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Aromatic Poly(α- and β-naphthylamino)amides and Poly(α and β-naphthyl)benzodiimidazoles. II

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ABSTRACT

Two new tetraamines, 1,5-di(α- and β-naphthylamino)-2,4-diaminobenzene, are prepared and used in a low-temperature solution polymerization with terephthaloyl and isophthaloyl chloride or 2,5-furoyl dichloride. The newly prepared poly-(α- and β-naphthylamino)amides are converted by polycyclodehydration with heating to the corresponding new heat-resistant poly(α- and β-naphthyl)benzodiimidazoles. The prepared polymers are characterized and the influence of the bulky naphthyl substituents on their solubility and on the thermal stability of the poly(naphthyl)benzodiimidazoles with respect to the corresponding unsubstituted polymers is discussed.

INTRODUCTION

In a previous paper [1], poly(amino)amides and polybenzodiimidazoles of 1,2,4,5-tetraaminobenzene with terephthalic, isophthalic or 2,5-furandicarboxylic acid were indirectly prepared from the corresponding poly(tosylamino)amides. Their properties and thermal stabilities were studied and compared with the similar polymers prepared by melt polymerization [2].

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Substituted aromatic polybenzodiimidazoles with phenyl [3-5] and methyl [6] substituents in the imidazole rings have been reported in the literature and generally showed [3, 5, 6] a slightly higher thermal stability in air and a lower one in nitrogen atmosphere than the corresponding unsubstituted polymers.

In this paper, new aromatic poly(α- and β-naphthylamino)amides (I) are prepared and converted by thermal polycyclodehydration to the corresponding new poly(α- and β-naphthyl)benzodiimidazoles (II) in order to study the influence of the bulky naphthyl substituents on their solubility and thermal stability (see Scheme 1). For this purpose two new tetraamines, 1,5-di(α- and β-naphthylamino)-2,4-diaminobenzene are prepared and used in a low-temperature solution polymerization with isophthaloyl and terephthaloyl chloride or 2,5-furoyl dichloride to prepare the poly(α- and β-naphthylamino)-amides.

The polymers are characterized by elemental analysis, infrared and ultraviolet spectroscopy, inherent viscosity measurements, molecular weight determination, and thermal analysis (DSC, TGA). The results of this study are discussed and compared with those of the corresponding unsubstituted [1, 2] and substituted [3, 5, 6] polymers reported in the literature.

EXPERIMENTAL

Materials

1,5-Di(α-naphthylamino)-2,4-diaminobenzene

1,5-Di(α-naphthylamino)-2,4-dinitrobenzene. In a 250 mL three-neck flask connected to a reflux condenser, 150 mL of N-methyl-2-pyrrolidone (NMP), 23.7 g (100 mmol) of 1,5-dichloro-2,4-dinitrobenzene [3, 7], and 42.9 g (300 mmol) of α-naphthylamine (puriss, Merck) were placed. The mixture was heated at 150°C with stirring for 4 h. After cooling to 70°C, 100 mL of methanol was added in portions and the reaction mixture was allowed to crystallize. The product was collected by suction filtration, washed with methanol, dissolved in 200 mL of hot N,N-dimethylformamide (DMF) and, after addition of 100 mL of methanol, allowed to crystallize. Red and yellow crystals (yield 35.6 g, 79%) were obtained which, when heated to 220°C, converted to yellow crystals, mp 241-243°C (Ref. 8: mp 202-203°C). These were insoluble in acetone, methanol, and benzene, and soluble in chloroform and DMF.

IR (nujol): 3350, 3320 cm^{-1} (ν_{NH}) and 1540, 1340 cm^{-1} (ν_{NO_2}). NMR (in DMF-d): δ 5.75 (s) and 7.1-7.9 (m). Analysis: Calculated for $C_{26}H_{18}N_4O_4$: C, 69.33%; H, 4.03%; N, 12.43%. Found: C, 70.00%, H, 4.24%; N, 12.23%.

