Investigations on Polyurethane Ionomers. II. 3,4-Dihydroxycinnamic Acid-Based Anionomers

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ABSTRACT: Polyurethanes of different compositions were synthesized by chain extending the prepolymer formed by the reaction of various polyols and diisocyanate with 3,4-dihydroxycinnamic acid. The polyurethanes were converted to their anionomers by treating with metal acetates. The polyurethanes were characterized using FTIR, FTNMR, TGA, and DSC analysis. The molecular weights of the polymers were determined using GPC. A detailed study of the effect of variation of molecular weight of the polyols and mol ratio of the various reactants on the glass transition temperature and molecular weight of the polyurethanes was made. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2105–2109, 1997

INTRODUCTION

Ionomers are polymers containing a small number of ionic groups (<10 mol %) in the polymer backbone. The presence of a small number of ionic groups in the hydrophobic polymer backbone significantly alters the properties of the material. Polyurethane ionomers are a very important class of block copolymers that can be tailored according to the end use. Polyurethanes with ionic moieties are of interest due to the possibility to disperse them in aqueous solutions. Polyurethane ionomers are synthesized predominantly by using an ionic diisocyanate or an ionic diol at the chain-extension stage and by postmodification of a preformed polyurethane. In the former case, polyurethane anionomers[1–8] (with carboxylic, sulfonic, and phosphoric acid groups), cationomers,[9–16] and zwitterionomers[17–21] were studied in great detail. In the latter case, polyurethanes were treated with NaH/NaOH and subsequently reacted with 1,3-propanesultone to give zwitterionomers.[22–24] A precisely required amount of ionic groups can be incorporated into the polyurethane by using a potentially ionic chain extender. Cinnamic acid systems have received wide attention in polymer synthesis due to the presence of unsaturated groups which can be photocured. To prepare polyurethanes containing ionic as well as a physicochemically modifiable group, 3,4-dihydroxy cinnamic acid was used as the chain extender.[25] In this article, we report the detailed studies on 3,4-dihydroxycinnamic acid-based polyurethanes, the effect of varying polyol, diisocyanate, mixed chain extenders, changing NCO/OH ratio on molecular weight, and the glass transition temperature.

EXPERIMENTAL

Materials

Poly(propylene glycol) of molecular weight 1000 (PPG$_{1000}$), polycaprolactone diol of molecular weights 530, 1250, and 2000 (PCL$_{530}$, PCL$_{1250}$, and PCL$_{2000}$), poly(ethylene glycol) of molecular weight 1000 (PEG$_{1000}$), and poly(tetramethylene oxide)glycol of molecular weight 1000 (PTMG$_{1000}$) (Aldrich) were dried under a vacuum for 24 h at 105°C prior to use. Tolylene diisocyanate (TDI; a mixture of 80% 2,4-TDI and 20% 2,6-TDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), and dibutyltindilaurate (DBTDL) (Aldrich) were used as received. 4,4-Methylene bisphenyl diisocyanate (MDI; Polysciences) was

pressure-filtered at 60°C to separate the monomers from the dimers and trimers. 3,4-Dihydroxycinnamic acid (DCA; Arrow Chemicals, India) was used as received. Sodium acetate and zinc acetate dihydrate (S.Ds, India) were used as received. The solvents dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and methanol were purified by standard procedures.

Measurements

Fourier transform infrared spectra (FTIR) of the polymers were recorded as neat films (prepared by casting purified polymer in DMF over a KBr window and evaporating the solvent under a vacuum at 50°C) using a Nicolet Impact 400 spectrometer. Fourier transform nuclear magnetic resonance (FTNMR) was recorded on a Bruker MSLp 300 MHz spectrometer. The molecular weights of the polymers were determined by using Water Associates gel permeation chromatography, the solvent being DMF stabilized with 0.01% of LiBr. Thermal analysis was carried out using a DuPont 910 differential scanning calorimeter and a DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen atmosphere.

