Polyurethane anionomers using phenolphthalins: 1. Synthesis and characterization

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(Received 31 August 1993; revised 23 November 1993)

Polyurethanes containing carboxylate groups were synthesized by using phenolphthalins as chain extenders. The resulting polymers were converted into ionomers by treating with metal acetates. The diols and polyurethanes were characterized by both Fourier transform nuclear magnetic resonance (*FT*n.m.r.) and Fourier transform infra-red (*FT*i.r.) spectroscopy. The thermal stabilities of the diols and polymers were analysed by thermogravimetric analysis.

(Keywords: polyurethane; anionomer; phenolphthalins)

INTRODUCTION

Polyurethane ionomers are an important class of block copolymers, used in a variety of fields for which the properties of the polymers are tailor made. The introduction of ionic groups on to the polymer backbone significantly changes the physical and morphological properties. In polyurethane ionomers, in addition to hydrogen bonding, coulombic attraction forces play a significant role in the properties of the polymers.

Polyurethane anionomers are prepared by the reaction of diisocyanates with aliphatic and aromatic diols and diamines containing sulfonic[1–8], carboxyl[9–14], or phosphoric acid groups[15]. The ionic groups are incorporated into the polymer backbone mainly during the chain-extension stage. Post-polymer introduction of ionic groups is carried out by the exchange of urethane protons by an initial ionization with sodium hydride, followed by reaction with sultone or lactone[16–18], or by the reaction with a carbon–carbon double bond on the polymer backbone[19]. Phenolphthalein has been used as a diol for the preparation of polyesters[20], poly(hydroxy ether)s[21,22], poly(imidoaryl ether ketone)s and poly(imidoaryl ether sulfone)s[23,24], polyarylates[25], poly(phosphoramide ester)s[26] and epoxy networks[27]. Earlier work from our laboratory involved the synthesis of polyurethanes using phenolphthalein as a chain extender[28]. This present work is based on a novel approach to synthesize polyurethanes with ionic chain extenders, thus enabling water dispersibility of the polymers. This has been achieved by using dihydroxy compounds containing triphenylmethane units, derivatized from phenolphthalein.

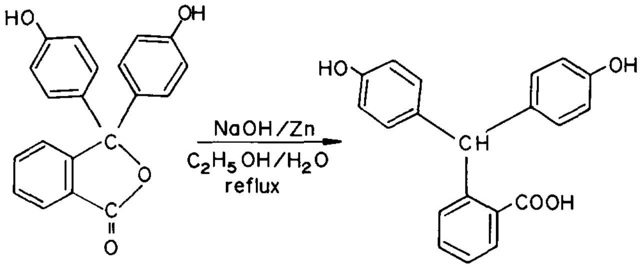
EXPERIMENTAL

Materials

Poly(tetramethylene oxide) glycol (PTMO) (Aldrich), with a molecular weight of 1000, was dried at 105°C in vacuum for 24 h before use. Dibutyltin dilaurate and tolylene diisocyanate (TDI) (Aldrich), phenolphthalein (BDH, India), thymolphthalein and sodium acetate (SD's, India) and zinc acetate (Sarabhai Chemicals, India), were used as received. Zinc powder (SDs, India) was activated before use. The solvents, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (SDs, India), were purified by standard distillation techniques and stored over molecular sieves until use.

Synthesis of diols (bisphenols) containing carboxylate groups

Phenolphthalins are derivatives of benzoic acid containing a triphenylmethane unit, prepared by the reduction of phenolphthalein or thymolphthalein (yield = 95%) (see *Scheme 1*). Tetrabromophenolphthalin was obtained by the bromination of phenolphthalin in glacial acetic acid (yield = 53%).



Scheme 1 Synthesis of phenolphthalins

The detailed procedures for the preparation of phenolphthalins are given elsewhere[29,30]. The structure of the various diols used in this work are given in *Figure 1*.

