

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>

### Synthesis of New Polymaleamides by Ring-Opening Polyadditi0N

R. Nagarathinam<sup>a</sup>; S. Viswanathan<sup>a</sup>

<sup>a</sup> Department of Polymer Science Guindy Campus, University of Madras, Madras, India

**To cite this Article** Nagarathinam, R. and Viswanathan, S.(1988) 'Synthesis of New Polymaleamides by Ring-Opening Polyadditi0N', *Journal of Macromolecular Science, Part A*, 25: 12, 1675 – 1682

**To link to this Article:** DOI: 10.1080/10601328808055094

**URL:** <http://dx.doi.org/10.1080/10601328808055094>

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 POLYMALEAMIDES BY RING-OPENING POLYADDITION

R. NAGARATHINAM and S. VISWANATHAN\*

Department of Polymer Science  
Guindy Campus, University of Madras  
Madras 600025, India

### INTRODUCTION

Ring-opening polyaddition (ROPA) of diamines to bisolides [1, 2] and bisultam [3] led to the production of polyamides. Ueda, Yabuuchi, and Imai reported the synthesis of polyamides with an unsaturation unit in the polymer backbone by the reaction of diamines with bisbutenolides [4]. Ueda, Kino, and Imai reported polyamides having unsaturated units in the backbone and pendent amide groups from diamines and bisazalactones [5]. On the basis of the reaction between isoimides and amines, *N,N'*-bisisomaleimides were prepared and allowed to undergo ROPA to diamines to yield polymaleamides [6, 7] and to *p*-aminophenol to yield polyester-maleamides [8]. *N,N'*-Disubstituted bisisomaleimides undergo ROPA to various diamines, affording homopolymaleamides and ordered alternating copoly-maleamides [9]. Similarly, bisisomaleimide has been polymerized with dihydrazines and also with dihydrazides to produce homo- and copolyhydrazides [10, 11]. Recently, we prepared polymaleamides from *N,N'*-methane-dianilinebisisomaleimide (MBIMI) and aliphatic diamines [12]. In this note we report ROPA of MBIMI to certain aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) at room temperature.

---

\*To whom correspondence should be addressed.

## EXPERIMENTAL/MATERIALS

Reagent-grade chemicals were purified by conventional methods. 1,4-Diaminobenzene (*p*-phenylenediamine, pPD) (BDH) was purified by distillation under reduced pressure (mp 140°C) [13]. 4,4'-Diaminobiphenyl (DABP) (LOBA) was recrystallized from hot water, and the monohydrate plates obtained were dried in vacuum to afford anhydrous diamine (mp 127°C) [14]. 4,4'-Diamino-3,3'-dimethoxybiphenyl (*o*-dianisidine, oAD) (Koch-Light) was twice recrystallized from aqueous methanol (mp 137°C) [13]. 1,5-Diaminonaphthalene (DAN) (Purum, Fluka AG) was vacuum sublimed to give white crystals (mp 170°C) [13]. 2,6-Diaminoanthraquinone (DAAQ) (Fluka AG) was recrystallized from hot DMF to afford orange crystals. MBIMI was synthesized as reported previously [12].

### Model Reaction

Aminobenzene (4.4 mmol) was allowed to react with MBIMI (2 mmol) in NMP (10 mL) at room temperature with stirring for 24 h under nitrogen (Eq. 1). The clear solution obtained was poured into water, and the pale yellow solid (model compound) was filtered, washed with water, and dried. Analysis: Calculated for  $(C_{33}H_{28}N_4O_4)_n$ : C, 72.79%; H, 5.15%; N, 10.29%. Found: C, 72.95%; H, 5.14%; N, 10.35%.

### Polymerization

MBIMI (5 mmol) was dissolved in NMP in an ice-cooled, two-necked polymerization kettle equipped with nitrogen inlet-outlet, stirrer, and drying tube. An appropriate diamine (5 mmol) in NMP was transferred quickly into the kettle and the outer cooling bath was allowed to attain ambient temperature slowly. The contents were stirred for 72 h under nitrogen to complete the polymerization (Eq. 2) and then poured into water. The precipitated poly-maleamide was filtered; washed successively with dilute HCl, water, dilute NaHCO<sub>3</sub> solution, and water; and then dried at 65–70°C in vacuum.

