

NOTES

Synthesis and Characterization of Newer Homopolymaleamides and Copolymaleamides from *N,N'*-Methanedianiline-bisomaleimide and Aliphatic Diamines

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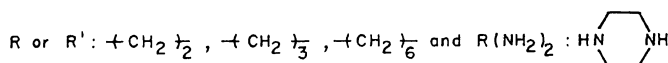
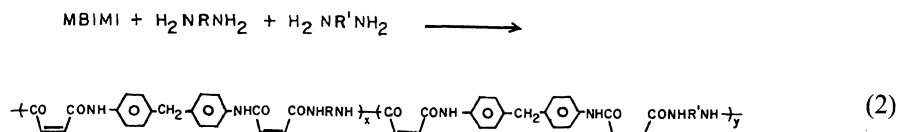
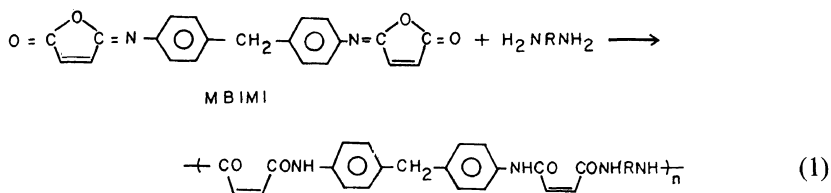
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Attempts have been made to prepare polyamides with carbon-alkenyl pendant groups, by reaction between diamines and *N*-malonic diesters of uracil and theophylline in solution phase.¹ In addition, diamines react with 2,2'-disubstituted bis(3-buten-4-olide)s² and 4,4'-disubstituted bisazalactones³ through ring-opening polyaddition (designated as ROPA) yielding polyamides with unsaturated unit in the backbone. Based on the reaction between isoimides and nucleophiles, first advocated by van der Meulen,⁴ biso-

imides have been prepared and allowed to undergo ROPA to various diamines,^{5,6} dihydrazines and dihydrazides^{7,8} and *p*-aminophenol.⁹ The aim of this paper is to polymerize a new likely candidate of this series, namely, *N,N'*-methanedianilinebisomaleimide (MBIMI) with some aliphatic diamines in *N*-methyl-2-pyrrolidone (NMP) at room temperature to produce homopolymaleamides and copolymaleamides. The ROPA reaction scheme is as shown in eq 1 and 2.



A model ROPA reaction was carried out which could explain the main features of polymers of this kind. The structure-property relationships of the polymaleamides are discussed.

EXPERIMENTAL

Materials

Maleic anhydride and 4,4'-diaminodiphenylmethane (DADPM) were purified by recrystallization, respectively, from trichloromethane and benzene. Aminobenzene was purified by distillation. The crystalline of piperazine (PPZ) was purified by recrystallization from ethanol to give hygroscopic plates preserved in vacuum. 1,6-Diaminohexane (DAH) was distilled in vacuum to give white crystals. 1,2-Diaminomethane (DAE), 1,3-diaminopropane (DAP), and dicyclohexylcarbodiimide (DCC) were all guaranteed grade reagents and used without further purification. Dichloromethane for UV spectrophotometry was purified by the following procedure.¹⁰ Commercial dichloromethane was washed with concentrated sulfuric acid, dilute sodium hydroxide and distilled water. The washed material was left standing overnight over calcium chloride and fractionally distilled; bp 40–41°C. Ether and NMP were purified by standard procedures.

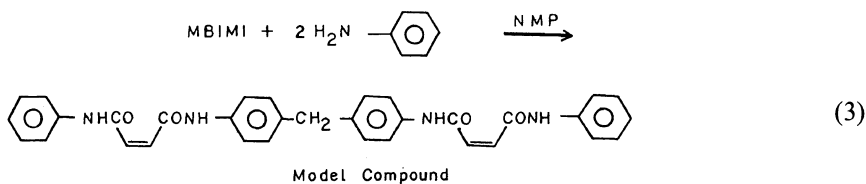
MBIMI

To an ice-cold solution of maleic anhydride

(0.2 mol) in dry ether, DADPM (0.1 mol) in dry ether was added with shaking and allowed to stand overnight.¹¹ The resulting compound, methanedianilinebismaleamic acid, was purified¹² by dissolution in dilute sodium hydrogen carbonate solution and reprecipitation with hydrochloric acid. The solid was washed with water and dried; mp 195°C. This methane dianilinebismaleamic acid (0.05 mol) was treated with DCC (0.1 mol) in dichloromethane and an ether mixture.¹³ The precipitated dicyclohexylurea was filtered off and the product MBIMI was recovered from the filtrate by removing the solvent under reduced pressure. MBIMI, after recrystallization from benzene-ether, melted at 155°C. MBIMI in dichloromethane has λ_{\max} at 353 and 226 nm. MBIMI was confirmed by elemental analysis. *Anal.* Calcd: C, 70.39%; H, 3.91%; N, 7.82%. Found: C, 70.55%; H, 3.90%; N, 7.79%.

