

Ionene Elastomers from Polytetramethylene Oxide Diamines and Reactive Dihalides. I.

Effect of Dihalide Structure on Polymerization and Thermal Reversibility

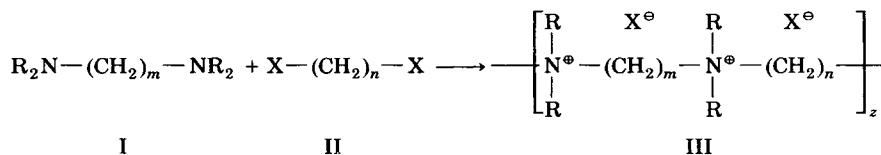
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Synopsis

The reaction of α,ω -bis(dimethylamino) polytetramethylene oxide with various dihalides provided a series of elastomeric ionenes. The influence of dihalide structure on the reaction was studied and a number of substituents were found which dramatically increased the rate of polymerization and ultimate molecular weights achieved. These ionene elastomers were thermoplastic and it was shown that in some cases this result was due at least in part to a depolymerization reaction via a dequaternization of the ammonium links. Again, structural features in the dihalide were important not only for the reverse reaction, but for the repolymerization to high molecular weight elastomer as well. An uncharged "analogue" was also prepared to address the feature of microphase separation and compared with the above ionene materials.

INTRODUCTION

Ionenes have been defined as polymers in which macromolecules contain cationic quarternary amines as integral links in the polymeric chain.¹ Although a variety of structural types are possible, the most thoroughly studied ionenes have been polyquaternary ammonium salts III, readily obtained from the Menshutkin reaction of aliphatic ditertiary amines I with dihalides II^{2,3}:

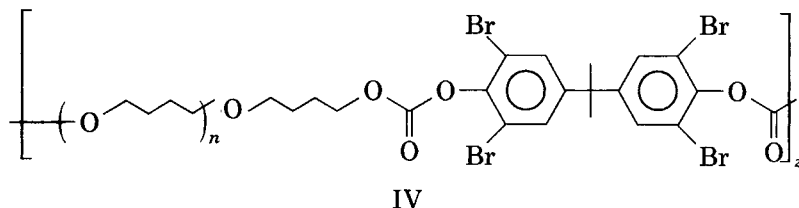


Scheme 1

In most cases, m and n have been small (1–16), giving ionenes with a high degree of ionic character and properties typical of polyelectrolyte–crystalline solids soluble in water and insoluble in organic solvents.⁴

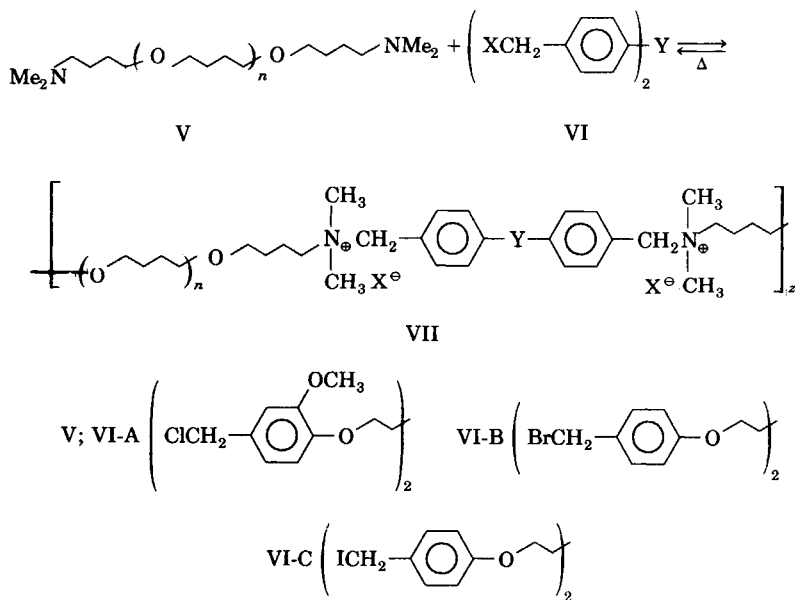
Ionenes in which a polymeric segment of low T_g is incorporated between the quaternary ammonium links have also been synthesized. Such ionene elastomers have seldom been prepared directly from the reaction of polymeric diamines with alkyl dihalides, however. Problems arise when the molecular weight of the diamine is high because the concentration of reactive chain ends is low at the outset and continues to decrease during the course of the polymerization, thus greatly reducing the overall rate and ultimate degree of polymerization.