Physico-chemical characterization

The molecular weights of the polyurethanes were determined by using a Waters Associates Gel Permeation Chromatograph equipped with a refractive index detector

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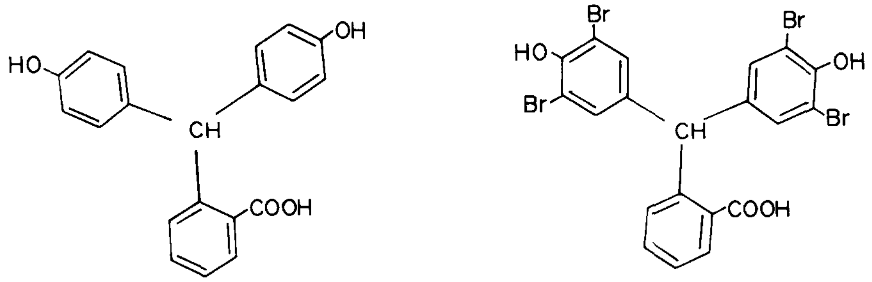
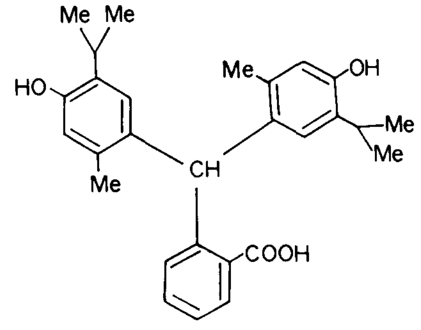


PHENOLPHTHALIN

TETRABROMO PHENOLPHTHALIN



THYMOLPHTHALIN

Figure 1 Structures of the diols used in this work

(Model 410): μ-styragel columns (10^3, 10^4, 10^5 and 10^6 Å) were used, with calibration being carried out by using polystyrene standards. The solvent used was DMF (flow rate = 1 ml min^{-1}). Infra-red spectra were recorded on a Nicolet 20DXB FTIR spectrometer. The diols were analysed by using the KBr pellet technique, with the polymers in the form of thin films, cast from DMF solutions over a pool of mercury. *FT*n.m.r. spectra were recorded on a Bruker CXP (90 MHz) spectrometer. The signals were denoted as follows: s, singlet; d, doublet; m, multiplet; w, weak; and b, broad. Thermogravimetric analysis was carried out in a nitrogen atmosphere using a Du Pont 951 thermogravimetric analyser, at a heating rate of 10°C min^{-1}.

Structures of the diols

2-[Bis(4-hydroxyphenyl)methylbenzoic acid (phenolphthalin). I.r. (KBr pellet) cm^{-1}: 1675 (C=O); 1597 (C=C, aromatic); 2920 (–CH–); 3130, 3410 and 3520 (–OH and –COOH (b)). ^{1}H n.m.r. (DMSO-d$_6$), δ (ppm): 6.4(s); 6.57–6.95(m); 7.65(d); 7.75(d); 9.17(b); 10.2(w). ^{13}C n.m.r. (DMSO-d$_6$), δ (ppm): 48.64; 114; 124; 128.7; 129.04; 129.58; 131; 133.58; 143.3; 154; 169.

2-[Bis(3,5-dibromo-4-hydroxyphenyl)methyl] benzoic acid (tetrabromophenolphthalin). I.r. (KBr pellet) cm^{-1}: 1680 (C=O); 1600 (C=C aromatic); 2915 (–CH–), 3120, 3420 and 3510 (–OH and –COOH (b)). ^{1}H n.m.r. (DMSO-d$_6$), δ (ppm): 6.4(s); 7.09–7.46(m); 7.96(d); 8.01(d); 5.41(b). ^{13}C n.m.r. (DMSO-d$_6$), δ (ppm): 48.64; 114; 124; 128.7; 129.1; 129.6; 131; 133.58; 143.3; 154; 169.

2-[Bis[4-hydroxy-2-methyl-5-(1-methylethyl)phenyl] methyl]benzoic acid (thymolphthalin). I.r. (KBr pellet) cm^{-1}: 1690 (C=O); 1595 (C=C, aromatic); 2920 (–CH–); 3100–3500 (–OH and –COOH (b)). ^{1}H n.m.r. (DMSO-d$_6$) δ (ppm): 0.94(d); 2.09(d); 6.39(s); 6.57(s); 7.30(m); 7.60(d); 4.9(b). ^{13}C n.m.r. (DMSO-d$_6$) (δ (ppm): 49.04; 111.4; 126.4; 129; 130; 131; 132; 136.8; 149; 176.

