added to the residual solid. To this solution, 2.27 g (0.0114 mol) of 4,4'-diaminobiphenylether was added at 0°C over a period of 5 min. After the mixture was stirred for 2 hr, 500 ml of water was added and the precipitated solid was filtered, washed thoroughly with water and methanol and dried at 80°C *in vacuo*. The obtained bisurethane weighed 6.35 g (82%).

Model Compound, 3-Phenyl-2,4(1H, 3H)-Quinazolinedione (IV)

A mixture of 3.87 g (0.0182 mol) of phenyl *N*-phenylcarbamate and 2.74 g (0.0182 mol) of anthranilic acid methyl ester in 40 ml of pyridine was heated at 120°C for 5 hr, and the reaction mixture was poured into 200 ml of water. The

solid was filtered and recrystallized from ethanol to produce colorless needles at 69% yield, mp 279°C (lit.,⁷ mp 280°C).

Anal. Calcd for C₁₄H₁₀N₂O₄: C, 70.58%; H, 4.23%; N, 11.76%. Found: C, 70.25%; H, 4.33%; N, 11.75%. By a similar procedure, (IV) was obtained in 85% yield from *N*-(phenylcarbamoyl)anthranilic acid methyl ester.

POLYMERIZATION

In Pyridine Solution

A general polymerization procedure of polymer VIA-3 is as follows: A mixture of 0.680 g (1.0 × 10⁻³ mol) of bisurethane IIA-3 and 0.301 g (1.0 × 10⁻³ mol) of 4,4'-diaminobiphenyl-3,3'-dicarboxylic acid methyl ester in 40 ml of pyridine was heated at 120°C for 12 hr. After cooling, the reaction mixture was poured into distilled water, filtered, washed with water and methanol, dried at 100°C *in vacuo*. The inherent viscosity of this polymer was 0.14 (0.5% H₂SO₄, 30°C). The polymer obtained weighed 0.579 g.

Anal. Calcd for C₄₂H₂₆N₆O₇: C, 69.40%; H, 3.58%; N, 11.56%. Found: C, 69.00%; H, 4.34%; N, 11.72% (after heat treatment of the polymer obtained in pyridine solution at 200–300°C for 4 hr).

In Solid State

A typical polymerization procedure for polymer VIA-7 is as follows: A mixture of 0.339 g (0.5 × 10⁻³ mol) of bisurethane IIA-3 and 0.157 g (0.5 × 10⁻³ mol) of 5,5'-methylenedianthranilic acid methyl ester was well mixed and charged into a one-necked flask. It was heated in a thin stream of nitrogen for 1 hr at 220–230°C. The flask was then evacuated to 1.0 mmHg. Heating was continued for 2 hr at 230–240°C, 3 hr at 250°C and finally 2 hr at 250–300°C. The obtained light yellow polymer weighed 0.317 g (86%). The inherent viscosity of this polymer was 0.30 (0.5% H₂SO₄, 30°C).

Anal. Calcd for C₄₃H₂₈N₆O₇: C, 69.80%; H, 3.78%; N, 11.35%. Found: C, 70.25%; H, 4.52%; N, 11.31%.

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