High-Temperature Polybismaleimide and Polybisnadimides Containing Keto and Ether Groups

Devendra Kumar[a]; Jasmeet Kaur[a]

[a] Polymeric Materials Laboratory, Department of Chemistry, University of Delhi, Delhi, India

PLEASE SCROLL DOWN FOR ARTICLE

HIGH-TEMPERATURE POLYBISMALEIMIDE AND POLYBISNADIMIDES CONTAINING KETO AND ETHER GROUPS

Devendra Kumar[*] and **Jasmeet Kaur**
Polymeric Materials Laboratory,
Department of Chemistry, University of Delhi,
Delhi-1100 07, India.

Abstract

High-temperature resistant polybismaleimide (XI) and polybisnadimides (XII), (XIII) and (XIV) were prepared from the reaction of 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BAPBB) (II) and 4,4'-bis(4''-aminophenoxy)benzophenone (4,4'-BAPB) (I) with maleic anhydride and nadic anhydride, respectively, followed by *insitu* cyclodehydration and polymerization. Thermal polymerization was performed at 225°C for 1.5 and 290°C for 0.5 h. Tough, brown polymers were obtained. Thermal polymerization was monitored using infrared (IR) spectroscopy. The thermal stabilities of the polymers were evaluated in nitrogen and in air by thermogravimetric analysis (TGA). The polymers were stable upto 400-430°C and had char yields of 50-65% at 800°C in nitrogen. The synthesised polymers were tested for solubility and were found insoluble in DMAC, DMSO and chloroform. The polymer precursors were characterized using IR and ^{1}H-NMR spectroscopy. The synthesised polymers are useful for the development of composites for high-temperature applications.

INTRODUCTION

The aerospace and electronics industries are actively looking for new and improved matrix resins for fiber-reinforced composites for elevated temperature applications. The aerospace industry in particular requires composites with hot wet envoirmental resistance which is achievable with high T_g resins, but the electronic industry favours high-temperature resins due to dimensional stability and low coefficient of thermal expansion (CTE) requirements. During the last few years endcapped bisimides and nadimides have found many applications for the formulation of the low cost, high temperature thermosetting resin systems. Grundschober[1] reported the homopolymerization of bismaleimides (BMIs) which can be achieved by a simple heating to temperatures between 150-400°C resulting in a highly crosslinked polymers involving addition reactions. Later nadic anhydride derivatives have been found suitable[2] for the synthesis of high-temperature resistant resins with improved processing characteristics. However, the developed resins were found to be inherently brittle because of the extensive crosslinking that occurs during

---

[*] Author to whom all correspondence should be addressed.

polymerization. Many BMI type resins are available commercially, but there is a continuous demand for improved matrix resins for numerous civil and defense applications. We[3-8] and several others[9-16] have developed modified BMI type resins.

An effective means of improving the solvent resistance and increasing the modulus in linear polymers has been by incorporating carbonyl and ether groups between the aromatic rings in the backbone. A notable example is polyetheretherketone (PEEK[R])[17] with a neat resin fracture energy, (G_{IC}, critical strain energy release rate) of 34 to 69 in. lb/in^2. In an effort to obtain processable, solvent and impact resistance addition polyimides, potentially useful as matrix resins for aerospace and electronics applications, we have synthesised polybismaleimide and polybisnadimides containing keto and ether groups. In this paper we present synthesis, characterization and thermal evaluation of keto and ether containing polybismaleimide and polybisnadimides.

