

Investigations on polyurethane anionomers using 3,4-dihydroxycinnamic acid. 1

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Polyurethanes of different compositions were synthesized by chain extending the prepolymer formed by the reaction of poly(tetramethylene oxide)glycol and tolylene diisocyanate with 3,4-dihydroxycinnamic acid. The polyurethanes were characterized using Fourier transform infra-red and Fourier transform nuclear magnetic resonance spectroscopies. The molecular weights of the polymers were determined using gel permeation chromatography. The polyurethane anionomers showed typical polyelectrolyte behaviour. The glass transition temperatures of the polyurethanes and their anionomers were determined by differential scanning calorimetry. The thermal stabilities of the polymers were evaluated using a thermogravimetric analyser. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polyurethanes with ionic moieties are of interest due to their water dispersibility. Polyurethane ionomers may be synthesized by using (a) an ionic diisocyanate, (b) an ionic diol or (c) post-synthesis modification of the polyurethane. Polyurethanes with carboxylic^{1–3}, sulfonic^{4–7} and phosphoric⁸ acid groups have been studied in great detail. The introduction of aromatic groups in polymers sometimes leads to improved properties⁹. Our group has been involved in the synthesis of chain-extended polyurethanes using aromatic chain extenders with different spatial architectures¹⁰. The introduction of aromatic moieties in polyurethanes enhances the thermal and mechanical properties of the polymers. Our earlier work was based on using phthaleins, pthalins and their derivatives, xantheins and pyridinium compounds as chain extenders^{10–12}. The cinnamic acid systems have received much attention in polymer synthesis owing to the presence of unsaturated groups which can be photocured. Photosensitive polymers with polyenic groups were obtained by synthesizing vinylogues of cinnamic derivatives¹³. Homopolymers and copolymers of vinyl phenylcinnamate were studied in detail. There have been reports in which incorporation of cinnamoyl groups gives polymers which exhibit non-linear optical properties¹⁴. In our attempt to bring both ionic as well as a physico-chemically modifiable group onto the polyurethanes, we have used 3,4-dihydroxycinnamic acid (caffeic acid) as the chain extender. In this work we present our investigation of the synthesis and characterization of polyurethanes and anionomers based on 3,4-dihydroxycinnamic acid.

EXPERIMENTAL

Materials

Poly(tetramethylene oxide)glycol of molecular weight 1000 (PTMG₁₀₀₀, Aldrich) was dried under vacuum for 24 h at 35°C prior to use. Tolylene diisocyanate (TDI, a mixture of 80% 2,4-TDI and 20% 2,6-TDI), dibutyltindilaurate (DBTDL, Aldrich), 3,4-dihydroxycinnamic acid (DCA, Arrow Chemicals, India), sodium acetate and zinc acetate dihydrate (S.D. Fine Chem, India) were used as received. The solvents dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and methanol were purified by standard distillation procedures.

Measurements

Fourier transform infra-red (FTi.r.) spectra of the polymers were recorded as neat films (prepared by casting purified polymer in DMF over a pool of mercury and evaporating the solvent at 60°C) using a Nicolet Impact 400 spectrometer. Fourier transform nuclear magnetic resonance (FTn.m.r.) spectra were recorded on a Bruker MSLp 300 MHz spectrometer. The molecular weights of the polymers were determined using a Water's Associates Gel Permeation Chromatograph, the solvent being DMF stabilized with 0.01% of LiBr. Thermal analysis was carried out using a Du Pont 910 differential scanning calorimeter and a Du Pont 951 thermogravimetric analyser at a heating rate of 10°C min⁻¹ under nitrogen atmosphere.

