The marked change in the copolymerization characteristics of monomers such as I and III is highly useful for preparing a variety of polymers with either the quaternary, aminimide, or isocyanate pendent groups. This was readily demonstrated in this work when it was shown that monomer III readily copolymerizes with styrene and by earlier work which had demonstrated that monomer I would not copolymerize with styrene.

Acknowledgment. The authors are indebted to M. R. Hallwachs, P. J. Menardi, and D. L. Gregerson for excellent technical assistance during this work.

Syntheses of Ladder Polymers. II.[1] Poly(isoindoloquinazolinediones)

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ABSTRACT: Two thermally stable isoindoloquinazolinedione polymers have been prepared by the cyclopolycondensation reaction of the aromatic diaminodiamides and 5,5′-bis(2-aminobenzamide) and 5,5′-methylenebis(2-aminobenzamide) with pyromellitic dianhydride in N-methylpyrrolidone at 22°. All of the polymers obtained were completely soluble in fuming nitric acid and concentrated sulfuric acid. TGA weight losses of less than 10% at 550° in nitrogen and at 530° in air were observed. The structure and polymerization route of poly(isoindoloquinazolinedione) were studied by the infrared spectral and ultraviolet spectral method, and it was established that the polymerization proceeded through the formation of tractable poly(amic acid amide) of high molecular weight (η_{inh} = 2.9), followed by cyclodehydration, yielding poly(imide amide); on subsequently being heated, this undergoes intramolecular rearrangement along the polymer chain, giving the thermodynamically stable poly(isoindoloquinazolinedione) with the structure of isoindolo[1,2-*b*]quinazoline-10,12-dione. In previous publications,[1,2] it was shown that polymer containing the isoindoloquinazolinedione ring has the thermodynamically stable structure with the isoindolo[1,2-*b*]quinazoline-10,12-dione ring and the model reaction of anthranilamide with phthalic anhydride afforded the kinetically stable isoindolo[2,1-*a*]quinazoline-5,11-dione and the thermodynamically stable isoindolo[1,2-*b*]quinazoline-10,12-dione. 5,11-Dione is thermally rearranged to 10,12-dione. In this paper, the detailed syntheses and structure of poly(isoindoloquinazolinediones) by the cyclopolycondensation reaction of aromatic diaminodiamides with pyromellitic dianhydride are disclosed.

Discussion

The preparation of a new type of ladder polymer, poly(isoindoloquinazolinediones) with an isoindoloquinazoline[2,1-*b*]quinazoline-10,12-dione ring was first reported by Gaudemaris, *et al.*[3] In a previous paper[1] the structure of thermodynamically stable poly(isoindoloquinazolinedione) with an isoindolo[1,2-*b*]quinazoline-10,12-dione ring was reported.

In order to confirm the possibility of the formation of the kinetically stable poly(isoindoloquinazolinedione) and the correct structure of thermodynamically stable poly(isoindoloquinazolinedione), new model compounds were synthesized as described in Scheme I. The reaction of anthranilamide with pyromellitic dianhydride in N-methylpyrrolidone (NMP) affords bis(*o*-carbamoylphenylcarbamoyl)benzenedicarboxylic acid (I) quantitatively at room temperature. When I is heated at 140–210°, the first intramolecular cyclodehydration takes place to afford bis(carbamoyl-2-phenyl)-N,N′-pyromellitimide (II) in quantitative yield. 7H,16H - Benzo[1′′,2′′:3,4:4′′,5′′:3′,4′]dipyrrolo[2,1-*b*:2′,1′-*b*′]diquinazoline-7,9,16,18-tetrone (IV) is obtained by heating II at 230–400°. The changing of I by heating was followed by ir (Figure 1), uv (Figure 2), and elemental analyses. Compound I had a strong carbonyl absorption band due to the carboxyl group at 1715 cm^{-1}, an amide carbonyl absorption band at 1660 cm^{-1}, NH stretching vibration bands at 3450 and 3350 cm^{-1} (A in Figure 1), and λ_{max} at 260, 303, and 315 mμ (A in Figure 2). The ir spectrum B in Figure 1 and the uv spectrum C in Figure 2 are interpreted as being due to compound II because of the imide carbonyl absorption bands at 1780 and 1720 cm^{-1}, the amide carbonyl absorption band at 1650 cm^{-1}, the characteristic absorption of the imide ring at 720 cm^{-1}, and further the λ_{max} at 250 and 310 mμ. The possibility of the formation of III was followed by observing the changes in the ir (Figure 1) and uv (Figure 2) spectra. Spectrum C in Figure 1 shows carbonyl absorption bands at 1780 cm^{-1} (five-membered ring carbonyl), 1700 cm^{-1} (six-membered ring carbonyl), and 1650 cm^{-1} (amide carbonyl), which are explained as a mixture of II and IV. The distinct spectral change of the uv spectrum due to the change from II to III was not observed in Figure 2. The formation of IV was confirmed by the appearance of new strong carbonyl absorption bands at 1780, 1700, and new absorption band at 1640 cm^{-1} (C=N double bond), and the disappearance of NH absorption peaks (3450, 3350 cm^{-1}) and amide carbonyl peaks (1650 cm^{-1}). New λ_{max} absorption peaks appear at 320 and 390 mμ due to the isoindoloquinazolinedione ring (Figure 2). Although Gaudemaris, *et al.*, have reported that III was obtained by heating