Synthesis of Polyurethane

Polyurethane prepolymer end-capped with isocyanate groups was prepared based on excess TDI (3.48 g, 0.02 mol) added drop by drop to PPG_{1000} (10 g, 0.01 mol) in a 100 mL three-necked flask at 60°C under nitrogen atmosphere. The abovementioned prepolymer was chain-extended with 3,4-dihydroxycinnamic acid (1.8 g, 0.01 mol) in DMF. Then, 0.01 g of a DBTDL catalyst was added, the temperature was increased to 70°C, and the reaction was allowed to continue to completion. The polyurethanes were precipitated by pouring into a 10-fold excess of distilled water and washed thoroughly with methanol. The polymers were dried under vacuum at 30°C for 1 week. Using a similar procedure, polyurethanes of other compositions as mentioned in Table I were synthesized. A detailed procedure, schematic representation of the synthesis, and conversion to anionomers of the polyurethanes was dealt with in detail in our earlier publication.[25] The sodium and the zinc anionomers are denoted using Na and Zn as suffixes. For example, C_1 Na and C_1 Zn denote the sodium and the zinc anionomers of C_1, respectively.

RESULTS AND DISCUSSION

Polyurethanes incorporated with ionic moieties are a very interesting material, the properties of which can be tailored according to the end user needs. The incorporation of ionic groups results in water dispersibility or even complete water solubility of these materials. To further enhance the properties of these materials, we introduced a photocrosslinkable unit along with the ionic groups into the polyurethane. Detailed investigations on the synthesis, characterization, and thermal behavior of C_1 and C_2 (cf. Table I) were reported by us recently.[25] All the polyurethane films (cf. Table I) on exposure to UV radiation were rendered insoluble even in polar solvents like DMF and DMSO, unlike with the unexposed films.

The codes of the polyurethanes, their composition, molecular weights, and polydispersity are given in Table I. The dispersity values for all the polyurethanes are toward a higher side due to the meager side reactions of the —COOH groups in the chain extender. As expected, the molecular weight of the polyurethane decreases from C_1 to C_4 due to the increase in the diisocyante content in the prepolymer formation stage. This results in decrease in the molecular weight of the prepolymer and therefore the molecular weight of the polyurethanes also decreases with increase in the diisocyanate content. Due to the higher reactivity of MDI, the molecular weight buildup in the case of C_5 is the highest. The molecular weights in the case of C_6 and C_7 are not appreciable due to the lower reactivity of the aliphatic NCO— groups of HDI and IPDI. Generally, the preparation of polyurethane through a prepolymer route rather than through a one-shot route leads to a high molecular weight buildup and narrow dispersity. C_{10} was prepared by a one-shot process and the molecular weight buildup was not as high as for C_1 (prepared by a two-stage prepolymer process).

The FTIR spectra of the polyurethanes and ionomers showed the splitting of the carbonyl peak of the urethane at 1728 and 1710 cm^{-1} due to the free and hydrogen-bonded groups. The same splitting was observed in the case of the ionomers showing the existence of hydrogen bonding even after the ionization of —COOH to —COONa. The frequency of acid carbonyl in the anionomers shifts toward 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 intensity of the carbonyl band at 1725 cm^{-1} in the case of the polycaprolactum diol-

Table I   Composition, Code, Molecular Weights, and Polydispersity of Polyurethanes

| Polymer Composition	Codes	Molecular Weights		
		$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
PTMG$_{1000}$/2TDI/DCA	C$_1$	3.76	15.40	4.10
PTMG$_{1000}$/3TDI/2DCA	C$_2$	2.80	7.10	2.54
PTMG$_{1000}$/4TDI/3DCA	C$_3$	2.23	4.43	1.99
PTMG$_{1000}$/5TDI/4DCA	C$_4$	1.39	2.96	2.12
PTMG$_{1000}$/2MDI/DCA	C$_5$	4.51	11.23	2.49
PTMG$_{1000}$/2HDI/DCA	C$_6$	1.26	3.02	2.40
PTMG$_{1000}$/2IPDI/DCA	C$_7$	0.76	1.84	2.42
PTMG$_{1000}$/3TDI/DCA + DMPA	C$_8$	1.00	1.74	1.74
PTMG$_{1000}$/3TDI/DCA + BD	C$_9$	1.77	2.32	1.31
PTMG$_{1000}$ + DCA/2TDI	C$_{10}$	1.63	5.90	3.62
PCL$_{530}$/2TDI/DCA	C$_{11}$	3.40	10.40	3.06
PCL$_{1250}$/2TDI/DCA	C$_{12}$	3.84	9.69	2.52
PCL$_{2000}$/2TDI/DCA	C$_{13}$	2.50	7.82	3.13
PPG$_{1000}$/2TDI/DCA	C$_{14}$	5.87	9.76	1.66
PEG$_{1000}$/2TDI/DCA	C$_{15}$	3.41	9.82	2.87

based polymers was high due to the ester linkages in the polyol segment. The amide II band due to the C—N stretching and N—H deformation was observed at 1531 cm^{-1}. The C—O—C stretching of the PTMG, PEG, and PPG backbone was observed at 1110 cm^{-1}. The urethane N—H stretching was observed at 3283 cm^{-1}.