Starting with dimethylamino terminated polytetramethylene oxide (PTMO) of up to 9000 molecular weight, Yamashita and co-workers have successfully prepared elastomeric ionenes via the Menshutkin reaction by utilizing a much more reactive aromatic dihalide, a dibenzyl chloride, in the polyquaternization.^{6,7} These polymers, despite their low ionic content, exhibited elastomeric behavior and it was of interest in our own work as to whether this was due to phase separation of the hard aromatic segments, ionic association, or a combination of both. Thus a nonionene block copolymer consisting of a PTMO soft segment and a brominated aromatic hard segment was prepared as a model for the study of the effect of ions on elastomeric properties, IV. It was found that this material exhibited no elastomeric behavior, indicating that ions are essential for the attainment of effective physical crosslinks (see later discussion):



In this article, we report our own studies of the reaction of bis(dimethylamino), PTMO, V, with a series of dibenzyl halides, VI, to form ionene elastomers, VII. We were particularly interested in the effects of structural modifications of the dihalide designed to further increase the rate of polymerization and ionene molecular weight. These novel ionenes were found to have outstanding elastomeric properties. The mechanical and morphological studies of these materials are described in an accompanying article.⁸

It is known that certain quaternary ammonium salts dissociate to tertiary amine and alkyl halide when heated.⁹ In the case of polymeric quaternary



Scheme 2

ammonium salts, this reaction, under carefully controlled conditions, has provided ionene elastomers thermoplastic by virtue of at least a partial depolymerization at elevated temperatures to amine and halide fragments of lower molecular weight. A repolymerization of amine and halide progressed at lower temperatures in the solid state. The influence of dihalide structure and other factors on these reactions is also discussed.

EXPERIMENTAL

Solvents and reagents were utilized as received from commercial suppliers unless otherwise noted. The dihalides 1,5-diiodopentane, 1,4-bis(chloromethyl) benzene, and 1,4-bis(bromomethyl) benzene were obtained from Aldrich Chemical Co., Milwaukee, WI. Tetrahydrofuran was dried prior to use by passage through a column of 3A molecular sieves. NMR Spectra were obtained on a Varian XL-200 NMR spectrometer at 200 MHz with tetramethyl silane as internal standard. Inherent viscosities were measured using a Canon-Fenske viscometer at 30°C at a concentration of 0.4 g/dL in chloroform. Thermal mechanical analysis (TMA) measurements were obtained on a Perkin-Elmer TMS-2 device at a scan rate of 10°C/min using a 5 g vertical load.

Limited solution light scattering measurements were made on one of the prepared ionenes for purposes of better quantifying absolute molecular weight (M_w). Dilute chloroform solutions were prepared of different concentration and studied following filtering through a 0.2 μm Acrodise CR filter. A Chromatix KMX-16 laser differential refractometer was operated at 633 nm (27°C) to determine the needed dn/dc values. A Chromatix KMX-6 LALLS spectrometer was used with a wavelength of 633 nm (27°C) for the solution scattering measurements. A 6–7° forward scattering angle was used which allowed the effects of intraparticle interference to be negligible.

Preparation of Polytetramethylene Oxide-Tetrabromobisphenol A Polycarbonate (IV)

Phosgene was bubbled into a solution of 102 g (0.1 eq) Teracol 2000, a 2000 molecular weight polytetramethylene oxide polyol, in 100 mL toluene until IR showed no remaining hydroxyl band. The excess phosgene and toluene were removed in vacuo to leave the bischloroformate.

A solution of 51 g (0.05 eq) of the bischloroformate in 50 mL CH_2Cl_2 was then added dropwise to a stoichiometric equivalent plus a 2.5% excess of tetrabromobisphenol A (13.6 g) with 5.1 g pyridine and 50 mL CH_2Cl_2 . The mixture was stirred and heated under reflux until the viscosity rose sufficiently to stop the magnetic stirrer. A film was cast on a glass plate and the solvent allowed to evaporate at RT prior to redissolving the THF. Precipitation in methanol removed the pyridine hydrochloride salts yielding a clear, light yellow film with a measured IV of 1.4.