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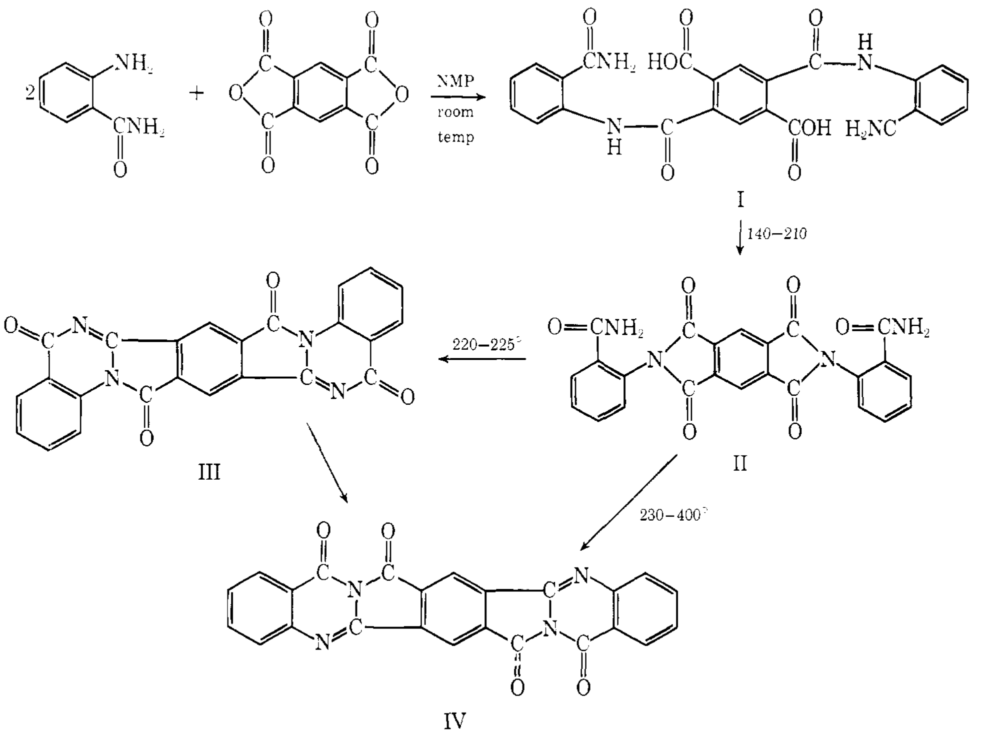
(1) M. Kurihara and N. Yoda, *J. Polym. Sci., Part B*, 2 (6), 875 (1968).

(2) M. Kurihara, *J. Org. Chem.*, **34**, 2123 (1969).

(3) G. Rabilloud, B. Sillion, and G. de Gaudemaris, *Makromol. Chem.*, **108**, 18 (1967).

SCHEME I



II at 300°, it is established that IV is obtained by thermal cyclization of II in this spectroscopic study.

The model reaction was extended to the cyclopolycondensation reaction of bifunctional aromatic diamides with aromatic dianhydrides, and the solution polymerization technique was employed for the polymerization of 5,5′-bis(2-aminobenzamide) (BABA) and 5,5′-methylenebis[2-aminobenzamide] (MABA) with pyromellitic dianhydride (PMDA) as shown in Scheme II.