Synthesis of polyurethanes

Poly(tetramethylene oxide) glycol (10 g, 0.01 mol) was placed in a 100 ml three-necked flask and 3.48 g of TDI (0.02 mol) was added slowly, with stirring, under a nitrogen atmosphere at 60°C. The reaction was allowed to proceed for one hour, after which time the reaction temperature was raised and maintained at 90°C for a further hour. After the NCO content had reached half the initial value (as determined by dibutylamine titration), the temperature of the reaction mixture was reduced to 60°C, and 5 ml of DMSO were added. In the next step, 3.73 g (0.01 mol) of phenolphthalin in 20 ml of DMSO were added slowly with stirring, followed by 0.01 g of the catalyst (dibutyltin dilaurate). The temperature of the reaction mixture was slowly raised to 90°C and kept there for two hours. After completion of the reaction the contents were poured into a tenfold excess of methanol to precipitate the polymer, which was separated by filtration and dried at 30°C under vacuum.

The corresponding polyurethanes, obtained by using tetrabromophenolphthalin and thymolphthalin, were prepared in a similar way. A polyurethane, chain extended with mixed aromatic and aliphatic diols, was prepared by the reaction of phenolphthalin and 1,4-butanediol with the isocyanate terminated prepolymer. A polyurethane without any carboxylate groups was prepared by using phenolphthalein as the chain-extender.

Conversion into ionomers

A stoichiometric amount of metal acetate in DMF was added to the required amount of polyurethane (10% solution in DMF) and the whole system was stirred rapidly for 2 h. The contents were then poured over the base of a silicone trough, and dried in an oven for 24 h at 90°C. The resulting film was dried at room temperature in vacuum for 7 days. The ionomers produced in this way were stored in a desiccator prior to characterization. The codes given to the various

Table 1 Compositions of the polyurethanes studied in this work

Polymer composition	Urethane code	Ionomer code
PTMO/2TDI/phenolphthalin	PH	PH-Na, PH-Zn
PTMO/2TDI/tetrabromophenolphthalin	BrPH	BrPH-Na, BrPH-Zn
PTMO/2TDI/thymolphthalin	TH	TH-Na, TH-Zn
PTMO/3TDI/phenolphthalin/1,4-butanediol	PHB	PHB-Na, PHB-Zn
PTMO/2TDI/phenolphthalein	PH_R	

polymers are indicated in *Table 1*. In this system of materials the polyol and isocyanate were present as fixed components, with the only variation being with respect to the nature of the chain extender. The following codes have been used: PH, phenolphthalin based; PH-Na (Zn), sodium (zinc) salts of the phenolphthalin-based polyurethanes, etc.; and PH_R, phenolphthalein based (reference) polyurethane (see *Table 1*).

RESULTS AND DISCUSSION

Molecular weight distribution data for the various polyurethanes, obtained from gel permeation chromatography (g.p.c.) are given in *Table 2*. All of the polymers have reasonably high molecular weights. Comparing the polydispersity values for the polymers based on phenolphthalin with that obtained for the phenolphthalein-based material, the high value observed for the former may be due to a certain amount of side reactions occurring between the isocyanate and the carboxyl groups. Among the polymers containing triphenylmethane units, those with substituent groups on the phenolic ring have lower molecular weights than the unsubstituted, simple phenolphthalin materials. This may be due to the steric effect of the alkyl and halogen groups, which hinders the approach of the isocyanate terminated prepolymers towards the hydroxyl group. For the PHB polymer incorporation of butanediol units creates a high degree of linearity and ordering. However, the low polydispersity value may be due to the removal of low-molecular-weight fractions, as a result of repeated reprecipitation in the g.p.c. sample preparation process.