Synthesis of polyurethanes

TDI (3.48 g, 0.02 mol) was added drop by drop to PTMG₁₀₀₀ (10 g, 0.01 mol) in a 100 ml three-necked flask at 60°C under nitrogen atmosphere. The temperature was then increased to 70°C and the reaction was allowed

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Table 1 Polymer compositions, molecular weight distribution and glass transition temperatures of polyurethanes and anionomers

Sample no.	Polymer composition	Polymer code	Molecular weight			T_g ($^{\circ}\text{C}$)
			$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	
1	PTMG ₁₀₀₀ /2TDI/DCA	C ₁	3.76	15.4	4.10	-59.5
1a	Sodium anionomer	C ₁ Na				-68.0
1b	Zinc anionomer	C ₁ Zn				-63.0
2	PTMG ₁₀₀₀ /3TDI/2DCA	C ₂	2.80	7.1	2.55	-45.0
2a	Sodium anionomer	C ₂ Na				-69.0
2b	Zinc anionomer	C ₂ Zn				-62.5

to proceed until the isocyanate content reached half the initial value (as determined by dibutylamine titration). The temperature was reduced to 60°C and the chain extender, DCA (1.8 g, 0.01 mol) in 20 ml of DMSO, was added drop by drop. Then 0.01 g of DBTDL catalyst was added, the temperature was increased to 70°C and the reaction was allowed to continue to completion. The polyurethane was precipitated by pouring into a 10-fold excess of distilled water and was washed thoroughly with methanol. The polymer was dried under vacuum at 30°C for a week. Polyurethanes of other compositions, see *Table 1*, were synthesized by the same procedure. The synthesis of the polyurethanes is represented in *Scheme 1*.