The polymerization of MABA with PMDA was partly described in a previous paper.[1] The polymerizations of BABA (Va) and MABA (Vb) with PMDA in NMP are summarized in Table I. In the first step poly(amic acid amides) of high molecular weight were prepared when MABA and solid PMDA were employed, using high monomer concentrations in the presence of lithium chloride. To prepare a tractable poly(amic acid amide) (VI) of high molecular weight, the effect of monomer concentration on the inherent viscosity was studied, and a total monomer concentration of 15% was found to be optimum in the polymerization as shown in Figure 3. The highest inherent

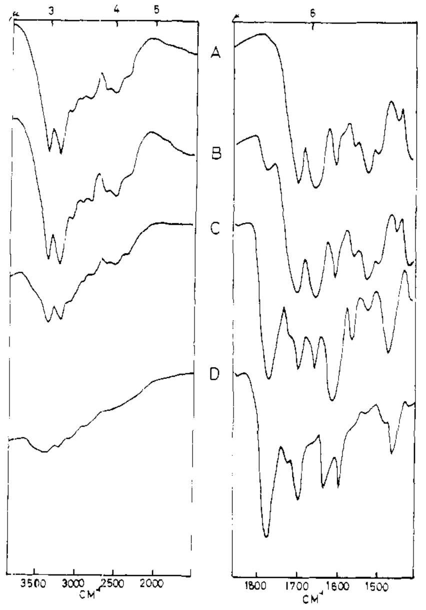


Figure 1. The infrared spectral changes of bis(2-carbamoylphenylcarbamoyl)benzenedicarboxylic acid (I): (A) at 75° for 30 min, (B) at 140–150° for 20 hr, (C) at 180–205° for 2 hr, (D) at 240° (2 mm) for 1.5 hr.

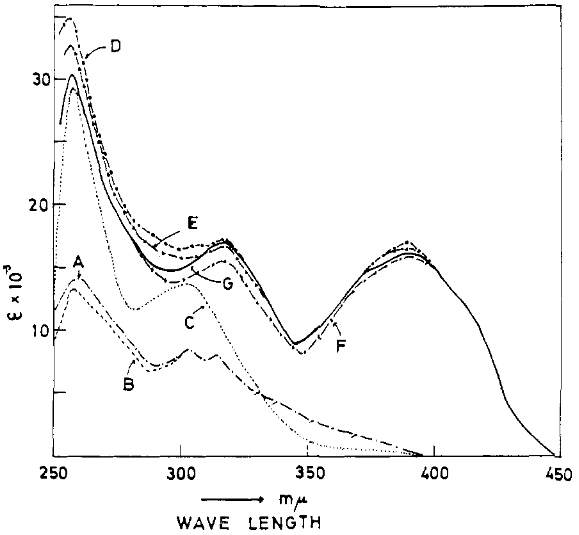


Figure 2. The ultraviolet spectral changes of bis(2-carbamoylphenylcarbamoyl)benzenedicarboxylic acid (I) in dimethyl sulfoxide: (A) at 75° for 30 min, (B) at 150° for 2 hr, (C) at 210° for 30 min, (D) at 230° for 30 min, (E) at 250° for 20 min, (F) at 300° for 20 min, (G) at 400° for 10 min.

