Studies on bismaleimides and related materials: 2. Synthesis and characterization of oligomeric maleimides derived from polystyrene and poly(phenylene methylene)

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Polystyrene and poly(phenylene methylene) of relatively low molar mass (2000–3000) have been converted through nitro and amino derivatives into maleimido-functionalized oligomers. The latter have been characterized spectroscopically and oligomers and cured resins derived therefrom studied by thermal gravimetric analysis. Both polystyrene and poly(phenylene methylene) show greater thermal and thermo-oxidative stability than the corresponding maleimido derivatives. This trend is also observed when comparing poly(phenylene methylene) with the crosslinked resin derived from maleimidopoly(phenylene methylene). The opposite trend is observed for polystyrene and the cured resin derived from maleimidopolystyrene.

(Keywords: bismaleimide; polystyrene; poly(phenylene methylene))

Introduction

There is widespread interest in the homopolymerization of bismaleimides (BMIs), particularly from the viewpoint of production of resin composite materials with high thermo-oxidative stability[1]. Unfortunately, limits to the utility of BMIs are imposed by their inherent brittleness resulting from high crosslink densities. Efforts have been made to overcome this problem by copolymerizing BMIs with 'reactive diluents' such as *o*-allylphenols[2] and styrenes[3]. In an alternative approach, Chisholm *et al.*[4] recently devised a system comprising an oligomeric mixture functionalized by maleimide rings as a precursor to the resin. Thus, for example, *N*-(4-phenoxyphenyl)-maleimide was treated with paraformaldehyde under non-aqueous acidic conditions to give an oligomeric mixture with the trismaleimide (**1**) as the major component[4].

In this paper, we describe an approach to novel oligomeric maleimides in which the imide rings are pendent to hydrocarbon backbones derived from polystyrene and poly(phenylene methylene). A restriction on synthetic approaches to oligomers of these types is imposed by the susceptibility of the maleimide ring to polymerization, hence oligomers in this work were generated by imidization of polyamines as a final step.

Experimental

Characterization. The molecular weight distribution of polystyrene was determined using a Waters modular g.p.c. system incorporating i.r. and u.v. detectors. Thermal gravimetric analysis was carried out on a Perkin–Elmer TGA-7 machine using a heating rate of 20°C min^{-1}. ^{1}H n.m.r. spectra were recorded at 200 MHz on a Bruker WP-200SY spectrometer. Solid state (CP/MAS) ^{13}C and ^{15}N n.m.r. spectra were recorded at 75.4 and 30.4 MHz, respectively, through the SERC service, University of Durham. Chemical shifts are quoted by reference to tetramethylsilane and nitromethane, respectively. I.r. spectra were recorded as KBr discs on a Perkin–Elmer 1600 FT instrument. Melting points were measured on a Gallenkamp electrothermal apparatus and are uncorrected. Elemental analyses were carried out at UMIST, UK.

Materials. Polystyrene (**2a**), $\bar{M}_w = 1800$, $\bar{M}_n = 1300$ (g.p.c., tetrahydrofuran (THF)), was prepared by anionic polymerization of styrene according to a literature procedure[5].

Poly(phenylene methylene) (**3a**), $\bar{M}_n = 2300$ (v.p.o., $CHCl_3$), 1290 (g.p.c., THF), was synthesized from benzyl alcohol and anhydrous hydrogen fluoride[6].

Nitropoly(phenylene methylene)[7], nitropolystyrene[8,9] and aminopolystyrene[8] have been previously reported but not fully characterized spectroscopically; full experimental details for these, and for aminopoly(phenylene methylene) are included below. See Structures **1**–**4**.

Synthesis. Preparation of nitropolystyrene (**2b**). Polystyrene (5.0 g) as a finely powdered solid was added slowly over 45 min to a mixture of fuming nitric acid, conc. sulfuric acid and water (11.0 g, reactant ratio = 70:21:9 vol%, respectively). The mixture was left stirring for 4 days at room temperature. The resulting cream-coloured semi-solid was added to ice/water (200 ml) whereupon a pale-cream-coloured solid precipitated. The solid was collected by filtration and washed with copious quantities of water until the washings were neutral. The material was air-dried to give a product that darkened on heating, and had m.p. ≈ 300°C. Found: C, 73.6; H, 5.7; N, 5.9%.