1,5 – di (α– or β –naphthylamino) – 2,4 – diaminobenzene

Ar =   or

Ia , IIa :   Ar =   ,   R =

Ib , IIb :   Ar =   »   ,   R =

Ic , IIc :   Ar =   »   ,   R =

Id , IId :   Ar =   ,   R =

Ie , IIe :   Ar =   »   ,   R =

If , IIf :   Ar =   »   ,   R =
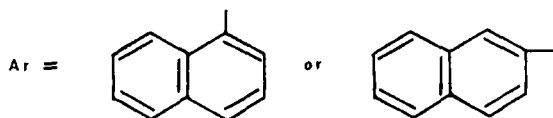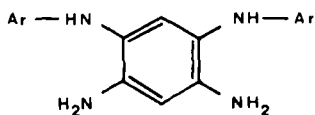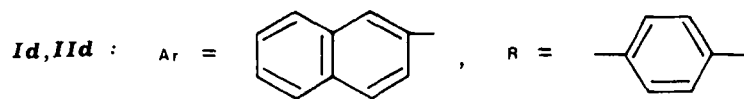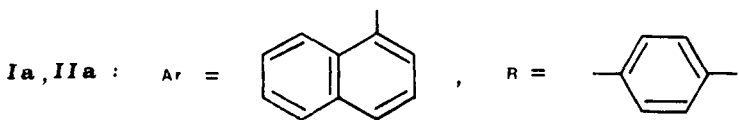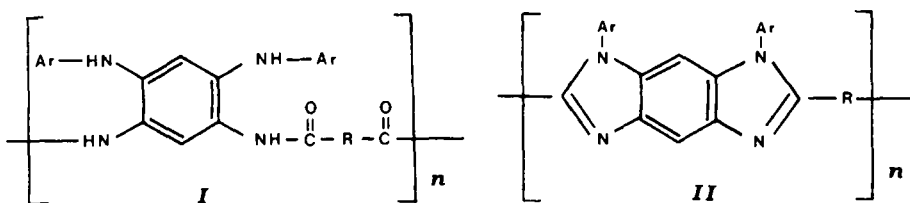
SCHEME 1.

Reduction of the 1,5-Di(α-naphthylamino)-2,4-dinitrobenzene. A Parr hydrogen pressure bomb was charged with 4.5 g (10 mmol) of 1,5-di-(α-naphthylamino)-2,4-dinitrobenzene, 150 mL of N,N-dimethylacetamide (DMAC), and 0.5 g of catalyst (10% palladium on powdered charcoal). The reduction was performed at room temperature in 1 h with hydrogen under a pressure of 50 psi. The reaction mixture was filtrated with suction through Celite under an inert atmosphere into 1 L of boiled oxygen-free water. Two drops of ammonium hydroxide solution (25%) was added to the emulsion which was formed, and the 1,5-di(α-naphthylamino)-2,4-diamino-benzene was precipitated. The precipitate was filtered with suction under nitrogen, washed with ice-cold methanol, and dried to constant weight at 60°C in vacuo (0.1 mmHg). The product was recrystallized from chloroform to yield white needles (yield 3.5 g, 90%), mp 260-262°C (sealed tube under nitrogen) which were insoluble in methanol and ethanol.

IR (nujol): 3420, 3320, 3280 cm^{-1} (ν_{NH}) and 1400 cm^{-1} (α-naphthalene). NMR (in DMF-d): δ 4.6 (br), 6.5 (s), and 7.2-7.8 (m). Mass (m/e): 390 (M$^+$), 375 (M$^+$–NH), 195 (M^{2+}). Analysis: Calculated for C$_{26}$H$_{22}$N$_4$: C, 79.97%; H, 5.68%; N, 14.35%. Found: C, 80.00%, H, 5.72%; N, 14.26%.