Preparation of 1,4-Bis(2-Methoxy-4-Chloromethylphenoxy) Butane (VI-A)

A solution of 31.0 g vanillin (0.20 mol) in 50 mL DMF (previously dried over molecular sieve) was added dropwise with stirring under nitrogen to a slurry

of 8.2 g 60% sodium hydride in mineral oil (previously washed with hexane) (0.21 mol) in 200 mL dry DMF. The mixture was stirred for 1 h until H₂ evolution ceased. Dibromobutane (21.0 g, 0.10 mol) was added and the reaction heated at 90°C for 2 h. The clear, dark brown solution was poured into 2 L water, and the precipitate filtered, washed with water, and partially air dried. The crude product was dissolved in chloroform, dried over MgSO₄, filtered, and evaporated to dryness on a rotary evaporator. Recrystallization from xylene gave 28 g (78%) of intermediate bisaldehyde.

This was reduced by heating a slurry of 26.8 g of the bisaldehyde in 200 mL EtOH with 4.2 g NaBH₄ under reflux. After 3 h, an IR spectrum of a sample indicated a small amount of aldehyde remained. Another 1.0 g NaBH₄ was added and heated an additional hour to complete the reduction. The reaction was poured into water, filtered, and the solid air dried. Recrystallization from 2-butanone gave 24.0 g (91%) of 1,4-bis(2-methoxy-4-hydroxymethylphenoxy) butane as a white crystalline solid.

Conversion to the dibenzyl chloride (VI-A) was accomplished by adding a solution of 22.0 g of dibenzyl alcohol in 200 mL warm CHCl₃ dropwise with stirring to a solution of 60 g SOCl₂ in 100 mL CHCl₃. Upon completion of addition, the solution was heated to boiling and the CHCl₃ allowed to distill while replacing with an equal volume of heptane. When the pot temperature reached 97°C, the solution was decanted from a small amount of yellow oil and allowed to cool. Decantation from oily impurities was continued until a white solid began to form. The solution was cooled in ice, and the product filtered, and washed with hexane. One more recrystallization gave a pure white crystalline solid which was one spot on TLC (EtOAc). IR and NMR confirmed the structure. The yield was 23.0 g (85%) of dibenzyl chloride VI-A, mp 116–118°C (see Scheme 2).

Preparation of 1,4-Bis(4-Bromomethylphenoxy) Butane (VI-B)

By a similar procedure as described above, 1,4-bis(4-hydroxymethylphenoxy) butane was prepared starting from *p*-hydroxybenzaldehyde and 1,4-dibromobutane. In a 1-L three-necked round-bottomed flask a slurry of 75 g of the dibenzyl alcohol, 250 mL CHCl₃, and 250 mL 48% hydrobromic acid was stirred mechanically and heated to 45°C. The diol slowly dissolved in the CHCl₃ layer until it was completely clear after 3 h. In another hour a precipitate began to form, and after 3 h, the slurry was cooled to room temperature, diluted with 250 mL cold water and filtered. The light orange crude product was washed with water and air dried. Two recrystallizations from 2-butanone gave the product, dibenzyl bromide VI-B (see Scheme 2), as buff needles which were pure by TLC. The yield was 75 g (70%), mp 138–140°C.

Preparation of 1,4-Bis(4-Iodomethylphenoxy) Butane VI-C

A solution of 3.9 g of 1,4-bis(4-bromomethylphenoxy) butane in 50 mL 2-butanone was added to a solution of 9.7 g NaI in 100 mL 2-butanone. After an initial exothermic reaction, a golden yellow precipitate formed. The product was filtered, washed with water, and air dried. Recrystallization from xylene gave the dibenzyl iodide as a golden yellow crystalline solid. The yield was 2.0 g.

Preparation of α,ω -Bis(Dimethylamino) Polytetramethylene Oxide (V)

The method of Smith and Hubin¹⁰ was modified as follows: A flame-dried 500 mL, three-necked round bottomed flask equipped with mechanical stirrer, N₂ inlet and thermometer was charged with 35 g CH₂Cl₂ and 50 g dry THF, and the contents cooled to 0–5°C under N₂ with an ice water bath. Trifluoromethane sulfonic anhydride (4.5 g) was added rapidly via syringe and the clear, colorless solution was stirred at 5–10°C for 15 min. THF (90 g) was added dropwise over a 15–20 min period keeping the temperature at 5°C. After addition was complete, the reaction was stirred for 90 min.

