

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>

### Homopolymerization of Four New Hydroxyamic Acids and Polycondensation of Glycerol With Dibasic Amic Acids

Thanun M. Pyriadi<sup>a</sup>; Nabeel Q. Smoka<sup>a</sup>

<sup>a</sup> Department of Chemistry, College of Science University of Baghdad, Baghdad, Iraq

**To cite this Article** Pyriadi, Thanun M. and Smoka, Nabeel Q.(1987) 'Homopolymerization of Four New Hydroxyamic Acids and Polycondensation of Glycerol With Dibasic Amic Acids', *Journal of Macromolecular Science, Part A*, 24: 7, 829 – 834

**To link to this Article:** DOI: 10.1080/00222338708082097

**URL:** <http://dx.doi.org/10.1080/00222338708082097>

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

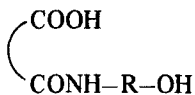
# HOMOPOLYMERIZATION OF FOUR NEW HYDROXYAMIC ACIDS AND POLYCONDENSATION OF GLYCEROL WITH DIBASIC AMIC ACIDS

THANUN M. PYRIADI and NABEEL Q. SMOKA

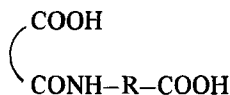
Department of Chemistry  
College of Science  
University of Baghdad  
Baghdad, Iraq

### INTRODUCTION

During the past 15 years or so, research in our laboratory has been mainly directed toward the synthesis of cyclic imides and isoimides for different purposes [1-4]. Thus a large number of substituted amic acids and bis-amic acids were prepared as intermediates. These amic acids were readily purified, crystallized, and obtained in excellent yields. In the present paper two types of amic acids are prepared. The first type is hydroxyamic acids of formula **A**, while the second type consisted of dibasic amic acids such as **B**:



**A**



**B**

Polycondensation of acids **B** with glycerol and homopolycondensation of **A** were investigated.

## EXPERIMENTAL

## Preparation of Amic Acids

Literature procedures [5] were followed with some modifications.

1. Preparation of *N*-(*O*-Carboxyphenyl)itaconamic Acid (1)

A two-necked 500-mL round-bottom flask was equipped with a reflux condenser having a  $\text{CaCl}_2$  tube on top and a dropping funnel. The flask was charged with 22.4 g (0.199 mol) itaconic anhydride, and enough THF was added and stirred to effect dissolution. 27.4 g (0.199 mol) 2-aminobenzoic acid was dissolved in 50 mL THF, added dropwise while heating the flask. Then the mixture was refluxed for 6 h. The solvent was evaporated under reduced pressure, and the residue purified by recrystallization from 1:1 acetone: water. The yield was 43 g (87.3%) of yellow crystals melting at 189–190°C. IR (in KBr):  $\nu_{\text{OH}}$ , 2700–3100  $\text{cm}^{-1}$ ;  $\nu_{\text{C=O}}$ , 1700  $\text{cm}^{-1}$ ;  $\nu_{\text{C=C}}$ , 1600  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$ , 3300  $\text{cm}^{-1}$ .

Analysis. Calculated: C, 57.83; H, 4.42; N, 5.62%. Found: C, 57.71; H, 4.21; N, 5.44%.

For NMR, see Table 1.

2. Preparation of 6-[Carbonyl-*N*-methyl-*N*-(2-ethanol)amino]bicyclo(2.2.1)hept-2,3-ene-5-carboxylic Acid (2)

A similar setup was charged with 5.0 g (0.03 mol) bicyclo(2.2.1)hept-2,3-ene-5,6-dicarboxylic anhydride, dissolved in 25 mL dry THF. 1.88 g (0.03 mol) of ethanolamine in 10 mL THF was added dropwise to the cooled flask in 15 min. A white precipitate settled out. The precipitate was filtered, washed with hexane, dried, dissolved in acetone, and reprecipitated with water. The white crystalline product (5.0 g, 72.7%) melted at 104–105°C. IR:  $\nu_{\text{OH}}$ , 3400  $\text{cm}^{-1}$  (alcoholic), 2600–3000  $\text{cm}^{-1}$  (carboxylic, broad);  $\nu_{\text{C=O}}$ , 1720  $\text{cm}^{-1}$ ;  $\nu_{\text{C=C}}$ , 1650  $\text{cm}^{-1}$ .

Analysis. Calculated: C, 60.25; H, 7.11; N, 5.85%. Found: 60.12; H, 7.01; N, 5.75%.

For NMR, see Table 1.

