Synthesis and characterization of fluorinated polybenzoxazoles via solution cyclization techniques*

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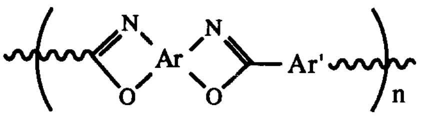
High molecular weight film-forming flexible fluorinated poly(arylene ether benzoxazole)s, which are suitable as gas separation membranes, adhesives and matrix resins, were synthesized in aprotic dipolar solvents such as *N*-methyl pyrrolidinone via an intermediate poly(hydroxy amide). The cyclodehydration was subsequently achieved at moderate temperatures (e.g. 150–195°C) in solution via an acid-catalysed (*p*-toluene sulfonic acid or pyridine hydrochloride) process. The water of dehydration could be azeotropically removed in an analogous manner to the well known synthesis of polyimides via intermediate poly(amide acid)s. The fluorinated monomers were bis(arylamino phenol)s based upon either the 6F or a novel 3F connecting link. Oxybis(benzoylchloride) appears to be a particularly attractive comonomer which allows the synthesis of soluble high molecular weight products. The amorphous macromolecules produced highly transparent ductile cast films with glass transition temperature values of about 300°C or higher. Semicrystalline morphologies could also be produced by incorporating more rigid comonomers. The synthetic procedures described herein are considered to be attractive relative to several alternative methods described in the literature for the synthesis of amorphous polybenzoxazoles.

(Keywords: fluorinated polybenzoxazoles; acid catalyst; solution cyclization)

INTRODUCTION

Polybenzoxazoles (PBOs) have long been of interest because of their excellent thermo-oxidative stability, high tensile modulus and strength.



A number of reviews have described their synthesis, processing and fibre properties and their potential benefits and drawbacks[1–7]. Traditional routes to rigid rod PBOs continue to be reported, but more recent investigations into the synthesis of PBOs have led to a number of novel polymerization methods[8–11]. The silylated monomer developed by Imai, and Reinhardt's silylated phosphorus catalyst route have shown great promise for the synthesis of soluble, fully cyclized materials. In addition, very active research efforts continue in the area of wholly aromatic PBOs[12,13]. More recent synthetic efforts have been aimed at developing polymerization techniques that would allow the direct application of reaction mixtures in subsequent processing steps, which is reminiscent of polyimides[14–16]. The development of a polymerization system that is as straightforward as the analogous polyimide systems would be very significant and was a major objective of our research. Furthermore, certain PBO material properties, such as the dielectric properties, hydrolytic stability and possibly thermo-oxidative stability and mechanical properties, would be expected to be equivalent or even superior to existing high performance aromatic polyimides. In addition, composites generated from a thermoplastic or thermosetting matrix resin consisting of PBO and a fibre reinforcement composed of highly ordered PBOs might have some characteristics of a molecular composite.

Based on the potential benefits attainable with PBO systems, our research efforts have focused on simplifying and better understanding the fundamental features controlling PBO synthesis. A major objective was to synthesize high performance materials that can withstand aggressive environmental conditions with minimal loss of physical properties. A second objective was to prepare highly transparent solvent- or melt-processable thermoplastic and thermosetting materials systems with a high glass transition temperature. To accomplish these objectives, a two-step polymerization system was developed[17]. The polymerization methodology consists of a low temperature amidation reaction followed by an acid-catalysed solution cyclization step. Fluorinated and/or kinked monomers were utilized to enhance

