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POLY(MALEIMIDE-AMINE)S AND POLY(MALEIMIDE-AMINE)ETHERS

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Abstract—Syntheses and properties of poly(maleimide-amine)s and poly(maleimide-amine)ethers from bischloromaleimide are reported. Three model compounds have been prepared and the polymers have been characterized spectrally by comparison with the model compounds. The polymers possess inherent viscosities in the 0.3 to 0.5 dl/g range.

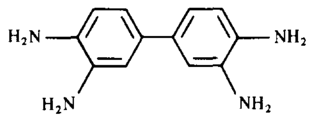
INTRODUCTION

The reactions of dichloromaleimides with amines, phenols, alcohols and thiols have received much attention [1] but the preparation of poly(maleimide-amine)s [2] is less documented. These polymers have always been prepared by reacting bischloromaleimides with di- and tetramines, aminophenols etc. with triethylamine as acid acceptor. In principle, transimidation by primary amines and quarternerization by tertiary amines used in the polymerization, are possible reactions in this method. According to published reports, transimidation does not occur for aromatic amines [3] and the replacement of chlorine is a faster reaction; also the triamine does not form quarternary salt [4] with the dichloromaleimide used during polymerization [4].

We now report the syntheses and characterization of several poly(amide-amines)s and poly(amide-amine) ethers from dichloromaleimides. Spectral data, elemental analysis viscosity values and thermal studies have been used for characterization.

EXPERIMENTAL

p-Aminophenol (BDH) and benzidine (SISCO, INDIA) were recrystallized before use. *p*-Phenylenediamine (BDH)



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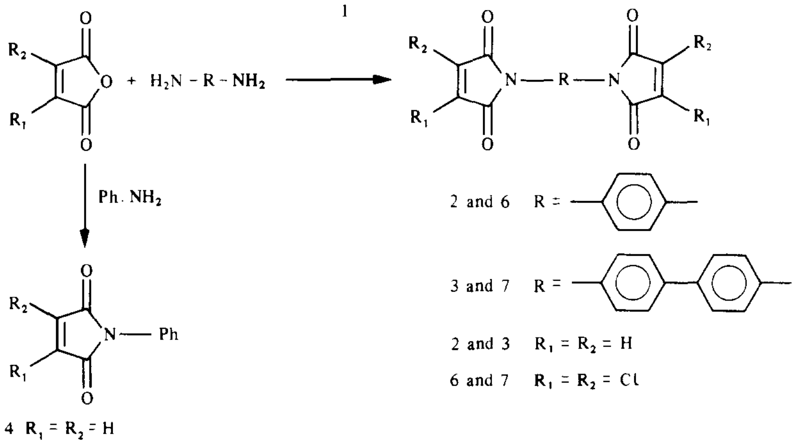
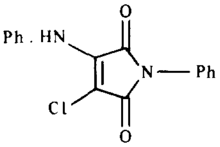
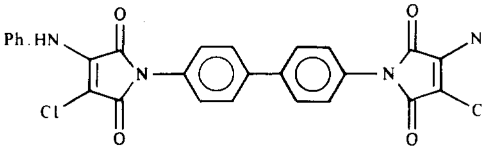


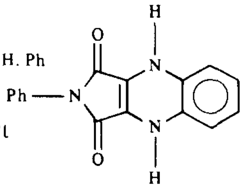
4 $R_1 = R_2 = H$
5 $R_1 = R_2 = Cl$



MC - 1



MC - 2



MC - 3

was distilled in vacuum and maleic anhydride (BDH) was resublimed. Thionyl chloride was treated with quinoline and distilled before use. Pyridine and dimethyl sulphoxide (DMSO), dimethylformamide (DMF), chloroform and methanol were commercial grade and were purified by distillation. Intrinsic viscosities were measured in a Ubbelohde suspended level viscometer, in DMSO at 30°C at a concentrations of 0.1 g/dl. The i.r. spectra were recorded on a PE-257 Spectrometer. ^{1}H-NMR were recorded on a XL-100 Varian instrument in $CDCl_3$ with TMS as internal standard.

