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CHAIN-EXTENDED POLYURETHANE ANIONOMERS USING FLUORESCIN

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Key Words: Polyurethane ionomers; Fluorescin; FT-IR; FT-NMR; T_g

ABSTRACT

Polyurethanes were synthesized by chain extension of isocyanate end-capped prepolymer based on poly(tetramethylene oxide) glycol and toluene diisocyanate using fluorescin. The polyurethanes were characterized using FT-IR and FT-NMR. The polyurethanes were converted to their anionomers by treatment with the respective metal acetates. To study the changes accompanying ionomer formation, especially in the soft segment, differential scanning calorimetry experiments were performed in the low temperature region. Thermal stabilities of the polymers and ionomers were studied using a thermogravimetric analyzer.

INTRODUCTION

Ionomers are polymers with a small number of ionic groups. The introduction of a relatively small number of ionic moieties into polyurethane significantly alters the properties of the material. The review article published by Dietrich and coworkers [1] in 1970 threw open the fascinating field of polyurethanes to academic researchers. In recent times they have evinced ample interest due to the ability to tailor-make them according to the fancy of the synthetic chemist. Two very impor-

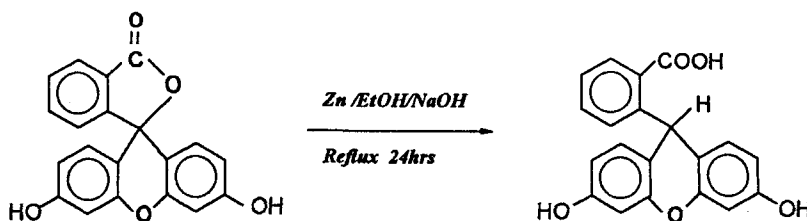
tant methods that have been employed are postmodification of polyurethanes [1–5] and the introduction of a potential ionic center or ionic moiety at the chain extension stage [6–15]. The introduction of aromatic moieties enhances the thermal and mechanical properties of the polymers [16–19].

Fluorescein and its derivatives have been used for various applications which are of great commercial importance. They are used in the field of recording materials [20, 21], color formers in color imaging [22], colored adhesives [23], high frequency ink jet printing [24], iridescent decorative boards [25], dyes in electrooptic polymers [26], antireflection layers on image screens [27], holograms [28], and in NLO materials [29]. Their most important impact is in the field of electrophotography where they are used as sensitizers and color toners [29–31]. The use of polymeric colorants is gaining interest due to their inherent nonleaching behavior coupled with products of good lightfastness. Fluorescein has been used as a unit in the preparation of polyesters [32], metal-containing polydyes [33–35], and as terminal units in polyethers [36]. In earlier work we used fluorescein, a bulky aromatic group, as a chain extender to prepare segmented polyurethanes [37]. Polyurethane ionomer chains extended with bulky aromatic groups containing potential ionic moieties have not been studied, unlike their analogous aliphatic chain extenders. Polyurethane anionomers were prepared from phenolphthalin in previous work from our group [38]. In order to introduce a colored moiety along with ionic groups into a polyurethane matrix, we derivatized fluorescein to fluoescin (Scheme 1) and used it as a chain extender. In this article we present the synthesis and properties of chain-extended polyurethane anionomers using fluoescin (a rigid aromatic molecule containing a carboxylic acid functionality).

EXPERIMENTAL

Materials

Poly(tetramethylene oxide) glycol of molecular weight 1000 (PTMG₁₀₀₀, Aldrich) was dried under vacuum for 24 hours at 35°C prior to use. Toluene diisocyanate (TDI, a mixture of 80% 2,4- and 20% 2,6-isomer) and dibutyltindilaurate (DBTDL, Aldrich) were used as received. Fluorescein (S.D. Fine Chem., India) was refluxed with HCl for 4 hours and recrystallized using benzene. Sodium acetate and zinc acetate dihydrate (S.D. Fine Chem., India) were used as received. The solvents *N,N*-dimethylformamide (DMF) and methanol were purified by standard procedures. Fluorescein was reacted with zinc dust, ethanol, and sodium hydroxide to



SCHEME 1.

give fluorescein, as reported earlier. Fluorescein was recrystallized from an ethanol/acetone mixture and used. [IUPAC name of fluorescein: 2-(3,6-dihydroxy-9H-xanthene-9-yl)-benzoic acid.]

