Structure–Property Relationships of Polyurethane Ionomers with Star Chain Architecture

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Synopsis

The effects of chain architecture, polyol chemistry and polyol molecular weight on the properties of elastomeric polyurethane ionomers were investigated. The type of polyol and its molecular weight had a strong influence on the rubbery modulus and tensile properties. Variations in chain architecture showed little impact on mechanical and thermal properties. Linear ionomers, three-arm ionomers, and six-arm ionomers had similar mechanical and thermal behavior.

INTRODUCTION

During the past 20 years the use of ion-containing polymers in high performance applications has become increasingly commonplace. Surlyn, Nafion, and other commercial ionomers have made significant headway in the marketplace. As a result, considerable effort has been directed at understanding the relationship between microstructure and physical properties in ionomers.[1] Both commercial and model systems have been the focus of extensive research. The type of polymer backbone, the polymer molecular weight, and the type and amount of neutralizing cation have all been observed to strongly influence material performance.[2]

Most studies aimed at understanding the structure–property relationships of ionomers have been carried out on systems consisting of a hydrophobic monomer randomly copolymerized with a minor amount of carboxylate or sulfonate containing comonomer. One system that has been extensively studied is lightly sulfonated polystyrene along with its analog carboxylated polystyrene. Lundberg and coworkers, among others, have investigated this family of materials.[3-7] Much of their work has focused on the effect of cation type on mechanical and rheological properties. One disadvantage in systems such as sulfonated polystyrene (SPS), which are prepared by free-radical polymerization is that the random arrangement of ionic groups may adversely affect phase separation. In turn, incomplete phase separation can complicate the investigation of structure–property relationships in the solid-state.

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Carefully synthesized model ionomers have in recent years become increasingly important research materials. Telechelic ionomers are model materials that have attracted substantial interest. In most ionomers, the ionic groups are randomly spaced along a high-molecular weight chain. In contrast, telechelic ionomers are low molecular weight polymers containing only ionic groups at the chain ends. Early studies[8–10] of telechelic ionomers concentrated on commercial materials such as Hycar, a carboxy-terminated polybutadiene produced by the B. F. Goodrich Co. More recently, studies have concentrated on specially tailored telechelics such as the carboxy-telechelic polyisoprenes synthesized by Jerome and co-workers.[11,12] These materials are very similar to Hycar in their mechanical behavior, but since they are prepared by anionic polymerization, samples with narrow-molecular-weight distribution can be obtained. Several studies have probed the structure–property relationships of these ionomers.[13–16]

Tant et al.[15] examined the tensile properties of Al^{3+}, Ba^{2+}, and Zr^{4+} salts of carboxy-telechelic polyisoprenes over the molecular weight range 15,000 to 45,000, and concluded that both the cation and the molecular weight played important roles in the materials' behavior. By changing the molecular weight of the telechelic backbone the investigators were able to conveniently vary the ion content while retaining a known molecular architecture.

Register et al.[16] also investigated structure–property relationships of telechelic ionomers. They used a battery of analytical techniques including SAXS, extended X-ray absorption fine structure (EXAFS) spectroscopy, thermal analysis, and mechanical testing to examine several narrow-molecular-weight distribution carboxy-telechelic vinyl polyisoprenes of 8000 molecular weight neutralized with different divalent cations. They found that those samples showing strain-hardening behavior have well-ordered ionic aggregates as probed by EXAFS. The investigators postulated that a high degree of local order would occur in aggregates in which the ionic groups are bound tightly. This explanation rationalizes the mechanical behavior well; if a sample has a cohesive aggregate it cannot relax by ion-hopping, and strain hardening will occur because of the finite extensibility of the polymer chains.

Another important model ionomer is the telechelic three-arm star sulfonated polyisobutylene of Kennedy and co-workers.[17–19] This material was designed to examine the effect of chain architecture on ionomer properties, and both its rheological and solid-state behavior have been well-characterized.[17–19] The three-arm star showed increased melt and solution viscosity relative to its linear analog. In addition, its solid-state behavior was marked by a proclivity toward strain-induced crystallization.