1,5-Di(β-naphthylamino)-2,4-diaminobenzene

1,5-Di(β-naphthylamino)-2,4-dinitrobenzene. This was prepared analogously to the above 1,5-di(α-naphthylamino)-2,4-dinitrobenzene from 1,5-dichloro-2,4-dinitrobenzene and β-naphthyl-amine (98%, Merck). Red crystals (yield 36.5 g, 82%) were obtained after recrystallization from DMF-methanol; mp 219-221°C [Ref. 9, mp 183).

IR (nujol): 3320 cm^{-1} (ν_{NH}) and 1540, 1340 cm^{-1} (ν_{NO_2}). NMR (in DMF-d): δ 6.8 (s) and 7.4-7.9 (m). Analysis: Calculated for C$_{26}$H$_{18}$N$_4$O$_4$: C, 69.39%; H, 4.03%; N, 12.43%. Found: C, 70.03%; H, 4.10%, N, 11.87%.

Reduction of the 1,5-Di(β-naphthylamino)-2,4-dinitrobenzene. This was performed as in the above reduction of the corresponding α-naphthylamino derivative. The product of the reaction was dissolved in hot pyridine and, after addition of methanol, allowed to crystallize to yield white needles (yield 3.4 g, 88%) soluble in methanol, ethanol, acetone, and in diethyl ether which melted at 114-116°C with decomposition (in a sealed under nitrogen tube).

IR (nujol): 3410 and 3270 cm^{-1} (ν_{NH}). NMR (in DMF-d): δ 4.65 (br), 6.50 (s), and 6.9-7.8 (m). Mass (m/e): 390 (M)$^+$, 375 (M$^+$–NH), 195 (M^{2+}). Analysis: Calculated for C$_{26}$H$_{22}$N$_4$: C, 79.97%; H, 5.68%; N, 14.35%. Found: C, 79.66%; H, 5.70%; N, 14.34%.

Terephthaloyl and Isophthaloyl Chloride

These were prepared and purified as in Ref. 10.

2,5-Furandicarbonyl Dichloride

This was prepared analogously to terephthaloyl chloride [10] in 82% yield by refluxing 2,5-furandicarboxylic acid with thionyl chloride for 24 h. Mp 78-79°C (Ref. 2: 79-80°C).

2,5-Furandicarboxylic acid was obtained from 2-furoic acid by successive conversion of the latter to methyl furoate [11], methyl 5-(chloromethyl)-2-furoate [12], and 2,5-furandicarboxylic acid [13].

N-Methyl-2-pyrrolidone (Fluka) was purified by fractional distillation in vacuo (bp 82-84°C/10 mmHg) over CaH_2 and stored over 4-Å molecular sieves. The water content was determined by the Karl Fischer method and found to be 0.004%.

Polymers

Poly(α- and β-naphthylamino)amides (Ia-If)

These were prepared by a low-temperature solution polymerization as reported in a previous paper [1]. The solid dicarboxylic acid dichloride (10.2 mmol) was added in portions with stirring under an inert atmosphere to a solution of 1,5-di(α-naphthylamino)-2,4-diaminobenzene (10 mmol) in dry NMP (40 mL), cooled to -10°C (overall reactants concentration 15% w/v).

The temperature was raised to room temperature and stirring was continued for 2 h. The resulting viscous polymer solution was poured into 300-500 mL of stirred distilled water. The polymer that precipitated was collected, washed with water, extracted with methanol in a Soxhlet apparatus for 6 h, and then dried in vacuo (3 mmHg) at 60°C to constant weight.

Poly[imino {2,4-di(α-naphthylamino)-1,5-phenyl-ene}iminoterephthaloyl] (Ia).   Yield 5.14 g (98.8%); orange powder. IR (KBr): 3320, 3190, 3160 cm^{-1} (ν_{NH}), 1665 cm^{-1} ($\nu_{C=O}$), 1530 cm^{-1} ($\delta_{NH} + \nu_{C-N}$) and 1400 cm^{-1} (α-naphthalene). Analysis: Calculated for $(C_{34}H_{24}N_4O_2)_n$: C, 78.44%; H, 4.65%; N, 10.76%. Found: C, 78.49%; H, 4.71%; N, 10.86%.