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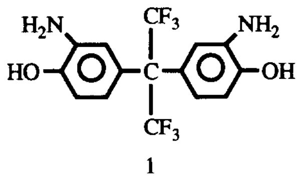
solubility and maintain good thermo-oxidative stability. This strategy was previously described for the synthesis of a series of high molecular weight, fully cyclized PBOs based on 2,2-bis(3-amino-4-hydroxyphenyl)isopropylidene and aromatic acid chlorides[18]. Unfortunately, when this technique was initially applied to the somewhat deactivated fluorinated systems, only modest molecular weights could be achieved under most conditions. Therefore, a systematic study of the cyclization conditions was conducted by systematically investigating the catalyst, catalyst concentration, solvent system and temperature, in an effort to determine the optimum conditions amenable to high molecular weight and complete cyclization. Using these optimal conditions, a series of fluorinated PBOs based on 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1-3,3,3-hexafluoropropane (6FAP) **1** and 2,2-bis(3-amino-4-hydroxyphenyl)-2-phenyl-1,1,1-trifluoroethane (3FAP) **2** and various fluorinated and non-fluorinated aromatic acid chlorides were synthesized and characterized with respect to solution, thermal, and mechanical behaviour.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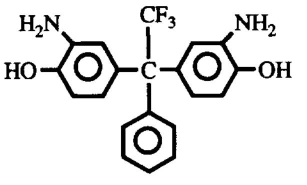
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The initial results of this research investigation are described herein. Additional details and modelling experiments will be reported later[19–21].

EXPERIMENTAL

Starting materials

3FAP was prepared as previously reported (m.p. = 216–217°C; lit.[22,23] m.p. = 216–217°C). 2,2-Bis(4-carbonyl chloride benzene)-2-phenyl-1,1,1-trifluoroethane (3FAC) was prepared by chlorinating the precursor diacid (synthesized via existing methods[24]) with $SOCl_2$ and two drops of dimethylformamide at 40°C. Two recrystallizations from hexane yielded a light yellow crystalline solid (m.p. = 67.2–69°C). Analysis calculated for $C_{22}H_{13}Cl_2F_3O_2$: C, 60.43; H, 3.00; Cl, 16.22. Found: C, 60.39; H, 3.01: Cl, 16.15.

Chlorination and purification of the other acid chlorides proceeded under similar conditions, and the first step was achieved via vacuum distillation. Terephthaloyl chloride (TC) (m.p. = 81–82°C; lit.[25] m.p. = 80–82°C) and isophthaloyl chloride (IC) (m.p. = 43–44°C; lit.[25] m.p. = 43–44°C) were obtained from Kodak, while 1,1′-oxybis(4-carbonyl chloride benzene) (ODB) (m.p. = 88–89°C; lit.[8] m.p. = 88°C) and 2,2-bis(4-carbonyl chloride benzene)-1,1,1-3,3,3-hexafluoropropane (6FAC) (m.p. = 96–97°C; lit.[8] m.p. = 94.5–95.5°C) were kindly donated by Hoechst. 6FAP (m.p. = 243–244°C; lit.[26] m.p. = 244–245°C) was purchased from Chriskev and recrystallized prior to use. *N*-Cyclohexyl-pyrolidinone (CHP) and *N*-methyl pyrrolidinone (NMP) were vacuum distilled from phosphorus pentoxide, while pyridine, *o*-dichlorobenzene (DCB) and toluene were distilled from calcium hydride prior to use. Pyridine hydrochloride and *p*-toluenesulfonic acid monohydrate (*p*-TSA) (Aldrich) were used as received.

Polymerization

A typical procedure was as follows. To a three-necked flask equipped with a mechanical stirrer, N_2/thermometer inlet and liquid addition funnel were added 3.6626 g (0.0100 mol) of 6FAP, 15 ml of NMP and 1.7 ml (0.0211 mol) of pyridine; the mixture was allowed to become homogeneous and cooled to 5°C. Immediately, a solution of 2.0302 g (0.0100 mol) of TC in 5 ml of NMP was added while maintaining the temperature at around 5°C. After complete addition, the temperature was slowly raised to room temperature and maintained for 6 h. The resulting poly(amide phenol) solution was precipitated into 50/50 methanol/water, washed with methanol/water and dried under vacuum at 160–170°C. Cyclization was accomplished by dissolving the polymer in CHP or NMP (20% solids, w/w) and 20–25% azeotroping solvent (v/v), along with the calculated quantity of catalyst (based upon hydroxyl groups in polymer) in a three-necked flask equipped with a mechanical stirrer, Dean-Stark trap and N_2/thermometer inlet. The catalysts were either pyridine hydrochloride or *p*-TSA. The reaction temperature was increased to the desired value by inserting the reaction vessel into a preheated oil bath. After 4 h the contents were cooled to room temperature, precipitated into methanol, washed with methanol and water and vacuum dried at 180°C for at least 48 h.