Model ROPA Reaction

A mixture of MBIMI (0.002 mol), aminobenzene (0.004 mol) and NMP (10 ml) was stirred for 24 h in a flask under nitrogen atmosphere. The clear solution was then diluted to 250 ml with water and a pale yellow solid thus obtained (Model compound, eq 3) was filtered, washed with water and dried. *Anal.* Calcd: C, 72.79%; H, 5.15%; N, 10.29%. Found: C, 72.95%; H, 5.14%; N, 10.35%.



Polymerization

Homo-polymerization was carried out in a two-necked kettle (with a side inlet for

nitrogen) equipped with a stirrer and a drying tube. MBIMI (0.002 mol) was placed in the kettle and dissolved in NMP by stirring

and the kettle was cooled in an ice-bath. The appropriate diamine (0.002 mol) in NMP was transferred quickly into the kettle and the outer cooling-bath was allowed to attain ambient temperature on its own accord. The stirring (3500 rpm) was continued for 24 h under a blanket of nitrogen to complete the polymerization. The clear solution was added dropwise to water (1000 ml) with stirring to precipitate the polymaleamide. The product was collected by filtration, washed with water and air-dried on a filter. Drying was completed at 65°C over P₂O₅ under high vacuum. Employing similar conditions, copolymaleamides were prepared by ROPA of MBIMI (0.002 mol) to two different diamines (0.001 mol each) in NMP.

Characterization

Elemental analysis of MBIMI, the model compound, and the polymers were carried out in a Perkin-Elmer 240 B analyzer. Absorption spectral data in the infrared region were recorded on a Perkin-Elmer 598 IR spectrophotometer. Thermal behavior of the polymers was followed using a du Pont 1090 thermogravimetric (TG) analyzer in a nitrogen atmosphere at a heating rate of 20°C min⁻¹ with a sample size 1–10 mg.

RESULTS AND DISCUSSION

Maleic anhydride undergoes a ring-opening reaction with DADPM to form methanedianilinebismaleamic acid, which is then cyclodehydrated by DCC to MBIMI. The fact that only an isoimide but not imide¹⁴ ring is formed is clear from the infrared absorptions of MBIMI at 1785 and 1670 cm⁻¹. On polymerization with diamines, MBIMI undergoes ROPA to produce amide and imidol groups,

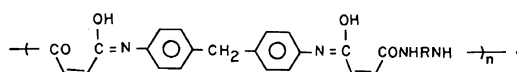


Table I. Polymerization^a of MBIMI with various diamines

Diamine(s)	Polymer	Yield	η_{inh}^b
		%	dl g ⁻¹
DAE	EMBM	92	0.12
DAP	PMBM	95	0.20
DAH	HMBM	99	0.27
PPZ	PZMBM	91	0.15
DAE+DAP	EPMBM	85	0.30
DAE+DAH	EHMBM	87	0.14
DAP+DAH	PHMBM	95	1.03

^a Polymerization was carried out with 0.002 mol of each monomer at a monomer concentration of 20 wt% in NMP.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 25°C.

Table II. Solubility of polymaleamides in various solvents^a

Solvent	Polymer	EMBM	PMBM	HMBM	PZMBM	EPMBM	EHMBM	PHMBM
Concentrated sulfuric acid		++	++	++	++	++	++	++
<i>N</i> -Methyl-2-pyrrolidone		s	s	s	+	s	s	s
Dimethylacetamide		s	s	s	+	s	s	s
Dimethyl sulfoxide		s	s	s	+	s	—	—
Dimethylformamide		—	—	—	—	—	—	—
Formic acid		—	—	—	—	—	—	—
<i>m</i> -Cresol		—	—	—	++	—	±	s
Tetrahydrofuran		—	—	—	—	—	—	—
Ethanol		—	—	—	—	—	—	—
Acetone		—	—	—	—	—	—	—

^a ++, soluble at room temperature; +, soluble on heating; ±, partially soluble; —, insoluble; s, swells.

The imidol immediately tautomerizes to the amide form. Table I summarizes the results of the solution polymerization of MBIMI with diamines. The polymaleamides are obtained in moderate to excellent yields. The value of inherent viscosity (η_{inh}), measured using a 0.5 g dl^{-1} solution in concentrated sulfuric acid (AnalaR grade) in a modified Ubbelohde viscometer at $25 \pm 0.1^\circ\text{C}$ having a solvent flow time exceeding 100s, ranges from 0.12 to 1.03.