SCHEME II

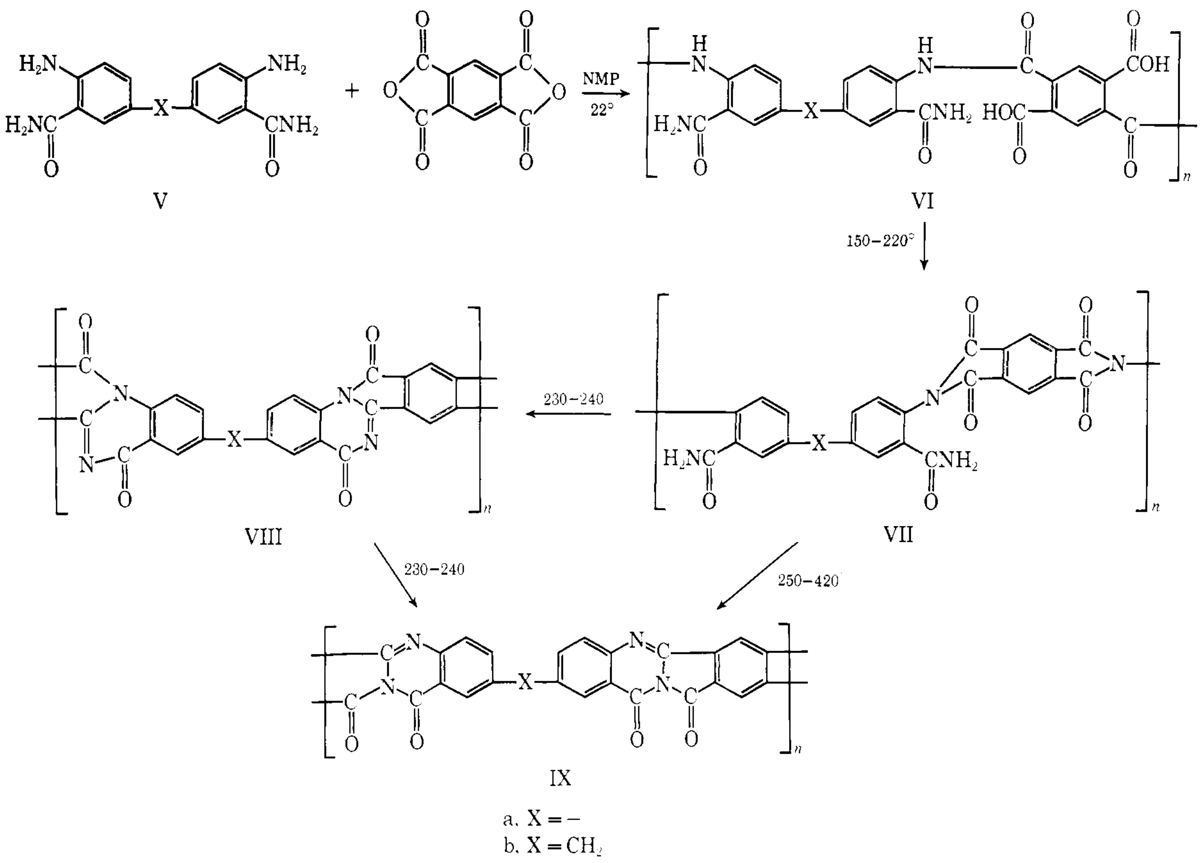


TABLE I
THE POLYMERIZATION OF POLY(AMIC ACID AMIDE) IN NMP

Expt no.	Monomer MABA,[a] g	 PMDA,[b] g	LiCl, g	Monomer[c] concn, %	Polymerzn conditions Temp, °C	 Time, hr	η_{inh}[d]
1	1.3514	1.0906	0.424	12	22	6	0.95
2	(BABA)[e] 4.2670	3.2718		15	22	6	1.6
3	1.4216	1.0906	0.424	15	22	4.5	2.9
4	1.4216	1.0906	0.424	5	22	4.5	1.36
5	1.4216	1.0906[f]	0.424	15	22	6	2.04
6	1.4216	1.0906		5	22	4	0.68

[a] Methylenebis(2-aminobenzamide). [b] Pyromellitic dianhydride. [c] Initial monomer concentration. [d] 25.0°, 0.5% concentration in NMP. [e] BABA; 5,5′-bis(2-aminobenzamide). [f] NMP solution.

viscosity η_{inh} = 2.9 (0.5% NMP, 25°) was attained when a monomer concentration of 15 wt % was employed. In the second step, intramolecular cyclodehydrations of poly(amic acid amide) (VI) along the polymer chain were followed by differential thermal analyses (DTA in air) and thermogravimetric analyses (TGA in nitrogen and in air). DTA analyses of VIa and VIb (Figure 4) show that the polymer have endothermic peaks at 90 and 190°, which is in good correlation with the maximum weight loss temperature of the TGA differential curves (Figure 5). Although the DTA curve in Figure 4 fails to show any heat change to accompany the rearrangement of VIII to IX which is presumed to occur >250°, as supported by TGA curves in Figure 5, it is presumed that the first cyclization begins at 80–90°, and the second cyclization begins at 180–190°. This is also established by the ir (Figure 6) and uv (Figure 7) spectra, and the rearrangement of VIII to IX occurs >250°.

The formation of poly(amic acid amide) (VI), polyimide amide) (VII), and poly(isoindoloquinazolinedione) (IX) was confirmed by comparisons of the ir and uv spectra of model compounds and the polymers (Figures 1, 2, 6, and 7). The changing of polymer structure by heating of poly(amic acid amide) (VIb) was followed in the region of both 2000–3500-cm^{-1} and 1500–1800-cm^{-1} in the ir spectra (Figures 1 and 6). The spectrum of VIb (Figure 6A) shows carbonyl absorption bands at 1660 and 1715 cm^{-1} and NH absorption bands of the amide group at 3350 and 3450 cm^{-1}, which closely resembled those of A in Figure 1. Figure 7B shows imide carbonyl bands at 1780 and 1720 cm^{-1}, an amide carbonyl absorption at 1650 cm^{-1}, and the characteristic absorption of the imide ring at 720 cm^{-1}, which are also in good agreement with those in Figure 1. Therefore, the structure of Figure 7B was confirmed as VII. The structural differences of isoindoloquinazolinedione rings in III and IV and in

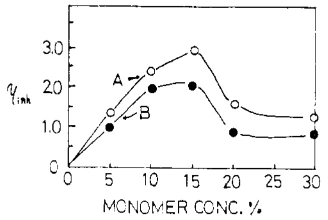


Figure 3. Effect of monomer concentration on extent of polymerization: A, η_{inh} of polymer solution; B, corrected η_{inh}; MABA–PMDA 1:1; MABA–LiCl 1:2; 22°, 4.5 hr; η_{inh} (0.5%, 25°, NMP).