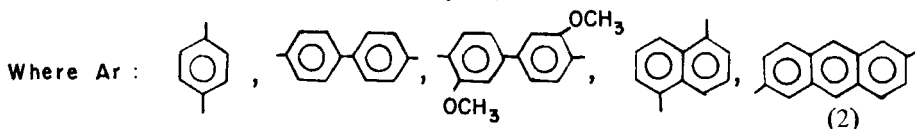
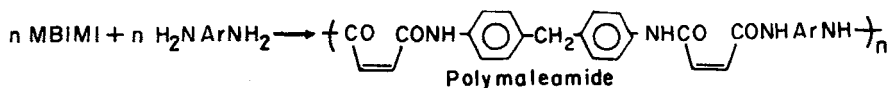
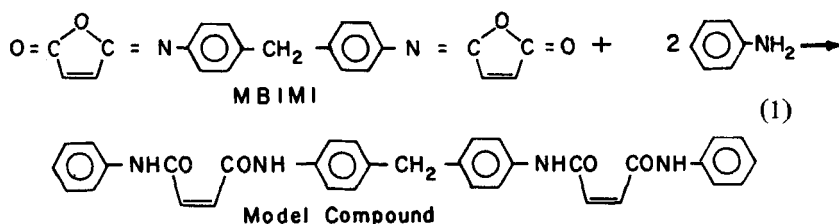
### Characterization

Elemental analysis was carried out with a Perkin-Elmer Model 240b instrument. The solubility of the polymaleamides in various solvents were recorded by adding 5 mg of the polymer to 1 mL of the solvent and allowing it to stand overnight. Inherent viscosities were measured at  $25 \pm 0.1^\circ\text{C}$  with an

Ubbelohde-type viscometer. The solutions of polymers for viscosity measurements were prepared by addition of 100.0 mL of concentrated sulfuric acid to 0.5 g of accurately weighed polymer. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer Model 598 using KBr pellets. The UV spectra were measured on concentrated sulfuric acid solutions with a Carl Zeiss UV-VIS Specord.

## RESULTS AND DISCUSSION

The synthesis of the model compound and the polymaleamides may be represented as follows:



Diamines attack at the bond between carbonyl carbon and lactonyl oxygen of MBIMI, resulting in amide and imidol groups. The latter undergoes immediate tautomerization to another amide group.

The polymaleamides are obtained in moderate to excellent yields. Their molecular compositions determined experimentally are in good agreement with the values calculated on the basis of the proposed repeat units in the respective polymers (Table 1). The polymers are freely soluble in concentrated  $\text{H}_2\text{SO}_4$  but insoluble in common organic solvents; they are soluble in amide-type solvents on heating (Table 2).

The IR spectra of MBIMI, the model compound, and the polymaleamides are presented in Fig. 1. The IR spectra of all the polymers are almost identical.

TABLE I. Ring-Opening Polyaddition of MBIMI to Various Diamines<sup>a</sup>

| Diamine | Polymer | Yield,<br>% | $\eta_{inh}^b$ ,<br>dL/g | Repeat<br>unit       | Molecular composition, % |      |       |       |      |       |
|---------|---------|-------------|--------------------------|----------------------|--------------------------|------|-------|-------|------|-------|
|         |         |             |                          |                      | Calculated               |      |       | Found |      |       |
|         |         |             |                          |                      | C                        | H    | N     | C     | H    | N     |
| pPD     | pPMBM   | 94          | 0.10                     | $C_{27}H_{22}N_4O_4$ | 69.53                    | 4.72 | 12.02 | 70.18 | 4.69 | 12.11 |
| DABP    | BPMBM   | 90          | 0.19                     | $C_{33}H_{26}N_4O_4$ | 73.06                    | 4.80 | 10.33 | 73.57 | 4.78 | 10.40 |
| oAD     | oAMBM   | 85          | 0.18                     | $C_{35}H_{30}N_4O_6$ | 69.77                    | 4.98 | 9.30  | 69.82 | 5.01 | 9.24  |
| DAN     | NMBM    | 85          | 0.13                     | $C_{31}H_{24}N_4O_4$ | 72.09                    | 4.65 | 10.85 | 71.30 | 4.63 | 10.97 |
| DAAQ    | AQMBM   | 75          | 0.09                     | $C_{35}H_{24}N_4O_6$ | 70.47                    | 4.03 | 9.40  | 71.03 | 4.06 | 9.46  |

<sup>a</sup>Polymerization was carried out at room temperature with 5 mmol of each monomer at a monomer concentration of 20 wt% in NMP.

<sup>b</sup>0.5% Solution in concentrated  $H_2SO_4$  at 25°C.