The materials designed for this study share some traits in common with the star ionomers prepared by Kennedy. The polyurethane ionomers have regularly spaced ionic groups and sulfonate functionalities. They differ from sulfonated polyisobutylenes, though, in some important aspects. The urethane ionomers are not telechelic; each arm in a multi-arm sample has several (on average 10) pendant ionic groups. Furthermore, the urethanes are prepared by condensation polymerization and as a result there is less control over the reaction product. The architectures described in the Experimental section of this study are the average structure of the products of each synthesis.

The advantage to studying structure–property relationships in polyurethane ionomers is the flexibility of the urethane chemistry. The diisocyanate and the polyol may be readily varied, as well as the type of anion and cation. In this study the effects of chain architecture, polyol chemistry, and polyol molecular weight on the properties of these materials are examined.

EXPERIMENTAL

Sample Preparation

The synthetic route followed in preparing samples for this study is summarized in Figure 1 which illustrates the preparation of a three-arm ionomer based on poly(tetramethylene oxide) (PTMO). The reaction path is derived from the approach outlined by Hwang et al.[20] for the synthesis of linear polyurethane ionomers. In the present work the base polymer is first synthesized, and then reacted with the appropriate alcohol to create the desired chain architecture. The polymer is then converted into the sodium ionomer by reaction with sodium hydride followed by propane sultone.

The polyols used to synthesize the ionomers discussed in this paper were PTMO (Quaker Oats Co., M_n = 1000, 2000), and hydroxy-terminated polybutadiene (PBD) (Polysciences, Inc., M_n = 2000). Before use, the polyols were degassed under vacuum at 50°C for 48 h. The diisocyanate used was toluene diisocyanate (TDI) (Aldrich), which was stored at 0°C until use. N,N-dimethyl acetamide (DMA) was used as the solvent and was degassed at room temperature for 48 h. Propane sultone (Aldrich) was purified by vacuum distillation. Sodium hydride (NaH, Aldrich), and Catalyst T-12 (M&T Chemicals) were used as received.

The base polyurethane copolymer was synthesized in the stoichiometric ratio 5 : 4 : 1, diisocyanate : polyol : isopropanol. The isopropanol was first reacted with TDI for 30 min at 70°C under an argon blanket. The polyol was then added to the reaction along with 0.5 wt % T-12 catalyst. To ensure complete reaction, the mixture was maintained at 70°C for 2 h. The molecular weight of the base polymer is very low because isopropanol acts to cap the growing chains. From stoichiometry, the average molecular weight is estimated to be approximately 5000.

Unique chain architectures were obtained by reacting a stoichiometric quantity of the base polymer with a multifunctional alcohol. Thus, the number of arms and not the molecular weight of each arm varies between samples synthesized from the same base polymer. The six-arm ionomer was synthesized by reacting base polymer with d-sorbitol in a 6 : 1 mole ratio. Three-arm ionomers were formed from base polymer and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol in a 3 : 1 mole ratio. Linear ionomers were formed by reacting base polymer with isopropanol in a 1 : 1 mole ratio. All the polyurethanes synthesized for this study have no chain extender, consequently these materials have no "hard segment" and no tendency to micro-phase separate. Evidence of the absence of phase separation was obtained by thermal analysis.

