

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Note Synthesis of New Poly(Amide-Hydrazide)s

J. Thanuja<sup>a</sup>; M. Srinivasan<sup>a</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Madras, India

**To cite this Article** Thanuja, J. and Srinivasan, M.(1989) 'Note Synthesis of New Poly(Amide-Hydrazide)s', Journal of Macromolecular Science, Part A, 26: 7, 1007 – 1014

**To link to this Article:** DOI: 10.1080/00222338908052027

**URL:** <http://dx.doi.org/10.1080/00222338908052027>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## NOTE

# SYNTHESIS OF NEW POLY(AMIDE-HYDRAZIDE)S

J. THANUJA and M. SRINIVASAN\*

Department of Chemistry  
Indian Institute of Technology  
Madras 600036, India

### INTRODUCTION

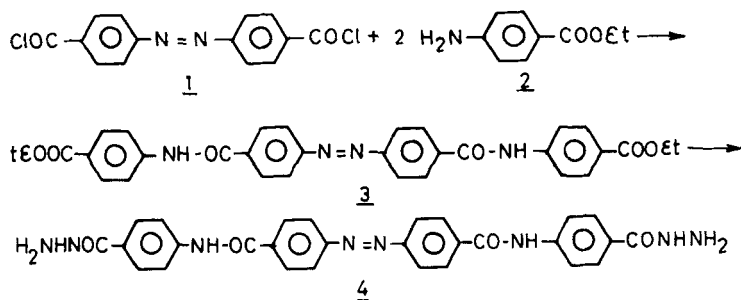
Poly(amide-hydrazide)s were originally developed to give fibers of high modulus and high strength [1]. They were generally prepared 1) from dicarboxylic acid chlorides and aminohydrazides by low-temperature polycondensation [2, 3]; 2) by the phosphorylation method [4, 5]; and 3) from dihydrazides with preformed amide linkages by low-temperature polycondensation [6]. These polymers were found to be thermally stable, but they showed poor solubility in polar aprotic solvents. In this paper we report the synthesis and characterization of some new poly(amide-hydrazide)s with azo groups in the backbone, which were introduced to improve solubility.

### EXPERIMENTAL

#### Azobenzene-4,4'-bis(*p*-amidobenzoic acid-hydrazide) (4) (Scheme 1)

To a solution of ethyl-*p*-aminobenzoate (2) (3.3 g, 0.02 mol) in dry benzene (15 mL), azobenzene-4,4'-biscarboxylic chloride (1) (3.07 g, 0.01 mol) in dry benzene (15 mL) was added, and the mixture was refluxed for 3 h. An orange yellow mass of azobenzene-4,4'-bis(ethyl-*p*-amidobenzoate) (3) was obtained and recrystallized from alcohol. Yield, 70%; mp, 244°C.

A mixture of 3 (0.564 g, 0.001 mol) in dry dioxane (10 mL) and hydrazine hydrate (99-100%, 3 mL) was refluxed gently for 72 h. On cooling, azobenzene-4,4'-bis(*p*-amidobenzoic acid-hydrazide) (4) was obtained as a solid. It was filtered and recrystallized from DMF. Yield, 65%; mp, 252°C.



SCHEME 1.

### Azobenzene-3,3'-bis(*p*-amidobenzoic acid-hydrazide) (7) (Scheme 2)

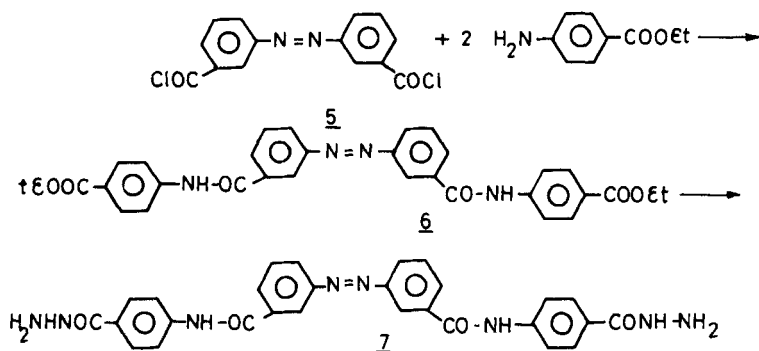
This compound was prepared in 72% yield in two steps exactly as described above, starting from azobenzene-3,3'-biscarboxylic chloride.