Characterization

Viscosity measurements. Intrinsic viscosity, $[\eta]$, and inherent viscosity, η_{inh}, (0.5% solutions) measurements were performed in NMP, tetrahydrofuran (THF), $CHCl_3$ or *m*-cresol at 25°C. Cannon-Ubbelohde viscometers (bore size 50–200) were employed.

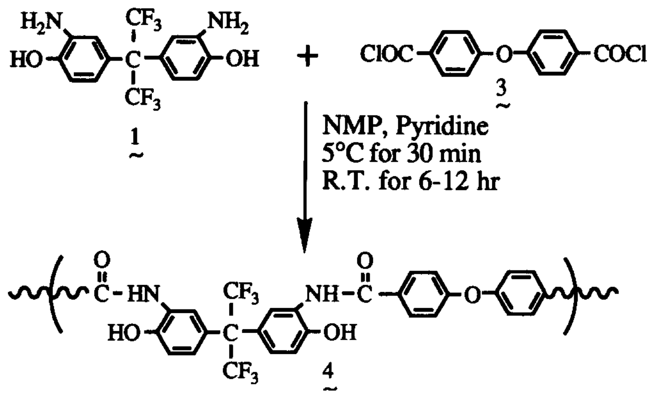
^1H n.m.r. analysis. ^1H n.m.r. analysis was conducted on a Varian 400 mHz instrument operating at 23°C. Samples were referenced to deuterated dimethylsulfoxide or $CDCl_3$.

Fourier transform infra-red (FT*i.r.*) *analysis.* *FT*i.r. studies provided qualitative information relative to the conversion of poly(hydroxy amide) (PHA) to PBO. Thin polymer films were analysed on a Nicolet MX-1 *FT*i.r.

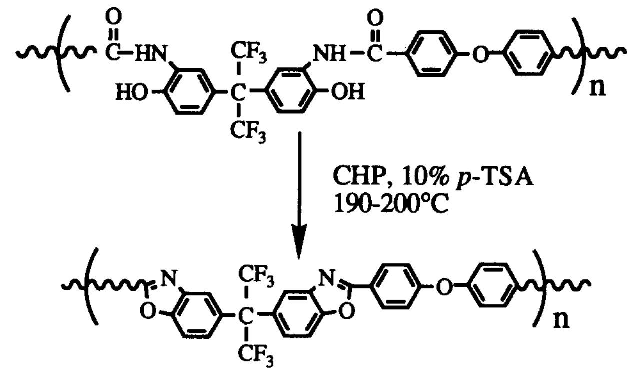
Thermal analysis. A DuPont 912 differential scanning calorimeter was used to determine T_gs as well as melting endotherms. Scans were run at a heating rate of 10°C min^{-1} in an atmosphere of N_2. Reported T_g values were obtained from the second heat after a slow cool. Thermo-oxidative stabilities were determined on a DuPont 951 thermogravimetric analyser at a heating rate of 10°C min^{-1} in an air atmosphere. Isothermal ageing studies were performed in a Blue-M circulating atmosphere oven. The sample films (0.13–0.25 mm thick) were dried to a constant weight and heated in the chamber to the test temperature. The samples were aged under an air atmosphere flowing over the samples at 25 cm^3 h^{-1}. The samples were periodically removed from the oven and weighed on an analytical balance.