To prepare the ionomers, the polyurethane polymers were first dissolved in DMA and mixed with a dispersion of NaH in toluene. The reaction mixture was maintained at −5°C under argon and vigorously stirred. Within approxi-
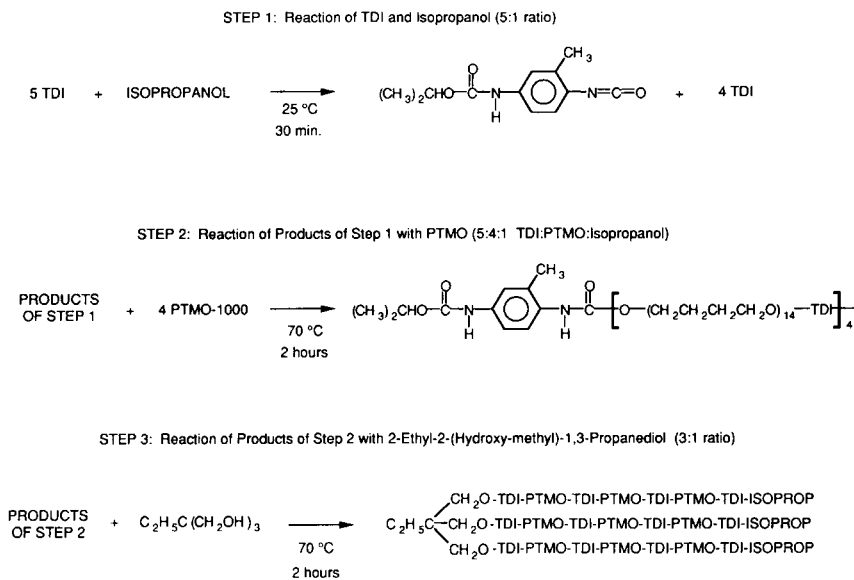
STEP 1: Reaction of TDI and Isopropanol (5:1 ratio)

5 TDI   +   ISOPROPANOL $\xrightarrow[\substack{25\,°C \\ 30\,min.}]{}$ $(CH_3)_2CHO-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}$—⟨ring, CH_3⟩—$N=C=O$ +   4 TDI

STEP 2: Reaction of Products of Step 1 with PTMO (5:4:1 TDI:PTMO:Isopropanol)

PRODUCTS OF STEP 1   +   4 PTMO-1000 $\xrightarrow[\substack{70\,°C \\ 2\,hours}]{}$ $(CH_3)_2CHO-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}$—⟨ring, CH_3⟩—$\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-[O-(CH_2CH_2CH_2CH_2O)_{14}-TDI]_4$

STEP 3: Reaction of Products of Step 2 with 2-Ethyl-2-(Hydroxy-methyl)-1,3-Propanediol (3:1 ratio)

PRODUCTS OF STEP 2   + $C_2H_5C(CH_2OH)_3$ $\xrightarrow[\substack{70\,°C \\ 2\,hours}]{}$ $C_2H_5C\begin{cases} CH_2O\text{-TDI-PTMO-TDI-PTMO-TDI-PTMO-TDI-ISOPROP} \\ CH_2O\text{-TDI-PTMO-TDI-PTMO-TDI-PTMO-TDI-ISOPROP} \\ CH_2O\text{-TDI-PTMO-TDI-PTMO-TDI-PTMO-TDI-ISOPROP} \end{cases}$

Fig. 1.   Five-step synthesis of sample ET13, a three-arm ionomer based on PTMO 1000 and TDI.

mately 7 min, a greenish-yellow color appeared. After 15 min, a stoichiometric amount of γ-propane sultone was added and the mixture was heated at 50°C for 2 h. Substitution of the urethane nitrogen was verified by examining the N—H stretch (3200 to 3500 cm^{-1}) in the Fourier-transform infrared spectrum of the final product. The reaction mixture was filtered to remove any unreacted NaH and the ionomer recovered by precipitation into toluene. This synthetic method provides the sodium salt directly.

The samples used in this study are listed in Table I. The first two letters of the mnemonic code refer to the polyol type ("ET" for PTMO, "PB" for PBD); the first number is the polyol molecular weight in thousands; and the second

STEP 4: Reaction of Products of Step 3 with Sodium Hydride
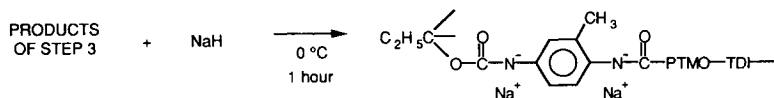
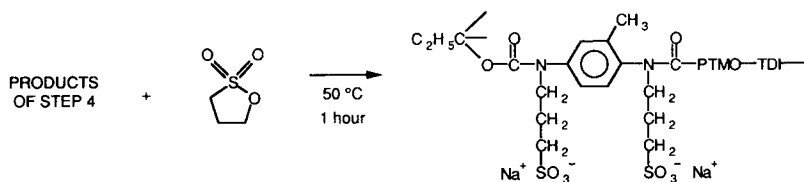STEP 5: Reaction of Products of Step 4 with Propane Sultone

Fig. 1. (*Continued from the previous page.*)

number is number of arms in the ionomer ("1" for a linear ionomers, "3" for three-arm ionomers, and "6" for six-arm ionomers). For example, sample ET23 is a three-arm ionomer with a PTMO 2000 soft segment.

