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Synthesis and characterization of new soluble polyaspartimides derived from bis(3-ethyl-5-methyl-4-maleimidophenyl)methane and various diamines

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Abstract

A series of new linear polyaspartimides was obtained via a Michael addition reaction from bis(3-ethyl-5-methyl-4-maleimidophenyl)-methane (BEMM) with various aromatic diamines in *m*-cresol in a 1:1 molar ratio. The molecular weight and yield of these polymers tend to increase with increasing monomer concentration. It was observed that a maximum molecular weight was reached at around 0.72 mol l^{-1} of monomer concentration. Both the yield and the molecular weight of the polymers increased with reaction times up to around 100 h. The inherent viscosities of the polymers varied from 0.42 to 0.70 dl g^{-1}. The polymers had number-average molecular weight and weight-average molecular weight in the range of 9400–20 000 and 24 000–68 000, respectively. All polymers are amorphous and soluble in *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, DMF, dimethyl sulfoxide, pyridine, *m*-cresol, cyclohexanone and tetrahydrofuran. The polymers had high glass transition temperatures in the range of 242–308°C and good thermal stability — 10% weight loss temperatures in the range of 408–459°C in air and 396–421°C in nitrogen. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaspartimides; Bis(3-ethyl-5-methyl-4-maleimidophenyl)methane; Aromatic diamines

1. Introduction

Polyimides have remarkable high temperature resistance and good mechanical and electrical properties. However, condensation type polyimides usually suffer from processing problems due to their insolubility, infusibility and the evolution of volatiles during the ring formation.

Bismaleimides (BMIs) are a leading class of thermosetting polyimides. Their excellent thermal and mechanical properties have made them extremely popular for advanced composites and electronics [1–3]. The BMIs can be self-polymerized through their reactive maleic double bonds to give highly crosslinked, brittle polyimides [4]. On the other hand, nucleophilic difunctional reagents can also add to the maleic double bonds to yield linear, high-molecular-weight polyimides [5]. In particular, diamines have been used to extend bismaleimides, resultig in polyaspartimides [6,7]. And numberous variations between the simple polybismaleimides and the polyaspartimides have afforded a broad choice of thermally stable polyimides which generally possess more facile processing characteristics than linear, high-molecular-weight condensation polyimides [8].

Recently, we have synthesized several novel polyimides based on new diamines containing flexible units such as aryl ether [9–17], sulfonyl [9] and bulky substituents such as *tert*-butyl group [10,11] as well as bulky pendent groups such as cyclododecyl [12], tricyclodecyl [13], norbornyl [14], *t*-butylcyclohexyl [14], adamantyl [16] and diphenylmethylene [17] groups. It was observed that these structural modifications could lower the polymer chain interactions by reducing the stiffness of the polymer chain, simultaneously maintaining the high temperature resistance [9–17]. Depending on the type and amount of structural modifications, the melting temperature can be lowered and the solubilities improved, resulting in processable materials.

In the continuation of preparation of new high-performance, processable polymers, it is of interest to synthesize processable polyaspartimides with high temperature resistance. This paper presents the synthesis and characterization of a series of novel polyaspartimides resulting from bismaleimide, bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (BEMM), with several new diamines [9–17] via a Michael addition reaction. The investigation was also conducted to study the effect of monomer concentration and reaction time

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on polymerization, and the effects of various structural modifications on the properties of polyaspartimides. So far there are few literature reports on systematic studies of such effects.

2. Experimental

2.1. Materials

Bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (BEMM) from TCI was used without further purification. Glacial acetic acid and *m*-cresol were purchased from Merck and used as received. The aromatic diamine monomers used for polymerization were synthesized and purified according to the method elsewhere reported [9–17].