EXPERIMENTAL

Materials: Aromatic diamines containing carbonyl and ether groups were synthesised by our modified method[18]. 1,3-Bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BAPBP)(II), m.p. 162-164°C (Lit[19]., m.p. 161.5-164°C) was synthesised from chlorobenzene and isophthaloyl chloride, followed by the reaction of the resulting 1,3-bis(4-chloro-4'-benzoyl)benzene with 4-hydroxyacetanilide and hydrolysis. 4,4'-Bis(4''-aminophenoxy)benzophenone (4,4'-BAPB)(I) was synthesised from 4,4'-difluorobenzohpenone and 4-aminophenol, m.p. 141-142°C (Lit[20], 141-142°C). Maleic anhydride (Aldrich) was purified by recrystallization from chloroform, m.p. 54°C. Endobicyclo[2,2,1]-hept-5-ene-2,3-dicarboxylic anhydride (nadic anhydride)(Aldrich) was purified by recrystallization from acetic anhydride, m.p. 165°C . Chloroform was dried by distillation over phosphorus pentoxide, b.p. 61°C. Solvent N,N'-dimethylacetamide and N,N'-dimethyl sulfoxide were dried and distilled from phosphorus pentoxide.

Techniques: Melting points were uncorrected and determined in a capillary tube by using an optical microscope melting point apparatus. Infrared (IR) spectra were recorded on a Shimadzu spectrometer IR-435 on a KBr disk. Elemental analysis was performed on a Heraeus CHN elemental analyzer. Dynamic thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Perkin-Elmer System 7/4 thermal analysis instrument attached to a Perkin-Elmer computer data station; heating rate 20°C/min, gas flow 100 mL/min, and the sample weight was 3-5 mg. Proton magnetic resonance (^{1}H-NMR) spectra were recorded on a Perkin-Elmer R32 (90 MHz) spectrometer. The chemical shift (δ) is given in ppm with tetramethyl silane (TMS) as an internal standard.

Synthesis

Reaction of diamine II with maleic anhydride (III): Formation of Bismaleamic acid (V).
     To a three-necked R.B. flask equipped with a nitrogen inlet, a calcium chloride guard tube and a magnetic stirrer, was dissolved 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (II) (1.0g, 0.002 mole) in dry chloroform. To this continuously stirring solution, granular maleic anhydride (I)(0.431g, 0.0044 moles) was added in one lot and the solution was stirred for 2 h. The resulting solution was poured in dry benzene. The solid obtained was filtered and dried in vacuum to give a yellow solid (V)(90% yield), m.p. 217-218°C.
ANAL for $C_{40}H_{28}N_2O_{10}$. Calculated: C, 68.96%; H, 4.03%; N, 4.03%. Found: C,67.97%; H, 4.13%; N, 4.69%.

NMR(DMSO-d$_6$)(δ): 10.0 (S, 2H, -COO<u>H</u>, exchangeable to D$_2$O), 9.80 (bS, 2H, -CO<u>NH</u>-, exchangeable to D$_2$O), 6.82-8.0 (m, 20H, aromatic) and 6.00-6.50 (q, 4H, cis olefinic, J=7 H$_z$).

In situ Imidization and polymerization

The bismaleamic acid (V)(1g) was prepared by dissolving the diamine (II) in DMAC (7 ml) using the method described above. The clear yellow solution was taken in an aluminium cup and placed in a preheated air oven maintained at 65-70°C for overnight and the solvent was allowed to evaporate-off. The cyclodehydration of the bismaleamic acid (V) was performed at 160°C for 0.5 h to bismaleimide (VIII). Thermal polymerization was carried out at 225°C for 1.5 h and at 290°C for 0.5 h to give a tough, brown polymer (XI).

Reaction of diamine (I) with nadic anhydride (IV): Formation of bisnadic acid (VII).