The *FT*i.r. spectra of the TH and PHB polyurethanes are given in *Figures 2* and *3*. The films were dried extremely thoroughly in order to avoid the characteristic sharp carbonyl peak which is observed even in the presence of traces of DMF. The observed splitting of the carbonyl peaks, at 1729 and 1711 cm^{-1}, is due to the presence of free and hydrogen bonded urethane groups. For the PHB polymer, the incorporation of butanediol units, along with phenolphthalin units, in the chain-extension stage, introduces more urethane linkages and flexibility, facilitating the production of more hydrogen bonding sites, and thus a clearer splitting is observed. Stretching, due to the aromatic double bonds of the phenyl groups, is observed at 1599 cm^{-1}. Bands, due to C–N stretching and N–H deformation (amide II band), are observed at 1531 cm^{-1}.

Table 2 Molecular weight and polydispersity values of the polyurethanes studied in this work, as obtained from g.p.c. measurements

Polyurethane	$\bar{M}_n$ ($\times 10^4$)	$\bar{M}_w$ ($\times 10^4$)	$\bar{M}_w/\bar{M}_n$
PH	11.7	95.9	8.16
BrPH	5.98	8.21	1.37
TH	5.71	14.6	2.56
PHB	4.01	4.33	1.08
PH_R	4.89	7.61	1.56

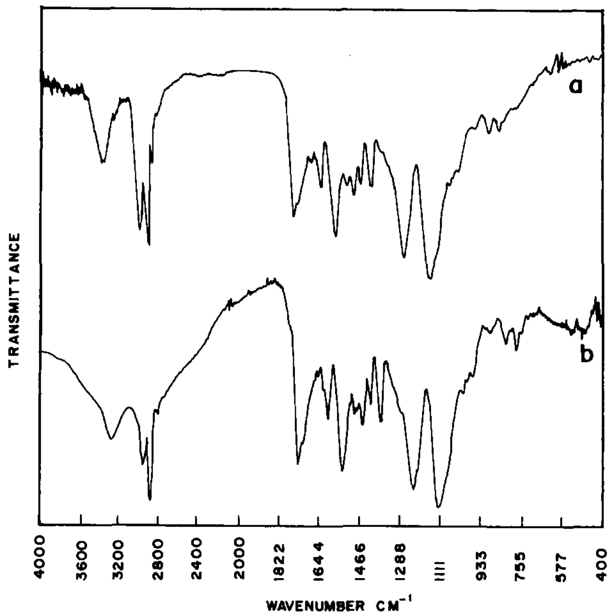


Figure 2 *FT*i.r. spectra of the polyurethanes TH (a) and PHB (b)

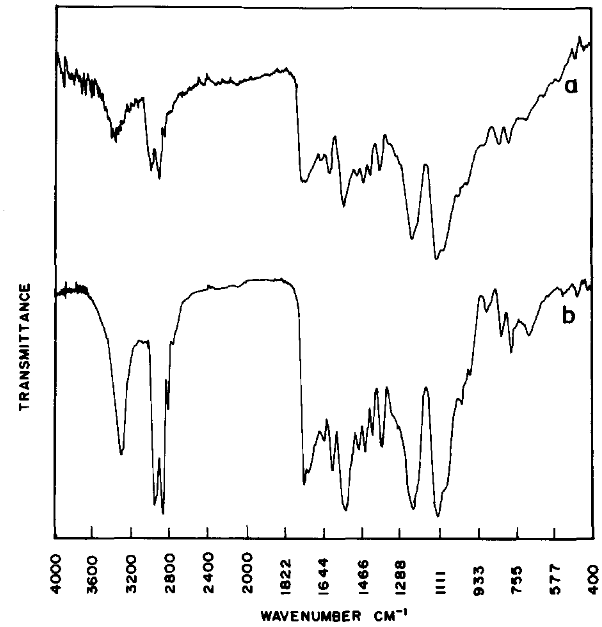


Figure 3 *FT*i.r. spectra of the polyurethane ionomers TH-Na (a) and PHB-Na (b)

The C=O stretching of the carboxyl groups in the polyurethanes are observed at 1704 cm^{-1}, and these are seen merged with the urethane carbonyl peaks. In polyurethane ionomers, where the –COOH group has been converted to a –COONa group, the frequency of the acid carbonyl shifts to 1600 cm^{-1} and merges with the double-bond absorption of the phenyl groups, thus resulting in an increase in the intensity of the absorption being observed. The existence of hydrogen bonding still remaining in the polyurethane chains is confirmed by the presence of an absorption at 1711 cm^{-1}, even after ionization.