RESULTS AND DISCUSSION

Polymerization of the fluorinated monomers with terephthaloyl chloride behaved quite differently than the bisphenol-A based aminophenol[18]. In general, it was



Scheme 1 Synthesis of PHA



Scheme 2 Conversion of 6FAP–ODB PHA to PBO

demonstrated that fluorinated bisaminophenols did not easily form high molecular weight polymers under what could be considered normal amidation conditions (*Scheme 1*). Fortunately, the PHA based on 6FAP **1** and ODB, **3**, shown in *Scheme 2*, easily afforded high molecular weight polymers[19]. Accordingly, this polymer was used as a model system for studying the cyclization reaction. In addition, the 6FAP–ODB PBO is soluble in THF, NMP, chloroform and *m*-cresol at various molecular weights, therefore facilitating characterization of the material via solution, spectroscopic and chromatographic techniques. Highly transparent and mechanically strong cast films were also prepared[19–21].

Optimal cyclization conditions for the fluorinated PHAs, such as **4**, were conducted using two different acid catalysts and various reaction temperatures. Dehydration of the reaction mixture was achieved by azeotroping the reaction mixture with various co-solvents. For instance, toluene was effective at removing water in the temperature range of 150–170°C, while DCB was useful at temperatures around 185°C. CHP was used as the solvent/dehydrating agent for even higher temperature reactions. The per cent cyclization was determined using the aromatic portion of the ^{1}H n.m.r. spectrum (*Figure 1*) obtained from aliquots of the reaction mixture at various times throughout the reaction. Dividing the integral for the two peaks at $\delta = 7.8$ ppm by the combined integrals from the peaks at $\delta = 7.8$ and $\delta = 7.05$ ppm results in the desired per cent PBO at a specific time or, conversely, the per cent PHA still remaining. *Figure 1* demonstrates quite clearly that complete cyclization has occurred and that monitoring the cyclization by ^{1}H n.m.r. is quite reliable. From the plot of per cent cyclization as a function of time for various concentrations of *p*-TSA and a range of reaction temperatures (*Figure 2*), one can clearly see that increasing catalyst concentration and temperature results in an increase in the rate of cyclization. Reactions conducted at or below 170°C, were allowed 8 h to completely cyclize, while temperatures greater than 180°C resulted in completely cyclized PBOs in as little as 2–5 h. Attempts to cyclize the PHA without the addition of an acidic description resulted in less than 1% conversion over a 5 h period.

To determine the effect of the acid catalyst on apparent molecular weight, solution viscosity measurements were performed on the precursor PHA and on the resulting PBOs. It was rationalized that polymers undergoing chain cleavage during the cyclization process would have η_{inh} values lower than the precursor PHA and that PBOs formed with minimal side reactions would display η_{inh} values higher than the precursor PHA. Unfortunately, a consequence of using this technique is that one can only compare the influence of catalysts and temperatures in relative terms. Furthermore, it is of course understood that PHA and PBO will have different

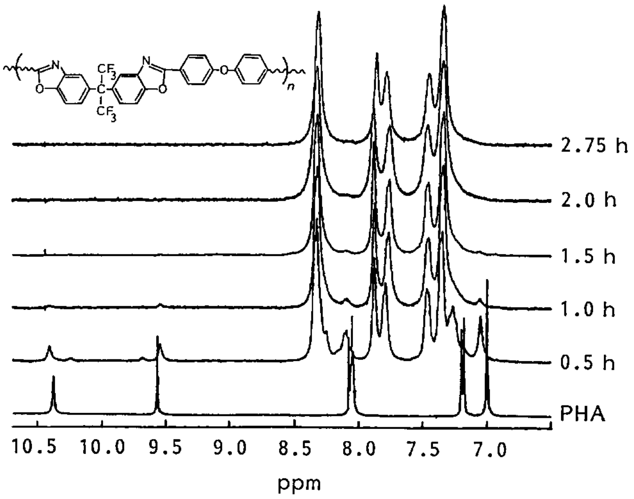


Figure 1 ^{1}H n.m.r. spectrum of the 6FAP–ODB polymers as a function of cyclization time (20% solids, w/v; NMP/DCB, 70/30 v/v; 185°C; 10% *p*-TSA)