All the products obtained were well characterized by UV, IR,  $^1\text{H}$  NMR, and elemental analysis.

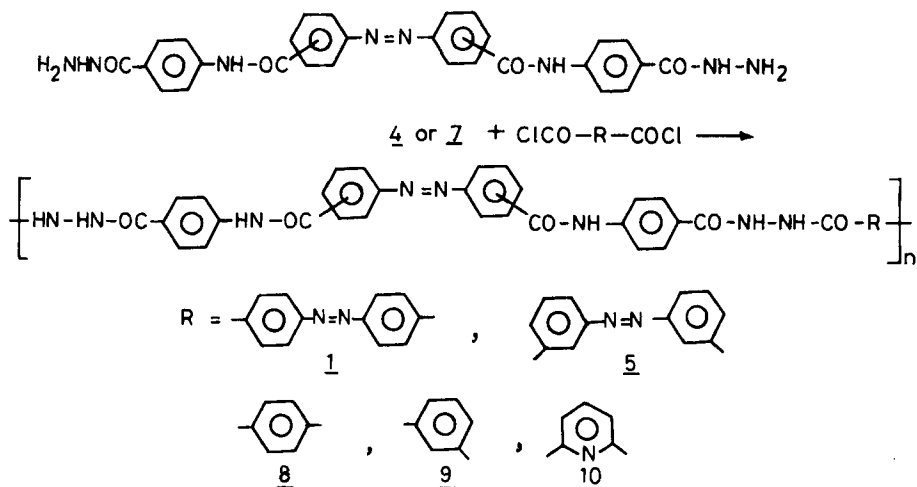
### Polymerization (Scheme 3)

A typical polymerization procedure was as follows.

A solution of 4 (5.36 g, 0.01 mol) in dimethylacetamide (40 mL) containing LiCl (5%) was reacted with diacid chloride (3.06 g, 0.01 mol) in DMAc (20 mL) under nitrogen at  $0^\circ\text{C}$ . The reaction mixture was stirred at room



SCHEME 2.



SCHEME 3.

temperature (30°C) for 24 h. The polymer was precipitated by pouring the reaction mixture into water. The isolated polymer was washed with methanol and dried. Yield, 80%.

### Measurements and Materials

The inherent viscosities of the polymers in DMAc at 30°C were determined. The IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer with KBr pellet samples. <sup>1</sup>H-NMR spectra were recorded on an EM-390 instrument. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were done on a Stanton Redcroft thermal analyzer at a heating rate of 10°C/min in static air. X-ray diffractograms were recorded on a Philip PW 1140 with nickel-filtered CuK<sub>α</sub> radiation. The densities of the polymers were determined using a pycnometer in hexane (a nonsolvent) at 30°C.

All reagents used were of Analar grade and recrystallized or distilled before use. 4,4'-Azodibenzoic acid and 3,3'-azodibenzoic acid were prepared by a literature procedure [7]. The acid chlorides were obtained by treating the corresponding acid with thionyl chloride.

TABLE 1. Some Physical Properties of Polymers

Polymer code	Dihydrazide	Diacid chloride	Yield, %	Density, g/mL	Viscosity, dL/g	Temperature for a 10% weight loss, °C
PAH-1	4	1	80	1.501	0.41	390
PAH-2	7	1	75	1.457	0.39	370
PAH-3	4	5	75	1.466	0.40	350
PAH-4	7	5	70	1.423	0.53	341
PAH-5	4	8	65	1.520	0.50	370
PAH-6	7	8	68	1.516	0.42	370
PAH-7	4	9	65	1.490	0.48	399
PAH-8	7	9	70	1.504	0.56	310
PAH-9	4	10	75	1.487	0.54	409
PAH-10	4	10	68	1.460	0.50	360

