Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Thermal Stability of Aromatic and Aliphatic Poly(N,N-Diacylhydrazone)s

Robert C. Troy[a]; David B. Sobanski[a]; Malcolm P. Stevens[a]
[a] Chemistry Department, University of Hartford, West Hartford, Connecticut

To cite this Article Troy, Robert C. , Sobanski, David B. and Stevens, Malcolm P.(1986) 'Synthesis and Thermal Stability of Aromatic and Aliphatic Poly(N,N-Diacylhydrazone)s', Journal of Macromolecular Science, Part A, 23: 2, 189 — 202

To link to this Article: DOI: 10.1080/00222338608063387

URL: http://dx.doi.org/10.1080/00222338608063387

J. MACROMOL. SCI.–CHEM., A23(2), pp. 189-202 (1986)

Synthesis and Thermal Stability of Aromatic and Aliphatic Poly(N,N-Diacylhydrazone)s

ROBERT C. TROY, DAVID B. SOBANSKI, and
MALCOLM P. STEVENS*

Chemistry Department
University of Hartford
West Hartford, Connecticut 06117

ABSTRACT

Poly(N,N-diacylhydrazone)s, which contain imide and imine functions linked by nitrogen-nitrogen bonds, were synthesized from terephthalaldehyde dihydrazone and aromatic and aliphatic dianhydrides. One of the aromatic polymers was also prepared from N,N'-diamino-1,4,5,8-naphthalenetetracarboxylic diimide and terephthaldehyde. The polymers exhibited moderate thermal stability and were shown to degrade initially by cleavage of nitrogen-nitrogen bonds.

INTRODUCTION

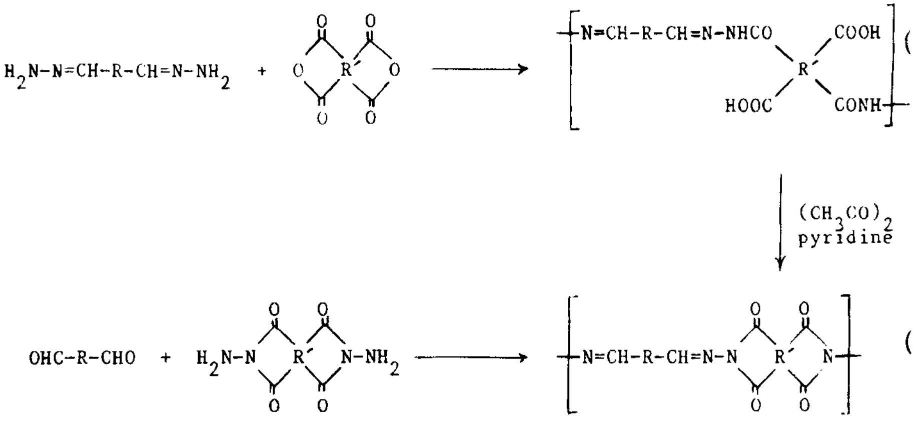
Poly(N,N-diacylhydrazone)s (I) combine the imide and imine functional groups through nitrogen-nitrogen bonds [1]. As such, they may also be called poly[N-(N'-imino)imide]s. In principle, they can be synthesized two ways: (1) reaction of dianhydride with dihydrazone

---

*To whom correspondence should be addressed.

0022-233X/86/2302-0189$3.50/0

followed by ring closure of the intermediate poly(N-acylhydrazone acid), and (2) condensation of N,N'-diaminodiimide with a dicarbonyl compound, preferably a dialdehyde.



(1)

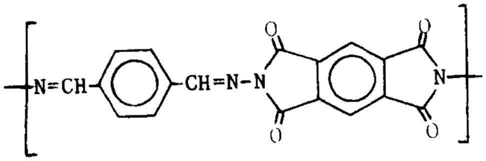
(2)

I

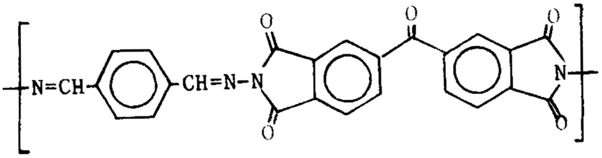
While Reaction (2), which is based on analogous condensation reactions of N-aminophthalimide reported by Drew and Hatt [2] and Hearn [3], affords poly(N,N-diacylhydrazone) in one step, it proved to be much less satisfactory because of difficulties in preparation or because of unexpectedly low reactivity of the N,N'-diaminodiimides. Consequently, this study concentrated on polymer synthesis by Reaction (1) using the readily available dihydrazone of terephthaldehyde.