Measurements

Fourier transform infrared spectra (FT-IR) of the polymers were recorded as neat films (prepared by casting a dilute solution of 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 (FT-NMR) spectra were recorded on a Bruker MSLp 300 MHz spectrometer using DMSO- d_6 as the solvent. The molecular weights of the polymers were determined by using Water's Associates gel permeation chromatography (GPC), with DMF as the solvent stabilized with 0.01% LiBr. The columns used were 10^6 , 10^5 , 10^4 and 10^3 Å μ -Styragel calibrated using polystyrene standards. Thermal analysis was carried out using a Du Pont 910 Differential Scanning Calorimeter and a Du Pont 951 Thermogravimetric Analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

Synthesis of Polyurethanes

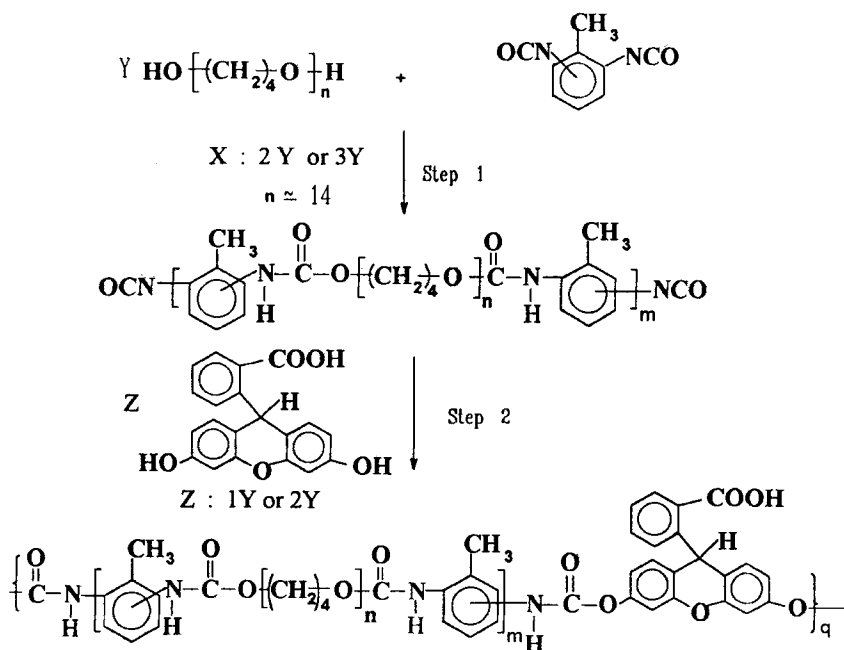
TDI (3.48 g, 0.02 mol) was added drop by drop to PTMG₁₀₀₀ (10 g, 0.01 mol) in a 100-mL 3-necked flask at 60°C under nitrogen atmosphere. The temperature was increased to 80°C and the reaction was allowed to proceed until the isocyanate content reached half the initial value (as determined by dibutyl amine titration). The temperature was reduced to 60°C and the chain extender fluorescein (3.34 g, 0.01 mol) in 20 mL of DMF was added drop by drop. Then 0.01 g of DBTDL catalyst was added, the temperature was increased to 80°C, and the reaction was allowed to go to completion (Scheme 2). The polyurethanes were precipitated by pouring them into a tenfold excess of distilled water and then washing thoroughly with methanol. The polymers were dried under vacuum at 30°C for a week. Polyurethane of another composition, as mentioned in Table 1, was synthesized by the same procedure.

Conversion to Anionomers

The polyurethanes dissolved in DMF were mixed with stoichiometric amounts of metal acetates (sodium and zinc) and cast over silicon troughs. The solvent was allowed to evaporate at a slow constant rate at a temperature of 60°C to give polyurethane anionomer films which were dried under vacuum.