In a three-necked R.B. flask equipped with a nitrogen inlet, a calcium chloride guard tube and a magnetic sitrrer, 4,4'-bis(4"-aminophenoxy)-benzophenone(I) (1.98 g, 0.005) was dissolved in acetone. To this continuously sitrring solution, granular nadic anhydride (IV) (1.71 g, 0.014 mole) was added in one lot and the solution was stirred for 1.5 h. The resulting solution was poured in dry benzene. The solid obtained was filtered and dried in vaccum to give a white solid of bisnadic acid (VII)(85%), m.p. 77-80°C.
ANAL for C$_{43}$H$_{36}$N$_2$O$_9$. Calculated: C, 71.27%; H, 4.97%; N, 3.87%. Found: C, 71.03%; H, 4.97%; N, 3.45%.
^{1}H-NMR(DMSO-d$_6$)(δ): 10.50 (bS, 2H, -COO<u>H</u> exchangeable to D$_2$O); 9.72 (S, 2H, -<u>NH</u>CO-, exchangeable to D$_2$O); 7.95-7.75 (d, 4H, aromatic, J=9 Hz); 7.20-7.00 (2d, 8H, aromatic, J=9 Hz); 6.50-6.18 (m, 4H, aromatic); 6.17-6.00 (2d, 2x2H, olefinic a,a'); 3.50 (2m, 2x2H, b,b'). 3.10-3.00 (2m, 2x2H, c,c') and 1.40-1.30 (m, 4H, d').

In situ Imidization and Polymerization

The bisnadic acid (VII)(1g) was prepared by dissolving the diamine (I) in DMAC (7.5ml) using the method described above. The clear yellow solution was taken in an aluminum cup and placed in a preheated air oven maintained at 65-70°C for overnight to evaporate off the solvent. The resulting solid was cyclodehydrated at 160°C for 0.5 h to bisnadimide (X). It was polymerized thermally at 225°C for 1.5 h and at 290°C for 0.5 h to give a tough, brown polymer (XIII).

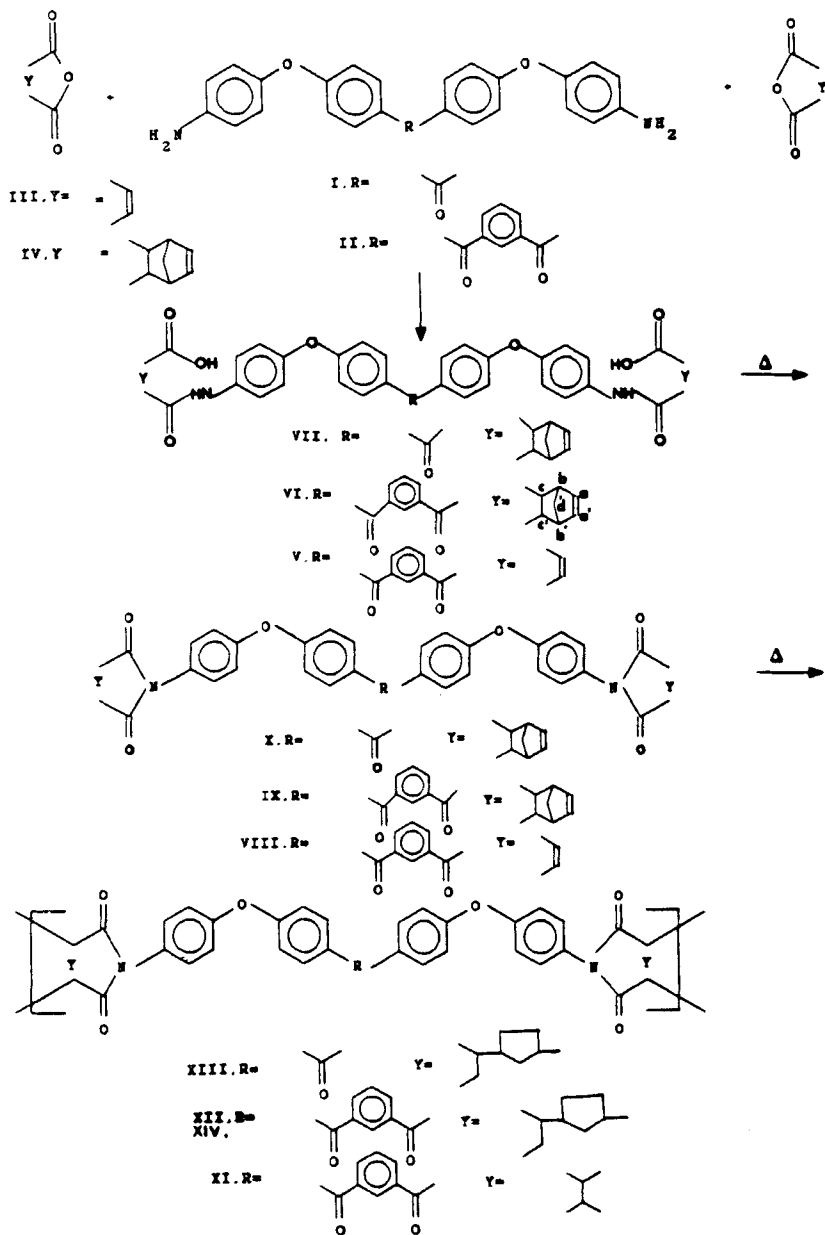### Reaction of diamine (II) with nadic anhydride (IV): Formation of bisnadic acid (VI).