Poly[imino {2,4-di(α-naphthylamino)-1,5-phenyl-ene}iminoisophthaloyl] (Ib).   Yield 5.08 g (97.5%); yellowish powder. IR (KBr): 3300, 3190, 3160 cm^{-1} (δ_{NH}), 1660 cm^{-1} ($\nu_{C=O}$), 1530 cm^{-1} ($\delta_{NH} + \nu_{C-N}$) and 1400 cm^{-1} (α-naphthalene). Analysis: Calculated for $(C_{34}H_{24}N_4O_2)_n$: C, 78.44%; H, 4.65%; N, 10.76%. Found: C, 78.46%; H, 4.68%; N, 10.69%.

Poly[(2,5-furylene)carbonylimino{2,4-di(α-naphthylamino)-1,5-phenylene}iminocarbonyl] (Ic). Yield 4.98 g (97.6%); yellow powder. IR (KBr): 3300, 3190, 3160 cm^{-1} (ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$), 1520 cm^{-1} ($\delta_{NH} + \nu_{CN}$) and 1400 cm^{-1} (α-naphthalene). Analysis: Calculated for $(C_{32}H_{22}N_4O_3)_n$: C, 75.28%; H, 4.34%; N, 10.97%. Found: C, 75.30%; H, 4.40%; N, 10.99%.

Poly[imino{2,4-di(β-naphthylamino)-1,5-phenylene}iminoterephthaloyl] (Id). Yield 4.73 g (91%); yellow powder. IR (KBr): 3320 (broad, ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$), and 1510 cm^{-1} ($\delta_{NH} + \nu_{C-N}$). Analysis: Calculated for $(C_{34}H_{24}N_4O_2)_n$: C, 78.44%; H, 4.65%; N, 10.76%. Found: C, 78.42%; H, 4.69%; N, 10.72%.

Poly[imino{2,4-di(β-naphthylamino)-1,5-phenylene}iminoisophthaloyl] (Ie). Yield 4.68 g (90%); yellowish powder. IR (KBr): 3350 cm^{-1} (broad, ν_{NH}), 1660 cm^{-1} ($\nu_{C=O}$), and 1510 cm^{-1} ($\delta_{NH} + \nu_{C-N}$). Analysis: Calculated for $(C_{34}H_{24}N_4O_2)_n$: C, 78.44%; H, 4.65%; N, 10.76%. Found: C. 78.47%; H, 4.68%; N, 10.76%.

Poly[(2,5-furylene)carbonylimino{2,4-di(β-naphthylamino)-1,5-phenylene}iminocarbonyl] (If). Yield 4.70 g (92%); green yellow powder. IR (KBr): 3350 cm^{-1} (broad, ν_{NH}), 1660,cm^{-1} ($\nu_{C=O}$), and 1515 cm^{-1} ($\delta_{NH} + \nu_{C-N}$). Analysis: Calculated for $(C_{32}H_{22}N_4O_3)_n$: C, 75.28%; H, 4.43%; N, 10.97%. Found: C, 74.99%; H, 4.24%; N, 10.93%.

Poly(α- or β-naphthyl)benzodiimidazoles (IIa-IIf)

These were prepared from the poly(α- and β-naphthylamino)amides precursors (Ia-If) (5 mmol) by thermal polycyclodehydration [1] at 290-300°C for 6 h in vacuo (0.01 mmHg) and similar reheating for 6 h after pulverizing.

Poly[[1,7-di(α-naphthyl)benzo{1,2-d: 4,5-d'}-diimidazole-2,6-diyl]-1',4'-phenylene] (IIa). Yield 2.40 g (99%); brown-yellow powder. IR (KBr): 1625 cm^{-1} ($\nu_{C=N}$), 1400 cm^{-1} (α-naphthalene), and 1365 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{34}H_{20}N_4)_n$: C, 84.28%; H, 4.16%; N, 11.56%. Found: C, 83.40%; H, 4.24%; N, 11.42%.