2.2. Preparation of polyaspartimides (PASI-1)

The general procedure for preparation of linear polyaspartimides was as follows. In a 100 ml three necked flask equipped with a magnetic stirrer, a reflux condenser, thermometer and nitrogen inlet, 0.553 g (1.25 mmol) of BEMM was added to 3.5 ml of *m*-cresol. When all the BEMM was dissolved, 0.648 g (1.25 mmol) of diamine DA-1 was added. Then 0.1 ml of glacial acetic acid, used as a catalyst, was added into the mixture when DA-1 was completely dissolved. The reaction mixture was immersed in an oil bath maintained at 100–110°C for 100 h. During this time an appreciable increase in the solution viscosity and darkening in color were noticed. The polymer was isolated by pouring the viscous reaction mixtures into excess ethanol with vigorous stirring to give the dark-brown fibrous polymers. The polymer precipitate was collected by filtration and washed thoroughly with ethanol and extracted with hot ethanol using a Soxhlet extractor and subsequently dried in a vacuum oven at 70°C for one day. The yield was nearly 94%. The polymer had an inherent viscosity of 0.42 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in *N*,*N*-dimethylacetamide (DMAc) at 30°C. The IR spectrum (KBr) exhibited absorptions at 3369 and 1632 cm^{-1} (N–H), 1695 cm^{-1} (C=O) Other polymers (PASI-2–PASI-10) were synthesized by an analogous procedure (Scheme 1).

2.3. Measurements

Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). IR spectra were recorded on a JASCO IR-700 spectrometer. The inherent viscosities of all polymers were measured using an Ubbelohde viscometer. Elemental analysis was made on a Perkin–Elmer 2400 instrument. Molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns 300 × 7.7 mm (guard, 10^5, 10^4, 10^3, 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 ml min^{-1}) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. Thermogravimetric data were obtained on a Du Pont 2100 in flowing nitrogen (60 $cm^3 min^{-1}$) at a heating rate of 20°C min^{-1}. Dynamic mechanical analysis (DMA) was performed on a Perkin–Elmer DMA 7e system at a heating rate of 5°C min^{-1} with a frequency of 1 kHz.