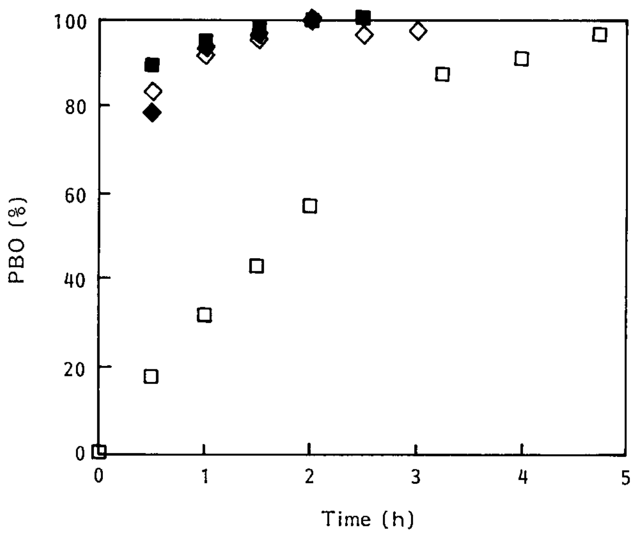


Figure 2 Conversion of 6FAP–ODB PHA to PBO as a function of reaction temperature and *p*-TSA concentration: □, 1% *p*-TSA; ◆, 10% *p*-TSA; ■, pyrHCl + 10% *p*-TSA; ◇, pyrHCl + 1% *p*-TSA (15% solids; NMP, toluene or DCB)

Table 1 Influence of cyclization conditions (20% w/v solids) on inherent viscosity values of poly(hydroxy amide)s (PHA) and derived polybenzoxazoles (PBO)

Polymer cosolvent	Catalyst	Temp. (°C)	Reaction time (h)	PHA η_{inh}^{a} (dl g^{-1})	PBO η_{inh}^{b} (dl g^{-1})
PHA	–	–	–	0.70	0.92
NMP/DCB	10% *p*-TSA	185	2.00	0.83	0.61[c]
NMP/DCB	1% *p*-TSA	185	4.75	0.92	–
NMP/DCB	100% PyrHCl + 10% *p*-TSA	185	2.75	0.76	–
NMP/DCB	100% PyrHCl + 1% *p*-TSA	185	3.00	0.61	–
CHP	10% *p*-TSA	195	3.00	1.08*	–

[a] Measured in THF, except * measured in *m*-cresol
[b] Measured in NMP
[c] Polymer not completely soluble

solvent–polymer interaction parameters and Mark–Houwink constants. Nevertheless, the results of this study (*Table 1*) suggest that higher temperatures and lower catalyst concentrations are required to maintain the η_{inh} at or above that of the PHA. The increase in η_{inh} was attributed to two different phenomena: (1) an increase in chain stiffness due to the formation of aromatic rings during cyclization; and/or (2) an increase in molecular weight after cyclization due to chain extension reactions. Theoretically, size exclusion chromatography should be able to better define these complementary effects. Nevertheless, it appears from the data in *Table 1* that molecular weight is not being dramatically affected by cyclization when *p*-TSA is used as the catalyst, but that combinations of *p*-TSA and pyridine hydrochloride appear to promote some degree of chain degradation. The optimum cyclization conditions found in this study were 10% *p*-TSA at 190–195°C in CHP for 4 h.

A number of fluorinated and non-fluorinated monomers (*Table 2*) were then used for the synthesis of fluorinated PBOs. Low temperature amidation in the presence of pyridine resulted in PHAs which were isolated and dried under vacuum to ensure removal of residual pyridine hydrochloride. Dissolution of the PHAs in CHP with 10% *p*-TSA and heating at 190–200°C for 4 h resulted in the formation of fully cyclized PBOs (*Scheme 1*). In most cases the PBOs remained in solution throughout the cyclization reaction. Exceptions to the trend were found for PBOs containing the terephthaloyl and isophthaloyl linkages. However, even in these cases, only some haziness in the reaction mixture was observed. Confirmation of ring closure was provided by thermogravimetric analysis (t.g.a.) and i.r. spectroscopy. With respect to the issue of molecular weight degradation during cyclization, it appears that the observations made in the model cyclization reaction did not apply (*Table 2*). The [η] values of the PBOs were lower than the η_{inh} values of the precursor PHA in nearly all cases, suggesting that chain degradation may be occurring during the cyclization process. More research is needed to clarify this issue.