A preliminary communication [1] described the synthesis of Polymers IA and IB from pyromellitic dianhydride and benzophenone-3,3',4,4'-tetracarboxylic dianhydride, respectively, and terephthalaldehyde dihydrazone. This study has now been expanded to include synthesis of Polymers IC and ID by reacting the dihydrazone with naphthalene-1,4,5,8-tetracarboxylic dianhydride and meso-butane-1,2,3,4-tetracarboxylic dianhydride, respectively. Polymer IC was also prepared by reaction of N,N'-diaminonaphthalene-1,4,5,8-tetracarboxylic diimide (II) with terephthalaldehyde. Earlier publications describe the preparation of polyimides containing nitrogen-nitrogen bonds from II [4] and the use of terephthalaldehyde dihydrazone to prepare 1,3,4-oxadiazole-containing polyamides [5], polyiminoureas [6], and poly(s-triazine)s [7].

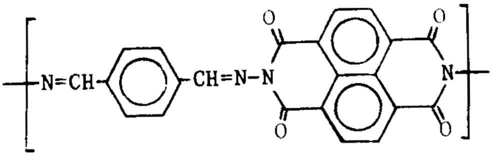
IA



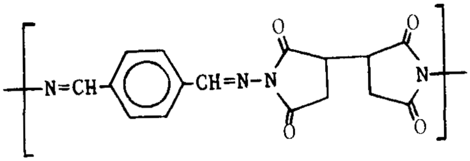
IB



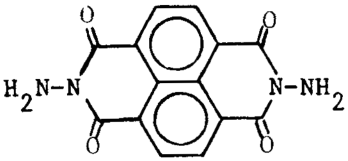
IC



ID



(meso)



II

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer using KBr pellets. DSC thermograms were measured with a Perkin-Elmer Model DSC-2 differential scanning calorimeter under nitrogen at a heating rate of 20°C/min. TGA thermograms were obtained with a Du Pont Model 951 thermogravimetric analyzer in both air and nitrogen atmospheres with a heating rate of 20°C/min. Long-term isothermal weight loss was determined in an air-circulating oven at 250°C for a period of 82 h. Microanalyses were performed by Mic-Anal Organic Microanalysis, Tuscon, Arizona.

Monomers

Terephthalaldehyde dihydrazone was prepared as previously described [1]. Terephthalaldehyde was recrystallized from water prior to reaction with II. Glutaraldehyde was extracted from a 50% aqueous solution with ether and fractionally distilled under vacuum. Aromatic dianhydrides were obtained from commercial sources and recrystallized from acetic anhydride. meso-Butane-1,2,3,4-tetracarboxylic dianhydride [8] was prepared by heating the corresponding tetracarboxylic acid 1 h under reflux with an equivalent amount of acetic anhydride in tetrahydrofuran. The dianhydride, which precipitates from solution during the reflux period, was obtained in yields of 60 to 63%.

N,N'-Diaminonaphthalene-1,4,5,8-tetracarboxylic diimide (II) was prepared by the method of Dine-Hart [4] and recrystallized from dimethylsulfoxide (DMSO). The compound gave unsatisfactory results upon elemental analysis; however, the sample left a combustion residue of approximately 3%. Calculated for $C_{14}H_8N_4O_4$: C, 56.75%; H, 2.72%; N, 18.92%. Found: C, 53.76%; H, 2.79%; N, 16.97%.

Polymerization

Intermediate poly(N-acylhydrazone acid)s were prepared by adding solid dianhydride in four approximately equal proportions every 15 min to a stirred solution of an equimolar quantity of terephthalaldehyde dihydrazone in previously dried solvent under a nitrogen atomsphere. Typically, 6.88 mmol each of dianhydride and dihydrazone were reacted in 40 mL of solvent. The solution or suspension was stirred for the time period indicated (Table 1) and the polymer was isolated by pouring the reaction mixture into water. The precipitated polymer was filtered, washed with methanol, and dried in a vacuum oven at 80°C. Experimental details are summarized in Table 1.

