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# *Polyaddition*

## Polymaleamidehydrazides
### Synthesis by ring-opening polyaddition of N,N'-bisisomaleimide with diamines

**R. Nagarathinam and S. Viswanathan**

Department of Polymer Science, University of Madras, Guindy Campus, Madras-600 025, India

### Summary

Some polymaleamidehydrazides were synthesized by the ring-opening polyaddition reaction between N,N'-bisisomaleimide and diamines(piperazine, phenylenediamines, 4,4'-diaminodiphenyl, 1,5-diaminonaphthalene, and 2,6-diaminoanthraquinone) in N-methyl-2-pyrrolidone (NMP) containing LiCl Characterization of the polymers was carried out by elemental analysis, solibility in various solvents, IR, UV-VIS, PMR spectra, TG and DSC as well as by inherent viscosity measurements. These polymers began to decompose around 250°C.

### Introduction

A number of reports are available on the synthesis of polyamides by ring-opening polyaddition(ROPA) of reactive heterocyclic compounds to diamines(1-7). In this paper we present the synthesis of polymaleamide-hydrazides(PMAHs) by ROPA of N,N'-bisisomaleimide(BIMI) to diamines. These polymers, with a cis C=C, are a new class of homo-and ordered alternating copolymers, which are unable to be synthesized by other preparative methods. They have potential cross-linking groups so that they can be cured to products, with no voids, having high thermal and chemical resistivities(8).

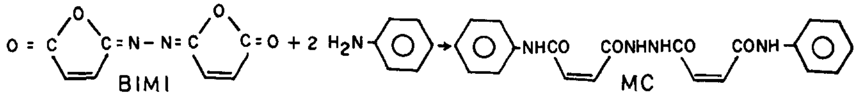
### Experimental

Piperazine(PPZ) and 4,4'-diaminobiphenyl(DABP) recrystallized respectively from ethanol and water were preserved in vacuum. o-Phenylenediamine(oPD) and m-phenylenediamine dihydrochloride(mPD) were recrystallized from water. p-Phenylenediamine(pPD) and 1,5-diaminonaphthalene(DAN) were purified respectively by distillation and sublimation in vacuum. 2,6-Diaminoanthraquinone(DAAQ) in hot dimethylformamide(DMF) was precipitated as red-orange diamine by the addition of water. Tetrahydrofuran(THF), dimethylsulfoxide(DMSO), dimethylacetamide(DMA), NMP and DMF were purified by employing standard procedures. BIMI was prepared as reported(1).

Model Compound(MC)

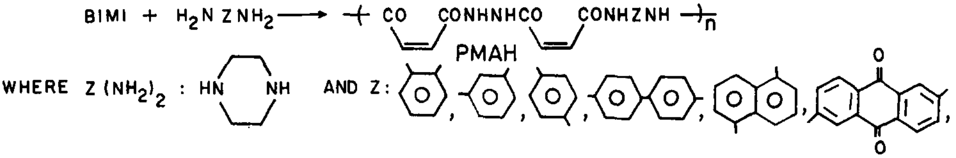
BIMI(0.96g,0.005mol), aniline(1.203g,0.011mol), and NMP(10mL) were stirred at room temperature for 24h under nitrogen and poured into water. This solid, model compound, was washed with water and dried. Anal.Calc. for $C_{20}H_{18}N_4O_4$ : C,63.49%; H,4.76%; N,14.81%.

Found: C,63.39%; H,4.78%; N,14.90%.



## Polymerization

Into a 20mL test-tube shaped, two-necked polymerization kettle with a side nitrogen inlet, fitted with a stirrer and a drying tube, was placed the appropriate diamine(0.005mol)and dissolved in the solvent by stirring. The kettle was cooled in an ice-water bath and BIMI(0.005mol)was added to it. The stirring(3500rpm) was continued for 72h at room temperature to complete the polymerization. The reaction mixture was poured into water and the precipitated polymer was washed and dried in vacuum at 65-70°C.