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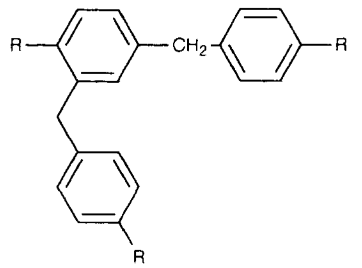
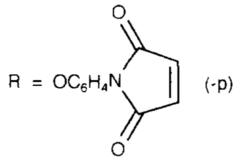
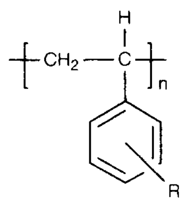
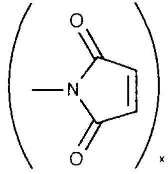


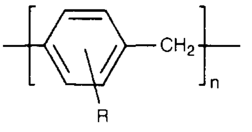
(1)





(2)

	R
a,	H
b,	$(NO_2)_x$
c,	$(NH_2)_x$
d,	



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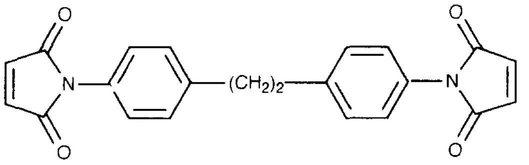
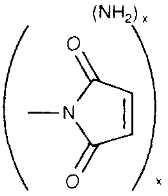


(4)

	R
a.	H
b,	$(NO_2)_x$
c	$(NH_2)_x$
d:	

$C_8H_{7.46}(NO_2)_{0.54}$ requires: C, 74.82; H, 5.81; N, 5.89%. I.r. ν_{max} (KBr) (cm^{-1}) 3024, 2921 (C–H stretch), 1600 (C=C stretch), 1516 and 1345 (NO_2 stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 40.8 (CH_2), 126.1 (non-quaternary aromatic), 146.3 (quaternary aromatic C–C), 152.4 (quaternary aromatic (C–N). ^{15}N n.m.r. (CP/MAS) δ (ppm) -3.8 (NO_2).

Preparation of aminopolystyrene (**2c**). Nitropolystyrene (**2b**) (1.0 g), stannous chloride dihydrate (5.5 g, 0.025 mol), conc. hydrochloric acid (6.5 ml) and ethanol (30 ml) were heated under reflux for 9 h. The mixture was cooled and the ethanol was evaporated under reduced pressure; aqueous sodium hydroxide (20%) was then added until the brown solution was basic to litmus. The alkaline solution was boiled for 20 min and then filtered while hot. The precipitate was added to 20% aqueous sodium hydroxide (100 ml), boiled again for 20 min, filtered, and the solid washed with copious quantities of water. The solid was dried, then ground into a fine powder and boiled with successive portions of water (5 x 200 ml). At the end of this treatment, the aqueous washings were clear after decantation. The solid was finally filtered and air-dried to give material that darkened on heating, but with m.p. > 360°C. Found: C, 74.6; H, 6.5; N, 7.4%. I.r. ν_{max} (KBr) (cm^{-1}) 3413 (N–H stretch), 3023, 2918, 2848 (C–H stretch), 1604 (C=C stretch), 1513 and 1344 (residual NO_2 stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 40.7 (CH_2), 115.8 (quaternary aromatic C–NH_2), 127.5 (aromatic C–H), 145.8 (quaternary aromatic C–C), 151.7 (quaternary aromatic C–NO_2). ^{15}N n.m.r. (CP/MAS) δ (ppm) -7.9 (NO_2) and -323.3 (NH_2).