TABLE 1. Poly(N,N-Diacylhydrazone)s and Corresponding Intermediate Poly(N-Acylhydrazone Acid)s

	Poly(N-acylhydrazone acid)[b]				Poly(N,N-diacylhydrazone)								
								Analysis calculated			Analysis found		
Polymer	Solvent[d]	Reaction time, h	Color	η_{inh}[e]	Yield, %	Color	Formula	C	H	N	C	H	N
IA	DMA	15	Yellow	0.22	72	Orange	$C_{18}H_8N_4O_4$	62.76	2.34	16.28	61.71	2.59	15.63
IB	DMF	16	Yellow	0.33	80	Orange	$C_{25}H_{12}N_4O_5$	66.96	2.70	12.50	65.99	2.81	11.73
IB	DMF	56	Yellow	0.43		Orange							
IC	DMF	24	Green	f	68	Brown	$C_{22}H_{10}N_4O_4$	67.01	2.56	14.21	62.10	3.04	11.54
IC	DMSO	24	Green	f	86	Brown							
IC[c]	DMSO	5	-	-	91	Brown							
ID	DMF	24	Yellow	f	90	Yellow-green	$C_{16}H_{12}N_4O_4$	59.25	3.73	17.28	60.39	4.06	16.80

[a] Polymerization and imidization procedures given in Experimental section.

[b] Prepared from terephthalaldehyde dihydrazone and dianhydride unless otherwise noted.

[c] Prepared from terephthalaldehyde and II at 120°C.

[d] DMA = N,N-dimethylacetamide; DMF = N,N-dimethylformamide; DMSO = dimethylsulfoxide.

[e] DMF solution (0.5 g/100 mL) at 30°C.

[f] Insoluble.

Soluble poly(N-acylhydrazone acid)s were converted to the corresponding poly(N,N-diacylhydrazone)s by reaction with acetic anhydride as described previously [1]. Insoluble polymers were heated overnight under reflux with an acetic anhydride-pyridine-benzene solution (equal volumes of each) to effect ring closure.

Alternate Synthesis of IC

Terephthalaldehyde (0.46 g, 0.0034 mol) and II (1.00 g, 0.0034 mol) were heated at 120°C for 5 h in 50 mL of DMSO, then stirred at room temperature overnight. The solution was poured into water, and the resultant brown precipitate was filtered, washed with methanol, and dried.

An attempt to prepare a similar polymer using glutaraldehyde was not successful. Equimolar amounts of the two monomers were heated at 120°C in dimethylsulfoxide for 24 h, but only unreacted II precipitated upon cooling.

Model Compound V

A solution of benzaldehyde (2.12 g, 0.02 mol) in tetrahydrofuran (15 mL) was added dropwise to a solution of hydrazine hydrate (1.00 g, 0.02 mol) in tetrahydrofuran (15 mL). Following the addition, the solution was stirred for 3 h, after which meso-butane-1,2,3,4-tetracarboxylic dianhydride (1.78 g, 0.01 mol) was added. The reaction mixture was stirred 15 min, then a solution of acetic anhydride-pyridine-benzene (10 mL of each) was added and allowed to react for 30 min. The solution was poured into 150 mL of water, and the resultant precipitate, which consisted of approximately equal amounts of colorless V and yellow benzylideneazine, was washed well with methanol to remove the latter. Compound V was isolated in 25% yield, mp 278-281°C. Calculated for $C_{22}H_{18}N_4O_4$: C, 65.66%; H, 4.51%; N, 13.93%. Found: C, 65.42%; H, 4.66%; N, 13.85%.

Polymer Degradation

Samples of Polymers IA, IB, and ID were heated in air at 500°C for 1 h in a quartz tube contained within a hot tube reactor. Sublimates were removed from the cool section of the tube and analyzed by infrared spectroscopy. For comparison of spectra, samples of pyromellitimide and benzophenone-3,3',4,4'-tetracarboxylic diimide were synthesized by reacting the corresponding dianhydrides with ammonia and heating the resultant ammonium salts strongly.

RESULTS AND DISCUSSION

Synthesis of Polymers and Model Compounds

An original goal of this research was to determine whether N,N'-diaminodiimides could serve as convenient monomers for introducing other functionalities into polyimides, as well as to investigate the properties of such polymers. As reported previously [1], however, attempts to synthesize the N,N'-diaminodiimide derivatives of pyromellitic dianhydride and benzophenone-3,3',4,4'-tetracarboxylic dianhydride using a published procedure [4] or procedures analogous to those reported for N-aminophthalimide [2] resulted in yields too low to be of practical value. Accordingly, to prepare poly(N,N-diacylhydrazone)s, the more conventional route from dianhydride and diamine (in this case, terephthalaldehyde dihydrazone) was employed. It was possible to prepare N,N'-diaminonaphthalene-1,4,5,8-tetracarboxylic diimide (II) [4] in good yield, but in this instance two problems were encountered. Although II could be recrystallized without difficulty, it failed to give satisfactory elemental analysis, apparently because of a tendency to form a poorly combustible char. This behavior was also noted in subsequent polymer combustion studies (vide infra). Furthermore, II proved to have unexpectedly low reactivity in polymerization with dialdehydes, considering analogous reactions of the monofunctional N-aminophthalimide [3].