3. Preparation of *N*-Methyl-*N*-(2-ethanol)succinamic Acid (3)

Following the above procedure [5], equimolar amounts of succinic anhydride and *N*-methylethanolamine were allowed to react. A yellow oil first settled. It was dissolved in acetone and reprecipitated with dry ether. After several repetitions, a sticky soft material was obtained which could not be

TABLE 1. NMR Spectral Data of the Prepared Amic Acids<sup>a</sup>

No.	Structure	Chemical shifts relative to TMS
(1)		$\delta$ 11.60(s, 1H, NH); $\delta$ 11.20(s, 1H, OH); $\delta$ 7.20-8.60(m, 4H, C <sub>6</sub> H <sub>4</sub> ); $\delta$ 3.40(s, 2H, CH <sub>2</sub> -); $\delta$ 6.10(d, 2H, vinylic CH <sub>2</sub> ).
(2)		$\delta$ 8.60(broad, 2H, 2OH <sup>b</sup> ); $\delta$ 6.05(s, 2H, H-C=C-H); $\delta$ 3.60(t, 2H, ); $\delta$ 3.10(s, 2H, ); $\delta$ 2.95(t, 4H, N-CH <sub>2</sub> -CH <sub>2</sub> OH); $\delta$ 1.18(s, 2H, ); $\delta$ 2.55(s, 3H, N-CH <sub>3</sub> ).
(3)		$\delta$ 7.88(s, 2H, 2OH); $\delta$ 3.80-3.30(m, 4H, N-CH <sub>2</sub> CH <sub>2</sub> O); $\delta$ 2.90-3.05(d, 4H, COCH <sub>2</sub> CH <sub>2</sub> CO); $\delta$ 2.60(s, 3H, CH <sub>3</sub> ).
(4)		$\delta$ 11.30(s, 1H, OH); $\delta$ 10.00(broad, 1H, NH); $\delta$ 7.2-8.65(m, 4H, C <sub>6</sub> H <sub>4</sub> ); $\delta$ 2.65(s, 4H, -CH <sub>2</sub> CH <sub>2</sub> -).

<sup>a</sup>NMR spectra were obtained in DMSO-*d*<sub>6</sub> using a 80 MHz Varian instrument.

<sup>b</sup>When D<sub>2</sub>O was added, NH and OH peaks disappeared.

crystallized. The gummy product (85.7%) gave the right neutralization equivalent (174.88). IR (in KBr):  $\nu_{\text{OH}}$ , 3400 cm<sup>-1</sup> (alcoholic), 3100-2600 cm<sup>-1</sup> (carboxylic);  $\nu_{\text{C=O}}$ , 1725 cm<sup>-1</sup>

Analysis. Calculated: C, 48.00; H, 7.43; N, 8.00%. Found: C, 47.96; H, 7.43; N, 7.70%.

For NMR, see Table 1.

#### 4. Preparation of *N*-(*O*-Carboxyphenyl)succinamic Acid (4)

10.0 g (0.099 mol) succinic anhydride and 13.7 g (0.099 mol) 2-aminobenzoic acid were allowed to react in refluxing benzene. The resulting precipitate

was recrystallized from methanol, and 18.0 g (75.9%) of yellow crystals, melting at 184–185°C, were obtained. IR:  $\nu_{\text{OH}}$ , 2700–3100  $\text{cm}^{-1}$ ;  $\nu_{\text{C=O}}$ , 1710  $\text{cm}^{-1}$ ;  $\nu_{\text{NH}}$ , 3250  $\text{cm}^{-1}$ .

Analysis. Calculated: C, 55.69; H, 4.64; N, 5.91%. Found: C, 55.58; H, 4.55; N, 5.70%.

For NMR, see Table 1.

## Glycerol

Glycerol was purified by distillation under reduced pressure. The distillate was protected from moisture before polymerization.

## Polymerization

### 1. Polymerization of Glycerol with Acid (1) or (4)

Glycerol (1.05 mol) and 1.0 mol of either Acid (1) or (4) were heated at 180°C for 2 h under nitrogen, and a viscous brown material formed. This was dried and then dissolved in  $\text{CHCl}_3$ . The polymer was reprecipitated twice with petroleum ether to give a yellow viscous product which was dried.

Polymer from amic acid (1) IR (thin film, major peaks): 3300  $\text{cm}^{-1}$  ( $\nu_{\text{NH}} + \nu_{\text{OH}}$ ); 2850  $\text{cm}^{-1}$  (residual OH of  $-\text{CH}-\text{CH}_2-\text{OH}$ ); 1720  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ , ester). NMR (in  $\text{CDCl}_3$ ),  $\delta$  6.65–8.05 (*m*, 5H,  $\text{C}_6\text{H}_4 + \text{NH}$ );  $\delta$  5.80 (broad, residual vinyl);  $\delta$  4.73 (broad, 2H,  $\text{O}-\text{CH}_2-$ );  $\delta$  4.38 (broad, 2H,  $-\text{COO}-\text{CH}_2-$ );  $\delta$  3.71 (broad, 1H,  $-\text{CH}-\text{O}-$ ).