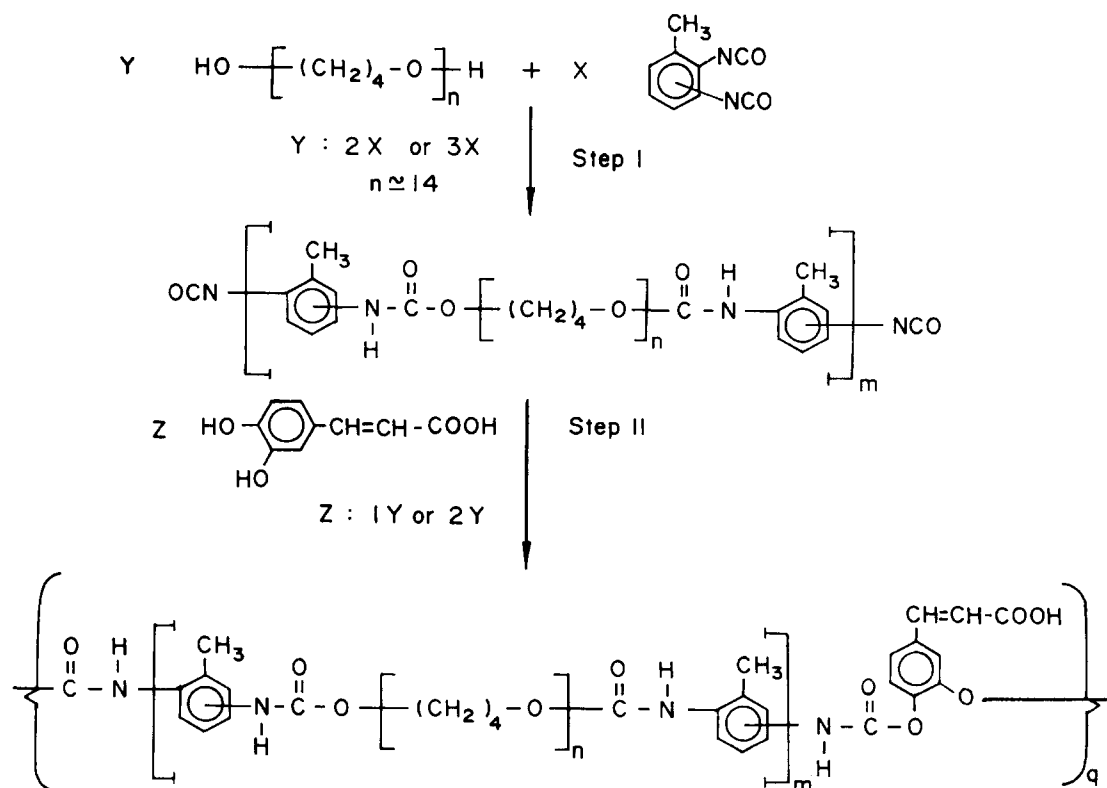
Conversion to anionomers

The polyurethanes dissolved in DMF were mixed with a stoichiometric amount of metal acetates (sodium and zinc) and cast over silicone troughs. The solvent was evaporated at a slow constant rate at a temperature of

60°C to give polyurethane anionomer films which were dried under vacuum.

RESULTS AND DISCUSSIONS

Both polyurethanes showed the expected molecular weight build-up. The molecular weights and dispersities are given in *Table 1*. The greater dispersity of both the polymers may be attributed to branching or to some amount of side reactions with the carboxylic acid groups. The FTi.r. spectra of the polyurethane and ionomers are shown in *Figure 1*. The observed splitting of the carbonyl peak of the urethane at 1728 cm^{-1} and 1710 cm^{-1} in C₂ is due to the free and hydrogen-bonded groups. The same splitting observed in the case of the ionomers shows the existence of hydrogen bonding even after the ionization of -COOH to -COONa. The frequency of acid carbonyl in the anionomers shifts towards the C=C stretching of the aromatic chain extender and aromatic isocyanate unit resulting in the increased intensity of the band at 1600 cm^{-1} . The amide II band due

**Scheme 1** Synthesis of DCA chain extended polyurethane

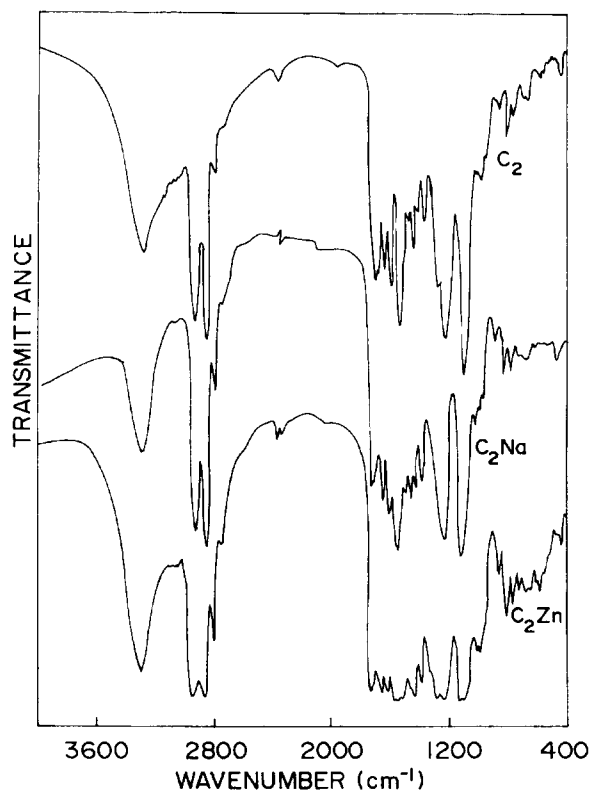


Figure 1 FTIR spectra of polyurethane and its anionomers

to the C–N stretching and N–H deformation is seen at 1531 cm^{-1} . The C–O–C stretching of the PTMG backbone is observed at 1110 cm^{-1} . The urethane N–H stretching is observed at 3283 cm^{-1} .

The ^1H n.m.r. spectrum of the polyurethane (C_2) was recorded using DMSO-d_6 solvent and is given in Figure 2. The methylene protons of the PTMG polyol segment absorb at 1.48 ppm and the methylene protons of $-\text{O}-\text{CH}_2-$ of PTMG absorb at 3.3 ppm, overlapping with the signal of water present in the solvent. The $-\text{O}-\text{CH}_2$ attached to the urethane linkage absorbs at 4.04 ppm.