Polymers were thus prepared satisfactorily from the corresponding dianhydrides and terephthalaldehyde dihydrazone by Reaction (1). For comparing thermal properties of aliphatic and aromatic poly(N,N-diacylhydrazone)s, polymer ID was prepared from meso-butane-1,2,3,4-tetracarboxylic dianhydride, a monomer previously used [9] to synthesize polyimides exhibiting good thermal stability. Polymer IC was also prepared from II and terephthalaldehyde by reaction (2); however, hot DMSO was necessary to provide a homogeneous reaction medium. Prolonged stirring of the monomers in DMSO at room temperature resulted only in recovery of unreacted II. Attempts to prepare an analogous polymer from II and glutaraldehyde failed, presumably because the dialdehyde undergoes homopolymerization more rapidly than copolymerization with II. Polymer IC gave very poor results upon elemental analysis. While imine-containing polymers are known [10] to give poor analyses, char formation is the most likely cause in this case in view of similar results with II. Results of the successful polymer syntheses are given in Table 1.

Infrared spectra of IC synthesized by the two methods show excellent agreement (Fig. 1). The six-membered ring imide carbonyl absorption at 1670 and 1710 cm^{-1} contrasts with those of the five-membered ring polyimides, which characteristically absorb at about 1700-1710 and 1770 cm^{-1}. Model compounds III and IV, analogous in structure to Polymer IA, and model compound V, analogous to Polymer ID,

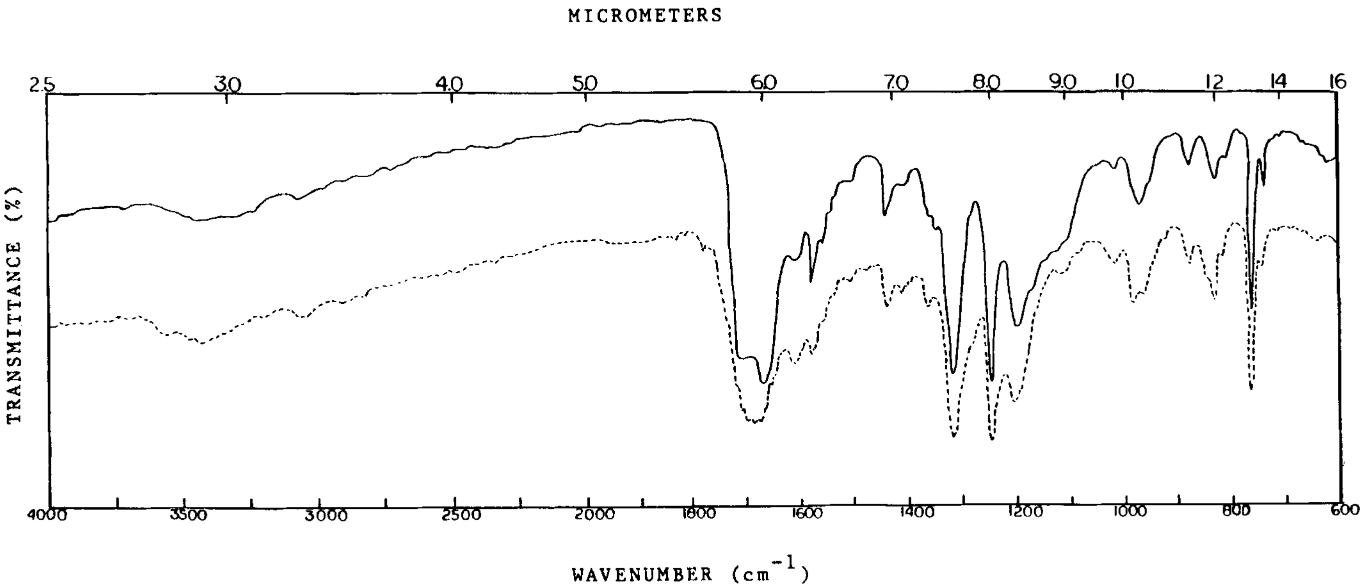
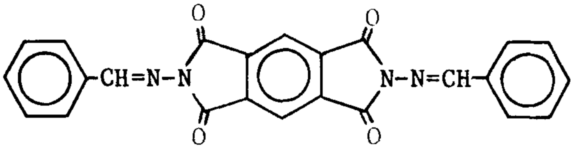
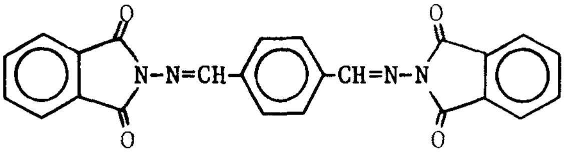