Using a similar method as descrebed above for the preparation of bisnadic acid (VII), bisnadic acid (VI) was synthesized by the reaction of diamine (II) with nadic anhydride in 90% yield, m.p. 161-162°C.
ANAL for C$_{50}$H$_{40}$N$_2$O$_{10}$. Calculated: C, 72.46%; H, 4.83%; N, 3.39%. Found: C, 72.16%; H, 5.19%; N, 3.40%.
^{1}H-NMR(DMSO-d$_6$)(δ): 10.45 (bS, 2H, -COOH, exchangeable to D$_2$O); 9.75 (S, 2H, -N<u>H</u>CO-, exchangeable to D$_2$O); 8.30-7.75 (m, 8H, aromatic); 7.45-6.85 (m, 8H, aromatic); 6.48-6.35 (bd, 4H, aromatic, J=9 Hz); 6.17-6.00 (2 m, 2x2H, Olefinic, a,a'); 3.35 (2m, 2x2H, b,b'); 3.10-3.00 (2,m 2x2H, c,c') and 1.50 (m, 4H, d').

In situ Imidization and Polymerization

The bisnadic acid (VI)(1 g) was prepared by dissolving the diamine (II) in DMAC (7 ml) using the above described method. The clear yellow solution was

III.Y=

IV.Y =

I.R=

II.R=

VII. R=   Y=

VI.R=   Y=

V.R=   Y=

X.R=   Y=

IX.R=   Y=

VIII.R=   Y=

XIII.R=   Y=

XII.R=
XIV.   Y=

XI.R=   Y=

Scheme 1

taken in an aluminum dish and placed in a preheated air-oven maintained at 65-70°C to evaporate-off the solvent. The resulting residue was cyclodehydrated at 160°C for 0.5 h to bisnadimide (IX). It was polymerized thermally at 225°C for 1.5 h and at 290°C for 0.5 h to give a tough, brown polymer (XII).

RESULTS AND DISCUSSION

Aromatic diamines containing keto and ether groups, viz., 4,4'-bis(4"-aminophenoxy)benzophenone (4,4'-BAPB) (I) and 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BAPBP) (II) were synthesized by our modified method[18]. These have been characterized[18] by FT-IR, Mass and ^{1}H-NMR spectroscopy.

Scheme 1 outlines the synthesis of polybismaleimide (XI) and polynadimides (XII), (XIII) and (XIV) by involving the reaction of diamine (I) and (II), with maleic anyhdride and nadic anhydride, respectively, followed by $in\ situ$ cyclodehydration and polymerization.

The reaction of diamine (II) with maleic anhydride (III) in chloroform gave the corresponding bismaleamic acid (V). The infrared spectrum of (V) (Fig. 1A) showed the presence of carboxylic and oiefinic groups, as can be inferred from the bands observed at 3400-3000 cm^{-1}, 1712 cm^{-1} and band at 1584 cm^{-1}, respectively. The ^{1}H-NMR spectrum of (V) recorded in DMSO-d$_6$ confirms the structure. The signals at 10.00 and 9.80 ppm are assigned respectively bo carboxylic and amido protons as these are exchangeable to D$_2$O. These, together with a quartet of four cis olefinic protons at 6.00-6.50 ppm and a multiplet of twenty aromatic protons at 6.82-8.00 ppm clearly indicate the maleic anhydride attachment at the amino terminals as maleamic acid units. The $in\ situ$ thermal cyclodehydration of the bismaleamic acid (V) at 160°C gave the bismaleimide (VIII). The IR-spectrum of bismaleimide VIII showed (Fig. 1B) the characteristic imide carbonyl bands at 1778, 1712 and 742 cm^{-1}. Also the presence of keto (1652 cm^{-1}) ether (1242 cm^{-1}) and the aromatic groups (1498 cm^{-1}) were clearly observed.