## Characterization

Elemental analysis was carried out in a Perkin-Elmer 240 B analyzer. Solubility of polymers in various solvents(0.005g/mL) were determined. IR(KBr) and UV-VIS(concentrated sulfuric acid) spectra were recorded respectively on Perkin-Elmer 598 IR Spectrophotometer and Carl Zeiss UV-VIS Specord. TG in nitrogen at a heating rate of 50°C/min and DSC in argon at 10°C/min of the polymers were recorded on TGS-2 and DSC-2 Perkin-Elmer analyzers. Inherent viscosities($\eta$inh) were measured at a concentration of 0.5g/dL in concentrated sulfuric acid using an Ubbelohde-type viscometer thermostated at 25±0.1°C.

## Results and Discussion

On reaction with an amine group the isoimide ring of BIMI opens up to produce an amide and imidol; the latter immediately tautomerizes to another amide group. The polymerization was conducted at room temperature to avoid the conversion of isoimide into imide(9).

BIMI was polymerized with DABP under various conditions and the results are summarized in Table 1. NMP containing LiCl(4%W/V) was found to be the most preferable polymerization solvent; LiCl influences the dissolution of the polymer more than that in NMP alone. Here, the positively charged solvent-Li species solvates the negatively charged polymer-chloride moiety and it is this collective, neutral entity which is soluble in the solvent(10). A change in the concentration from 5 to 20 weight % showed regular increase in the $\eta$inh. The stirring speed and $\eta$ inh

Table 1. Polymerization of N,N'-Bisisomaleimide with 4,4'-Diaminobiphenyl

| Solvent | Monomer concentration, weight % | Stirring speed, rpm | Reaction time, h | $\eta$inh, dL/g |
|---|---|---|---|---|
| DMSO | 5 | 1200 | 24 | 0.12 |
| DMSO | 10 | 1200 | 24 | 0.13 |
| DMSO | 15 | 1200 | 24 | 0.18 |
| DMSO | 15 | 3500 | 24 | 0.20 |
| DMSO | 20 | 1200 | 24 | 0.24 |
| DMSO | 20 | 3500 | 72 | 0.30 |
| DMF | 20 | 3500 | 72 | 0.15 |
| DMF+LiCl | 20 | 3500 | 72 | 0.18 |
| NMP | 15 | 1200 | 24 | 0.28 |
| NMP | 15 | 3500 | 24 | 0.30 |
| NMP+LiCl | 15 | 3500 | 24 | 0.33 |
| NMP+LiCl | 20 | 3500 | 24 | 0.35 |
| NMP+LiCl | 20 | 3500 | 72 | 0.45 |

Table 2. Polymerization of N,N'-Bisisomaleimide with Various Diamines

| Diamine | Polymer | Yield (%) | inh (dL/g) | Elemental Analysis Repeat Unit | Calc. (%) C | H | N | Found(%) C | H | N |
|---|---|---|---|---|---|---|---|---|---|---|
| PPZ | PZBM | 90 | 0.11 | $C_{12}H_{14}N_4O_4$ | 51.80 | 5.04 | 20.14 | 52.35 | 5.01 | 19.97 |
| oPD | oPBM | 72 | 0.19 | $C_{14}H_{12}N_4O_4$ | 56.00 | 4.00 | 18.67 | 55.80 | 3.98 | 18.72 |
| mPD | mPBM | 95 | 0.17 | $C_{14}H_{12}N_4O_4$ | 56.00 | 4.00 | 18.67 | 56.05 | 4.01 | 18.55 |
| pPD | pPBM | 97 | 0.17 | $C_{14}H_{12}N_4O_4$ | 56.00 | 4.00 | 18.67 | 55.95 | 4.04 | 18.80 |
| DABP | BPBM | 98 | 0.45 | $C_{20}H_{16}N_4O_4$ | 63.83 | 4.26 | 14.89 | 64.07 | 4.29 | 15.09 |
| DAN | NBM | 86 | 0.09 | $C_{18}H_{14}N_4O_4$ | 61.71 | 4.00 | 16.00 | 62.06 | 3.93 | 16.04 |
| DAAQ | AQBM | 75 | 0.12 | $C_{22}H_{14}N_4O_6$ | 61.40 | 3.25 | 13.02 | 61.84 | 3.27 | 12.94 |

are in the same trend; it is to note that in the rpm range studied no thermal effect was observed and hence, 3500rpm employed. There was no significant change in $\eta$inh after the reaction time of 72h.