Preparation of maleimidopolystyrene (**2d**). Aminopolystyrene (0.77 g) and maleic anhydride (0.50 g, 5.1 mmol) were stirred in *N*,*N*-dimethylformamide (DMF) (30 ml) under an atmosphere of nitrogen for 8 h at 40°C. After standing at room temperature overnight, anhydrous sodium carbonate (1.0 g, 9.43 mmol) and acetic anhydride (0.82 g, 8.04 mmol) were added, and the mixture was stirred at 45°C for 8 h under a nitrogen atmosphere. The product was cooled and added to ice/water (100 ml) and allowed to stand overnight. The dark-brown precipitate was filtered and washed with water (800 ml). The solid was then stirred with saturated sodium bicarbonate solution (100 ml) and the mixture was filtered and washed with copious quantities of water. The product was air-dried to give material that darkened on heating, but with m.p. > 360°C. Found: C, 64.2; H, 4.9; N, 5.4%. I.r. ν_{max} (KBr) (cm^{-1}) 3025, 2920 (C–H stretch), 1713 (C=O stretch), 1514 and 1347 (NO_2 stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 40.9 (CH_2), 127.9 (aromatic C–H), 146.4 (quaternary aromatic) and 169.8 (imide C=O). ^{15}N n.m.r. (CP/MAS) δ (ppm) −4.4 (NO_2), −213.9 (imide) and −237.0 (unassigned).

Preparation of nitropoly(phenylene methylene) (**3b**). Poly(phenylene methylene) (4.0 g) was added to fuming nitric acid (100 ml) at −3°C with rapid stirring and the mixture stirred for 1 min. The product was poured into ice/water (800 ml) and the yellow solid was filtered and washed with copious quantities of water until the washings were neutral to litmus. The resulting pale-brown solid was dissolved in chloroform (200 ml) to give a soluble and an insoluble portion. The mixture was filtered and the filtrate was evaporated under reduced pressure to give the title material as a golden–brown solid (5.1 g), softening ~95°C, m.p. 102–104°C. Found: C, 55.2; H, 3.1; N, 11.7%. $[C_7H_{4.7}(NO_2)_{1.3}]_n$ requires: C, 56.57; H, 3.16; N, 12.26%. I.r. ν_{max} (KBr) (cm^{-1}) 3076 (C–H stretch), 1522 and 1345 (NO_2 stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 36.5 (CH_2), 125.6 (aromatic C–H) 132.7, 140.1 and 146.8 (quaternary aromatic). ^{15}N n.m.r. (CP/MAS) δ (ppm) −5.4 (NO_2).

Preparation of aminopoly(phenylene methylene) (**3c**). Nitropoly(phenylene methylene) (2.5 g), stannous chloride dihydrate (13.75 g, 0.06 mol), conc. hydrochloric acid (16 ml) and ethanol (30 ml) were heated under reflux for 6 h. The dark-brown solution was cooled and ethanol was evaporated under reduced pressure. Aqueous sodium hydroxide (250 ml, 20%) was added and the mixture was boiled for 20 min. A dark-brown powder deposited upon cooling, and most of the aqueous layer was decanted. This procedure was repeated with two further aliquots (125 ml) of aqueous sodium hydroxide. The residue was finally filtered, and the solid washed with warm water (600 ml). The solid was then boiled for 10 min with three separate aliquots of water (300 ml). After decantation and filtration, the solid was finally washed with water (800 ml) and air-dried to give a product (1.45 g), m.p. >360°C. Found: C, 71.7; H, 6.0; N, 13.1% (Sn, 1.5%). $[C_7H_{4.7}(NH_2)_{1.3}]_n \equiv [C_7H_{7.3}N_{1.3}]_n$ requires: C, 76.7; H, 6.67; N, 16.62%. I.r. ν_{max} (KBr) (cm^{-1}) 3344 (NH stretch), 3008, 2912 (CH stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 35.9 (CH_2), 116.1 (aromatic *C*–H), 128.8 (quaternary aromatic), 130.5 (aromatic C–H), 145.1 (quaternary aromatic). ^{1}H n.m.r. (d^6-DMSO) δ (ppm) 3.4–3.6 (br s, NH_2, exchangeable with D_2O), 4.1–5.0 (br, 2H, CH_2), 6.0–6.9 (br, m, ~2.8 H, Ar–H). ^{15}N n.m.r. (CP/MAS) δ (ppm) −320.9 (NH_2).