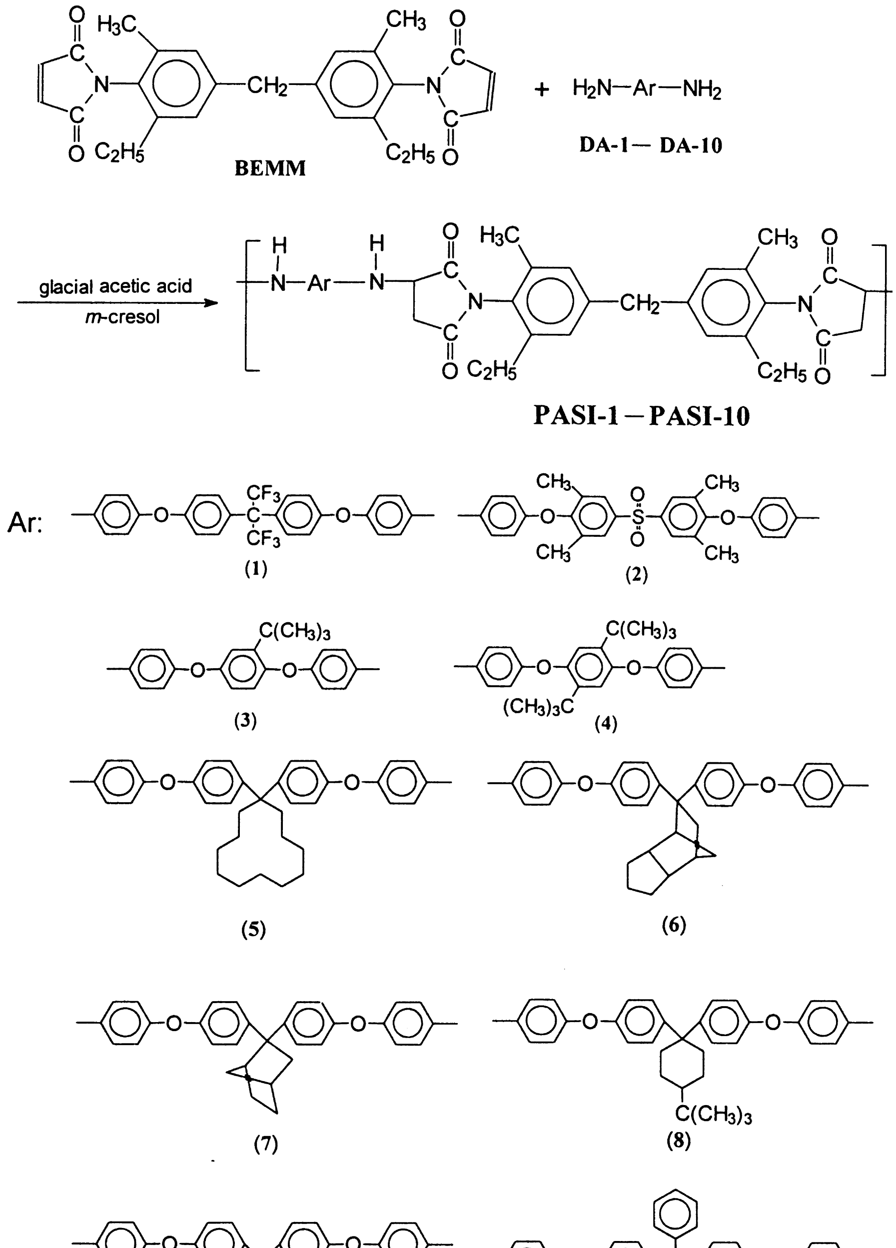
3. Results and discussion

3.1. Prepartion of polymers

A series of new linear polyaspartimides (PASI-1–PASI-10) was obtained via a Michael addition reaction (Scheme 1). The procedure used in the polymerization was the addition of the solid diamine to a solution of the bismaleimide (BEMM) with *m*-cresol in a 1:1 molar ratio. There is little literature reporting the effect of the monomer concentration on the polymerization results such as yield and molecular weight. To obtain the highest molecular weight, determination of the suitable monomer concentration in the study is important. The concentration of the reactants was varied from 0.38 to 1.0 mol·l^{-1}. Glacial acetic acid was used as the catalyst. The data for these reactions are shown in Table 1. The molecular weight and yield of these polymers tend to increase with increasing monomer concentration. However, it appears that a maximum molecular weight can be reached at around 0.72 mol·l^{-1} of monomer concentration (Run 2, Table 1). At monomer concentrations around 1.0 mol·l^{-1}, the reaction solution becomes extremely viscous and difficult to stir and begins to gel (Run 1, Table 1). However, the gel could be dissolved in the mixture by adding additional *m*-cresol.

The effect of the reaction time on the polymer yield and molecular weight of BEMM with various diamines was investigated using 0.72 mol·l^{-1} monomer concentration. As shown in Fig. 1, both the yield and the molecular weight of the resulting polymers increased with reaction times up to around 100 h. There was no significant molecular chain growth and increase of polymer yield when reaction time was prolonged. Therefore the polymerization time of 100 h was adopted in this study.

Table 2 shows the polymerization results and IR spectra data of various polyaspartimides. The polymers (PASI-1–PASI-10) were obtained in quantitative yields with moderate to high inherent viscosities of 0.42–0.70 dl g^{-1}, which were measured in DMAc solutions. GPC measurement revealed that these polymers exhibited number-average molecular weight $\bar{M}_n$ and weight-average molecular weight $\bar{M}_w$ in the ranges of 9400–20 000 and 24 000–68 000, respectively. In the IR spectra of the Michael addition product, the C=O stretching of the imide group of the polymers is in the range of 1695–1713 cm^{-1}. Furthermore, the absence of the bands around 666 cm^{-1} due to the maleimide ring (C=C stretching) of BEMM and the bands around 3380 and 1630 cm^{-1} for the N–H group confirmed the addition



Scheme 1.

reaction. The dark-brown and brittle polymer films, except PASI-7 and PASI-8, could be obtained by casting from their DMAc solutions. Polymers PASI-7 and PASI-8 with higher molecular weight were flexible and tough.

3.2. Characterization of polymers

The solubility of the polyaspartimides in various solvents is shown in Table 3. Nearly all of the polymers were easily soluble at room temperature in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), DMAc, DMF, dimethyl sulfoxide (DMSO), *m*-cresol and pyridine, as well as in common organic solvents such as tetrahydrofuran (THF), cyclohexanone and chloroform.

The crystallinity of the polymers was evaluated by wide angle X-ray diffraction measurement with 2θ from 8 to 40°.