3,3′-Diaminobenzidine (**1**), *p*-phenylenebis(maleimide) (**2**), 4,4′-biphenylbis(maleimide) (**3**), *N*-phenylmaleimide (**4**) and dichloro-*N*-phenylmaleimide (**5**), were obtained by published methods [5, 6] and were purified by recrystallization.

p-Phenylene-bis(dichloromaleimide) (*6*)

To a solution of **2** (1.34 g, 0.005 mol) in dry thionyl chloride (20 ml), pyridine (1.6 g, 0.02 mol) was added at 0°C, and stirred for 24 hr at room temperature. It was then refluxed for 2 hr. Thionyl chloride and pyridine were removed under vacuum and the resulting white solid was recrystallized from chloroform–methanol to give 1.01 g (40%) of title compound. m.p. 242° (dec.). i.r. (KBr) 1730, 1600, 1385 and 830 cm^{-1}. Analysis: found C = 41.64, H = 0.91 and N = 6.8. $C_{14}H_4N_2O_4Cl_4$ requires C = 41.58, H = 0.99 and N = 6.9%.

4,4′-Biphenyl-bis(dichloromaleimide) (*7*)

This was prepared from **3** (1.72 g, 0.005 mol) thionyl chloride (20 ml) and pyridine (1.66 g, 0.02 mol) as in the case of compound **6**. Yield 1.21 g (43%) m.p. 273° (dec.) i.r. (KBr) 1720, 1595, 1380 and 850 cm^{-1}. Analysis: found C = 50.11, H = 1.65 and N = 5.95. $C_{20}H_8N_2O_4Cl_4$ requires C = 5.00, H = 1.6 and N = 5.8%.

MODEL REACTION

2-Phenylamino-3-chloro-N-phenylmaleimide (MC-1)

To a solution of **5** (2.41 g, 0.01 mol) in DMSO (15 ml) was added aniline (1.3 g, 0.015 mol) with stirring under N_2, at room temperature. After 3 hr it was poured into water; the solid was filtered off, washed well with water, rectified spirit and water and dried. It was then recrystallized from dry ethanol. Yield 2 g (60%). m.p. 290° (dec.). i.r. (KBr): 3300 (NH), 1720 (>=O), 1655 (conjugation), 1595 (C=C) 1380 (t-Nitrogen) and 880 cm^{-1} (C–Cl). Analysis: found C = 64.41, H = 3.63, N = 9.39 $C_{16}H_{11}N_2O_2Cl$ requires C = 64.43, H = 3.69 and N = 9.40%.

NN′-bis(2-phenylamino-3-chloromaleimido)-4,4′-biphenyl (MC-2)

This was prepared in the same manner as MC-1 starting from **7** (2.43 g, 0.005 mol) and purified by recrystallization from dry ethanol. Yield 1.9 g (65%) m.p. 320°C (dec.). i.r. (KBr): 3320, 1730, 1655, 1590, 1520, 1380 and 875 cm^{-1} Analysis: found C = 64.8, H = 3.45, N = 9.5 $C_{32}H_{20}N_4O_4Cl_2$ requires C = 64.65, H = 3.37 and N = 9.43%.

N-Phenylmaleimide and o-phenylenediamine (MC-3)

MC-3 was prepared from *o*-phenylenediamine (1.08 g, 0.01 mol) and **5** (2.41 g, 0.01 mol) as a colourless solid 1.4 g (:2%) in the same manner as MC-1. It was recrystallized from dry DMF–methanol (m.p. 303) (dec.). i.r. (KBr): 3330, 1730, 1650, 1590, 1320 and 870 cm^{-1}. Analysis: found C = 69.30, H = 3.92, N = 15.13 $C_{16}H_{11}N_3O_2$ requires C = 69.31, H = 3.97, N = 15.16%.

POLYMERIZATION

The polymerization was effected by extending the method used for model compounds. Three typical cases are given.

Poly(maleimide-amine)PMA-1

To a solution of **6** (1.25 g, 0.003 mol) in DMSO (10 ml) was added triethylamine (0.6 g, 0.006 mol) followed by *p*-phenylenediamine (0.324 g, 0.003 mol) in DMSO (10 ml). The mixture was stirred at room temperature for 6 hr and poured into water. The solid was filtered off, washed well with water and methanol and then dried at 100°C in vacuum. Yield 0.821 g (65%) recrystallized from DMF–methanol (1:1) mixture, m.p. >360°. i.r. (KBr): 3310, 1510 (NH), 1720 (>=O) 1660 (conjugation), 1595 (–C=C–) 1375 (t-nitrogen) and 880 cm^{-1} (C–Cl). Analysis: found C = 54.51, H = 2.7 and N = 12.71 $(C_{20}H_{10}N_4O_4Cl_2)_n$: requires C = 54.55, H = 2.73 and N = 12.73%.