Poly[[1,7-di(α-naphthyl)benzo{1,2-d:4,5-d'}diimidazole-2,6-diyl]-1',3'-phenylene] (IIb). Yield 2.41 g (99.5%); brown powder. IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$), 1400 cm^{-1} (α-naphthalene), and 1345 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{34}H_{20}N_4)_n$: C, 84.28% H, 4.16%; N, 11.56%. Found: C, 83.45%; H, 4.20%; N, 11.47%.

Poly[[1,7-di(α-naphthyl)benzo{1,2-d:4,5-d'}-diimidazole-2,6-diyl]-2',5'-furylene] (IIc).   Yield 2.36 g (99.5%); brown-red powder. IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$), 1410 cm^{-1} (α-naphthalene), and 1340 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{32}H_{18}N_4O)_n$: C, 81.00%; H, 3.82%; N, 11.81%. Found: C, 80.20%; H, 3.96%; N, 11.62%.

Poly[[1,7-di(β-naphthyl)benzo{1,2-d:4,5-d'}-diimidazole-2,6-diyl]-1',4'-phenylene] (IId).   Yield 2.40 g (99%); yellow powder. IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$) and 1360 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{34}H_{20}N_4)_n$: C, 84.28%; H, 4.16%; N, 11.56%. Found: C, 80.38%; H. 4.37%; N, 11.53%.

Poly[[1,7-di(β-naphthyl)benzo{1,2-d:4,5-d'}-diimidazole-2,6-diyl]-1',3'-phenylene] (IIe).   Yield 2.40 g (99%); white powder. IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$) and 1340 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{34}H_{20}N_4)_n$: C, 84.28%; H, 4.16%; N, 11.56%. Found: C, 81.98%; H, 4.54%; N, 12.30%.

Poly[[1,7-di(β-naphthyl)benzo{1,2-d:4,5-d'}-diimidazole-2,6-diyl]-2',5'-furylene] (IIf).   Yield 2.34 g (98.5%); yellow powder, IR (KBr): 1630 cm^{-1} ($\nu_{C=N}$) and 1340 cm^{-1} (tertiary nitrogen). Analysis: Calculated for $(C_{32}H_{18}N_4O)_n$: C, 81.00%; H, 3.82%; N, 11.81%. Found: C, 80.66%; H, 4.05%; N, 11.96%.

Measurements

Elemental analysis was carried out with a Perkin-Elmer model No. 240. Melting points were taken on a Kofler or in a Buchi (Dr Tottoli) melting point apparatus and are uncorrected. The IR absorption spectra were recorded with a Perkin-Elmer spectrophotometer model No. 281-B as nujol mulls or KBr pellets. The UV spectra were measured on concentrated sulfuric acid solutions (C = 5×10^{-4} g/100 mL) of the poly(α- or β-naphthyl)benzodiimidazoles, with a Pye-Unicam SP-8000 spectrophotometer. The NMR spectra of the new tetraamines and their intermediates were recorded with a 60 MHz Varian-A-60A instrument with tetramethylsilane (TMS) as internal standard and DMF-d as solvent. Mass spectra of the new tetraamines were obtained with a Hitachi-Perkin-Elmer RMU-GL mass spectrometer.

Inherent viscosities were measured at 25°C with Ubbelohde viscometers. Molecular-weight determinations were carried out by a "Knauer" membrane osmometer using Sartorius regenerated cellulose membranes and DMF as solvent.

The thermal properties of the polymers were determined on a

Perkin-Elmer DSC-2 Differential Scanning Calorimeter (ΔT = 20°C/ min) and on a Perkin-Elmer Thermobalance TGS-2 (ΔT = 5°C/min). Samples of approximately 5 mg were dried in the instrument in nitrogen atmosphere at 105°C for 0.5 h before carrying out the runs.