TABLE 2. Solubility of Polymaleamides in Various Solvents<sup>a</sup>

| Solvent                        | pPMBM | BPMBM | oAMBm | NMBM | AQMBM |
|--------------------------------|-------|-------|-------|------|-------|
| Concentrated sulfuric acid     | ++    | ++    | ++    | ++   | ++    |
| <i>N</i> -Methyl-2-pyrrolidone | ++    | +     | +     | +    | +     |
| <i>N,N</i> -Dimethylacetamide  | ++    | +     | +     | +    | +     |
| <i>N,N</i> -Dimethylformamide  | ++    | ±     | ±     | ±    | -     |
| Dimethylsulfoxide              | ++    | +     | +     | +    | +     |
| Formic acid                    | -     | -     | -     | -    | -     |
| <i>m</i> -Hydroxytoluene       | ±     | -     | ±     | -    | -     |
| Tetrahydrofuran                | -     | -     | -     | -    | -     |
| Ethanol                        | -     | -     | -     | -    | -     |
| Acetone                        | -     | -     | -     | -    | -     |

<sup>a</sup>++, Soluble at room temperature; +, soluble on heating; ±, partially soluble; -, insoluble.

The disappearance of the two characteristic frequencies of MBIMI at 1785 and 1670  $\text{cm}^{-1}$  (corresponding to a five-membered lactone ring and the  $\text{>C=N}$  group) with the appearance of the two new frequencies at 1600 and 3300  $\text{cm}^{-1}$ , respectively, for the amide I (overlap of C=C and C=O stretching [15, 16]) and N-H stretching indicate the establishment of amide links by ROPA of iso-imide to diamine [6-12]. The N-H stretching band is broad due to the involvement of N-H group in hydrogen bonding [17]. The C-H stretching vibration of the  $\text{CH}_2$  group between the aromatic rings appears in the region 2960-2840  $\text{cm}^{-1}$  [18]. All these polyamides show multiple bands in the region 1200-700  $\text{cm}^{-1}$  due to C-H in-plane and out-of-plane bending vibrations of the aromatic systems. The absorptions at  $\sim 1415$  and at  $\sim 670$   $\text{cm}^{-1}$  are assigned, respectively, to in-plane and out-of-plane deformations of the vinylic C-H with a *cis* configuration. The absence of absorption around 970  $\text{cm}^{-1}$  for the corresponding *trans* configuration also corroborates this [18, 19]. Thus the *cis* geometry of MBIMI is retained in ROPA to diamines under mild conditions.

In the electronic spectra, the red shifts in cases of pPMBM (370 nm) and BPMBM (373 nm) compared to the model compound (368 nm) are very small