RESULTS AND DISCUSSION

The molecular weight buildups of both polyurethanes were appreciable and are given in Table 2. The polydispersity values are to the high side, which is justified by taking into account the sluggish side reactions of the carboxylic acid group with TDI, which would lead to some amount of branching.



SCHEME 2.

FT-IR spectra of the polyurethanes and the ionomers are shown in Fig. 1. The N—H stretching of the urethane linkage is observed as a broad peak at 3296 cm^{-1} . Symmetric and asymmetric stretching of the $-\text{CH}_2-$ groups of PTMG are observed from 3000 to 2750 cm^{-1} . Carbonyl stretching due to urethane carbonyl and acid groups in FC_1 is seen as a broad band from 1736 to 1710 cm^{-1} , showing the hydrogen-bonded nature of the carbonyl groups. However, in the case of FC_1Na and FC_1Zn , the single peak in the case of acid carbonyl splits into two peaks at 1736 and 1709 cm^{-1} , corresponding to hydrogen-bonded and nonhydrogen-bonded carbonyl groups, further accompanied with a decrease in intensity of the carbonyl group. This is expected since anionomer formation would shift the carbonyl stretching of the carboxylic acid group to lower frequencies. This falls closer to $\text{C}=\text{C}$

TABLE 1. Polymer Compositions and Codes of Polyurethanes and Their Anionomers

Polymer composition	Polymer code
PTMG ₁₀₀₀ /2TDI/Fluorescein	FC ₁
Na ionomer	FC ₁ Na
Zinc ionomer	FC ₁ Zn
PTMG ₁₀₀₀ /3TDI/2Fluorescein	FC ₂
Na ionomer	FC ₂ Na
Zinc ionomer	FC ₂ Zn

TABLE 2. Molecular Weights, Polydispersity, and Glass Transition Temperature of Polyurethane and Anionomers

Polymer code	Molecular weights			$T_g, ^\circ\text{C}$
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n	
FC ₁	4.49	7.75	1.72	-32
FC ₁ Na	—	—	—	-41
FC ₁ Zn	—	—	—	-38
FC ₂	5.55	10.7	1.92	-17
FC ₂ Na	—	—	—	-21
FC ₂ Zn	—	—	—	-20

stretching of the aromatic groups, resulting in a more intense peak at 1604 cm^{-1} . This is ample evidence for the conversion of polyurethanes to their ionomers. The peak at 1551 cm^{-1} is due to C—N stretching and N—H deformation. The broad nature of the C—O—C stretching shows that the ether group also actively participate in hydrogen bonding.

The $^1\text{H-NMR}$ spectrum of polyurethane was recorded using $\text{DMSO-}d_6$ as the solvent and is given in Fig. 2. The methylene protons of PTMG resonate at 1.46 ppm. The methylene protons of $-\text{O}-\text{CH}_2-$ of PTMG are seen at 3.3 ppm, which merge with the water signal in the solvent. The peak at 4.02 ppm is due to the methylene protons of $\text{O}-\text{CH}_2$ attached to the urethane linkage. The methyl protons of TDI absorbs at 2.16 ppm. The aromatic protons of the chain extender and TDI resonate from 6 to 8 ppm. The N—H of the urethane linkage and carboxylic acid protons of the chain extender were fixed using a D_2O exchange technique. The N—H protons of the urethane linkage absorb from 8 to 10 ppm, and the carboxylic acid protons of the chain extender part resonate as a weak signal at 10.2 ppm.

For the ^{13}C NMR data the carbon of the methylene groups of PTMG resonates at 26 ppm. The carbon of the $-\text{OCH}_2-$ groups absorbs at 69 ppm. The carbons of the aromatic chain extender and TDI resonate between 100 to 140 ppm. The urethane carbon resonates at 157 ppm. The acid carbonyl carbon resonates at 170 ppm.