RESULTS AND DISCUSSION

The poly(α-naphthylamino)amides were isolated in almost quanti- tative yields, whereas the corresponding poly(β-naphthylamino)amides were isolated in lower yields. The elemental analysis and IR spectra for both poly(naphthylamino)amides were consistent with the expected chemical structures (Ia-If).

The yellowish to orange naphthyl-substituted poly(amino)amides were insoluble in aprotic solvents such as DMF, DMAC, dimethyl- sulfoxide (DMSO), hexamethylphosphoric triamide (HMPT), and NMP, whereas their corresponding unsubstituted poly(amino)amides [1] were insoluble. A similar increase of solubility for poly(amino)- amides with tosyl [1] and phenyl [4, 5] substituents was also observed.

The inherent viscosity (η_{inh}), the number-average molecular weight ($\overline{M}_n$) determined osmometrically, and the calculated number- average degree of polymerization of the poly(naphthylamino)amides are given in Table 1.

TABLE 1. Inherent Viscosities, Molecular Weights, and Degrees of Polymerization of Poly(α- and β-naphthylamino)amides Ia-If

Polyamide	η_{inh} [a] dL/g	$\overline{M}_n$ [b]	$\overline{DP}_n$ [b]
Ia	0.20	11,800	23
Ib	0.13	8,200	16
Ic	0.13	10,800	20
Id	0.11	–	–
Ie	0.10	–	–
If	0.10	–	–

[a]Measured at a concentration of 0.5 g/dL in DMF at 25°C.
[b]Number-average molecular weight ($\overline{M}_n$) and number-average degree of polymerization ($\overline{DP}$) determined osmometrically.

A remarkable difference between the polyamides of 1,5-di(α-naphthylamino)- and 1,5-di(β-naphthylamino)-2,4-diaminobenzene concerning their molecular weights was observed (Table 1). Thus the poly(β-naphthylamino)amides showed relatively low molecular weights (less than 6000), which were below the accuracy limits of the osmometric method and therefore are not tabulated in Table 1. This fact and also the lower yields obtained from the polymerization of 1,5-di(β-naphthylamino)- than of 1,5-di(α-naphthylamino)-2,4-diaminobenzene should not be attributed to a lower basicity (reactivity) of the former amine because of the lower electrophilic character of the β-naphthyl than of the α-naphthyl substituent. Solution of poly(α-naphthylamino)amides in DMF afforded brittle films where as no films were obtained from poly(β-naphthylamino)amides because of their low molecular weights.

The DSC and TGA thermograms ($\Delta T = 20°C/min$) in nitrogen showed that the polycyclodehydration of the poly(naphthylamino)-amides (Ia-If) to the polybenzodiimidazoles (IIa-IIf) started in the 230-250°C range, similar to that of the corresponding unsubstituted poly(amino)amides [1]. No second-order transition (T_g) could be detected in the DSC-curves for the polymers. The appearance of a second endotherm peak at a higher temperature in some DSC curves for the polynaphthylaminoamides was proved by TGA to be due to the completion of their cyclodehydration, because a total percentage weight loss, in agreement with that calculated for their conversion to the corresponding polybenzodiimidazoles, resulted.

Poly(α- and β-naphthyl)benzodiimidazoles (IIa-IIf) were prepared from the corresponding poly(α- and β-naphthylamino)amides in theoretical yield. Their IR spectra showed the disappearance of the amide bands (ν_{NH}, $\nu_{C=O}$, δ_{NH} + ν_{C-N}) and the appearance of the characteristic bands of benzimidazole and the N-substituted benzimidazole ring ($\nu_{C=N}$, tertiary nitrogen). Polyamides and polybenzimidazoles with α-naphthyl substituents showed also a characteristic absorption band at 1400 cm^{-1} due to the α-naphthyl substituent.