The C–O–C band from the PTMO soft segment is observed at 1107 cm^{-1} for the TH polymer, indicating the presence of hydrogen bonding between the soft and hard segments. On ionization of the carboxylate group the amount of hydrogen bonding is reduced, and the band shifts to a higher frequency, i.e. 1112 cm^{-1}. For the PHB polymer, a hydrogen bonded C–O–C absorption is observed at 1103 cm^{-1}, which shifts to 1112 cm^{-1} in the case of the ionomer.

Urethane N–H stretching was observed at 3290 and 3283 cm^{-1} for TH and PHB, respectively, indicating that both are hydrogen bonded. The broadening of this band for the polyurethane ionomer on the high-frequency side indicates that a certain amount of hydrogen bonding is disrupted here, leading to the presence of free –NH groups in the polymer chain.

The ^{1}H n.m.r. spectrum of the TH polyurethane is given in *Figure 4*. The spectra were recorded in a mixed solvent system ($CDCl_3$/DMSO-d_6 (1/1)) in order to enhance the solubility of the different segments. A proton exchange technique, using D_2O, was used to fix the –NH protons. The multiplet observed at 1.6 ppm is due to the aliphatic methylene protons of the PTMO unit, while that at 3.26 ppm is due to the $-OCH_2$ units. The peaks at 2.16 and 2.94 ppm are due to the aliphatic protons of the alkyl groups on the phenyl rings, and the peak at 4.14 ppm is due to the NH–CO–O–CH_2 groups of the PTMO backbone. The aromatic phenyl protons are observed as multiplets at 6.85–7.35 and 7.88 ppm. Since the TDI used is a mixture of 2,4 and 2,6 isomers the urethane protons are observed, as weak signals, at 8.35, 8.54 and 9.4 ppm

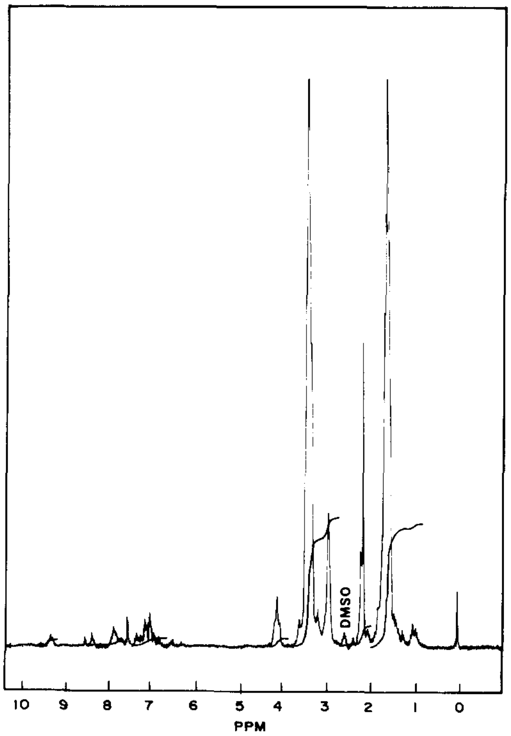


Figure 4 ^{1}H n.m.r. spectrum of the TH polyurethane

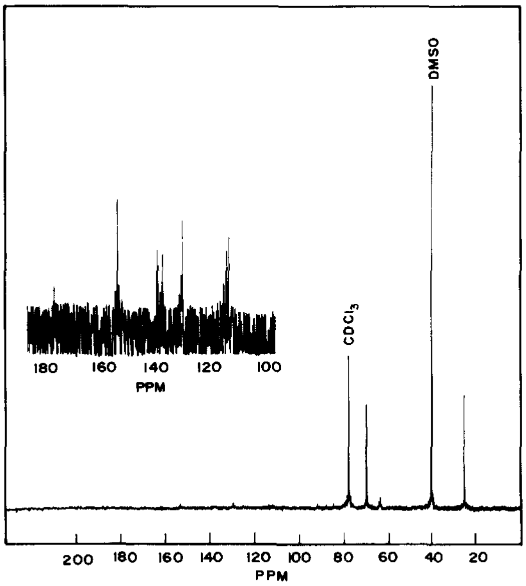


Figure 5 ^{13}C n.m.r. spectra of the TH polyurethane

The ^{13}C n.m.r. spectrum of the TH polyurethane is given in *Figure 5*. The carbon of the methylene units of PTMO are observed at 26 ppm and those of the $-O-CH_2$ units at 69.6 ppm, while the carbons of the aromatic rings are seen at 114–137 ppm. The carbonyl carbons of the urethane unit and the acid are observed at 158 and 176 ppm, respectively.