Preparation of maleimidopoly(phenylene methylene) (**3d**). Aminopoly(phenylene methylene) (**3c**) (1.0 g) and maleic anhydride (0.934 g, 9.52 mmol) in DMF (50 ml) were stirred at 35°C for 8 h under an atmosphere of nitrogen. After standing at room temperature overnight, anhydrous sodium carbonate (0.20 g, 1.89 mmol) and acetic anhydride (3.11 g, 0.03 mol) were added and the mixture was stirred at 45°C for 24 h. The product was cooled and the solvent evaporated under reduced pressure to leave a dark-brown solid. After washing with water (800 ml), the product was air-dried to give material with m.p. >360°C. Found: C, 65.3; H, 3.7; N, 7.0%. $[C_7H_{4.7}(NC_4H_2O_2)_{1.3}]_n \equiv [C_{12.2}H_{7.3}N_{1.3}O_{2.6}]_n$ requires: C, 68.57; H, 3.42; N, 8.53%. I.r. ν_{max} (KBr) (cm^{-1}) 3099 (CH stretch), 1712 (C=O stretch). ^{13}C n.m.r. (CP/MAS) δ (ppm) 35.9 (CH_2), 130.3, 138.1 (aromatic), 169.6 (imide CO). ^{15}N n.m.r. (CP/MAS) δ (ppm) −214.7 (NH_2), −189.2 (minor, unassigned resonance).

Oligomer solubility properties. **2b**, insoluble in most organic solvents including dimethylsulfoxide (DMSO), but soluble in DMF; **2c** and **2d**, insoluble in organic solvents; **3b**, soluble in halogenated solvents, e.g. dichloromethane and chloroform; **3c** and **3d**, insoluble in most organic solvents, but soluble in DMF and DMSO.

Polymerizations. Cure cycles for the quantitative preparation of resins from maleimidopolystyrene (**2d**) and maleimidopoly(phenylene methylene) (**3d**) were as follows: consecutively, 1 h at 180°C, 2 h at 200°C, 2 h at 250°C, then 6 h at 300°C.

Results and discussion

Synthesis. In order to achieve efficient chemical imidization of polyamines in solution, it was decided to use polystyrenes and poly(phenylene methylene) of relatively low molar mass. The former (**2a**) was prepared by controlled anionic polymerization of styrene by a literature method[5]. Poly(phenylene methylene) (**3a**) was readily prepared by oligomerization of benzyl alcohol in anhydrous hydrogen fluoride[6]; it may be noted that this procedure offers an efficient, inexpensive route to the oligomer that is easily adaptable to industrial-scale use. The desired nitro (**2b**[8,9] and **3b**[7]) and amino (**2c**)[8] derivatives have been reported in earlier literature, but have not been fully characterized spectroscopically; aminopoly(phenylene methylene) (**3c**) has not previously been reported. Full preparative and spectral data on all materials derived from polystyrene and poly(phenylene methylene) are described in the Experimental section with particular reference to solid state ^{13}C and ^{15}N n.m.r. data.

The nitration of polystyrene (**2b**) was effected[8] in a mixture of fuming nitric acid and conc. sulfuric acid to give nitropolystyrene (**2b**) as a pale-yellow, high-melting solid, analytical data for which indicated a degree of nitration around 0.5 (see **2b**, $x = \sim 0.5$). Presence of the nitro group in **2b** was easily recognized from the i.r. spectrum (NO_2 stretch at 1516 and 1345 cm^{-1}) and also by a single resonance ($\delta = -3.8$ ppm) in the solid state ^{15}N n.m.r. spectrum (cf. values of $\delta = -10$ to -14 ppm for nitroarenes in solution)[10]. The nitropolystyrene (**2b**) was reduced with stannous chloride and conc. hydrochloric acid in ethanol according to a literature procedure[8]. It was apparent, however, from the i.r. spectrum (NO_2 stretching at 1513 and 1344 cm^{-1}) and the solid state ^{15}N n.m.r. spectrum ($\delta = -7.9$ ppm (NO_2) and −323.3 ppm (NH_2), cf. values of $\delta = -321$ to -329 ppm for aminoarenes in solution[10]) that the reduction was incomplete; the use of longer reaction times did not effect completion of the reaction and impure aminopolystyrene (**2c**) was imidized without further purification. Thus sequential treatment of **2c** with maleic anhydride in DMF then acetic anhydride and sodium carbonate gave a brown, high-melting material. From i.r. (imide (C=O stretch at 1713 cm^{-1}), solid state ^{13}C n.m.r. (*C*=O, $\delta = 169.8$ ppm) and solid state ^{15}N n.m.r. spectra ($\delta = -213.9$ ppm) it was apparent that the maleimidopolystyrene had been formed (see, for example, ^{15}N n.m.r. resonances $\delta = -212.4$ ppm for the BMI (**4**)[11] in the solid state and $\delta = -217$ ppm in solution for the BMI derived from 4,4′-diaminodiphenylmethane[12]). It was also clear from the ^{15}N n.m.r. spectrum that the product was contaminated not only with the nitro derivative (**2b**)