Analysis for alternating glycerol-amic acid. Calculated: C, 59.01; H, 4.91; N, 4.59%. Found: C, 52.62; H, 5.15; N, 4.45%.

$[\eta]$  0.056 dL/g. Conversion 52.17%.

Polymer from amic acid (4): 3350  $\text{cm}^{-1}$  ( $\nu_{\text{NH}} + \nu_{\text{OH}}$ ); 1750  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ , ester); 1700  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ , amide). NMR (in  $\text{CDCl}_3$ ),  $\delta$  6.60–8.05 (*m*, 5H,  $\text{C}_6\text{H}_4 + \text{NH}$ );  $\delta$  4.20 (broad, 4H,  $-\text{OCH}_2-\text{CH}_2-\text{O}$ );  $\delta$  3.60 (broad, 1H,  $-\text{CH}-\text{O}$ );  $\delta$  2.88 (*s*, 2H,  $-\text{CH}_2-\text{COO}$ );  $\delta$  2.60 (*s*, 2H,  $-\text{CH}_2\text{CONH}$ ).  $[\eta]$  was 0.061.

Analysis for linear chains. Calculated: C, 55.51; H, 5.33; N, 4.98%. Found: C, 54.33; H, 4.93; N, 4.43%.

### 2. Homopolymerization of Hydroxamic Acids (2) and (3)

5.0 g of (2) or (3) was dissolved in 25 mL pure DMF, and two drops of  $\text{H}_2\text{SO}_4$  were added before refluxing for 8 h. The solution was poured into

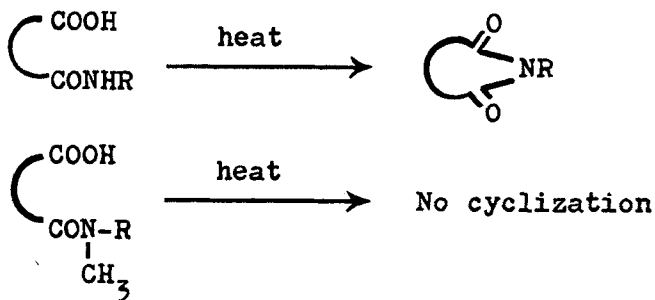
200 mL methanol, and an oily material precipitated. The product was isolated, purified by dissolving in chloroform, and reprecipitated with ether. The viscous product was dried under reduced pressure, yielding 70.5% conversion for amic acid (2) and 65.4% for (3).

$[\eta]$  of polymer obtained from (2) was 0.027, and from (3) 0.082.

## RESULTS AND DISCUSSION

Although glycerol is known to produce three-dimensional crosslinked polyesters when it polycondenses with diols [6], soluble polymers of low molecular weights were obtained here by careful control of reaction conditions. Temperatures higher than 180°C or reaction times longer than 2 h resulted in the formation of insoluble material. The NMR spectrum of the polyester obtained from condensation of glycerol with (1), which revealed the presence of a big portion of the vinylic protons, indicates that the vinyls groups of itaconamic acid did not participate in crosslinking even at 180°C. The allylic nature of this vinyl may have been a reason for the sluggish nature of such groups in free-radical polymerization.

Attempts to prepare the methyl esters of (1) or (4) or their chlorides were not encouraging. Low yields or none in some of these attempts obliged us to perform direct polycondensation, which normally requires high temperatures. We wanted to avoid high temperature polymerization to minimize crosslinking and side reactions [7], and also to avoid cyclization of the amic acids to the corresponding imides. Such cyclization was found during distillation of *N*-allylmaleamic acid [2, 8], producing *N*-allylmaleimide in low yield. To avoid this, amic acids (2) and (3), which have methyl groups on the amidic nitrogen, were prepared by the reaction of *N*-methylethanolamine with the desired anhydride (see Experimental),



When the methylated amic acids (2) and (3) were polycondensed in refluxing DMF, again the products were of rather low molecular weight and no cyclic imides were isolated or detected.

#### REFERENCES

- [1] T. M. Pyriadi and H. J. Harwood, *J. Org. Chem.*, **36**, 821 (1971).
- [2] T. M. Pyriadi and H. J. Harwood, *Polym. Prepr.*, p. 60 (1970).
- [3] T. M. Pyriadi and M. Fraih, *J. Macromol. Sci.-Chem.*, **A18(2)**, 159 (1982).
- [4] T. M. Pyriadi and H. Kaleefa, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 129 (1984).
- [5] *Organic Synthesis*, **41**, 94 (1961).
- [6] R. Lenz, *Organic Chemistry of Synthetic High Polymers*, Wiley-Interscience, New York, 1967, p. 96.
- [7] G. Odian, *Principles of Polymerization*, Wiley, New York, 1970, p. 103.
- [8] T. M. Pyriadi, PhD Thesis, University of Akron, Akron, Ohio, 1970.

Received June 2, 1986