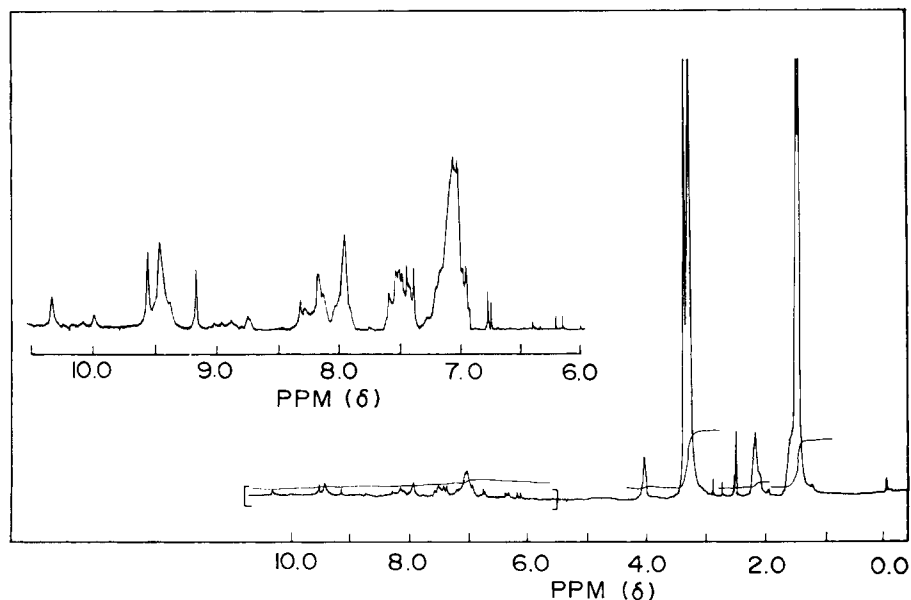


Figure 2 ^1H FT n.m.r. spectrum of C_2

The absorption of methyl protons of TDI occurs at 2.18 ppm. The aliphatic $\text{HC}=\text{CH}$ of the chain extender and the aromatic protons of TDI absorb at 6–8 ppm. The urethane N–H protons absorb in the range 8–10 ppm as observed by Lesar *et al.*¹⁵. The proton of the acid absorbs at 10.4 ppm. To find whether the unsaturated site in the chain extender is intact in the polyurethane and to simplify the complex spectra of the chain-extended polyurethane, a simple $\text{NCO}:\text{OH}$ reaction in the ratio of 1:1 was performed under the same reaction conditions and the spectrum was recorded. The spectrum showed the absorption of the aliphatic $\text{HC}=\text{CH}$ *trans* hydrogen (of cinnamic acid) as doublets at 6.12 ppm and 7.37 ppm.

The ^{13}C spectra of the polyurethane C_2 is given in Figure 3. The methylene groups of PTMG absorb at 26 ppm and $-\text{O}-\text{CH}_2$ of PTMG at 69 ppm. The carbons of the aromatic chain extender, $\text{C}=\text{C}$ and TDI absorb in the region from 110 to 140 ppm. The carbonyl group of the urethane absorbs at 158 ppm and carboxylic acid at 172 ppm.

Dilute solution behaviour

There are several important parameters such as molecular weight, ionic content, solvent polarity, counter-ion binding, etc., that influence the solution properties of ionomers. Solution behaviour of ionic polymers with sulfonate and carboxylate groups has been studied extensively^{16–19}. In this work viscosity measurements were carried out in DMF as the solvent. The anionomers showed typical polyelectrolyte behaviour as shown in Figure 4, i.e. polymer coil expansion at lower dilutions, which disappears on addition of a strong electrolyte like LiBr. The chemical crosslinking in the case of the divalent zinc ionomer rendered the anionomer insoluble and therefore the solution properties could not be evaluated.