The ^{1}H-NMR spectra of the polyurethane were recorded using DMSO-d_6 solvent and are given in Figures 1–4. The urethane N—H protons of TDI, MDI, HDI, and IPDI absorbs in the range from 8 to 10 ppm, at 9.4 ppm, at 5.7 ppm, and in the range 4.7–5.9 ppm, respectively. The methylene protons of the PTMG polyol segment absorbs at 1.48 ppm and the methylene protons of —O—CH$_2$— of PTMG absorbs at 3.3 ppm, overlapping with the signal of water present in the solvent.
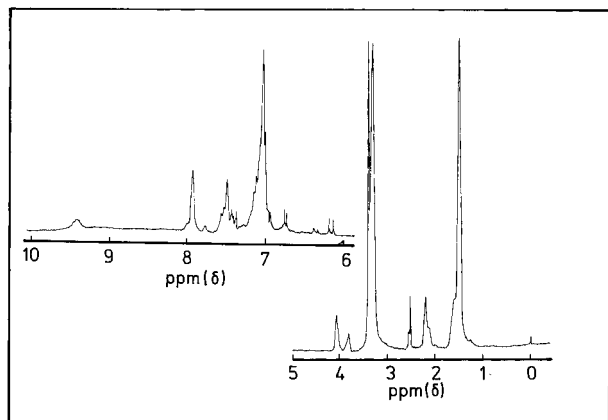
The —O—CH$_2$ attached to the urethane linkage absorbs at 4.04 ppm. The methylene protons of PCL-based system absorbs between 1 and 2 ppm and 3.7 and 4 ppm. The absorption of methyl protons of TDI occurs at 2.18 ppm (b) and the methylene protons of MDI absorbs at 3.8 ppm. The methylene protons of HDI and IPDI absorb between 1 and 2.5 ppm. The aromatic protons of TDI and the chain extender and the aliphatic C=C of the chain extender absorbs from 6 to 8 ppm. The proton of the acid carbonyl absorbs at 10.4 ppm as a weak signal in some cases and is absent in others. The spectra showed the absorption of the aliphatic C=C *trans*-hydrogen (of cinnamic acid) as doublets at 6.12 and 7.37 ppm. The peak at 2.5 ppm is due the traces of DMSO present in the deuterated solvent.

DSC study of the ionomers gave insight into the morphological structure of the polymers. The

Figure 1 ^{1}H-FTNMR spectrum of C$_5$.
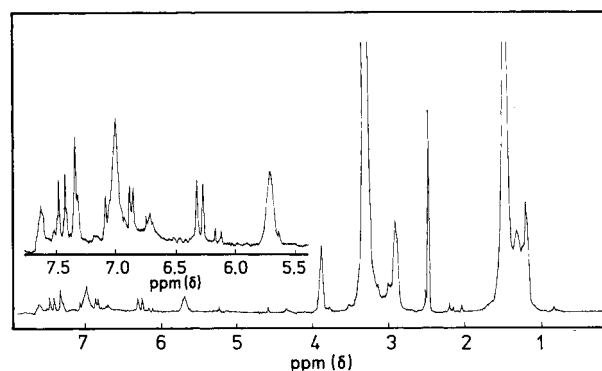
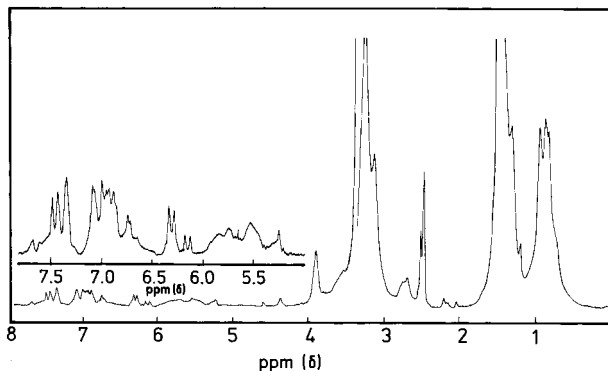**Figure 2** ^{1}H-NMR spectrum of C$_6$.