Table 2 Solution and thermal properties of various fluorine-containing polybenzoxazoles

Polymer	η_{inh}^{a} (dl g^{-1})	$[\eta]^{b}$ (dl g^{-1})	T_g^{c} (°C)	5 wt% t.g.a.[d] (°C)
6FAP–ODB	0.92	1.08*	280	534
3F–ODB	0.48	0.29	299	547
6FAP-3FAC	0.44	0.48	310	529
3FAP-3FAC	0.29	0.27	330	514
6FAP–IC	0.62	0.54*	296	512
3FAP–IC	0.31	0.26	301	524
6FAP–TC	0.65	0.45*	361	531
3FAP–TC	0.37	0.20*	369	536
6FAP–6FAC	0.56	0.41*	336	531
3FAP–6FAC	0.27	0.26	334	520

[a] PHA precursor measured in NMP
[b] Fully cyclized PBO measured in NMP, except * measured in *m*-cresol
[c] Heating rate 10°C min^{-1}, atmosphere N_2
[d] Heating rate 10°C min^{-1}, atmosphere air

Table 3 Solubility characteristics[a] of various fluorinated polybenzoxazoles (10% solids (w/v))

Polymer composition	Solvent				
	$CHCl_3$	THF	NMP	DCB	*m*-cresol
6FAP–ODBC	S	S	S	S	S
3F–ODBC	SS	S	S	S	S
6FAP–3FAC	S	S	S	S	S
3FAP–3FAC	S	S	S	S	S
6FAP–IC	SS	I	I	SS	S
3FAP–IC	SS	I	SS	S	S
6FAP–TC	SS	I	I	I	S
3FAP–TC	SS	I	I	S	S
6FAP–6FAC	SS	I	S	I	S
3FAP–6FAC	S	S	S	S	S

[a] S, Soluble; I, insoluble; SS, slightly soluble

A preliminary comparison of the solution and thermal properties of these materials is provided in *Tables 2* and *3*. The η_{inh} and [η] values for the 6F PBOs suggest higher molecular weight and, in general, the films formed from these PBOs had a better appearance than those from the respective 3F counterparts. Although not shown, the solubility differences between the 3F and 6F polymers were noticed and, in general, the 3F PBO tended to be more soluble than the 6F PBOs. The PHAs, on the other hand, showed no real difference in their solubilities. Dynamic t.g.a. (5% weight loss) in air was not sensitive to molecular structure and with all of the values exceeded 500°C. Perhaps most interesting is the effect on the T_g of substituting a 3F for a 6F linkage. In most cases the T_g is barely affected by replacing a 6F linkage with a 3F linkage. For example, 6FAP–TC and 3FAP–TC, 6FAP–IC and 3FAP–IC, and DHB–6FAC and DHB–3FAC have nearly the same T_g values, although PBOs 6FAP–3FAC and 3FAP–3FAC have T_g values differing by about 20°C (ref. 19). Recent model efforts[20] suggest that the 3F system should be more rigid.

CONCLUSIONS

A number of novel fluorinated PBOs have been successfully synthesized in high molecular weight using a two-step polymerization/cyclization technique. Based upon model studies carried out on 6FAP and ODB, optimum cyclization conditions were achieved when 10 mol% *p*-TSA was used as the catalyst in CHP at 195°C for 4 h. Not all of the fluorinated PHAs resulted in high molecular weight, and further mechanistic studies are required to elucidate this feature. Nevertheless, numerous novel fluorine-containing PHAs and PBOs have been generated, which show T_g values between 280 and 370°C. Dynamic thermo-oxidative stability proved to be quite good[19] and, in general, PBOs containing the 3F linkage displayed enhanced solubility relative to their 6F counterparts, although both produced transparent ductile films. Modelling efforts have provided some interesting differences between the two systems[20].