The polymerization was terminated by pouring the viscous syrup into a rapidly stirred ice cold solution of 12.0 g anhydrous dimethylamine in 50 mL dry THF. After stirring at room temperature for 15 min, the mixture was transferred to a 500-mL round-bottomed flask with 150 mL toluene and the CH₂Cl₂ and unreacted dimethylamine and THF were stripped on a rotary evaporator. The residue was diluted to 400 mL with more toluene, treated with 50 mL 25% aqueous NaOH, and heated to reflux with rapid stirring. Heating was continued for 10–15 min until the evolution of dimethylamine was complete. The still warm mixture was transferred to a separatory funnel, the aqueous layer discarded, and the organic phase dried over powdered MgSO₄ and filtered through a pad of Super Cel filter aid. The clear, colorless filtrate was evaporated to dryness on a rotary evaporator to give bis(dimethylamino) PTMO as a light yellow syrup which solidified on standing. The yield was 85.0 g (61%). The molecular weight was determined by titration of a THF–isopropyl alcohol solution of a sample of the polymer with 0.1N HCl to a bromphenol blue end point, and in this case was found to be 8000, assuming a functionality of 2.0. Higher molecular weight diamines were obtained by increasing the weight ratio of THF to trifluoromethane sulfonic anhydride initiator. Following this procedure, bis(dimethylamino) PTMO's of 14,000 and 27,500 molecular weight were also prepared.

Reaction of α,ω -Bis(Dimethylamino)–Polytetramethylene Oxide (V) with Dihalides (VI)

A solution of 10.0 g of bis(dimethylamino) PTMO and a stoichiometric equivalent plus a 2.5% excess of the dihalide (VI) in 50 mL dry THF was stirred and heated under reflux until the viscosity rose sufficiently to stop the magnetic stirrer. An antioxidant (0.1 g) such as Irganox 1010 was dissolved in the syrup which was cast on a glass plate. The solvent was allowed to evaporate at room temperature (4–6 h). After heating in a forced air oven at 65°C for 16 h, the resulting ionenes were obtained as clear, colorless, strong elastomeric films.

RESULTS AND DISCUSSION

Factors Affecting Ionene Formation

Similar to the formation of polyurethane elastomers, the reaction of polymeric ditertiary amines with dihalides is a condensation polymerization. In

TABLE I

Reaction no.	Molecular weight diamine	Dihalide	Polym. time	IV ^a 0.4 g/dL
1	8000		16 h	1.4
2	8000		18 h	1.6
3	8000	$\left(\text{ClCH}_2\text{-C}_6\text{H}_3(\text{OCH}_3)\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	8 h	2.4
4	8000	$\left(\text{ClCH}_2\text{-C}_6\text{H}_3(\text{OCH}_3)\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	8 h	3.1
5	8000		20 min	2.8
6	8000	$\left(\text{BrCH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	10 min	4.7
7	8000	$3 \left(\text{ClCH}_2\text{-C}_6\text{H}_3(\text{OCH}_3)\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$ $1 \left(\text{BrCH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	1 h	4.6
8	8000	$\left(\text{ICH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	30 s	5.1
9	14000	$\left(\text{ClCH}_2\text{-C}_6\text{H}_3(\text{OCH}_3)\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	72 h	2.6
10	14000	$\left(\text{BrCH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	30 min	3.8
11	14000	$3 \left(\text{ClCH}_2\text{-C}_6\text{H}_3(\text{OCH}_3)\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$ $1 \left(\text{BrCH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	3.5 h	3.3
12	27500	$\left(\text{BrCH}_2\text{-C}_6\text{H}_4\text{-O-CH}_2\text{CH}_2\text{CH}_2 \right)_2$	1 h	3.0

^a CHCl₃ solution, measured at 30°C in a Cannon-Fenske #50 viscometer.

order to develop optimum elastomeric properties, a sufficiently high degree of polymerization must be achieved. To accomplish this, it is imperative not only that the functionality of the reactants be as close to 2.0 as possible, but also that the reactivity of the amine with halide be high enough to provide a rapid rate of polyquaternization to high molecular weight ionene.