Poly(maleimide-amine)PMA-5

The polymerization was carried out as before from **6** (1.22 g, 0.003 mol) and 3,3′-diaminobenzidine (**1**) (0.64 g, 0.003 mol). Yield 1.3 g, (52%). It was recrystallized from hot DMF–methanol (1:1) m.p. >360°. i.r. (KBr): 3330, 1730, 1665, 1520 and 1370 cm^{-1}. Analysis: found C = 65.99, H = 3.0, N = 17.7 $(C_{26}H_{14}N_6O_4)_n$ requires C = 65.8, H = 2.95 and N = 17.7%.

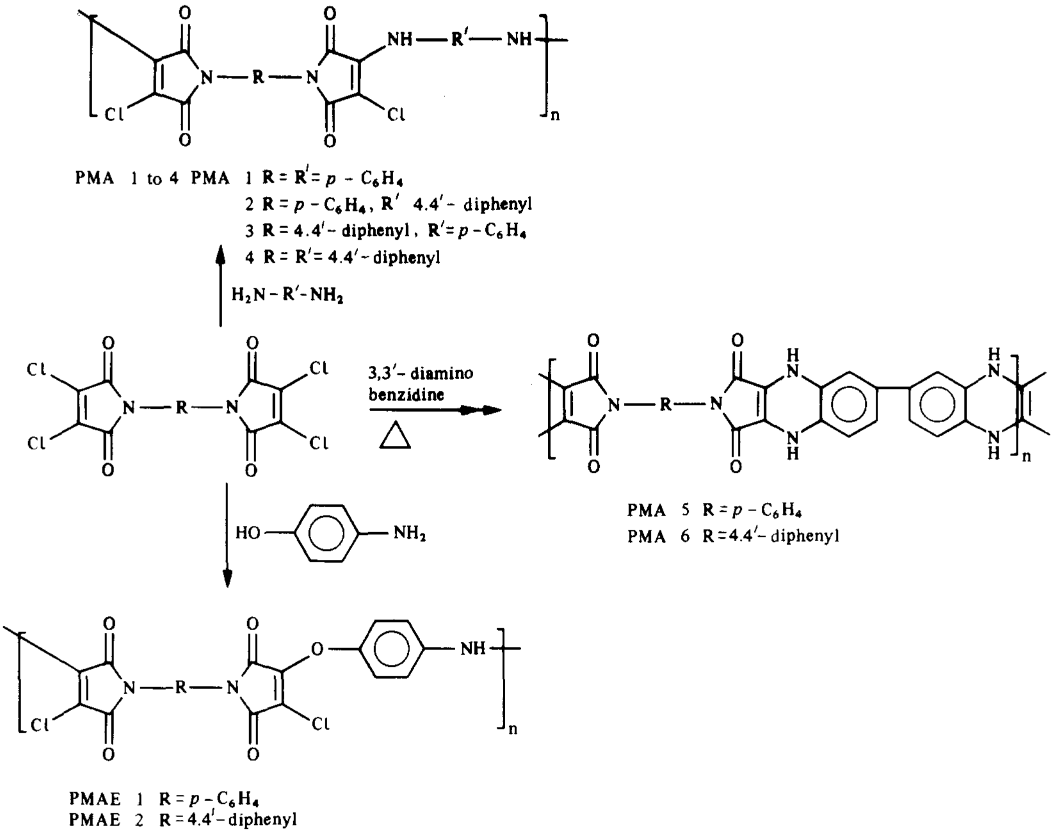
Poly(maleimide-amino)ether:PMAE-1

To *p*-aminophenol (0.33 g, 0.003 mol) in dry DMSO (20 ml), triethylamine (0.6 g, 0.006 mol) and a solution of **6** (1.2 g, 0.003 mol) in DMSO (5 ml) were added at room temperature and stirred for 4 hr. It was then poured into water; the solid was filtered off, washed with water and methanol and finally dried. It was recrystallized from DMF–methanol (1:1) yield 0.82 g (62%). i.r. (KBr): 3320, 1730, 1665, 1590, 1515, 1370, 1250 and 880 cm^{-1}. Analysis: found C = 54.50, H = 1.98, N = 9.6 $(C_{20}H_9N_3O_5Cl_2)_n$ requires C = 54.42, H = 2.04 and N = 9.52%.