Samples for mechanical testing and thermal analysis were spin-coated from DMA and stored in a vacuum oven at 50°C until use.

Instrumental Conditions

Dynamical mechanical data were collected at 110 Hz using a computer controlled Toyo Rheovibron DDv-IIC. Film samples, approximately $0.04 \times 3 \times 20$ mm in size, were tested under a nitrogen blanket from -100 to 200°C at a heating rate of 2°C/min. DSC thermograms over the temperature range -130 to 200°C were recorded on a Perkin-Elmer DSC-II interfaced with a thermal

TABLE I
Sample Code

Sample	Polyol	Isocyanate	Chain architecture
ET11	PTMO 1000	TDI	Linear
ET13	PTMO 1000	TDI	Three arm
ET16	PTMO 1000	TDI	Six arm
ET23	PTMO 2000	TDI	Three arm
PB23	PBD 2000	TDI	Three arm

analysis data station (TADS). The experiments were carried out at a heating rate of 20°C/min under a helium purge on samples weighing 16 ± 2 mg. Calibration was done using indium and mercury standards. A scanning autozero module was used to minimize instrumental nonlinearity over the temperature range of interest. Uniaxial stress–strain measurements were made at room temperature using an Instron TM with a crosshead speed of 0.5 in./min. Dumbbell-shaped film samples were stamped out with an ASTM D1708 die. Reported data are the average of three tests.

RESULTS AND DISCUSSION

Dynamic Mechanical Thermal Analysis

Figure 2 shows the dynamic mechanical responses of PTMO 1000/TDI ionomers with different chain architectures (samples ET11, ET13, and ET16). Both the E' and E'' data for these materials are nearly identical. Chain architecture appears to have little influence on the plateau modulus or the plateau width. This result is consistent with earlier investigations which have dem-
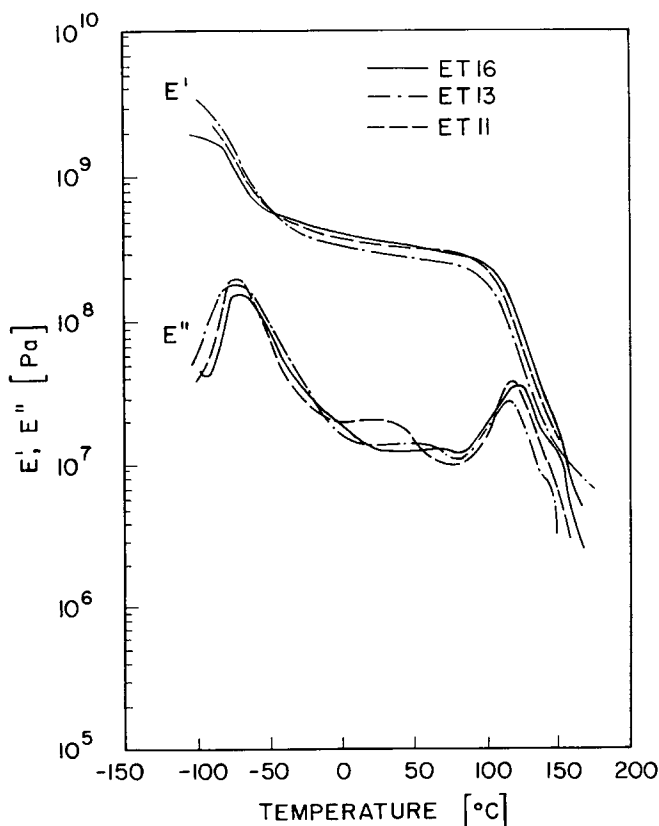

Fig. 2. DMTA of polyurethane ionomers: effect of chain architecture. (– – –) ET11; (– · –) ET13; (———) ET16.

onstrated that elastic modulus is principally a function of ionic crosslink density.[21] ET16 and ET13 differ from ET11 by the addition of a covalent tie point at the center of the star. This covalent "crosslink" causes only a very small increase in the overall crosslink density since the number of ionic groups per arm, and hence the number of potential ionic crosslinks, is large.