Figure 3 ^{1}H-FTNMR spectrum of C_7.

glass transition temperature of the polyurethane depends on the nature of the polyol used. The main factor that operates in polyurethanes is hydrogen bonding. By the introduction of ionic groups in the polyurethane matrix, coloumbic forces operate along with hydrogen bonding. A detailed investigation was done by Cooper and co-workers. They studied a model system of polyurethane based on $PTMG_{1000}$ and TDI and then replaced the urethane hydrogen with ionic groups.[26] The introduction of ionic groups into the polyurethane significantly reorients the hydrogen bonding in the polyurethane, leading to an increase in the phase purity of the soft and the hard segments. When the molecular weight of the polyol increases, a crystallization phenomenon was observed in PCL_{1250}- and PCL_{2000}-based systems. The polyurethane based on PCL_{2000}, on conversion to ionomers, does not have any effect on the soft-segment T_g due to the tendency of the soft segment to crystallize. The driving force for phase separation due to soft-segment crystallization is so large that upon ionization no further increase in phase purity occurs and, hence, the T_g does not change. In the PPG-based systems due to their
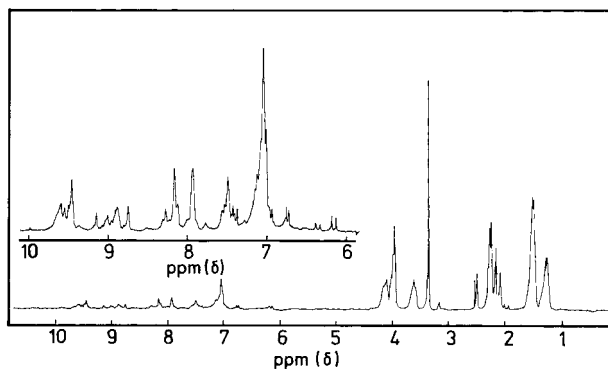
axial methyl groups attached to the secondary carbon atom which hinders the efficient packing, their T_g's were on the higher side than those of the PTMG systems. The PEG-based system showed a lower T_g when compared to the PPG system. In an earlier study based on chain-extended polyurethane by Frisch and co-workers,[27] a change in T_g with a change in the metal ions in the case of anionomers containing carboxylate groups was reported. In our study[28] also on the use of ionic chain extenders, we observed a shift in T_g toward lower values. But the magnitude of the T_g shift was less in the case of divalent metal ions. This is due to ionic chemical crosslinking between the chains. This phenomenon was observed in this case also. The T_g of the sodium anionomers was lower than that of the zinc anionomers. The glass transi-

Table II Glass Transition Temperature of Polyurethanes and Anionomers

Polymer Code	T_g (°C)
C_1	−59.5
C_1Na	−68.0
C_1Zn	−63.0
C_2	−45.0
C_2Na	−69.0
C_2Zn	−62.5
C_3	−40.0
C_4	−33.5
C_5	−38.0
C_5Na	−46.0
C_5Zn	−42.5
C_6	−52.0
C_6Zn	−56.5
C_7	−40.0
C_7Zn	−43.0
C_8	−22.0
C_8Zn	−31.0
C_9	−45.0
C_9Zn	−51.0
C_{10}	−29.0
C_{10}Zn	−32.5
C_{11}	—
C_{11}Na	−10.5
C_{11}Zn	+5.0
C_{12}	−28.0
C_{12}Na	−45.5
C_{12}Zn	−40.0
C_{13}	−25.0
C_{13}Na	−26.0
C_{13}Zn	−25.5
C_{14}	−15.0
C_{14}Zn	−19.0
C_{15}	−16.0
C_{15}Zn	−19.5

Figure 4 ^{1}H-NMR spectrum of C_{11}.

tion temperature of the polyurethanes and their anionomers are given in Table II.

CONCLUSIONS

Polyurethanes containing cinnamic acid groups were synthesised using a variety of polyols and diisocyanates. FTNMR measurements were made to fix the —NH protons of the urethane linkages. FTIR studies also showed the existence of hydrogen bonding in the case of the ionomers. The introduction of ionic groups into the polyurethane causes increased microphase separation, thereby decreasing the T_g of the soft segment.

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