Table 1 Thermal and thermo-oxidative stability of polystyrene, poly(phenylene methylene), the maleimido oligomers (**2d** and **3d**) and cured resins derived from **2d** and **3d** from thermal gravimetric analysis

	Air			Nitrogen		
Structure	Temp. (°C) for 5% weight loss	Temp. (°C) for 10% weight loss	Residue at 1000 K (%)	Temp. (°C) for 5% weight loss	Temp. (°C) for 10% weight loss	Residue at 1000 K (%)
2a	367	386	< 1[a]	400	413	0[b]
2d	302	355	5.0[c]	259	360	37.5
Crosslinked resin derived from **2d**	389	427	8.8	393	450	63.6
3a	428	463	3.1	440	490	12.4
3d	317	425	30.2	315	458	59.5
Crosslinked resin derived from **3d**	387	428	1.8	410	466	63.2

[a] Value quoted is for 459°C
[b] Value quoted is for 466°C
[c] <7% present at 580°C

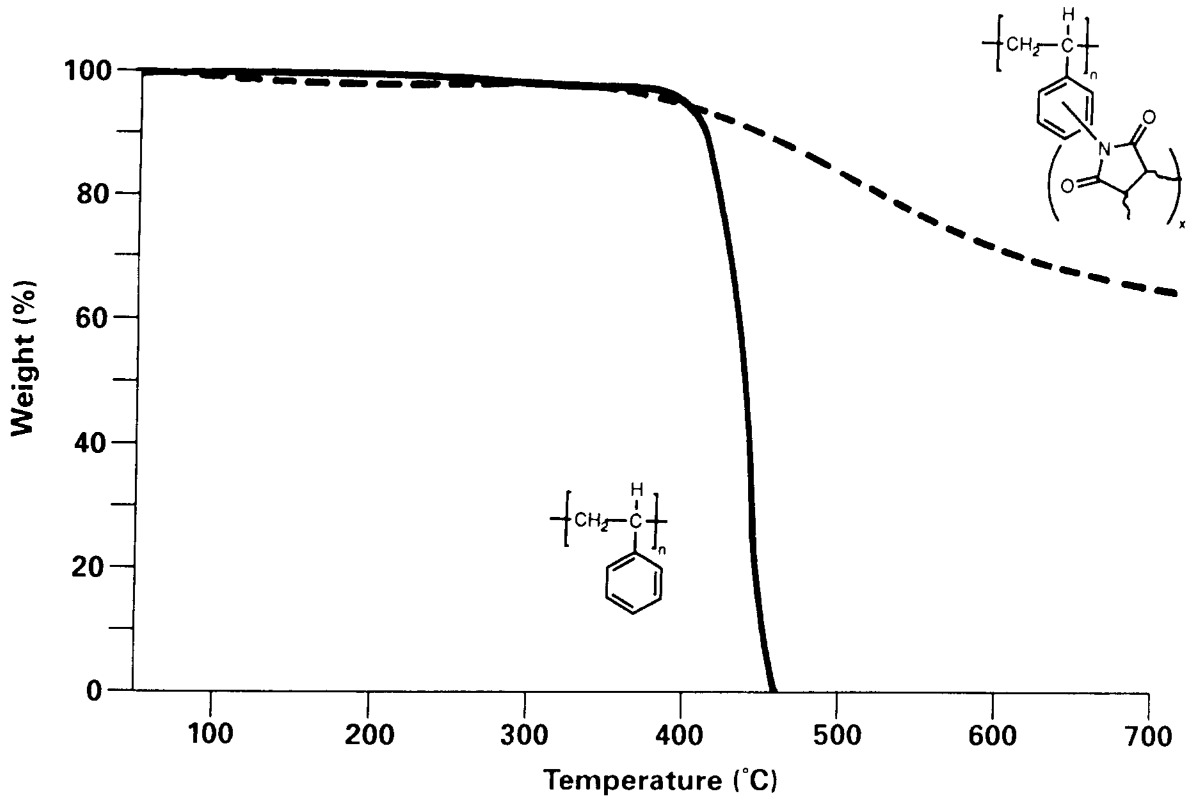


Figure 1 Stability profiles of polystyrene and the cured resin derived from maleimidopolystyrene (**2d**), obtained by thermal gravimetric analysis under a nitrogen atmosphere

($\delta = -4.4$ ppm) but with another species giving rise to an unassigned resonance at $\delta = -237$ ppm; despite these impurities, the imidized material (**2d**) was used for oligomer characterization (see below).