Figure 3 displays the E' and E'' data for ionomers with the same chain architecture but different soft segments. The difference in elastic modulus between ET13 and ET23 is also consistent with the observation that elastic modulus is a strong function of ionic crosslink density. The higher molecular weight PTMO decreases the density of ionic groups, resulting in a lower elastic modulus material. The low modulus of PB23 is consistent with earlier investigations of polybutadiene-based polyurethanes.[22] The magnitude of the difference in moduli between PB23 and the other samples, though, is surprising, and may indicate that this sample has a lower ionization level than expected. The dynamic mechanical responses also demonstrate the effect of soft segment on crystallinity. ET23 is the only sample to show polyol crystallinity.

Differential Scanning Calorimetry

The DSC curves for the ionomers studied are shown in Figure 4. The materials based on PTMO 1000 have identical thermal behavior. Each shows a
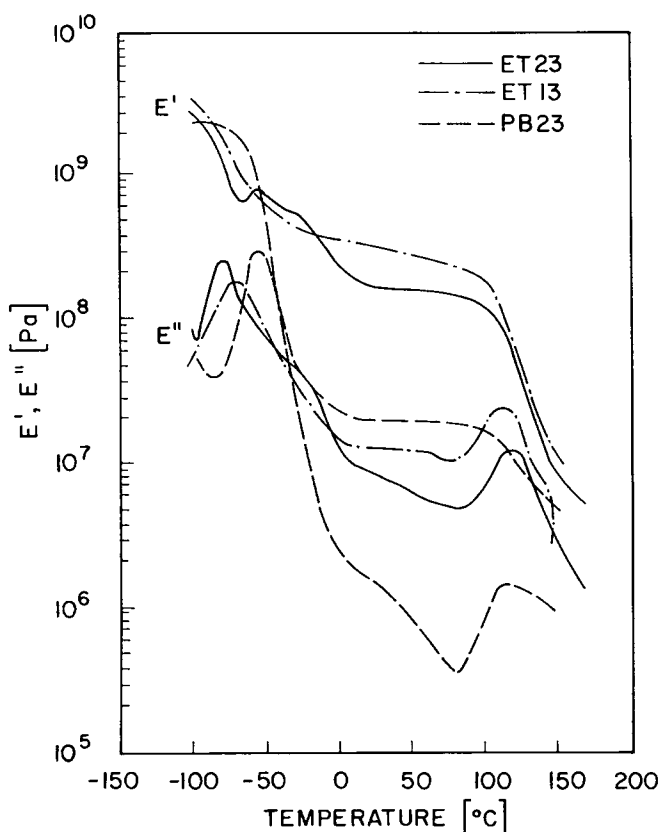

Fig. 3.   DMTA of polyurethane ionomers: effect of soft segment chemistry and molecular weight. (– ·–) ET13; (———) ET23; (– – –) PB23.
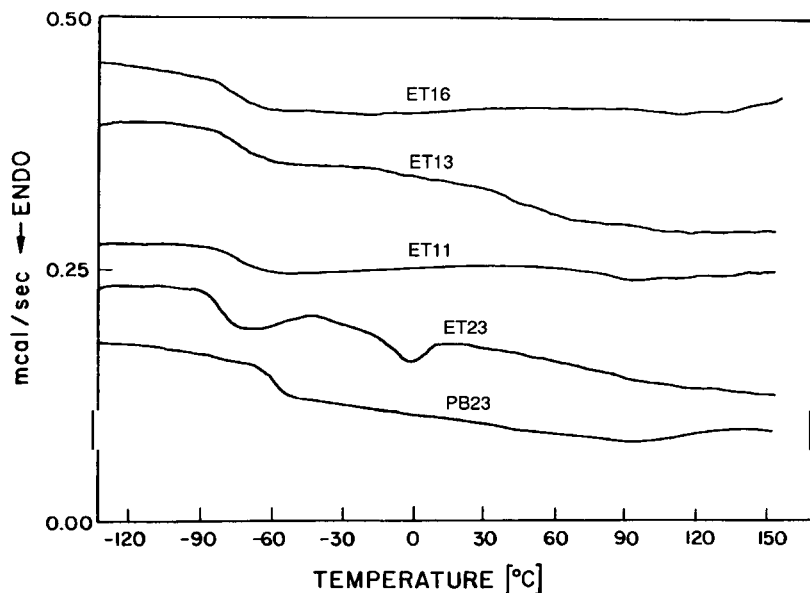
Fig. 4.   DSC of polyurethane ionomers.