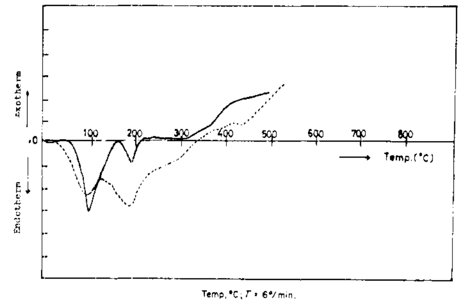


Figure 4. Differential thermal analyses of poly(amic acid amide) (VIa, VIb) in air (Δt = 6°/min): (——, VIa; – – –, VIb.

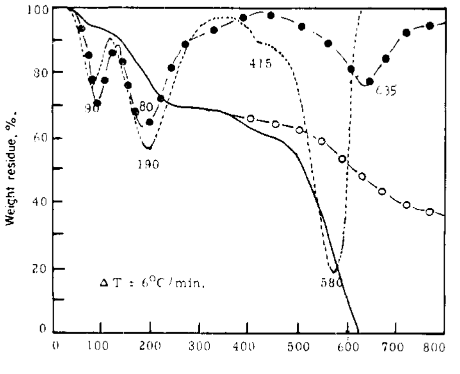


Figure 5. Thermal analyses of poly(amic acid amide) (VIb) in nitrogen and in air: -O-O-O-, in nitrogen; -●-●-●-, differential curve in nitrogen; ——, in air; ------, differential curve in air.

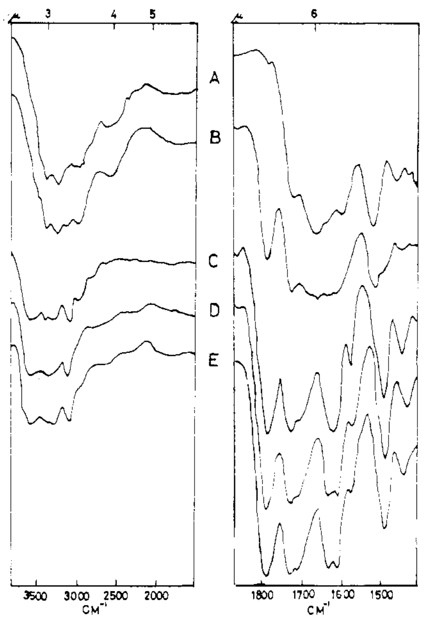


Figure 6. The infrared spectral changes of a film of poly(amic acid amide) (VIb): (A) at 75° for 16 hr, (B) at 150° for 2 hr, (C) at 250° for 30 min, (D) at 300° for 30 min, (E) at 420° for 2 min.

VIII and IX were presumed to be confirmed by comparing the characteristic quinazolone carbonyl and >C=N absorption bands in the ir spectra and the $\lambda_{\max}$ in the uv spectra as described in a previous paper.[2] The formation of poly(isoindoloquinazolinedione) (IX) was confirmed by the appearance of new carbonyl absorption band at 1780 and 1720 cm^{-1} and the disappearance of the amide carbonyl band at 1650 cm^{-1} as shown in Figure 7C, D, and E. In these assignments by ir spectra, it was presumed that the polymers consist of a predominant component and other components due to the complexity of this cyclization reaction, and that the predominant component in the final product was the poly(isoindoloquinazolinedione) (IX). The formation of poly(amic acid amide) (VI), poly(imide amide) (VII), and poly(isoindoloquinazolinedione) (IX) is also confirmed by the changes in the uv spectra of the polymer films (Figure 7). A in Figure 7 corresponds to structure VI, B to VII, and E to IX, in comparison with those of Figure 2 and those of Figure 6, respectively. It is shown that the structure of poly(isoindoloquinazolinedione) (IXb) is confirmed by the appearance of new absorption bands at 310 and 380 mμ which are characteristic absorption bands of poly(isoindoloquinazolinedione). The possibility of the formation of kinetically stable poly(isoindoloquinazolinedione) (VIII) by cyclodehydration of VII and acyl rearrangement of VIII to IX was described in a previous paper.[1] However, kinetically stable poly(isoindoloquinazoline) VIII is not obtained by heating VII as