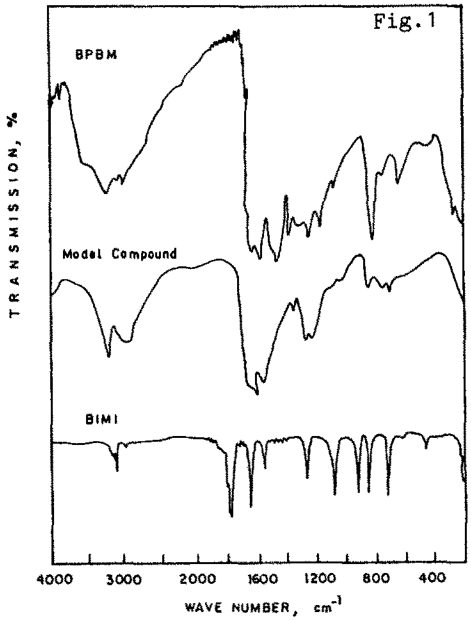
The yield and $\eta$inh data on the ROPA of BIMI to various diamines(at a monomer concentration of 20 weight % in NMP+LiCl) and the % compositions of the resulted PMAHs are given in Table 2. The PMAHs were obtained in moderate to excellent yields. The results of elemental analysis agree with the values calculated for the proposed repeat unit in the respective PMAH.

The polymers are insoluble in common organic solvents like THF,EtOH, and acetone(Table 3). They are freely soluble only in concentrated sulfuric acid but undergo slow decomposition and the % decrease in the $\eta$inh after 24h are: oPBM,16; mPBM,29; pPBM,35; BPBM,15; AQBM,9.

The establishment of the amide unit is characterized primarily by IR spectra(Fig.1 and Table 4). The disappearance of the two characteristic frequencies, 1790 and 1680 cm$^{-1}$ , of BIMI and the appearance of two new bands for the polymers at 3400-3200 cm$^{-1}$ (N-H stretching) and at 1600 cm$^{-1}$ (overlap of C=O and C=C stretchings(11)), justify the formation of amide units by ROPA. The N-H stretching band is broad due to hydrogen bonding(12). The additional amide I band is due to the CONHNHCO unit(13). The absorption at ~680 cm$^{-1}$ has been assigned to the C-H out-of-plane deformation about cis C=C; the absence of a band at 980-960cm$^{-1}$ due to trans isomeric form corroborates this view(1). The PMR signals for pPBM in $CD_3SOCD_3$ in the $\delta$(ppm) scale are; 6.4(4H), 7.6(4H), 10.4(2H), and 11.2(2H). The 6.4 $\delta$ signal is assigned to four protons attached to C=C with a cis configuration; 7.6$\delta$, four aromatic protons; 10.4$\delta$, two amide protons; 11.2$\delta$, two hydrazide protons(14). Thus the retention of the cis geometry of BIMI is possible only through ROPA to diamines under mild conditions.

Table 3. Solubility of Polymaleamidehydrazides(++, soluble at room temparature; +, soluble on heating; ±,partially soluble; -, insoluble)

| Solvent / Polymer | $H_2SO_4$ | NMP | DMSO | DMA | DMF | HCOOH | m-Cresol | THF | EtOH | $Me_2CO$ |
|---|---|---|---|---|---|---|---|---|---|---|
| PZBM | ++ | ++ | + | ++ | ± | + | ± | - | - | - |
| oPBM | ++ | + | + | + | + | ± | ± | - | - | - |
| mPBM | ++ | + | + | + | + | - | ± | - | - | - |
| pPBM | ++ | + | + | + | + | - | - | - | - | - |
| BPBM | ++ | + | ± | + | ± | - | - | - | - | - |
| NBM | ++ | + | + | + | + | - | - | - | - | - |
| AQBM | ++ | + | + | + | + | - | ± | - | - | - |