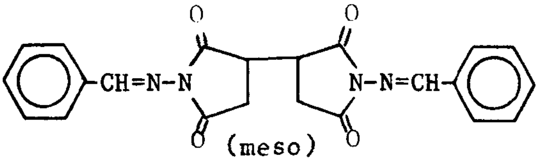
FIG. 1. Infrared spectra of Polymer IC prepared by Reaction (1) (- -) and Reaction (2) (—).



III



IV



V

were prepared for spectroscopic comparison. Infrared and ultraviolet spectra of III and IV compared favorably with those of polymer IA, as reported previously [1]. Model compound V exhibited infrared absorptions in good agreement with those of Polymer ID (Fig. 2), with the exception of expected differences in the aromatic C–H out-of-plane bending region arising from mono- and para-disubstitution, respectively.

Despite introduction of the imine group, polymer solubility was poor. None of the ring-closed polymers dissolved in the usual polymer solvents, and the intermediate poly(N-acylhydrazone acid)s of IC and ID were also insoluble. Brittle films could be cast from N,N-dimethylformamide solutions of the intermediate polymers of IA and IB. In the presence of concentrated sulfuric acid, the polymers degraded rapidly. No glass transition temperatures were detectable in DSC thermograms.

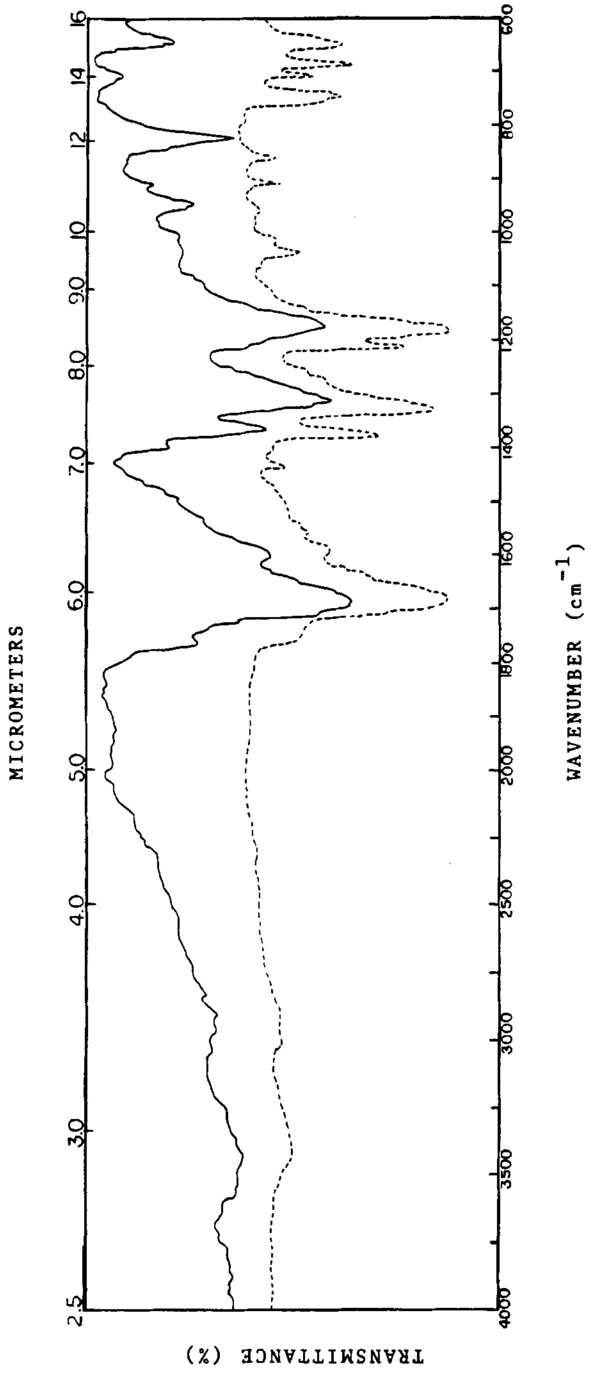


FIG. 2. Infrared spectra of Polymer ID (—) and model compound V (- -).