Thermogravimetric Analysis

TGA thermograms of fluorescein, polyurethanes and ionomers are given in Figs. 3 and 4. Fluorescein decomposes beyond 135°C , corresponding to about a 15% weight loss. The polyurethanes and their ionomers are comparable in their thermal stabilities. There is only a marginal weight loss up to 130°C , and it is caused by the moisture taken up due the presence of ionic groups. The urethane linkage cleaves above 175°C . The weight loss beyond this may be due to a combination of the various chemical segments in the polymers. The apparently high thermal stability of these aromatic-based polyurethanes is due to the nonisothermal experimental conditions combined with the nonvolatile nature of the decomposition products.

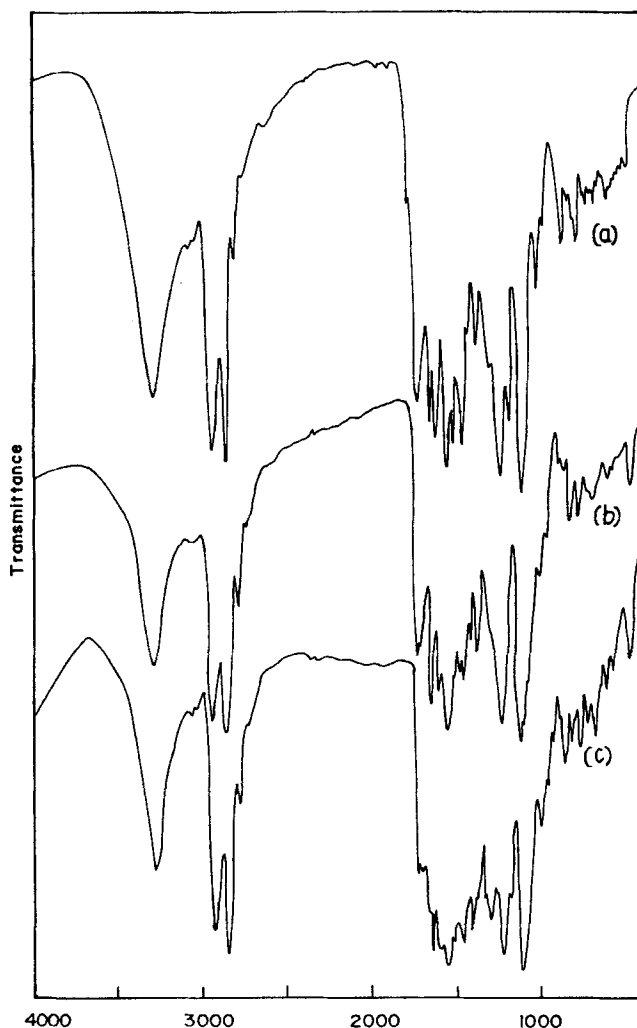
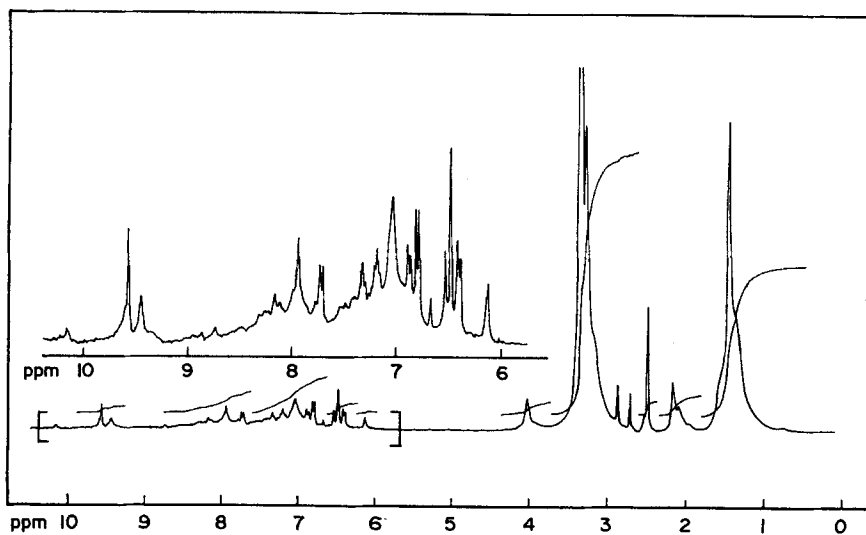
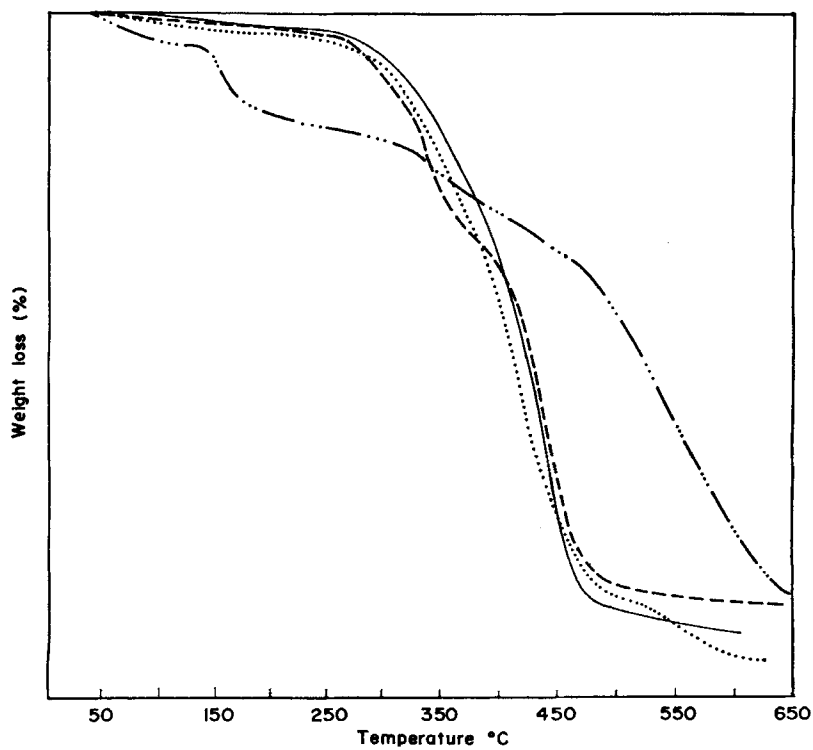