RESULTS AND DISCUSSION

Bismaleimides (**2** and **3**) were obtained in over 80% yield from maleic anhydride and *p*-phenylenediamine or benzidine. **2** and **3** reacted with thionyl chloride in presence of pyridine to give the dichloromeleimides **6** and **7**. The observed yields were however much less than those reported previously. Compounds **6** and **7** were characterized by i.r. and elemental analysis.

Three model compounds were prepared. From aniline and dichloro-*N*-phenylmaleimide (**5**), MC-1 was obtained. 4,4′-Biphenylbischloromaleimide (**7**) and aniline gave MC-2 while dichloro-*N*-phenylmaleimide and *o*-phenylenediamine yielded MC-3. DMSO was identified as the best solvent for good yields and was used in the preparation of model compounds and for polymerization. MC-1 and MC-2 had characteristic absorption from imide, C–N and –C=C– in the 1720, 1380 and 1595 cm^{-1} region. The



conjugation of secondary nitrogen with carbonyl gave an additional but expected absorption at around 1650 cm^{-1}. The secondary amine absorption was seen at 1520 and 3300 cm^{-1} and C–Cl at 880 cm^{-1}. Model compound MC-3 involves replacement of both chlorines in the maleimide ring and there was no C–Cl absorption at 880 cm^{-1}.

The polymerization was carried out using triethylamine as acid acceptor. All polymers were insoluble solids. In the reaction between dichloromaleimides and tetramines, the polymer started to precipitate in one hour. Variation of temperature from ambient to 150°C during polymerization did not improve the yields and hence all polymerizations were done at room temperature only, to give the polymers in 50–70% yields as yellow to dark brown crystalline materials. The i.r. spectra of polymers compared well with model compounds in the functional region. The chlorine content of PMA-1 and PMA-4 were determined by gravimetric precipitation of AgCl and the theoretical and experimental values were in good accord.

The polymers had viscosities in the 0.3–0.5 dl/g range.

In amide solvents, the solubility of the diamine derived polymers were about 10% w/v at room temperature. The tetramine derived polymers were however soluble only in conc. H_2SO_4; all polymers however decomposed rapidly in sulphuric acid.

Thermal studies indicated that the polymers degraded gradually around 300°C in air. The decomposition was rapid at 500°C. The poly(maleimide

Table 1. Properties of polymers

Polymer	Yield (%)	η_{inh}* (dl/g)	Decomposition temperature‡ Air	N_2	% Residue at 700° Air	N_2
PMA-1	68	0.52	340	362	8	42
PMA-2	65	0.48	332	378	12	33
PMA-3	70	0.59	323	352	13	40
PMA-4	60	0.61	334	376	7	38
PMA-5	52	0.27†	369	407	15	55
PMA-6	50	0.31†	358	398	10	49
PME-1	62	0.48	282	338	7	38
PMAE-2	65	0.51	279	317	5	42

*DMSO at 30°C [C = 0.5 g/dl].
†Conc. H_2SO_4 at 30°C [C = 0.5 g/dl].
‡Observed in TGA (10% wt. loss): heating rate, 6°C/min.

amine)ethers were much less stable, losing 10% weight even at 280°C. Under N_2, the decomposition was significantly less. For example poly(maleimide-amine) PMA-1 had a residue of only 8% at 700°C which 42% was left behind under N_2 at the same temperature. The various polymers prepared, yields, viscosities and thermal data are given in Table 1.

In DTA, all poly(maleimide-amine) had a strong exotherm in the 350–420°C region. The exotherm for poly(maleimide-amino)ethers PMAE-1 and PMAE-2 were seen between 250 and 300°C.

PMA-1 was heated to various temperatures in air and the i.r. spectrum of heat treated polymer was studied. Up to 200°C, the i.r. spectrum of PMA-1 remained unchanged. Even at 300°C, the spectrum remained unaffected but band broadening was observed. By 400°C, the intensity of absorption due to secondary amine at $3300\,cm^{-1}$ and conjugated carbonyl at $1660\,cm^{-1}$ started decreasing and by 500°C all original absorptions disappeared. This clearly shows that poly(maleimide-amine)s and poly(maleimide-amino)ethers are not thermally very stable. This weakness may be due to secondary amino group and aliphatic imido links.

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