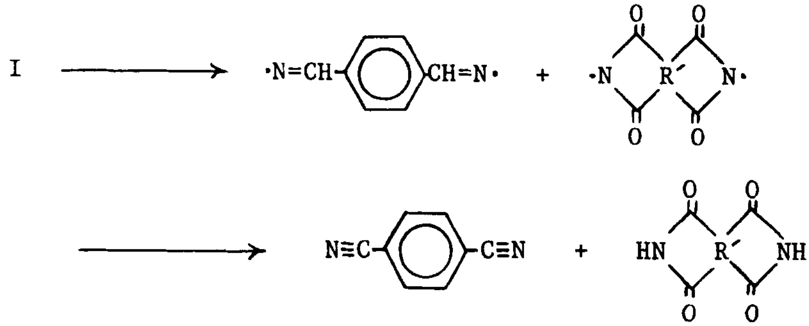
Polymer Degradation

TGA thermograms obtained in both air and nitrogen atmospheres are shown in Figs. 3 and 4. The following conclusions may be drawn from these data:

1. Polymers IA and IB begin to degrade in air or nitrogen at approximately 400°C whereas IC and ID degrade initially between 300 and 350°C. (Some loss of retained solvent is also evident with IA and IB.)
2. Secondary degradation of IA and IB occurs between 450 and 500°C, at lower temperatures for IC and ID.
3. Polymer IC exhibits the greatest weight retention at high temperatures, although ID has remarkably high retention in nitrogen.

Initial weight loss is undoubtedly due to cleavage of the nitrogen-nitrogen bond, with some possible concomitant breakdown of the aliphatic system of ID. The remarkable difference in thermal stability of ID between air and nitrogen was not unexpected in view of similar results observed by Loncrini and Witzel [9]. It is not clear why IC degrades at a lower temperature than the other aromatic polymers, but a steric influence on the nitrogen-nitrogen bond strength is a possibility. The apparent char formation with IC at higher temperatures probably accounts for the poor elemental analysis and would be consistent with the combustion residue noted for monomer II.

Samples of IA, IB, and ID were heated in air at 500°C in a tube reactor, and sublimates collected from the cool part of the tube exhibited infrared spectra consistent with nitrogen-nitrogen cleavage. Spectra of the sublimates from IA and IB closely resembled those of pyromellitimide and benzophenone-3,3',4,4'-tetracarboxylic diimide, respectively, with additional absorbances at 2220 and 840 cm^{-1} consistent with 1,4-dicyanobenzene [11]. The spectrum of the sublimate from ID exhibited a relatively complex spectrum including a significant absorption in the strained ring carbonyl region at 1760 cm^{-1} but the predominant bands were again those at 2220 and 840 cm^{-1}, suggesting significant degradation of the aliphatic portion of the polymer. Initial degradation may thus be depicted according to Reaction (3), a homo-



(3)