The compositions of the polymaleamides agree quite well with those calculated on the basis of proposed repeat units for these polymers. The values of solubility of the polymaleamides in various solvents are qualitatively recorded and given in Table II. These polymers are soluble in concentrated sulfuric acid but not in common organic solvents such as tetrahydrofuran, ethanol and acetone. It is to be pointed out that these polymers undergo swelling in amide type solvents. The

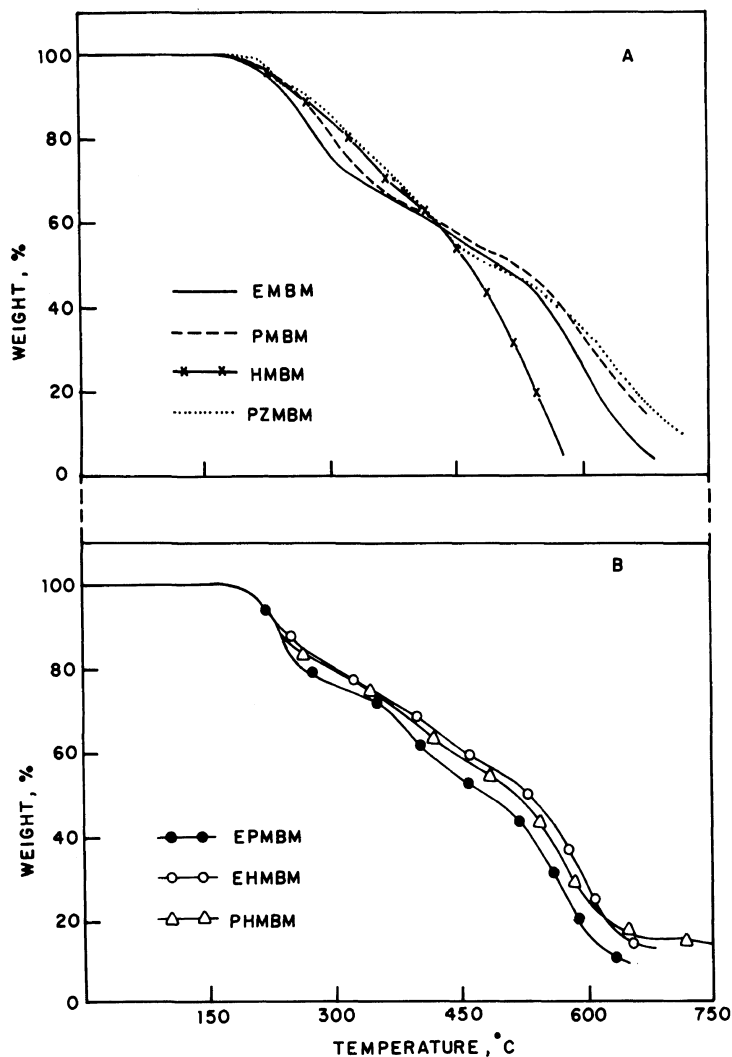


Figure 1. Thermogravimetric curves of polymaleamides in nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$.

absence of hydrogen on nitrogen (from PPZ) of the amide unit, established by the ROPA of MBIMI to PPZ (a secondary amine), results in a decrease in the extent of hydrogen bonding in PZMBM compared to other polymaleamides studied, and hence, the solubility of PZMBM in the solvents.

Structures of the polymaleamides prepared are elucidated primarily by infrared spectra. On polymerization, the two characteristic frequencies (1785 and 1670 cm^{-1}) disappear, indicating scission of the isoimide ring, while two new peaks make their appearance one at 1600 cm^{-1} (amide I assigned to overlapped stretching of $\text{C}=\text{C}$ and $\text{C}=\text{O}$) and another at about 3400 cm^{-1} (NH stretching) confirming the formation of amide units.^{5,9,15} These results indicate that the ROPA has proceeded exactly according to the scheme shown in eq 1 and 2.

Figure 1 shows the thermal characteristics of these polymers observed by thermogravimetry. All these polymaleamides began to decompose at $190\text{--}215^\circ\text{C}$. PZMBM (having cyclic diamine units) prepared from MBIMI and piperazine was found to have a higher thermal stability than the others.

In conclusion, the above results indicate the ROPA under the condition used to result in polyamides retaining *cis*-configuration about $\text{C}=\text{C}$ as is evident from the IR spectra.

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