Thermogravimetric analysis

Figures 6–9 show the t.g.a. curves obtained for the diols, polyurethanes and polyurethane anionomers. The rigid, aromatic diols undergo decomposition over the temperature range 240–265°C. PTMO is thermally stable up to 175°C, and then undergoes decomposition by a single-stage process. The polyurethanes containing

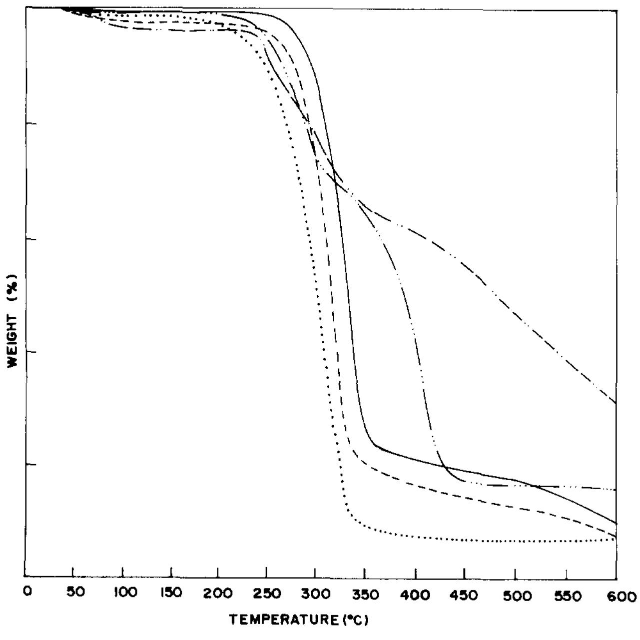


Figure 6 T.g.a. traces of: (——) phenolphthalin; (– – –) thymolphthalin; (– – · · – –) tetrabromophenolphthalin; (— · · · —) PH$_R$; and (· · ·) PTMO

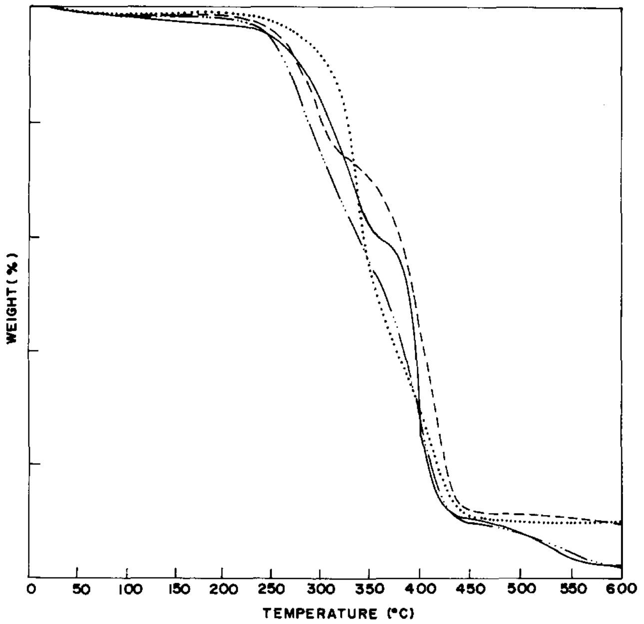


Figure 7 T.g.a. traces of: (——) PH; (– – –) TH; (· · · ·) BrPH; and (— · · · —) PHB