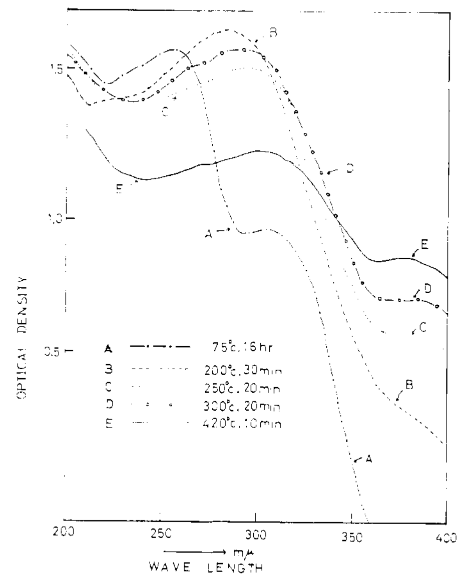


Figure 7. The ultraviolet spectral changes of a film of poly(amic acid amide) (VIb): (A) at 75° for 16 hr, (B) at 200° for 30 min, (C) at 250° for 20 min, (D) at 300° for 20 min, (E) at 420° for 10 min.

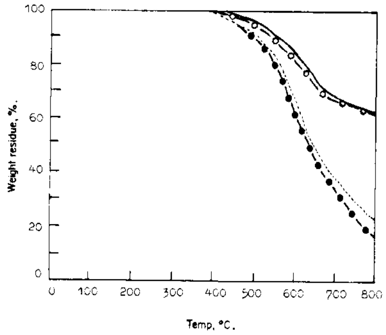


Figure 8. Thermogravimetric analyses curves for poly(isoindoquinazolinedione) (IXa, IXb) in nitrogen and in air: ——, IXa in nitrogen; ——, IXa in air; -O-O-O-, IXb in nitrogen; -●-●-●-, IXb in air.

shown in Figure 7, which is in good agreement with cyclizations of model compounds (Figure 2). Although the formation of VIII was not confirmed by this spectral data, it is presumed that the formation of IX by means of the intramolecular cyclization of VII proceeds through the formation of VIII and its rearrangement to IX because the kinetically stable isoindoloquinazolinedione ring (VIII) is thermally unstable to high temperatures (230–420°).[2]

The poly(isoindoloquinazolinedione) (IX) thus obtained is highly resistant to hydrolytic degradation by strong acid or alkali, and is insoluble in most organic solvents; it is soluble in concentrated sulfuric acid and fuming nitric acid.

The thermal stability of the resulting fully aromatic poly(isoindoloquinazolinedione) was measured either in nitrogen or in air by the thermogravimetric method, as shown in Figure 8. These isoindoloquinazolinedione polymers have excellent thermal stabilities which are a coalescence of the most thermally stable features of the poly(imidazopyrrolones).[4] The thermal stability of the step ladder polymer, poly(isoindoloquinazolinedione), in both nitrogen and air is considerably greater than that of the corresponding single-strand polymers, poly(quinazolinedione),[5] poly(benzoxazinone),[6] poly(quinazolone),[7] in the same six-membered ring systems derived from aromatic diaminodicarboxylic acid.

Experimental Section[8]

1. **Materials. 4,4′-Diamino-3,3′-biphenyldicarboxylic acid (BDC) (Va)** was prepared by published procedure.[9]

5,5′-Methylenedianthranilic acid (Vb) was obtained from Ihara Chemicals Co., mp 222–223°.

Pyromellitic dianhydride (PMDA) was obtained from Tokyo Kasei Co., CP grade, and was purified by recrystallization from acetic anhydride and by sublimation before use.

Anthranilamide was prepared by published procedures.[2]

***N*-Methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc)** were obtained from Kishida Chemical, CP grade, and distilled from calcium hydride and phosphorus pentoxide at 3 mm.

2. **[6,6′-Bi-2*H*-3,1-benzoxazine]-2,2′,4,4′(1*H*,1′*H*)-tetraone.** A 9.6-g (0.035 mol) portion of 4,4′-diamino-3,3′-biphenyldicarboxylic acid was dissolved in the mixture of 500 ml of concentrated hydrochloric acid and 2.5 l. of water. Phosgene gas was then gradually added into the solution with vigorous stirring at room temperature over 3 hr, to yield a light green precipitate. The precipitate was filtered and washed several times with water. The yield was 1.5 g (93%). Recrystallization from DMAc yielded light green crystals: mp >360°; ir (KBr) 1760, 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{16}H_8O_6N_2$: C, 59.26; H, 2.49; N, 8.64. Found: C, 59.01; H, 2.62; N, 8.42.