Table 1
Effect of reaction concentration on the preparation of polyaspartimides. Polymerization was carried out using 1.25 mmol of BEMM and 1.25 mmol of diamine DA-1 with 0.1 ml of glacial acetic acid in *m*-cresol for three days

Run no.	Amount of solvent (ml)	Monomer concentration (mol l^{-1})	$\bar{M}_n \times 10^{-4}$[a]	Yield (%)	Remark[b]
1	2.5	1.00	1.28	95	G
2	3.5	0.72	1.47	93	S
3	4.5	0.56	1.12	90	S
4	5.5	0.45	1.04	85	S
5	6.5	0.38	0.79	81	S

[a] Measured by GPC in THF; polystyrene was used as standard.
[b] S, homogeneous solution; and G, gelation.

Table 2
Polymerization results and IR spectra of various polyaspartimides. Polymerization was carried out using 1.25 mmol of BEMM and 1.25 mmol of diamine (DA-1–DA-10) with 0.1 ml of glacial acetic acid in 3.5 ml of *m*-cresol for 100 h

Polymer code	Yield (%)	η_{inh}[a] (dl g^{-1})	$\bar{M}_n \times 10^{-4}$[b] (g.mol^{-1})	$\bar{M}_w \times 10^{-4}$[b] (g.mol^{-1})	IR spectra (cm^{-1})		Film quality[c]
					C=O	N–H	
PASI-1	94	0.42	1.5	4.5	1695	1632, 3369	B
PASI-2	95	0.42	1.6	4.9	1707	1630, 3334	B
PASI-3	97	0.63	1.4	4.4	1705	1625, 3358	B
PASI-4	97	0.66	1.2	3.6	1700	1636, 3348	B
PASI-5	95	0.45	0.94	2.4	1701	1631, 3382	B
PASI-6	98	0.68	1.1	3.5	1705	1633, 3379	B
PASI-7	97	0.66	1.8	6.2	1713	1632, 3378	F, T
PASI-8	96	0.51	2.0	6.8	1704	1636, 3352	F, T
PASI-9	98	0.70	1.1	3.0	1703	1626, 3375	B
PASI-10	98	0.70	1.4	4.6	1710	1630, 3360	B

[a] Inherent viscosity measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C.
[b] Measured by GPC in THF; polystyrene was used as standard.
[c] B, brittle; F, flexible; and T, tough.

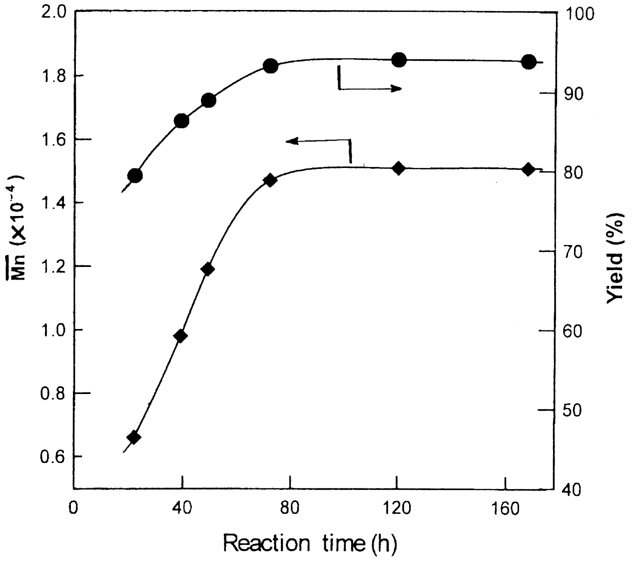


Fig. 1. Effect of reaction time on polymerization of BEMM with DA-1 in *m*-cresol with 0.72 mol·l^{-1} monomer concentration.

All the polymers showed amorphous diffraction patterns. The excellent solubility and highly amorphous nature of the polymers could be attributed to the structural modification through the incorporation of flexible units such as hexafluoroisopropylidene (PASI-1), sulfone (PASI-2), and ether groups (PASI-1–PASI-10). It could also be attributed to the incorporation into the polymer structure of bulky substituent and pendent groups like the *tert*-butyl group (PASI-3 and PASI-4) as well as the pendent cardo groups (PASI-5–PASI-10). There was a considerable decrease in the rigidity and a lowering of energy of internal rotation for the polymer chain due to the presence of the flexible units, thus reducing the crystallinity and improving polymer solubility. Incorporating a bulky *tert*-butyl substituent and the pendent cardo groups in a *para*-linked polymer chain decreases the intermolecular forces between the polymer chains, due to a looser packing of polymer chains as compared with the unsubstituted polymers. Therefore, the crystallization tendency is markedly reduced and the solubilities are significantly enhanced [18].