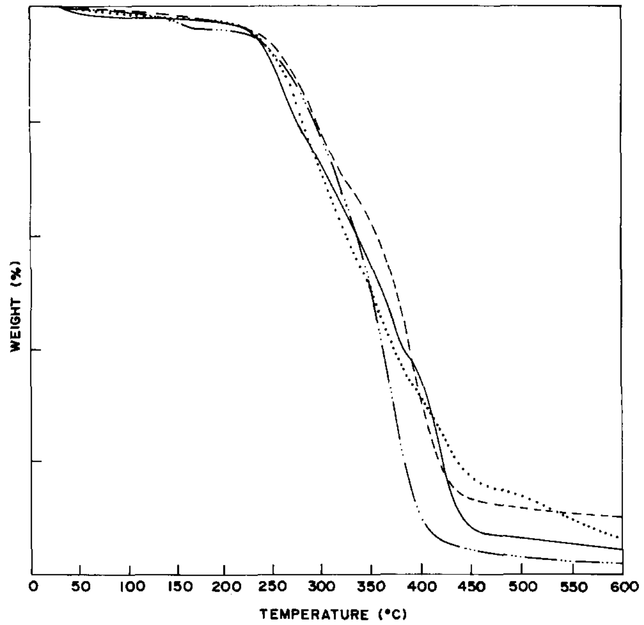


Figure 8 T.g.a. traces of: (——) PH-Na; (– – –) TH-Na; (— · · · —) BrPH-Na; and (· · · ·) PHB-Na

carboxylate groups are stable up to 230°C, after which temperature decomposition starts. The multi-stage decomposition process observed here is due to the combination of chemically different segments in the polymer chain. Polyurethanes, which are chain extended with only aromatic diols (i.e. PH, BrPH, TH), are relatively more stable in the first stage of decomposition than the polyurethane that is chain extended with a mixed aromatic and aliphatic diol species (PHB). Among the ionic polyurethanes, those with divalent metal cations have shown a slightly improved thermal stability than those with monovalent cations, as a result of ionic crosslinking between the chains.

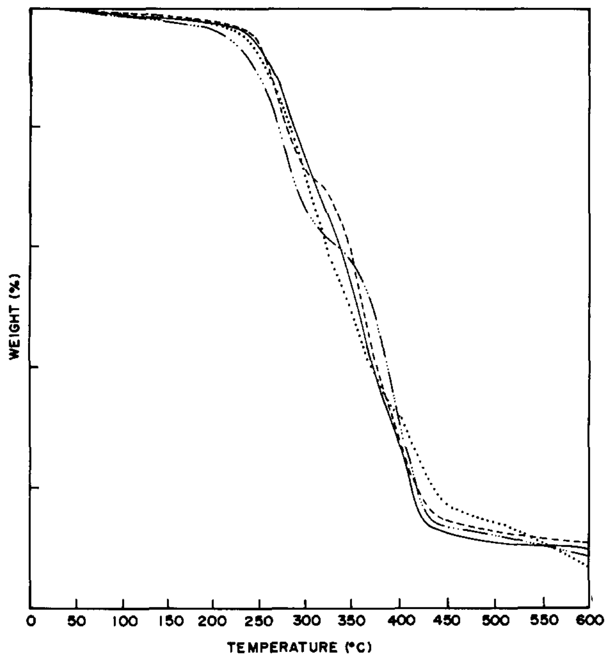


Figure 9 T.g.a. traces of: (——) PH-Zn; (– – –) TH-Zn; (· · · ·) BrPH-Zn; and (— · · · —) PHB-Na

CONCLUSIONS

Chain-extended polyurethanes, containing –COOH groups, were synthesized using phenolphthalins (derivatives of phenolphthaleins). The corresponding metal-containing ionomers were prepared with sodium and zinc counterions. Molecular weight analysis (g.p.c.) confirmed the molecular weights to be in the expected, significant ranges. *FT*i.r. spectroscopic studies indicated the presence of hydrogen bonding among the –NH and –C=O functional groups of the urethanes. Thermogravimetric analysis shows that fully aromatic polyurethanes have relatively higher thermal stabilities when compared to aliphatic systems. The polyurethane ionomers incorporating zinc have higher thermal stabilities than the corresponding sodium materials, as a result of ionic crosslinking.

ACKNOWLEDGEMENT

One of the authors (S. Ramesh) wishes to thank the Council of Scientific and Industrial Research (CSIR), India for a fellowship.

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