Dimethylamine-terminated polytetramethylene oxide was chosen as the rubbery segment for this study because it is readily prepared in any desired molecular weight having excellent difunctionality by the method of Smith and Hubin.¹⁰ For best results in reactions with dihalides care was taken to convert the organic soluble byproduct, dimethylammonium trifluoromethane sulfonate, to the sodium salt for complete removal by aqueous extraction during workup of the diamine. The results of a number of reactions of PTMO diamines with a series of reactive dihalides are listed in Table I.

In this table, the polymerization time is recorded from the start of reflux to the attainment of viscosity high enough to stop the magnetic stirrer. It is a measure, as is the inherent viscosity of the final ionene elastomer, of the reactivity of the dihalide with the diamine. As expected, the reactivity is profoundly influenced by the structure of the dihalide.

Characterization of these ionene systems using GPC has not been practical to undertake because of possible ionic interactions with the column support. Hence, to give further support to the inherent viscosity data that high molecular weight was achieved, a dibenzyl bromide-based ionene having a 3500 dimethyl-amino-terminated polytetramethylene oxide soft segment was investigated by solution light scattering for purposes of determining absolute molecular weight (M_w). Using the procedures described earlier, the data given in Figure 1 were obtained which are a conventional plot of $Kc/\bar{R}(\theta)$ vs. c

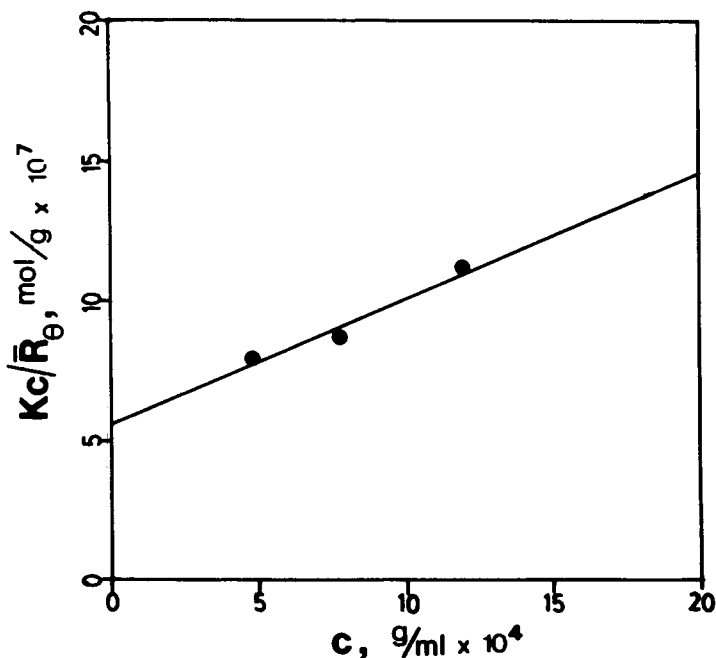
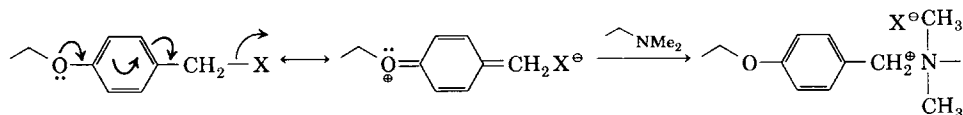


Fig. 1. Plot of reduced Rayleigh ratio vs. concentration for 1B-NS-3500 ($M_w = 1/\text{intercept} = 1.8 \times 10^6$ g/mol).

where K is a constant, c is concentration, and $\bar{R}(\theta)$ is the reduced Rayleigh ratio. Such a plot, if linear at dilute concentrations, provides an intercept that is the inverse of \bar{M}_w , which in this specific case is 1.8×10^6 g/mol. Furthermore, this value supports the inherent viscosity parameter as an indication of high molecular weight. Additional data points at higher concentrations were not considered due to the du/dc values going off scale believed to arise from potential association of the ionic moieties in the system. While the lower concentration data provide good linearity, the reader is cautioned that the \bar{M}_w value of 1.8×10^6 g/mol reported herein is *indicative* of the overall molecular weight and should not be considered as an absolute value of the ionene polymer.