The reaction of diamine (II) with nadic anhydride (IV) in chloroform gave the corresponding bisnadic acid (VI). Its infrared spectrum showed the presence of carboxylic (3250-3000 cm^{-1} and 1705 cm^{-1}) and olefinic (1610 cm^{-1}) groups. The ^{1}H-NMR spectrum of (VI) recorded in DMSO-d$_6$ showed signals at 10.45 and 9.75 ppm. These are assigned respectively to carboxylic and amido protons as these are exchangeable with D$_2$O. These, together with two multiplets at 6.17-6.00 ppm, corresponding to the four olefinic protons, the eight aliphatic protons at 3.35 and 3.10-3.00 ppm, and the four protons of the norbornene bridge-head methylene (multiplet at 1.50 ppm) confirmed the nadic anhydride attachement at the amino terminals. Besides these signals, the rest of the ^{1}H-NMR spectrum of (VI) remains almost identical to that observed[18] for the parent diamine (II). The $in\ situ$ thermal cyclodehydration of bisnadic acid (VI) at 160°C gave the bisnadimide (IX). Its infrared (IR) spectrum showed the characteristic imide carbonyl bands at 1770, 1715 and 745 cm^{-1}. Also the presence of keto (1650 cm^{-1}), ether (1240 cm^{-1}) and the aromatic groups were clearly observed.

Using the similar method of condensation and $in\ situ$ cyclodehydration, other nadimide polymer precursor (X) was synthesized from bisnadic acid (VII) by involving the reaction of diamine (I) with nadic anhydride and were characterized spectroscopically.

THERMAL POLYMERIZATION

Thermal polymerization of bismaleimide (VIII) and   bisnadimide (IX) and (X) was performed above 225°C to form tough, crosslinked polymers. The curing cycles
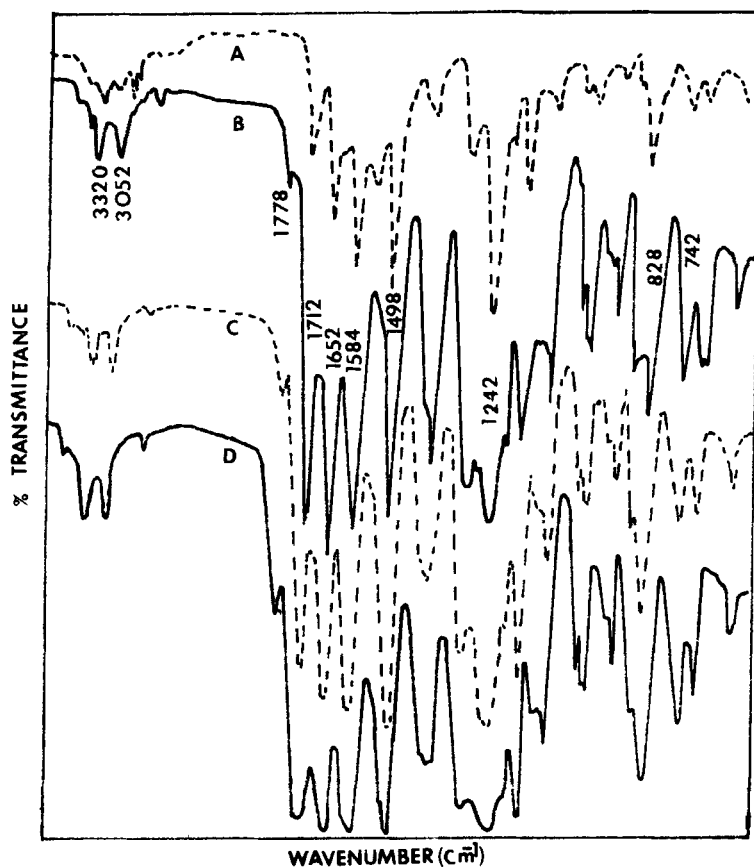
Figure 1. Infrared spectra on a KBr disk of :
A. Bismaleamic acid (V) ; B. Bismaleimide (VIII);
C. After heating VIII at 225°C for 1.5 h ;
D. Polymer XI.