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REFERENCES

1 Culbertson, B. M. and Murphy, R. *J. Polym. Sci., Polym. Lett.* 1966, **4**, 249

2 Kubota, T. and Nakanishi, R. *J. Polym. Sci., Polym. Lett.* 1964, **2**, 655

3 Imai, Y., Taoka, I., Uno, D. and Iwakura, Y. *Makromol. Chem.* 1965, **83**, 167

4 Moyer, W. W. Jr, Cole, C. and Anyos, T. *J. Polym. Sci., A* 1965, **3**, 2107

5 Wolfe, J. F. in 'Encyclopedia of Polymer Science and Engineering', (Ed. N. M. Bikales), 2nd edn, Vol. 11, Wiley-Interscience, New York, 1988, p. 601

6 Arnold, C. Jr *Macromol. Rev.* 1979, **14**, 265

7 Wolfe, J. F. and Arnold, F. E. *Macromolecules* 1981, **14**, 909

8 Tanaka, Y., Oishi, Y., Kakimoto, M. A. and Imai, Y. *J. Polym. Sci., Polym. Chem.* 1991, **29**, 1941

9 Reinhardt, B. A. *Polym. Commun.* 1990, **31**, 453

10 Ueda, M., Sugita, H. and Sato, M. *J. Polym. Sci., Polym. Chem.* 1986, **24**, 1019

11 Hilborn, J. G., Labadie, J. W. and Hedrick, J. L. *Macromolecules* 1990, **23**, 2854

12 Krause, S. J., Haddock, T. B., Vezie, D. L., Lenhert, P. G., Hwang, W. R., Price, G. E., Helminiak, T. E., O'Brien, J. B. and Adams, W. W. *Polymer* 1988, **29**, 1354

13 Tsai, T. T. and Arnold, F. E. *Am. Chem. Soc., Polym. Prepr.* 1988, **29** (2), 324

14 Feger, C., Khojastech, M. M. and McGrath, J. E. 'Polyimides: Materials, Chemistry, and Characterization', Elsevier, 1989

15 Wilson, D., Stenzenberger, H. D. and Hergenrother, P. M. 'Polyimides', Chapman Hall, New York, 1990

16 Kim, Y. J., Glass, T. E., Lyle, G. D. and McGrath, J. E. *Macromolecules* 1993, **26**, 1344

17 Joseph, W. D., Abed, J. C., Mercier, R. and McGrath, J. E. *Am. Chem. Soc. Polym. Prepr.* 1993, **34** (1), 397

18 Joseph, W. D., Mercier, R., Prasad, A., Marand, H. and McGrath, J. E. *Polymer* 1993, **34**, 866

19 Joseph, W. D. PhD Thesis, Virginia Polytechnic Institute and State University, 1993

20 Vasudevan, V., Abed, J. C. and McGrath, J. E. MacroAkron IUPAC Preprints, 11–14 July 1994

21 Joseph, W. D., Abed, J. C., Yoon, T. H. and McGrath, J. E. *Am. Chem. Soc. Polym. Prepr.* 1994, **35**(1), 551

22 McGrath, J. E., Grubbs, H., Rogers, M. E., Gungor, A., Joseph, W. D., Mercier, R., Rodrigures, D., Wilkes, G. L. and Brennan, A. 23rd International SAMPE Technical Conference, 1991, Vol. 23, p. 119

23 McGrath, J. E., Grubbs, H. J., Woodard, M. H., Rogers, M. E., Gungor, A., Joseph, W. D., Mercier, R. and Brennan, A. *Composite Structures* 1994, **27**, 7

24 Alston, W. B. and Gratz, R. F. US Patent 4 758 380, 1988

25 Weast, R. C. (Ed.), 'CRC Handbook of Chemistry and Physics', 67th Edn, CRC Press, Boca Raton, 1987

26 Lau, K. S. Y., Landis, A. L., Kelleghan, W. J. and Beard, C. D. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 2381