The rates of polymerization are in accordance with the well-known order of reactivity of halides toward nucleophilic displacement, with benzyl halides being faster than alkyl halides and $\text{Cl} < \text{Br} < \text{I}$. Interestingly, the most reactive alkyl halide, diiodopentane, is comparable to the least reactive benzyl halide, 1,4-bis(chloromethyl) benzene (reaction 1 with reaction 2). A substantial increase in reactivity is realized when a strongly electron donating substituent is incorporated *para* to the benzyl group (reaction 2 with reaction 3). This effect is attributed to a resonance interaction which enhances the leaving ability of the halide¹¹:



Scheme 3

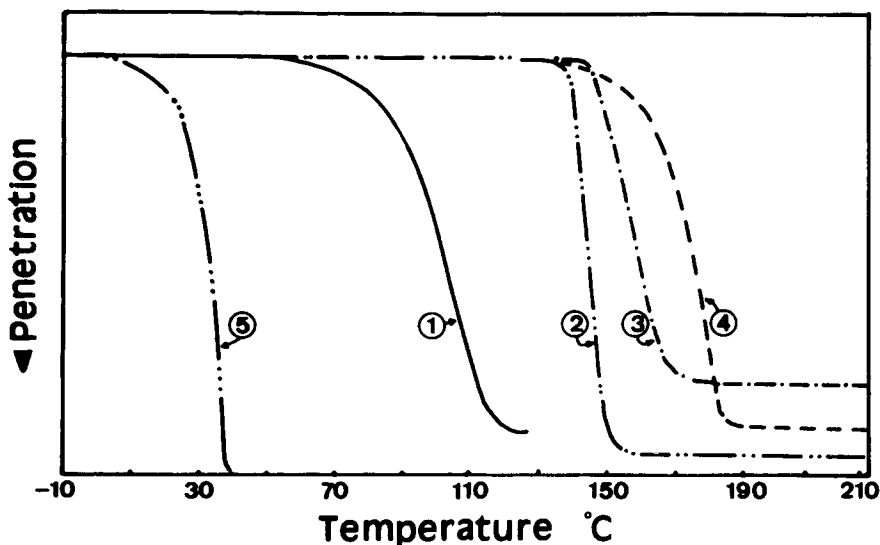
Changing the leaving group from Cl to Br provides a dramatic increase in the rate of polymerization (reaction 2 with reaction 5). Further activation of the benzyl bromide with the electron donating substituent had little effect on the rate, but did give a substantially higher ultimate molecular weight (reaction 5 with reaction 6). Of course, the fastest rate of polymerization to the highest molecular weight ionene was achieved with the best leaving group, iodide, on an activated benzyl group (reaction 8).

As the molecular weight of the PTMO diamine is increased, the rate of polymerization with even activated dibenzyl chlorides decreases significantly (reaction 9 with reaction 3), while that of the bromides is much less affected by the decrease in reactive chain end concentration (reactions 10 and 12 with reaction 6).

By utilizing mixtures of dichlorides with small amounts (ca. 25 mol %) of dibromides, it was found that the rate of polyquaternization approached that of the pure dibromides (reaction 7 with reaction 6 and reaction 11 with reaction 10).

Factors Affecting Thermal Behavior

The ionene elastomers were found to be thermoplastic as evidenced by some representative thermal mechanical analysis (TMA) curves as shown in Figure 2. For comparison, Figure 2 also includes the response of the noncharged block



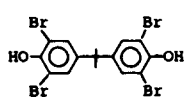
Curve	Ionene Linking Agent	Softening Point °C
1	Kraton 1107	105
2	3:1 $(\text{ClCH}_2-\text{C}_6\text{H}_4-\text{O})_2$ + $(\text{BrCH}_2-\text{C}_6\text{H}_4-\text{O})_2$	144
3	$(\text{BrCH}_2-\text{C}_6\text{H}_4-\text{O})_2$	157
4	$\text{BrCH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$	179
5		32

Fig. 2. Thermal mechanical analysis spectra of ionene polymers.

polymer, tetrabromo bisphenol-A (see structure IV), and of a typical commercial thermoplastic elastomer (Krayton 1107) which represents a styrene-isoprene-styrene block polymer of ca. 120,000 molecular weight with 10,000 molecular weight styrene end blocks and 100,000 molecular weight isoprene midblock (17% styrene).