The elemental analysis of some poly(naphthyl)benzodiimidazoles showed a somewhat lower carbon and a higher hydrogen content in respect to the theoretical values, due probably to incomplete ring closure which has also been reported for analogous polymers [14, 15].

All poly(naphthyl)benzodiimidazoles (IIa-IIf) were insoluble in aprotic polar solvents and slightly soluble in formic and concentrated sulfuric acid. Thus the presence of the bulky naphthyl substituents in the structure of IIa-IIf did not affect their solubility in aprotic polar solvents. Their solubility was slightly increased in sulfuric and formic acid (solubility 0.2-0.3%) in comparison with the solubility of the corresponding unsubstituted polybenzodiimidazoles [1] which were insoluble in sulfuric acid and very slightly soluble in formic acid (0.08%).

TABLE 2. Inherent Viscosities and Ultraviolet Data for Poly(α- and β-naphthyl)benzodiimidazoles

Polymer	η_{inh}[a] dl/g	η_{inh}[b] dl/g	λ_{max} nm[c]	$E_{1cm}^{1\%}$
Ia	3.47	d	215	1280
			365	460
Ib	1.39	d	217	1220
			325	520
Ic	0.65	0.19	218	1380
			416	440
Id	0.30	0.23	222	1070
			360	400
Ie	0.19	0.14	220	1170
			325	500
If	0.16	0.14	222	1570
			420	570

[a]Measured at a concentration of 0.2 g/dL in formic acid at 25°C.
[b]Measured at a concentration of 0.2 g/dL in concentrated sulfuric acid at 25°C.
[c]The ultraviolet spectra were measured on concentrated sulfuric acid solutions of the polymers.
[d]No inherent viscosity could be measured in this concentration because of the lower solubility of the polymer.

The inherent viscosities and ultraviolet data obtained for poly-(naphthyl)benzodiimidazoles are given in Table 2.

The lower inherent viscosities of the poly(β-naphthyl)benzodiimid-azoles than those of poly(α-naphthyl)benzodiimidazoles is evidently due to the lower molecular weights of their precursors (Table 1).

The λ_{max} of the ultraviolet absorption bands between the corre-sponding polybenzodiimidazoles with α-naphthyl and β-naphthyl sub-stituents were approximately similar, whereas their corresponding absorption coefficients $E_{1\ cm}^{1\%}$ were different. Also, these λ_{max} appeared to be similar to those for the corresponding unsubstituted polymers [1]. However, a characteristic difference in the ratio of
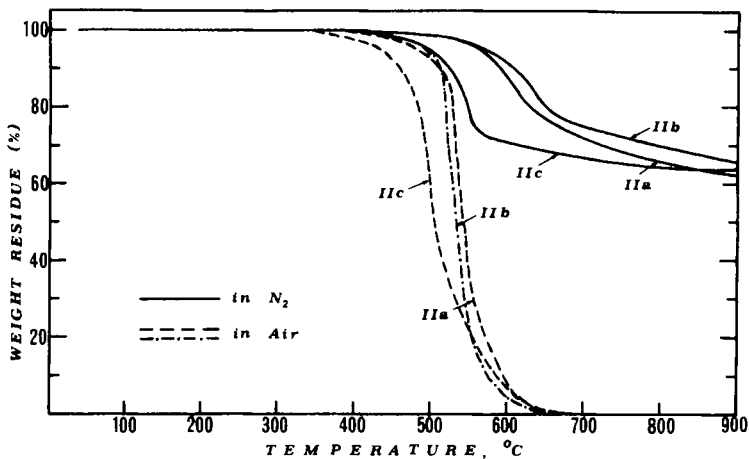
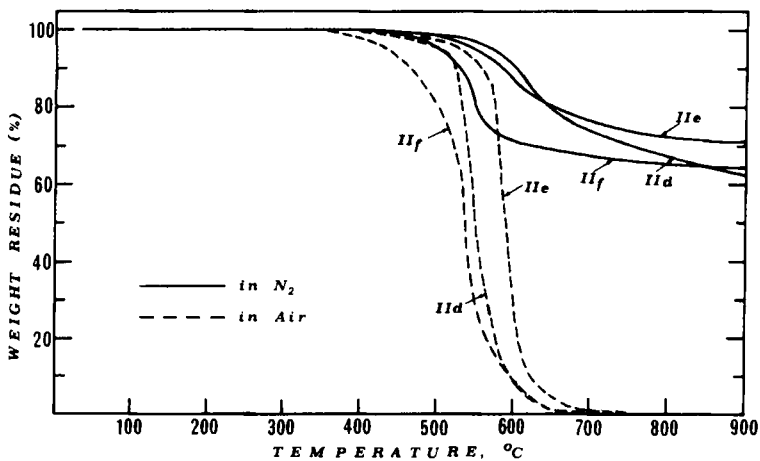FIG. 1. Thermogravimetric curves of poly(α-naphthyl)benzodi-imidazoles.