3. **5,5′-Bis(2-aminobenzamide) (BABA) (Va).** A 30-g portion (0.092 mol) of solid [6,6′-bi-2*H*-3,1-benzoxazine]-2,2′,4,4′(1H,1′H)-tetraone was added immediately to a stirring solution of 84 ml of 28% aqueous ammonium hydroxide solution. The solution was stirred for 2 hr at 25°. The green precipitate was filtered and washed with 5% aqueous sodium carbonate solution and water. It was recrystallized two times from NMP, washed with benzene, and dried under reduced pressure (10^{-4} mm) at 100°: mp 314°; yield 10 g (40%); ir (KBr) 3400 (NH), 1600 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{14}O_2N_4$: C, 61.93; H, 5.48; N, 20.30. Found: C, 62.21; H, 5.22; N, 20.70.

4. **6,6′-Methylenebis[2H-3,1-benzoxazine-2,4(1H)-dione]** was prepared in 95% yield according to the same method described in the synthesis of [6,6′-bi-2H-3,1-benzoxazine]-2,2′,4,4′(1H,1′H)-tetraone (VIa). Recrystallization from the mixture of DMAc and water yielded white crystals melting above 360°.

Anal. Calcd for $C_{17}H_{10}O_6N_2$: C, 60.36; H, 2.98; N, 8.28. Found: C, 60.51; H, 3.05; N, 8.15.

5. **5,5′-Methylenebis[2-aminobenzamide] (MABA) (Vb).** A 10-g (0.030 mol) portion of solid 6,6′-methylenebis[2H-3,1-benzoxazine-2,4(1H)-dione] was added to the 149 ml of 1% aqueous ammonium hydroxide solution at 23° with vigorous stirring; after 15 min, a precipitate was obtained and the solution was stirred for 5 hr. The precipitate was filtered, washed with water, recrystallized from the mixed solvent of methanol, pyridine, and benzene to yield white crystals melting at 285° in 75.0% yield.

Anal. Calcd for $C_{15}H_{16}O_2N_4$: C, 63.36; H, 5.67; N, 19.71. Found: C, 63.51; H, 5.42; N, 19.48.

6. **Model Compounds. A. Bis(O-carbamoylphenylcarbamoyl)benzenedicarboxylic Acid (I).** A 1.09-g (0.005 mol) portion of PMDA was added to a stirring solution of 1.36 g (0.01 mol) of anthranilamide in 14 ml of NMP, and stirred at 10° for 3 hr. After stirring at 25° overnight, the solution was poured into 500 ml of water to obtain white crystals. It was filtered and washed with ether. The yield was 1.3 g (52%). Recrystallization from dimethylformamide and ethyl acetate yielded white crystals melting above 400°.

Anal. Calcd for $C_{14}H_{18}O_8N_4$: C, 58.77; H, 3.70; N, 11.43. Found: C, 58.60; H, 4.00; N, 11.67.

B. Bis(carbamoyl-2-phenyl)-N,N′-pyromellitimide (II) was obtained by heating I at 150° for 2 hr, mp 400°.

Anal. Calcd for $C_{24}H_{14}O_6N_4$: C, 63.44; H, 3.11; N, 12.33. Found: C, 63.16; H, 3.21; N, 12.15.

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(4) V. L. Bell and G. F. Pezdirtz, *Polym. Lett.*, **3**, 977 (1965).

(5) (a) M. Kurihara and N. Yoda, *J. Polym. Sci., Part A*, **1**, 1765 (1967); (b) S. Tohyama, M. Kurihara, K. Ikeda, and N. Yoda, *ibid., Part A-1*, 2523 (1967).

(6) (a) N. Yoda, K. Ikeda, M. Kurihara, S. Tohyama, and R. Nakanishi, *ibid., Part A*, **1**, 2359 (1967); (b) M. Kurihara and N. Yoda, *J. Macromol. Sci.*, **A1**, 1069 (1967).

(7) M. Kurihara and Y. Hagiwara, *Polym. J.*, in press.

(8) All the melting points were taken on a Büchi melting apparatus and were uncorrected. Microanalyses were carried out by the Microanalytical Section of this laboratory. Infrared spectra were recorded with Hitachi Model EPI-S recording spectrophotometer in potassium bromide disk or film. Ultraviolet spectra were obtained in dimethyl sulfoxide solution or film on a Cary Model 14 recording spectrophotometer. Differential thermal analysis was made with the Shimazu DT-10 instrument using 50 mg of sample at the rate of 6°/min. Thermal gravimetric analyses (TGA) in nitrogen and air were obtained with the Shimazu RT-3 using 100 mg of sample at the rate of 6°/min.

(9) M. Kurihara and N. Yoda, *Bull. Chem. Soc. Jap.*, **40**, 2429 (1967).

C. 7H,16H-Benzo[1′′,2′′:3,4:4′′,5′′:3′,4′]dipyrrolo[2,1-*b*:2′,1*b*′]diquinazoline-7,9,16,18-tetrone (IV) was obtained by the treatment of II of 240–250° for 2 hr. Yellow crystals melting at 444° were obtained.