Nitration of poly(phenylene methylene) (**3a**) was carried out using fuming nitric acid by the method of Shriner and Berger[7]. The chloroform-soluble portion of the product is similar to that reported by them in terms of analytical data and softening/melting temperature (95°C/102–104°C; cf. 117°C/132°C[7]); the material approximates in structure to **3b** ($x = \sim 1.3$). It is characterized spectroscopically by i.r. bands at 1522 and 1345 cm^{-1} (NO_2 stretch) and by a single resonance ($\delta = -5.4$ ppm, NO_2) in the solid state ^{15}N n.m.r. spectrum; there is no evidence for the presence of 'polybenzoyl' impurity $(C_6H_4CO)_n$ (anticipated[11] C=O stretching frequency at 1660 cm^{-1}) that might be expected to arise as a by-product from oxidation[7]. Treatment of nitropoly(phenylene methylene) (**3b**) with stannous chloride and conc. hydrochloric acid caused reduction of the nitro group (i.r. and solid state ^{15}N n.m.r.) and the appearance of a single resonance ($\delta = -320.9$ ppm) in the ^{15}N n.m.r. spectrum. Despite thorough washing with aqueous sodium hydroxide and water, this material (**3c**) retained tin-containing residues (1.5% from elemental analysis). Imidization of this polyamine (**3c**) was carried out without further purification to give the maleimidopoly(phenylene methylene) (**3d**) which was recognized by imide carbonyl ($\delta = 169.6$ ppm) and imide nitrogen ($\delta = -214.7$ ppm) resonances in solid state ^{13}C and ^{15}N n.m.r. spectra, respectively.

Polymer characterization. Attempts to establish cure profiles for oligomers **2d** and **3d** using differential scanning calorimetry proved unsuccessful, with traces being relatively featureless over the range 50–400°C; no evidence for a polymerization exotherm could be adduced.

Cured resins from the imidized oligomers were prepared using a heating cycle with a relatively high final temperature (300°C). The heating cycle was based on that previously used for BMI monomers with a relatively high cure onset temperature, and is described in the Experimental section.

Thermal gravimetric analysis was used to study both the thermal and thermo-oxidative stability of polystyrene (**2a**), poly(phenylene methylene) (**3a**), the corresponding maleimido derivatives (**2d** and **3d**) and cured resins derived from the maleimido oligomers (see *Table 1*). Both polystyrene and poly(phenylene methylene) exhibit greater thermal and thermo-oxidative stability than the corresponding maleimido derivatives. It was anticipated that the crosslinked resins derived from the maleimido oligomers would possess higher thermal and thermo-oxidative stability than the parent hydrocarbon, and this is the case in comparing polystyrene and **2d** (see *Table 1* and *Figure 1*). In contrast, and surprisingly, the cured resin derived from maleimido poly(phenylene methylene) (**3d**) is less stable thermally, both in air and under nitrogen, than is poly(phenylene methylene) itself (see *Table 1*). It is possible that the doubly benzylic reactive methylene group of poly(phenylene methylene) (**3a**) is rendered even more labile by the influence of a neighbouring *ortho* substituent. It may also be noted that the imidized oligomer was unavoidably contaminated by tin-containing residues which could, in turn, have had a detrimental effect on the thermal properties of the resulting resin; it has been noted[13] that resins prepared from certain high purity BMI monomers have higher thermal stability than impure products (96%) from initial reaction mixtures.

Summary

Novel imidized materials with polystyrene and poly(phenylene methylene) backbones have been prepared in three steps from low molar mass parent hydrocarbons. Further evaluation of these materials should be facilitated by the low cost and easy large-scale synthesis of polystyrene and poly(phenylene methylene).

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