FIG. 1. FT-IR spectra of (a) FC₁, (b) FC₁Na, and (c) FC₁Zn.

Differential Scanning Calorimetric Analysis

DSC thermograms are given in Fig. 5, and T_g values in Table 2. The presence of ionic moieties in the polyurethanes drastically alters the thermal properties. The low T_g values of the polyurethanes are generally due to the polyol employed. Due to dispersion of the hard segment (comprised of the chain extender and TDI) in the soft polyol segment, the T_g s of these polymers are higher than those of the parent polyol. When we compare the T_g s of the two parent polymers FC₁ and FC₂, the higher T_g in the second series could be due to the high degree of hard segment content. Although the T_g s shift to lower temperatures in the case of FC₂Na and FC₂Zn compared to FC₂, all the transitions were of a very broad nature due to the

FIG. 2. FT-NMR spectrum of FC_2 .FIG. 3. TGA curves of FC (-·-·-·), FC_1 (—), FC_1Na (- - -), and FC_1Zn (· · · · ·).

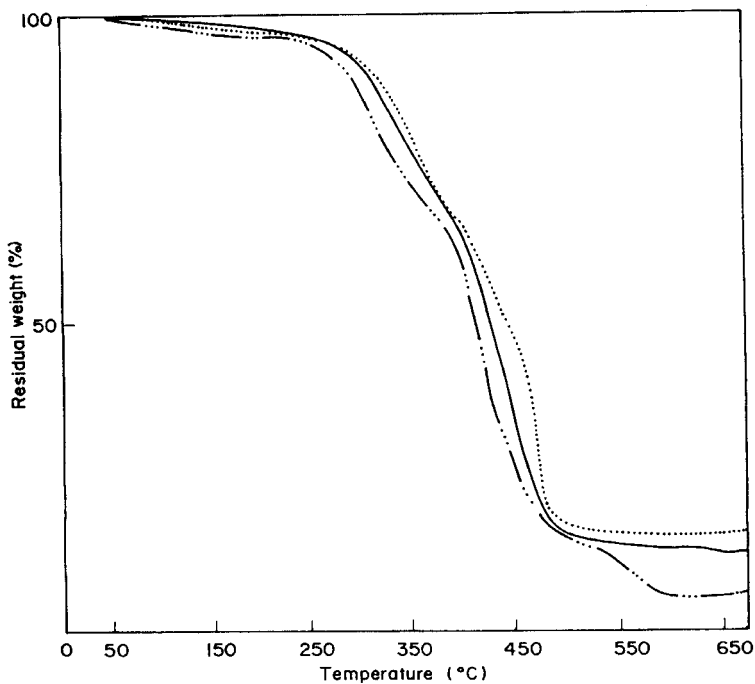


FIG. 4. TGA curves of FC₂ (—), FC₂Na (---), and FC₂Zn (····).

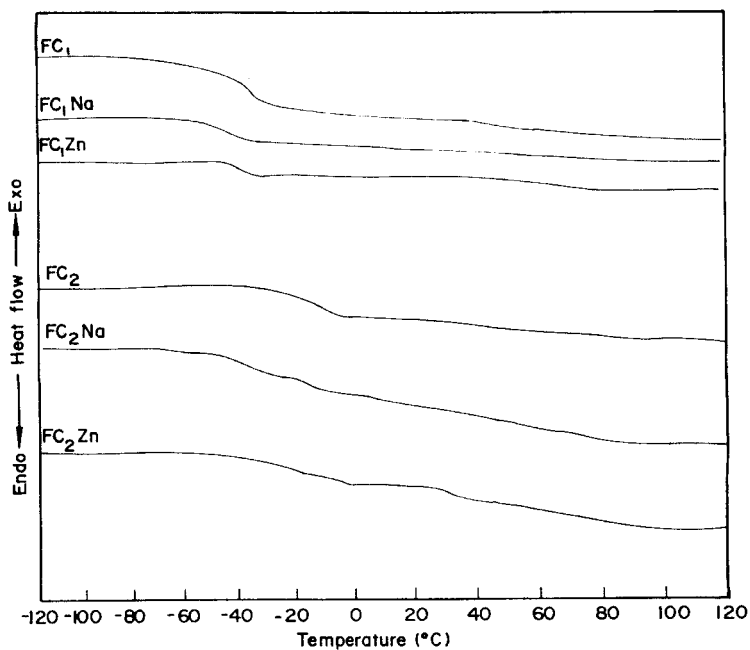


FIG. 5. DSC thermograms of polyurethanes and ionomers.

large amount of mixing of the soft and hard segments. The introduction of ionic groups significantly reorients the hydrogen bonding in the polyurethanes and results in an increased degree of phase separation between the soft and hard segments. This is true even for bulky aromatic chain extenders [38] when the percentage of hard segment content is not high. Such shifting of the T_g is observed as we go from FC₁ to FC₁Na and FC₁Zn. The higher T_g of the zinc ionomer when compared to the sodium ionomer is due to chemical crosslinking caused by the divalent metal ion, which partially inhibits segmental mobility. For the glass transitions of FC₁ and FC₂ series polymers, where the hard segment content is higher in the latter, even the introduction of ionic groups does not cause complete phase separation as is evident from the broad transitions of FC₂, FC₂Na, and FC₂Zn, although the ionic groups present significantly shift the glass transition temperatures to lower temperatures.

CONCLUSION

Polyurethanes with rigid aromatic moieties containing ionic groups were synthesized. FT-IR spectra of the ionomers showed the presence of hydrogen bonding, even in the anionomers. The introduction of an ionic group shifts the glass transition temperature to a lower temperature. The thermal stabilities of the polyurethanes and the anionomers were comparable.

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