The thermal behavior of the polymers was evaluated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). Table 4 presents the thermal

Table 3
Solubility of various polyaspartimides. Solubility: ++, soluble at room temperature; +, soluble on heating at 70°C; +−, partially soluble at 70°C; −, insoluble at 70°C

Polymer code	Solvent[a]									
	NMP	DMAc	DMF	DMSO	*m*-cresol	Pyridine	THF	Cyclo-hexanone	Acetone	Chloroform
PASI-1	++	++	++	++	++	++	++	++	+−	+−
PASI-2	++	++	++	++	++	++	++	++	+−	++
PASI-3	++	++	++	++	++	++	++	++	+−	++
PASI-4	++	++	++	++	++	++	++	++	++	++
PASI-5	++	++	++	++	++	++	++	++	++	++
PASI-6	++	++	++	++	++	++	++	++	−	+
PASI-7	++	++	++	++	++	++	++	++	−	++
PASI-8	++	++	++	++	++	++	++	++	−	++
PASI-9	++	++	++	++	++	++	++	++	−	++
PASI-10	++	++	++	++	++	++	++	++	−	++

[a] Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMSO, dimethylsulfoxide; DMAc, *N*, *N* -dimethylacetamide; and THF, tetrahydrofuran.

properties of the polyaspartimides. Since no distinct glass transition could be observed in the differential scanning calorimetry (DSC) trace, the T_g value of the polymers was determined by DMA using film species. It could be seen that the T_gs of polymers, except PASI-4 and PASI-5, are reasonably high, varying between 242 and 308°C [7,19,20]. The high T_g value of the polymers may be due to the presence of the polar groups such as sulfone (PASI-2) group, a bulky *tert*-butyl substituent (PASI-3) as well as the cardo groups (PASI-6–PASI-10). In general, cardo groups showed a high T_g value due to the bulky pendent group that inhibited the free rotation of the polymer backbone [21,22]. It is observed that polymer PASI-9 containing adamantane group showed the highest T_g value. It has been recognized that incorporation of adamantane groups in the polymer backbone leads to an enhanced T_g value [23,24]. It was noted that polymer PASI-10 bearing a pendent phenyl group showed a lower T_g value than the other cardo polymers. It may be ascribable to the presence of the kink linkage of the diphenylmethylene unit in the polymer backbone. The kink linkage would lower the rigidity of the polymer backbone [25].

Table 4
Thermal properties of various polyaspartimides

Polymer code	T_g[a] (°C)	Decomposition temperature (Td_{10})[b]	
		In N_2	In air
PASI-1	294	403	459
PASI-2	274	396	408
PASI-3	287	415	447
PASI-4	–[c]	400	415
PASI-5	–[c]	407	430
PASI-6	304	411	448
PASI-7	263	403	437
PASI-8	268	404	445
PASI-9	308	421	448
PASI-10	242	414	449

[a] From dynamic mechanical analysis (DMA) measurements conducted at a heating rate of 5°C $\min^{-1}$.

[b] Decomposition temperature at 10% weight loss was determined by TGA at a heating rate of 20°C $\min^{-1}$.

[c] Could not be detected by DMA.

TG analyses revealed that these polymers were stable up to a temperature of approximately 350°C. Their decomposition temperatures of 10% weight loss (Td_{10}) were in the range 396–421°C in nitrogen and 408–459°C in air. It was observed that the Td_{10} values of the polymers in air atmosphere are higher than those in nitrogen, which is reasonable considering the high aliphatic content of these polymers. It was possibly because of the oxidative cross-linking, or an early weight-gained oxidation of the aliphatic groups when thermally degraded in air [26–28]. For instance, the oxidation of methyl group (CH_3) on the polymer backbone may form carbonyl (C=O) and hydroxyl groups (O–H) and then cause weight gain [26–28].

4. Conclusions

The new polyaspartimides resulted from a Michael addition reaction of bismaleimide BEMM and various diamines were successfully prepared. These polymers exhibited amorphous behavior and excellent solubility. The polymers had high T_g values in the range 242–308°C and good thermal stability. Thus these materials could be considered as new processable polymeric materials.

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