soft segment glass transition temperature (T_g) near $-70°C$, and no other distinguishable transitions. The PBD 2000 based ionomer also shows this type of response. A polybutadiene matrix transition is observed near $-60°C$. The ionomer synthesized with PTMO 2000 shows a crystalline melting endotherm near $5°C$ in addition to the matrix glass transition. A small exotherm near $-40°C$ can also be identified; this results from PTMO crystallization in the temperature region between T_g and the melting point, T_m.

The glass transition temperatures obtained from the DSC measurements are listed in Table II. The T_m and enthalpy of melting, H_m, values for ET23 are also given.

Stress–Strain Analysis

Uniaxial stress–strain data for PTMO 1000/TDI ionomers with different chain architectures are shown in Figure 5. There are no large qualitative or

TABLE II
Thermal Analysis Data

Sample code[a]	T_g DSC (°C)	T_g DMTA (°C)	T_m DSC (°C)	H_m DSC (cal/g)
ET11	−68.7	−72	—	—
ET13	−70.3	−71	—	—
ET16	−69.6	−72	—	—
PB23	−59.4	−61	—	—
ET23	−77.6	−76	0	.98

[a] All samples cast from methanol except PB23 which was cast from a 5 : 1 mixture of chloroform and methanol.
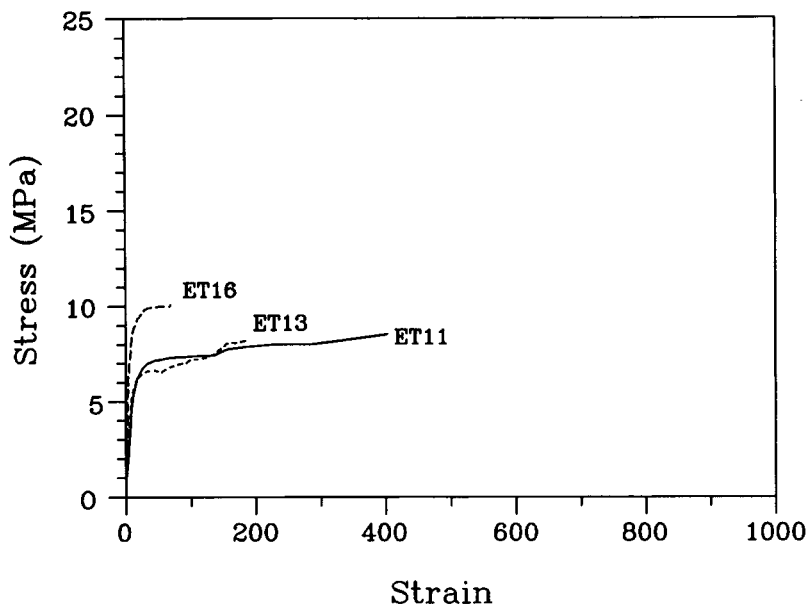
Fig. 5.   Tensile properties of polyurethane ionomers: effect of chain architecture. (———) ET11; (- - - - -) ET13; (– – –) ET16.

quantitative differences in the stress–strain response among ET11, E13, and ET16. The chain architecture of these materials appears to exert little influence on their Young's modulus or large deformation behavior.