Thermogravimetric analysis

The thermogravimetric analysis curves of DCA, polyurethanes and the polyurethane ionomers are given in Figure 5. The chain extender decomposes above

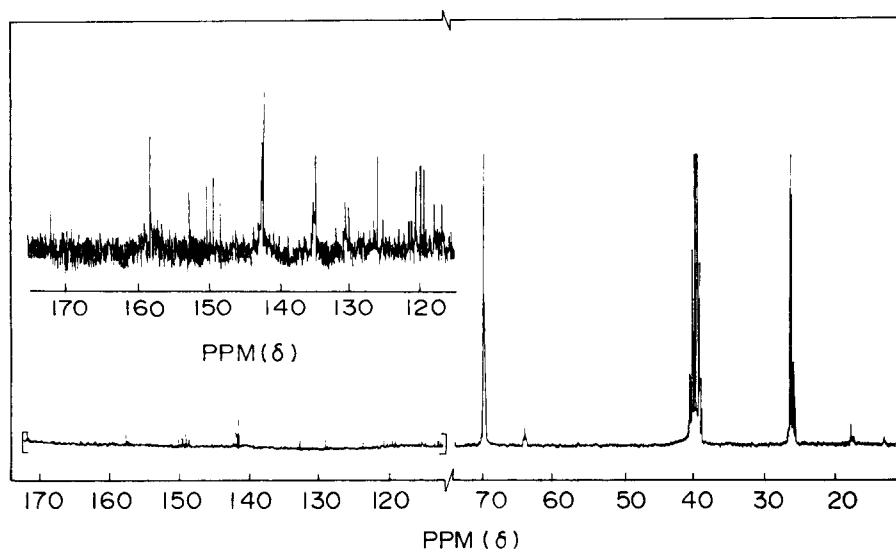


Figure 3 ¹³C FT n.m.r. spectrum of C₂

200°C. The weight loss in the case of the polyurethanes up to around 150°C is low. In the case of the anionomers the initial loss of weight up to 150°C is due to the free and bound water. Although the urethane linkages cleave at above 180°C, there is an apparent increase in the thermal stability of the polymeric systems on the use of aromatic chain extenders. This is due to the formation of non-volatile decomposition products and to the non-isothermal experimental conditions employed. The decomposition beyond 180°C could be due to a combination of various chemical segments (chain extender, urethane linkage, PTMG, etc.) in the polymer.

Differential scanning calorimetric analysis

The glass transition temperature (*T_g*) of the poly-

urethanes depends mainly on the nature of the polyol. The low *T_g* obtained in all cases is due to the nature of the PTMG₁₀₀₀ polyol used. As the polyurethanes are converted to their ionomers, the *T_g* shifts to lower temperatures as seen in Figure 6. This is expected since the introduction of ionic groups significantly alters the hydrogen bonding between the polyol segment and the hard segment, resulting in increased freedom for the polyol segment. Furthermore, when the hard segment content is increased, as in the case from C₁ to C₂, the *T_g* shifts to higher temperatures due to the increased concentration of hard segment dispersed in the soft segment inhibiting efficient phase separation. The phase separation between the hard and the soft segment in the case of zinc ionomers is not as profound as in the case of the sodium ionomers. This is due to the chemical