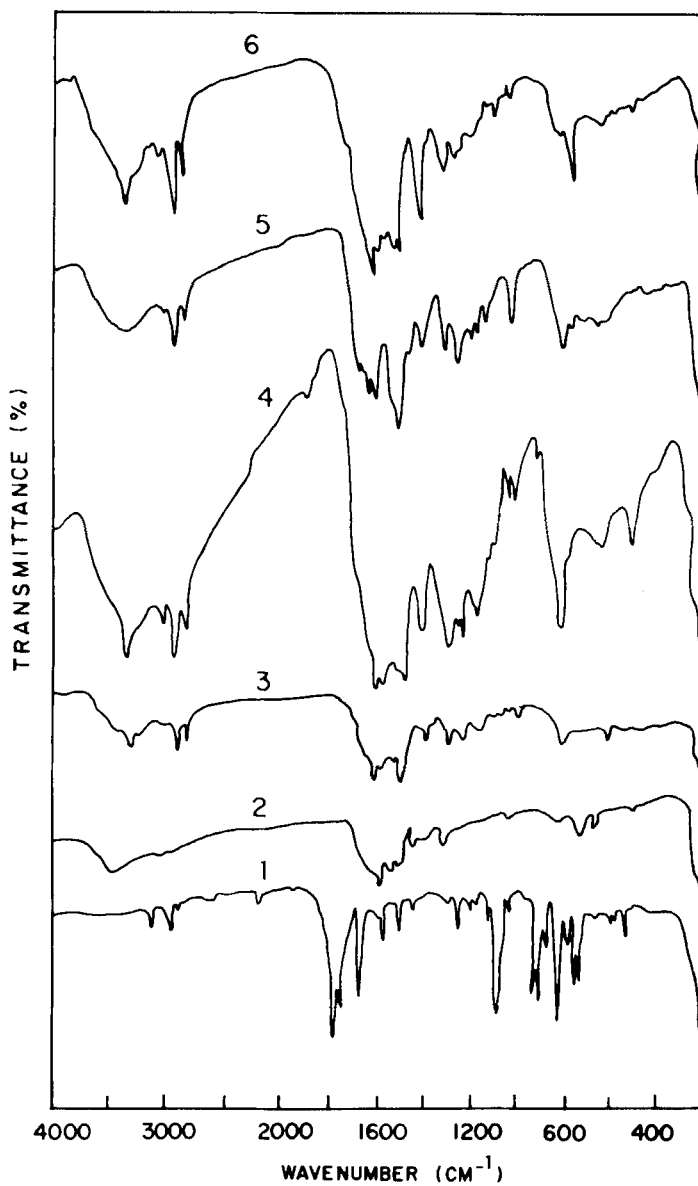


FIG. 1. IR spectra of (1) MBIMI, (2) model compound, (3) pPMBM, (4) BPMBM, (5) oAMBm, and (6) NMBM.

TABLE 3. UV-VIS (concentrated H<sub>2</sub>SO<sub>4</sub>) Absorption Spectral Data on Polymaleamides

| Polymaleamide  | UV-VIS<br>(wavelength, nm) |
|----------------|----------------------------|
| Model compound | 205, 288, 368              |
| pPMBM          | 229, 272, 370              |
| BPMBM          | 204, 245, 373              |
| oAMBM          | 207, 240, 373              |
| NMBM           | — 220, 371                 |
| AQMBM          | 220, 257, 347              |

(Table 3) even though there is an extension of conjunction through benzene rings [7] (corresponding  $\lambda_{\max}$  values are not available under the conditions of study). In the case of oAMBM, both mesomeric and possible steric effects of the methoxyl group operate and nullify each other and, hence, the absorption occurs at the same wavelength as in BPMBM. The absorption due to the  $\pi^* \leftarrow \pi$  transition in BPMBM (245 nm) undergoes a blue shift in NMBM (220 nm) due to difference in the extent of delocalization over the number of carbon atoms. The electron-withdrawing nature of the carbonyl groups in AQMBM causes a blue shift to 347 nm.

## REFERENCES

- [1] Y. Iwakura, K. Hayashi, M. Shimizu, and T. Watanabe, *Makromol. Chem.*, **95**, 228 (1966).
- [2] M. Ueda, M. Takashashi, and Y. Imai, *Ibid.*, **179**, 2783 (1978).
- [3] Y. Imai, H. Hirukawa, K. Okuyama, and M. Ueda, *Ibid.*, **180**, 25 (1979); *Chem. Abstr.*, **90**, 122102p (1979).
- [4] M. Ueda, M. Yabuuchi, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 2641 (1977).
- [5] M. Ueda, K. Kino, and Y. Imai, *Ibid.*, **13**, 659 (1975).
- [6] Y. L. Fan, *Macromolecules*, **9**, 7 (1976).
- [7] R. Nagarathinam and S. Viswanathan, *Polym. Bull.*, **16**, 147 (1986).
- [8] R. Nagarathinam, N. Rajeswari, S. Viswanathan, and H. Kothandaraman, *Ibid.*, **14**, 287 (1985).



- [9] Y. Imai, M. Ueda, and S. Kanno, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1691 (1975).
- [10] M. Ueda, S. Kanno, and Y. Imai, *Ibid.*, **13**, 2735 (1975).
- [11] Y. L. Fan, *Macromolecules*, **10**, 469 (1977).
- [12] R. Nagarathinam and S. Viswanathan, *Polym. J.*, **18**, 865 (1986).
- [13] R. C. Weast (ed.), *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Boca Raton, Florida, 1987.
- [14] F. G. Mann and B. C. Saunders, *Practical Organic Chemistry*, Longman, London, 1974, p. 216.
- [15] M. G. Gherasim and I. Zugravescu, *Eur. Polym. J.*, **14**, 985 (1978).
- [16] O. E. Edwards and T. Singh, *Can. J. Chem.*, **32**, 683 (1954).
- [17] J. E. Riordan and H. S. Blair, *Polymer*, **20**, 196 (1979).
- [18] A. D. Cross, *Introduction to Practical Infrared Spectroscopy*, 2nd ed., Butterworths, London, 1964.
- [19] I. K. Varma and Veena, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 163 (1979).

Received December 5, 1987

Revision received February 18, 1988