One method of interpreting these results is to use rubber elasticity theory. In this approach tensile modulus is given by

$$E = 3[(f - 2)/f]\nu RT \tag{1}$$

where f is the crosslink functionality, ν is the density of elastically effective chains, R is the gas constant, and T is the absolute temperature. For sample ET11 the application of this equation is straight forward. If we consider the effective network element to be the PTMO chain, and we assume that all the sulfonate groups reside within aggregates, we can approximate a value for ν equal to 1.0×10^{-3} mol/cm^3. If we assume further that the functionality of an ionic crosslink is large, such that the bracketed quantity in eq. (1) approaches unity, we can calculate an upper bound on E equal to 8.0 MPa.

For samples ET13 and ET16 the application of eq. (1) is more complicated. Because of their star-shape architecture, these materials have a small fraction of covalent crosslinks in addition to their ionic crosslinks. However, since the density of the covalent crosslinks is small relative to the ionic crosslinks, the overall crosslink density ν remains essentially unchanged. Thus, from eq. (1) the expected enhancement to the modulus brought about by the presence of the covalent crosslinks will be small.

This approach clearly demonstrates that ET11, ET13, and ET16 are very similar in their network structure in spite of their different chain architectures. Significant differences in their stress–strain properties should not be expected.

In contrast, large differences in stress–strain response are observed for materials that vary in soft segment molecular weight. Figure 6 shows the tensile data for ET23 and ET13.

The differences in the stress–strain curves for ET23 and ET13 require a two-part explanation. At small strains, the mechanical behavior of these materials can again be described in terms of network theory. The crosslink density in ET13 is twice that in ET23, and as eq. (1) suggests, their Young's moduli reflect this difference. At higher elongations their mechanical behavior begins to be affected by strain-induced crystallization. The higher molecular weight soft segment in ET23 makes it more likely to crystallize. As a result ET23 shows more pronounced strain hardening behavior than ET13, and has a high ultimate tensile stress which is unusual for low molecular weight ionomers. Other low molecular weight ionomers have tended to have poor ultimate properties.[16,19]

Tensile data for PB23 was not obtained because the sample was found to have crosslinked prior to testing.

CONCLUSIONS

A series of model polyurethane ionomers based on TDI with different chain architectures and polyols have been synthesized and characterized. The effect of chain architecture on mechanical and thermal properties was small. The absence of significant differences in properties was attributed to the fact that changes in chain architecture had little effect on the overall crosslink density.
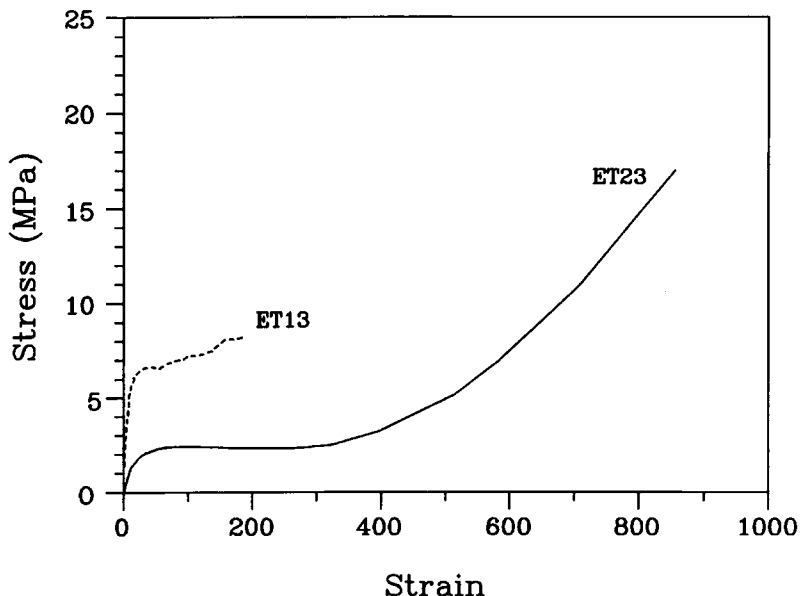

Fig. 6. Tensile properties of polyurethane ionomers: effect of soft segment molecular weight. (- - - -) ET13; (——) ET23.

Conversely, differences in soft-segment chemistry and soft segment molecular weight had large effects on the mechanical behavior of these materials.

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