were selected based on our earlier studies.[5] The bismaleimide (VIII) was *in situ* thermally polymerized in an air oven maintained at 225°C for 1.5 h. The temperature of the oven was then raised for further curing at 290°C for 0.5 h. A tough, brown polymer (X) was obtained. The thermal polymerization was monitored using IR spectroscopy on a KBr disk heated along with the sample. Fig. 1C and 1D shows the pattern of IR obtained at 225°C for 1.5 h and at 290°C for 0.5 h, respectively. A general braodening of the IR bands at this stage indicated polymerization. Similarly, *in situ* thermal polymerization of bisnadimide (IX) and (X) was carried out thermally in an air oven. Tough polymers (XII) and (XIII) were obtained. Thermal
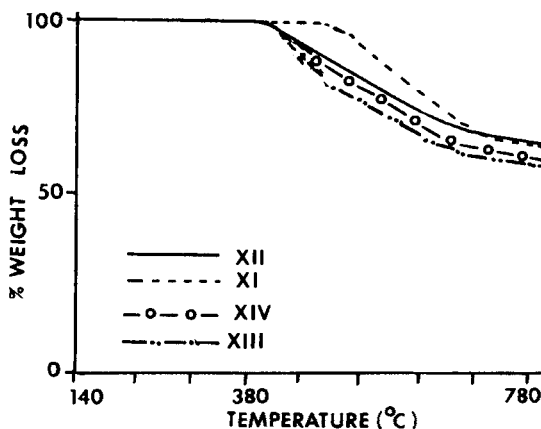
Figure 2. Dynamic Thermogravimetric Analysis of Polymers
in Nitrogen.

TABLE 1

Decomposition Temperature and Char Yield of the Polymers
in Nitrogen Atmosphere

Polymer	PDT(°C)	PDT_{max}(°C)(W_r^a,%)	Char Yield at 800°C
XI	430	590 (85)	64
XII	410	550 (82)	65
XIII	400	590 (68)	60
XIV	410	520 (67)	50

$^a W_r$ = percentage weight remaining at that temperature.

polymerization of bisnadimide (IX) in a evacuated sealed tube at 225°C for 1.5 h and 290°C for 0.5 h gave a tough polymer (XIV).

The synthesized polymers were evaluated for their thermal stability using dynamic thermogravimetric analysis (TGA) in air and nitrogen atmosphere. Figure 2 shows TGA thermograms in nitrogen of the polymers (XI), (XII), (XIII) and (XIV). In table 1, polymer decomposition temperature PDT, temperature of maximum weight of rate loss PDT_{max} (obtained from the differential thermograms recorded simultaneously), and anaerobic char yields at 800°C are given. Interestingly, these polymers showed higher polymer decomposition temperature PDT, (410-460°C) and PDT_{max} (520-590°C) than those reported earlier from addition polymerization of polynadimides[2,6,16] or polybismaleimides. These polymers showed char yield in
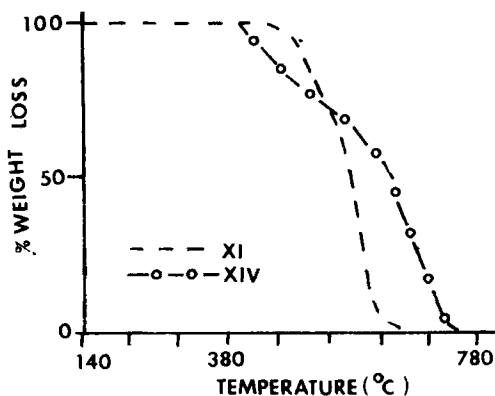
Figure 3. Dynamic Thermogravimetric Analysis of Polymers
in Air.