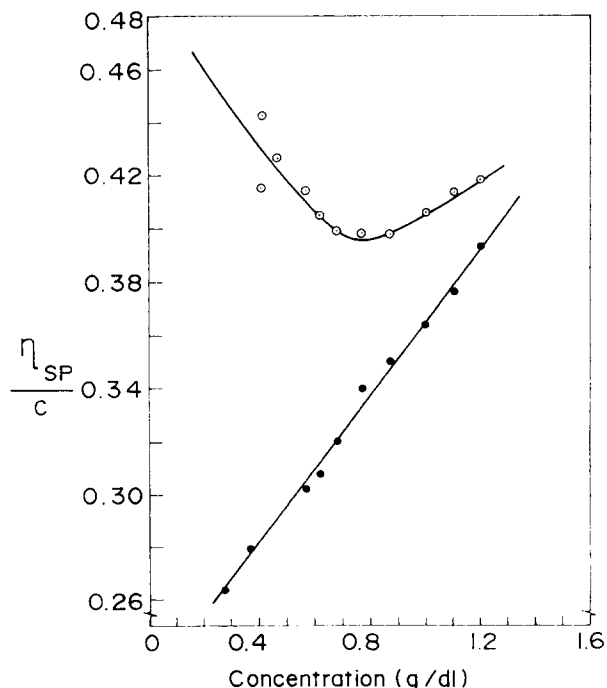


Figure 4 Reduced viscosity versus concentration behaviour of C₂ (●) and C₂Na (○)

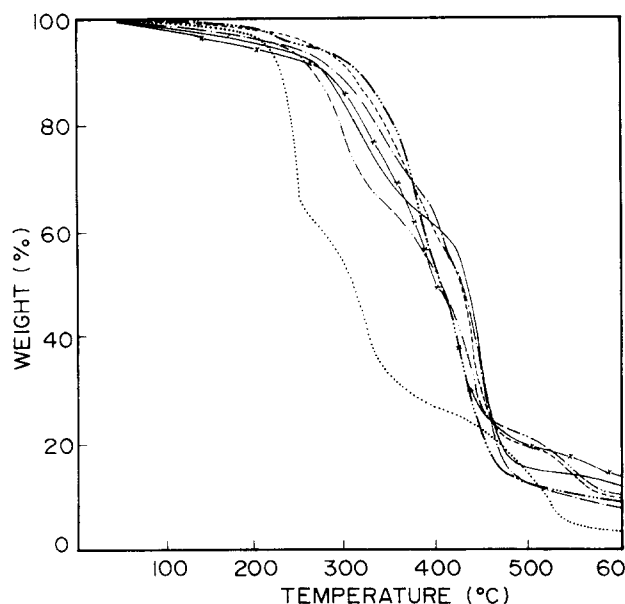


Figure 5 T.g.a. curves of DCA (.....), polyurethanes and C₁ (---) C₂ (---) and their anionomers C₁Na (---·---), C₁Zn (---x---), C₂Na (—) and C₂Zn (---·---·)