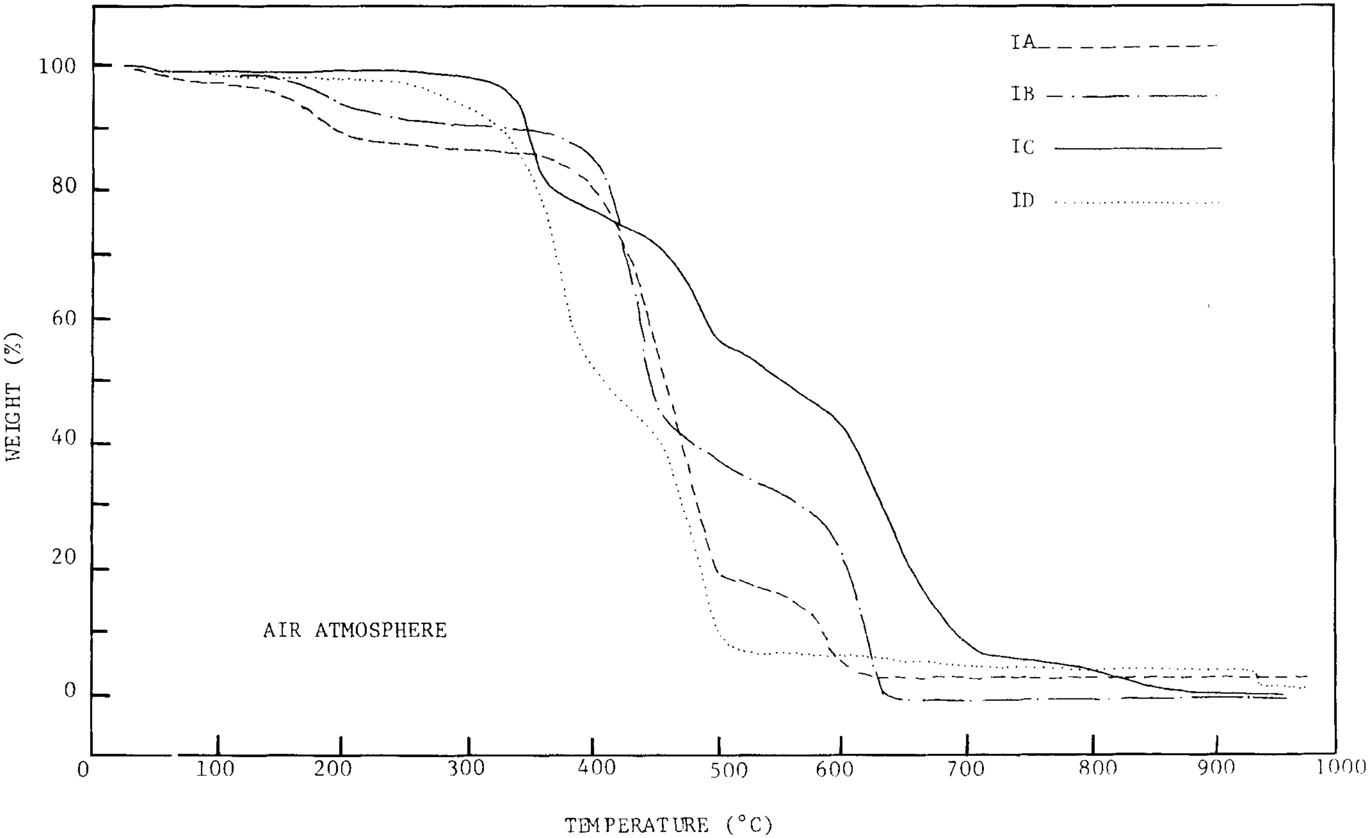


FIG. 3. Thermogravimetric analyses of poly(N,N-diacylhydrazone)s in air.