the range of 60-65%. The higher char yield obtained from the polymers XI and XII can be attributed due to the presence of diketo, ether groups and may be explained by the fact that during decomposition, the crosslinked units change in such a way that the weight loss is comparatively less, which may be attributed to particular aromatization reactions. In air (Fig. 3) all the polymers decompose catastrophically above 620°C with no or negligible char yield at 800°C. The synthesized polymers were tested for solubility. All the polymers were forund insoluble in DMAC, DMSO and chloroform.

The developed polymers, particularly XI and XII are potential candidates for the preparation of fiber-reinforced (graphite/glass/kevlar) composites for high-temperature applications.

REFERENCES

1.   F. Grundschober and J. Sambeth, U.S. Pats. 3,380,964 (1968)), 3, 523, 996 (1970); Fr. Pat. 1,455,514; *Chem. Abstr., 65,* 10746 (1966).
2.   H.R. Lubowitz, U.S. Pat., 3,528,950 (1970).
3.   D. Kumar, *Chem. & Ind.(London), 21,* 189 (1981).
4.   D. Kumar, G.M. Fohlen and J.A. Parker, *J. Polym. Sci., Polym. Chem. Ed., 21,* 245-267 (1983).; U.S. Pat. 4,579,782, April 1, 1986; U.S. Pat. 4,600,769 July 15, 1986.
5.   D. Kumar. G.M. Fohlen and J.A. Parker, *J. Polym. Sci.. Polym. Chem. Ed., 21,* 565-578 (1981).
6.   D. Kumar, G.M. Fohlen and J.A. Parker, *Macromolecules,* 1250-1257 (198 \textgrave{ }. U.S. Pat. 4, 634,759, Jan. 06, 1987.
7.   A.D. Gupta and D. Kumar, *J. Appl. Polym. Sci, 30,* 3879-3889 (1985).
8.   A.D. Gupta and D. Kumar, *J. Polym. Materials, 1,* 189-192 (1984).
9.   G.T. Kwaitkovski, G.E. Brode, U.S. Pat. 3,839,287 (1974).
10.   S. Street and D. Beckley, U.S. Pat. 4,351,932 (1982).

11. H.D. Stenzenberger, M. Herzog, W. Romer and R. Scheiblich, *SAMPE*, 1568-1585 (1985).
12. J.J. King, M. Chaudhari and S. Zahir, 29th National SAMPE Symposium, 29, 392-408 (1984).
13. J.V. Crivello, Am. Chem. Soc. Meeting, *Polymer Priprints*, *14*, 294 (1973).
14. A.J. Kinboch, S.J. Shaw, ACS, *Polymer Material Science and Engineering*, *49*, 307 (1983).
15. a) Tito T. Serafini and P. Delvigs, *Appl. Polym. Sym.*, *22*, 89-100 (1973).
    b) T.T. Serafini, P. Delvigs and G.R. Lightsey, *J. Appl. Polym. Sci.*, *16*, 905 (1972).
16. D.A. Scola and M.P. Stevenes, *J. Appl. Polym. Sci.*, *26*, 231-247 (1981).
17. a) Imperial Chemical Industres, Wilmington, DE.;
    b) D. Hunston, National Bureau of Standards, Gaithesburg, MD, private communication, February 1986.
18. D. Kumar and J. Kaur, unpublished work.
19. P.M. Hergenrother, N.T. Wakelyn and S.J. Havens, *J. Polym. Sci., Polym. Chem. Ed.*, 25, 1093 (1987).
20. Matsui Toatsu Co. Ltd., Japan.