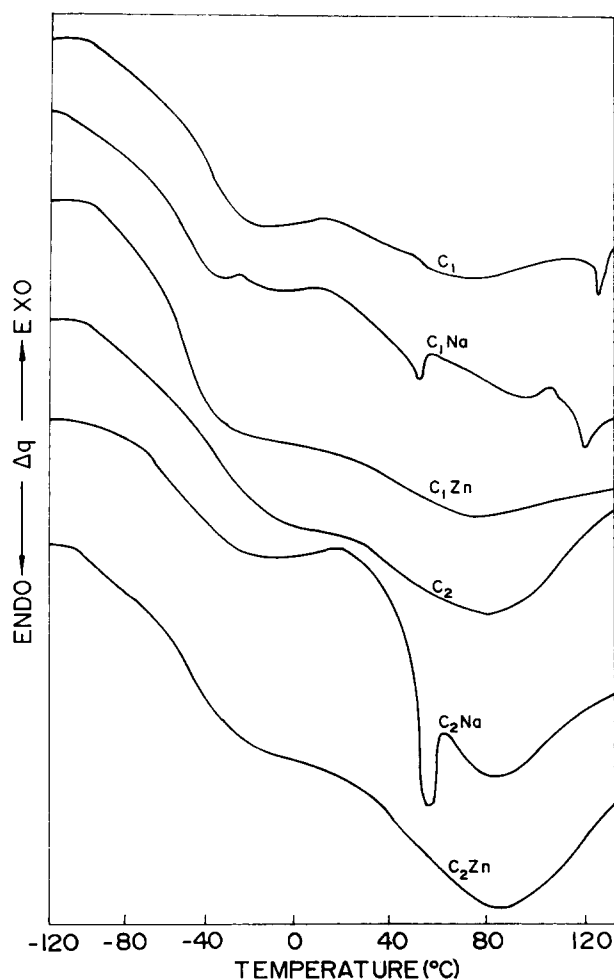


Figure 6 D.s.c. curves of polyurethanes and their anionomers

crosslinking caused by the divalent metal ion which hinders phase separation. The endotherm observed at around 55°C in the case of sodium anionomers disappeared on quenching the samples again from 150 to -130°C and repeating the heat scan. This is probably due to the short-range ordering among the ionic hard segments which is dependent on the thermal history of the polymers. Such observations have been reported by Miller *et al.*⁷.

CONCLUSION

The FTi.r. study of the chain-extended polyurethanes showed the presence of hydrogen-bonded carbonyl groups even in the case of the ionomers. The glass transition temperature of the anionomers shifted to lower temperatures as compared to the polyurethanes. The anionomers showed typical polyelectrolyte behaviour which disappeared on the addition of a strong electrolyte. Further work is in hand to study the effect of physico-chemical modification of the cinnamyl groups in these systems.

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REFERENCES

- 1 Yang, C. Z., Grasel, T. G., Bell, J. L., Register, R. A. and Cooper, S. L. *J. Polym. Sci. Part B, Polym. Phys.* 1991, **29**, 581
- 2 Ramesh, S. and Radhakrishnan, G. *Polymer* 1994, **35**, 3107
- 3 Kim, B. K. and Kim, T. K. *J. Appl. Polym. Sci.* 1991, **43**, 393
- 4 Dietrich, D., Keberle, W. and Witt, H. *Angew. Chem. Int. Edn* 1970, **9**(1), 40
- 5 Lam, P. K. H., George, M. H. and Barrie, J. A. *Polym. Commun.* 1989, **30**, 2321
- 6 Ramesh, S. and Radhakrishnan, G. *J. Macromol. Sci., Macromol. Rep.* 1993, **A30**(Supp.) 3-4, 251
- 7 Miller, J. A., Hwang, K. K. S. and Cooper, S. L. *J. Macromol. Sci. Phys.* 1983, **B22**, 321
- 8 Lam, P. K. H., George, M. H. and Barrie, J. A. *Polym. Commun.* 1991, **32**, 80
- 9 Cuve, L., Pascault, J. P., Boiteux, G. and Seytre, G. *Polymer* 1991, **32**, 343
- 10 Ramesh, S. PhD thesis, University of Madras, India, 1994
- 11 Ramesh, S. and Radhakrishnan, G. *J. Macromol. Sci., Macromol. Rep.* 1995, **A32**(1-2), 91
- 12 Ramesh, S. and Radhakrishnan, G. *J. Polym. Mater.* 1995, **12**, 71
- 13 Tsuda, M., Tanaka, H. and Nakanishi, H. *J. Polym. Sci.* 1972, **A-1**(10), 1729
- 14 Hanemann, T. and Haase, W. *ACS Polym. Prepr.* 1994, **35**(2), 254
- 15 Lesar, M., Zigon, M. and Malavasic, T. *J. Appl. Polym. Sci.* 1993, **47**, 805
- 16 Tharanikkarasu, K., Rajalingam, P. and Radhakrishnan, G. *Polymer* 1992, **33**, 3643
- 17 Hara, M., Wu, J. and Lee, A. H. *Macromolecules* 1989, **22**, 754
- 18 Hara, M., Lee, A. H. and Wu, J. *J. Polym. Sci. Part B, Polym. Phys.* 1987, **25**, 1407
- 19 Rajan, H., Rajalingam, P. and Radhakrishnan, G. *Polym. Commun.* 1991, **32**, 93