Anal. Calcd for $C_{24}H_{10}O_4N_4$: C, 68.89; H, 2.40; N, 13.39. Found: C, 68.23; H, 2.21; N, 13.63.

7. Polymerizations. Typical Preparation of a Poly(amic acid amide) (VI). The low-temperature solution polymerization was carried out by the reaction of MABA with PMDA in NMP. To a solution of purified MABA (4.267 g, 0.015 mol) in NMP (50 ml) was added freshly sublimed PMDA (3.272 g, 0.015 mol) at 22° in a heterogeneous system with rapid stirring in an inert atmosphere. After 10 min, a light yellow, clear solution was obtained and the viscous polymer solution was quenched by pouring it into ethanol after 6 hr. The fibrous polymer was filtered, washed thoroughly with ethanol, and dried under vacuum at 75°. The yield of polymer was nearly quantitative and the inherent viscosity was 2.9 in NMP (0.5% concentration, 25°). The polymer solution was poured onto a glass plate and heated at 75° for 15 hr to afford a transparent, tough film of poly(amic acid amide) (VIb).

Anal. Calcd for $C_{25}H_{18}O_8N_4$: C, 59.76; H, 3.61; N, 11.15. Found: C, 57.21; H, 4.05; N, 10.48.

The poly(amic acid amide) thus obtained was soluble in DMAc, NMP, dimethylformamide, and dimethyl sulfoxide, and concentrated sulfuric acid.

8. Conversion to Poly(amic acid amide) (VIb) and Poly(isoindoloquinazolinedione) (IXb). The poly(amic acid amide) film was heated on a frame in an oven at 150° for 2 hr. The polymer undergoes the first intramolecular dehydration to form a poly(imide amide) (IXb) of high molecular weight.

Anal. Calcd for $(C_{25}H_{14}O_6N_4)_n$: C, 64.38; H, 3.06; N, 12.01. Found: C, 64.06; H, 3.30; N, 11.88.

The dehydration was also effected by treating poly(amic acid amide) film (VIb) with a solvent pair of acetic anhydride and pyridine (1:1). The poly(isoindoloquinazolinedione) (IXb) was obtained by heating the poly(imide amide) (VIIb) or poly(amic acid amide) (IXb) in nitrogen at 250° for 30 min.

Anal. Calcd for $(C_{25}H_{10}O_4N_4)_n$: C, 69.78; H, 2.34; N, 13.02. Found: C, 69.30; H, 2.50; N, 12.78.

Acknowledgment. The author gratefully acknowledges the interest and encouragement of Dr. N. Yoda of Pioneering Research and Development Laboratories, Toray Ind. Inc. The author is indebted to Messrs. T. Mizushima and T. Suzuki for the thermal analyses and the nomenclature of the monomer and polymers, and Dr. A. Ishitani for the measurement and valuable discussion of ultraviolet spectra. Thanks are due to Mr. A. Kobayashi for technical assistance.

Conformational Analysis and Chain Statistics of Poly(isobutylene)[1a]

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ABSTRACT: The conformational analysis of poly(isobutylene) is performed, with explicit allowance for elastic bending of the chain ∠CCC bond angles. The corresponding effect consists of a drastic flattening of the conformational energy function *vs.* ψ_1 and ψ_2 (the chain rotation angles on the general monomer unit). Furthermore, the differences among the energy minima, calculated either allowing for all H···H, H···C, and C···C nonbonded interactions, or treating the methyl groups as spherically symmetrical bodies and assigning different values to their van der Waals' radius, are very similar; quite the opposite is obtained if the chain bond angles are kept fixed. The chain conformation in the crystalline state is unambiguously verified to be close to that proposed by Wasai, Saegusa, and Furukawa:[5] it corresponds to an 8_3 helix. The chain conformation in the unperturbed state is shown to be satisfactorily described in terms of a statistical sequence of "staggered" (T, G, and G′) rotational states. Both the mean-square end-to-end distance and its temperature derivative, evaluated with the conformational energy values obtained for the chain in the crystalline state, are in excellent agreement with experiment.

The problem of the chain conformation of poly(isobutylene), both in the crystalline state and in solution, has aroused considerable controversy.[2–9]

For the crystalline state, Fuller, Frosch, and Pape[2a] first proposed a definite chain conformation, containing eight monomer units in one turn (8_1). Liquori, on the basis of the qualitative distribution of the diffracted X-ray intensities on the fiber spectrum, showed that an 8_1 or an 8_7 conformation is unlikely. He proposed a uniform 8_5 helix,[2b] which should have constant values of the bond angles, and internal rotation angles on the chain backbone equal to 114 and 98°, respectively

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