FIG. 2. Thermogravimetric curves of poly(β-naphthyl)benzodi-imidazoles.

TABLE 3. Data of Thermal Degradation of Poly(α- or β-naphthyl)-benzodiimidazoles

	Decomposition temperature of 5% weight loss		Half-volatili-zation point[a] (°C)	Integral proce-dural de-composi-tion tem-perature[a] (°C)	% of total weight loss[a] at 900°C	Activation energy[a] E (kcal/mol)
Polymer	in air	in nitrogen				
IIa	480	558	620	635	38	40
IIb	485	569	627	640	35	41
IIc	420	490	536	561	37	35
IId	502	580	630	654	37	42
IIe	427	560	603	660	28	43
IIf	441	504	540	562	36	37

[a]Determined in nitrogen atmosphere.

the absorption intensities $E_{1\ cm}^{1\%}$ of the two bands between the unsubstituted [1] and naphthyl-substituted polybenzodiimidazoles was observed.

The thermal stability of the poly(naphthyl)benzodiimidazoles was evaluated from their TGA thermograms (Figs. 1 and 2) [16, 17].

The half-volatilization point (the temperature at which half of the ultimate weight loss occurred) [16] and the integral procedural decomposition temperature [16, 18] were determined for the temperature range 50-900°C in nitrogen. The activation energy in nitrogen was determined by the multiple heating rate procedure [17] as reported in a previous paper [1]. The results obtained are given in Table 3.

The thermal stability of poly(α- and β-naphthyl)benzodiimidazoles of terephthalic and isophthalic acid was respectively similar and higher than that of the poly(α- and β-naphthyl)benzodiimidazoles from 2,5-furandicarboxylic acid (Table 3). However, the latter ones did not show a higher total weight loss at 900°C (in nitrogen). Such an inferior thermal stability for thermally stable polymers with a furan ring, in respect to the corresponding polymers with a phenylene ring (m- and p-), was also observed for polybenzodiimidazoles [1] and polydibenzimidazoles [2].

The polybenzodiimidazoles with β-naphthyl substituents (IId-IIf) showed a higher thermal stability in air than the corresponding polymers with α-naphthyl substituents (IIa-IIc), even though their molecular

weights were much lower. Also, no such characteristic difference for their thermal stability in nitrogen was generally observed (Table 3).

Comparison of the thermal stability of poly(naphthyl)benzodiimidazoles with that of the corresponding unsubstituted polymers [1] showed that the presence of their naphthyl-substituents slightly increased the thermal stability in air and reduced it in nitrogen.

An analogous effect was also reported for the phenyl substituents [3, 5], whereas a relative reduction of thermostability both in air and nitrogen was deduced for the corresponding methyl-substituted polybenzodiimidazoles on the basis of the available data [1, 2, 6].

In comparison with phenyl substituents [3, 5], naphthyl substituents caused a slightly higher thermostability in air for the corresponding substituted polybenzodiimidazoles.

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