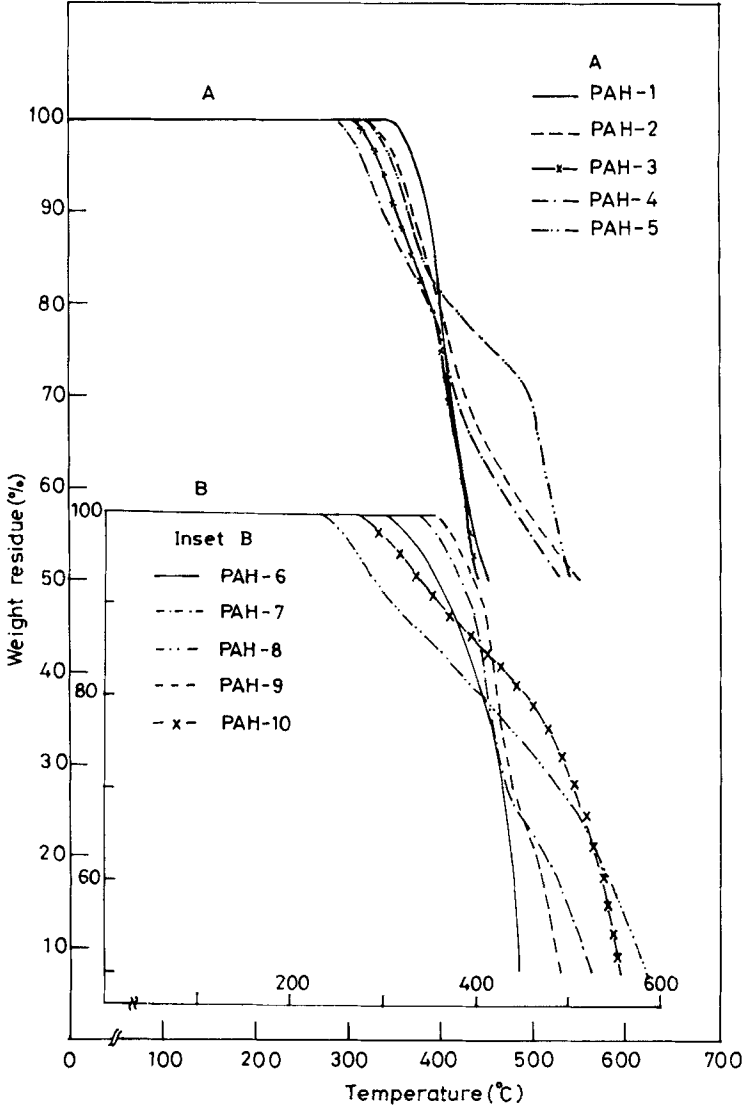


FIG. 1. TGA curves of PAH 1-10 (Table 1).