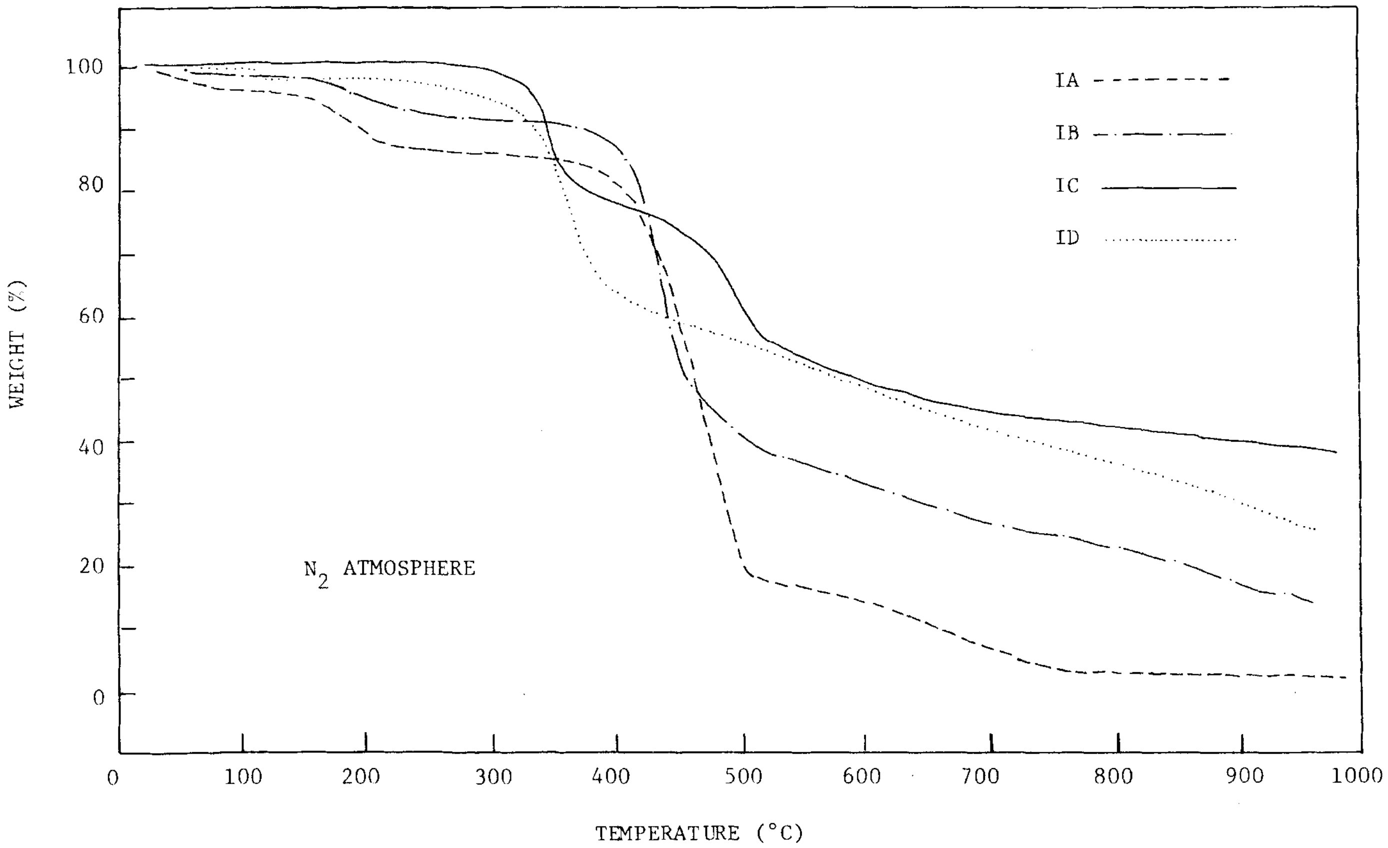


FIG. 4. Thermogravimetric analyses of poly(N,N-diacylhydrazone)s in nitrogen.

lytic process similar to that reported previously for polymers containing imide and 1,3,5-triazine rings linked through nitrogen-nitrogen bonds [12].

Samples of IA and IB were also subjected to a constant temperature of 250°C in an air circulating oven. An initial weight loss arising from entrapped solvent was observed (3% in 2 h from IA, 13% in 2 h from IB), but after 82 h IA and IB retained 94 and 85% of their weights, respectively.

ACKNOWLEDGMENTS

This research was supported by a Cottrell College Science Grant from Research Corporation and a Vincent Brown Coffin Grant from the University of Hartford. The authors are also grateful to Mr John Vontell and Dr Daniel Scola of United Technologies Corporation for the TGA measurements, to Dr Roscoe Pike of United Technologies Corporation for a sample of meso-butane-1,2,3,4-tetracarboxylic acid, to Gulf Oil Chemicals for a sample of benzophenone-3,3',4,4'-tetracarboxylic dianhydride, and to Dr Michael Hearn of Wellesley College for his interest and helpful discussions.

REFERENCES

[1] R. C. Troy and M. P. Stevens, J. Polym. Sci., Polym. Lett. Ed., 22, 113 (1984).
[2] H. D. K. Drew and H. H. Hatt, J. Chem. Soc., p. 16 (1937).
[3] M. J. Hearn and S. B. Prisch, Proceedings of the 11th Northeast Regional Meeting, American Chemical Society, Rochester, New York, 1981.
[4] R. A. Dine-Hart, J. Polym. Sci., Part A-1, 6, 2755 (1968).
[5] S. Fukuoka, T. Fujiwara, S. Goto, K. Nagasawa and T. Tsumaki, Japanese Kokai, 75,09,695 (January 31, 1975); Chem. Abstr., 83, P29736u (1975).
[6] A. Zochniak and J. Ossowski, Plaste Kautsch., 21, 744 (1974); Chem. Abstr., 82, 4829t (1975).
[7] E. Oikawa and H. Tatsuishi, J. Appl. Polym. Sci., 15, 913 (1971).
[8] J. R. Ladd, U.S. Patent 3,915,997 (December 25, 1973), to General Electric Co.; Chem. Abstr., 84, 30463e (1976).
[9] D. F. Loncrini and J. M. Witzel, J. Polym. Sci., Part A-1, 7, 2185 (1969).
[10] E. W. Neuse and M. S. Loonat, Macromolecules, 16, 128 (1983).
[11] C. J. Pouchert, The Aldrich Library of Infrared Spectra, Aldrich Chemical Co., 1970, p. 829.
[12] R. Takatsuka, T. Unishi, and I. Honda, J. Polym. Sci., Polym. Chem. Ed., 15, 1785 (1977).

Received November 13, 1984