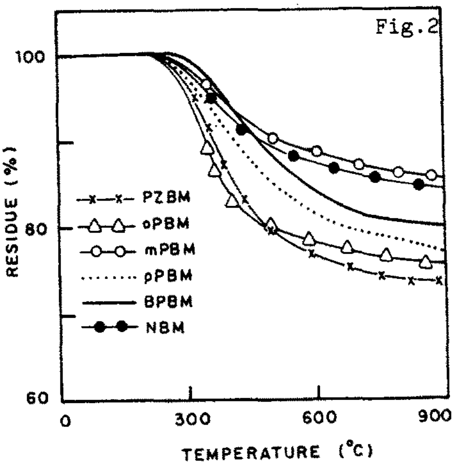


Fig.1. Infrared absorption spectra

Fig.2. TG curves of polymers

Table 4. IR(KBr) and UV-VIS($H_2SO_4$) Absorption Spectral Data

| Polymer | IR (Wave number, cm⁻¹) | | | | | | | UV-VIS |
|---|---|---|---|---|---|---|---|---|
| | N-H stretch | amide I | | amide II | amide III | | C-H of $HC=CH$ | Wavelength, nm |
| MC | 3320,3250 | - | 1600 | 1550 | 1340 | - | 695 | 197, 233, 320 |
| PZBM | - | - | - | - | - | - | - | 196, 220, 250 |
| oPBM | 3250 | 1670 | 1610 | 1520 | 1320,1200 | | 680 | 197, 234, 340 |
| mPBM | 3250 | 1660 | 1600 | 1540 | 1305,1220 | | 685 | 198, 234, 353 |
| pPBM | 3300 | 1670 | 1625 | 1530 | 1340,1280 | | 680 | 196, 234, 373 |
| BPBM | 3240 | 1655 | 1600 | 1530 | 1320,1250 | | 670 | 200, 258, 415 |
| NBM | 3220 | 1660 | 1600 | 1540 | 1340,1280 | | - | - 220, 322 |
| AQBM | 3350 | 1665 | 1630 | 1570 | 1350,1300 | | 665 | 204, 255, 327 |

Table 5. Thermal Analysis Data on Polymaleamidehydrazides

| Polymer | TG | | | | DSC |
|---|---|---|---|---|---|
| | Initial decomposition temperature, °C | Rapid weight-loss temperature, °C | ipdt T*, °C | Oxygen Index | Transition temperature, °C |
| PZBM | 235 | 400 | 432 | 0.47 | - |
| oPBM | 235 | 350 | 398 | 0.48 | 237,347 |
| mPBM | 245 | 460 | 467 | 0.52 | 187,202,247,431, 462 |
| pPBM | 250 | 440 | 463 | 0.49 | - |
| BPBM | 265 | 465 | 496 | 0.50 | 167,262 |
| NBM | 245 | 375 | 474 | 0.51 | - |
| AQBM | 155 | 240 | 364 | 0.35 | - |

T* integral procedural decomposition temperature(1).

In the UV-VIS spectra(Table 4) compared to MC, there is a blue shift for PZBM since there is no extension of conjugation in the polymer chain. The λmax for oPBM, mPBM, pPBM, and BPBM has undergone a red shift by conjugation extension. The area of delocalization of electrons in NBM is smaller than that in BPBM and hence, a blue shift; the blue shift for AQBM is due to electron-withdrawing carbonyl groups.

Thermal analysis data on the PMAHs are given in Fig.2 and Table 5. Of the polymers studied, BPBM(with extension of conjugation over two rings) is the most stable one. NBM is less stable than BPBM($\lambda$max values). The CO groups in AQBM reduce its thermal stability. The high char yields obtained(Fig.2) at 700°C in cases of oPBM, mPBM, and pPBM indicate their good stability(15,16). Thermal stability of PZBM is lower than that of pPBM due to the absence of aromatic system, and there is no hydrogen available on the amide N for hydrogen bonding. The oxygen index values of the polymers point out their flame retarding nature(17). In spite of the low $\eta$inh values, these polymers are found to have low weight-loss in the temperature range studied: although the aliphatic diacid segment of these polymers may undergo thermal decomposition(18), the hydrazide unit may cyclise to oxadiazole(19,20). In cases of oPBM, mPBM and BPBM the intitial decomposition temperature and the rapid weight-loss temperature correspond to the values of endothermic transition and exothermic transition, respectively(Table 5).

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