Downloaded At: 17:55 24 January 2011

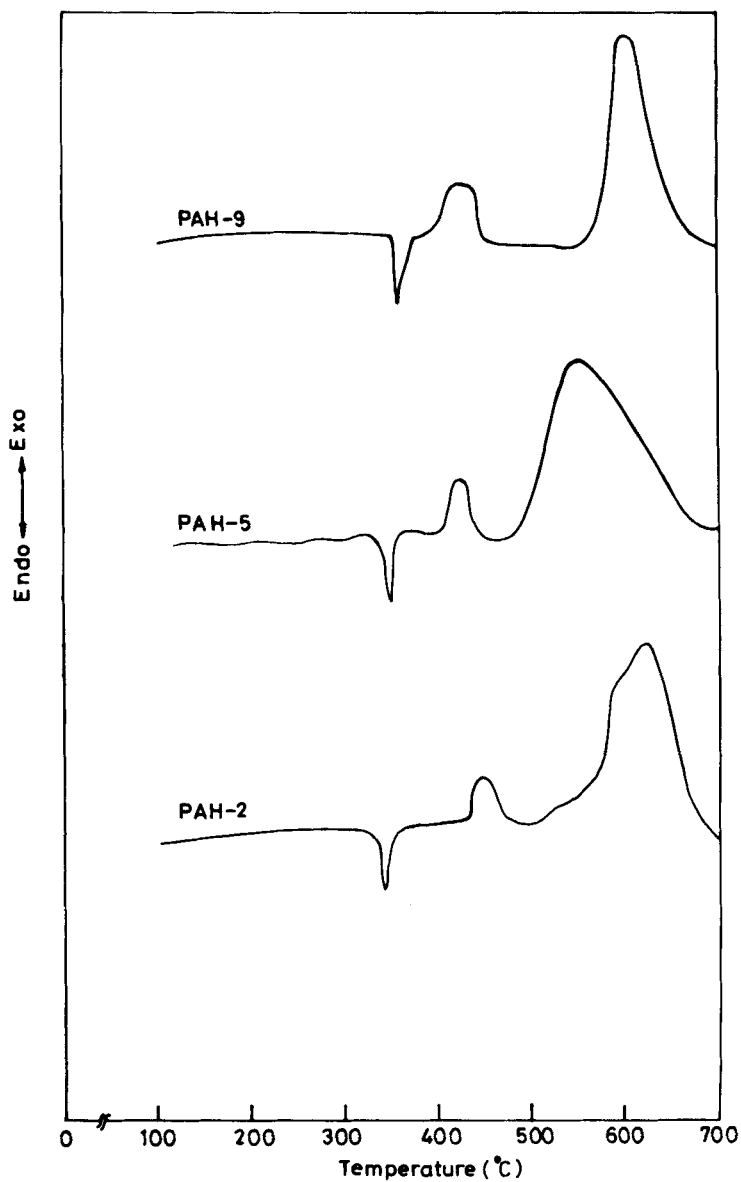


FIG. 2. DTA traces of PAH.

## RESULTS AND DISCUSSION

The polymers were obtained in reasonably good yields and characterized by spectroscopic techniques. Some of their physical properties are listed in Table 1.

To characterize the polymer solubility, a 10% (w/v) solution was taken as a criterion. All the polymers were found to be soluble in concentrated sulfuric acid, trifluoroacetic acid, and DMSO. The polymers derived from *meta*-oriented monomers showed better solubility than the *para*-oriented ones.

The x-ray diffractograms of these polymers showed crystalline peaks in the range  $2\theta = 10-42^\circ$ .

Thermal studies (TGA) showed that the decomposition temperature of the polymers varied from 310-409°C (Fig. 1). The DTA curves (Fig. 2) of the polymers showed two exotherms and one endotherm. The endotherm at 340-360°C may be due to secondary transitions. The first exotherm around 400°C may be due to the elimination of water or nitrogen from the polymer [8, 9]. The large exotherm at 539-619°C can be assigned to the complete destruction of these polymers.

## ACKNOWLEDGMENTS

The authors thank IIT, Madras, for financial assistance and RSIC, IIT, Madras, for spectral data.

## REFERENCES

- [1] J. Preston, "Synthesis and Properties of Rodlike Condensation Polymers," in *Liquid Crystalline Order in Polymers* (A. Blumstein, ed.), Academic, New York, 1978, Chap. 4.
- [2] J. Preston, W. B. Black, and W. L. Hofferbert Jr., *J. Macromol. Sci.—Chem.*, **A7**(1), 45 (1973).
- [3] J. Preston, W. B. Black, and W. L. Hofferbert Jr., *Ibid.*, **A7**(1), 67 (1973).
- [4] J. Preston and W. L. Hofferbert Jr., *J. Polym. Sci., Polym. Symp.*, **65**, 13 (1978).
- [5] F. Higashi and N. Kokubo, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1639 (1980).
- [6] J. S. Shukula and H. Dwiredi, *J. Macromol. Sci.—Chem.*, **A16**(3), 681 (1981).



- [7] M. L. Tomlinson, *J. Chem. Soc.*, p. 756 (1946).
- [8] J. E. Riordan and H. S. Blair, *Polymer*, 20, 196 (1979).
- [9] V. V. Korshak, in *Heat Resistant Polymers*, Academy of Sciences of the U.S.S.R. (Israel Programme of Scientific Translation), 1971, p. 198.

Received May 6, 1988

Revision received August 8, 1988