From the curves, it is apparent that the ionene elastomers soften and flow at much higher temperatures than the S-I-S Krayton block polymer. Furthermore, the shapes of the curves are different with most of the ionenes exhibiting a much sharper softening or "melting-like" behavior. Only the highest softening ionene, that linked with 1,4-bis(bromoethyl)benzene, provides a curve similar to that of a typical thermoplastic elastomer. It is noted that the noncharged tetrabromo bisphenol-A species shows only a softening of around 30°C which results from the melting behavior of the PTMO segment ($2000\bar{M}_w$) which will crystallize when cooled to subambient conditions. Following this softening (melting), there is no sign of a rubbery plateau region as

would be the case if microphase separation had been induced by the presence of the tetrabromo bisphenol-A containing segment. The TMA results therefore strongly indicate that little or no phase separation occurs in this material, thereby suggesting that there is not sufficient incompatibility between the PTMO segment and that of the so-called hard segment. This is in contrast to the ionene systems which must promote the phase separation on the basis of charge (coulombic interactions). More detail will be presented on verifying these latter statements in Part II of this series.

TABLE II

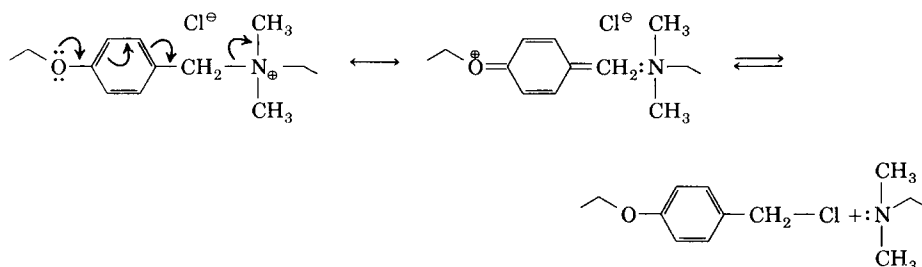
Ionene from reaction number ^a	Diamine MW	Dihalide	TMA softening point ^b (°C)
7	8000	$3 \left(\text{ClCH}_2 - \text{C}_6\text{H}_2(\text{OCH}_3) - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$ $+ 1 \left(\text{BrCH}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$	144
3	8000	$\left(\text{ClCH}_2 - \text{C}_6\text{H}_2(\text{OCH}_3) - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$	146
9	14000	$\left(\text{ClCH}_2 - \text{C}_6\text{H}_2(\text{OCH}_3) - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$	149
2	8000	$\text{ClCH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2\text{Cl}$	157
6	8000	$\left(\text{BrCH}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$	157
10	14000	$\left(\text{BrCH}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{CH}_2\text{CH}_2\text{CH}_2 \right)_2$	160
5	8000	$\text{BrCH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2\text{Br}$	179

^aSee Table I.

^bMeasured at a scan rate of 10°C/min., the softening point is recorded as the intersection point of tangent lines drawn from onset and complete penetration.

The TMA softening points of the ionenes as obtained by TMA have been listed in Table II and show no dependence on the molecular weight of the PTMO diamines (and thus ionic content), but are indeed directly related to the structures of the dihalide linking agents. For the TMA scan rate utilized, the benzyl chlorides were observed to soften at lower temperatures than bromides with the lowest softening point obtained when there is an electron donating substituent present in the para position. Interestingly, the same mixture of activated halides which provides the rapid rate of polyquaternization of a bromide was found to have the lower softening point of a pure chloride. Presumably, this phenomenon is the result of a rapid equilibration of bromide ion with benzyl chloride to continually regenerate the more reactive (toward amine) benzyl bromide and chloride ion.

These results are in accordance with the concept that the softening or melting type behavior of these ionenes is actually a depolymerization from the dequaternization of the ammonium ion links. This is a displacement reaction in which the nucleophile is the halide ion and the leaving group is tertiary amine.



Scheme 4

Most of the same structural features which enhanced the quaternization reaction also favor the reverse reaction; namely, benzyl greater than alkyl and the resonance contribution of electron donating substituents. However, in the absence of hydrogen bonding substituents or solvents, chloride ion is a stronger nucleophile than bromide,¹² and thus quaternary ammonium chlorides undergo the reverse reaction more readily (at a lower temperature) than bromides.

Depolymerization–Repolymerization Efficiency

The main advantage anticipated for an elastomer that is thermoplastic as a result of depolymerization would be a significantly lower melt viscosity than conventional TPEs. Ideally, in the case of an ionene elastomer, it should dequaternize rapidly and without side reactions to give a readily processable syrup of lower molecular weight amines and halides which would requaternize rapidly and completely to its original molecular weight. The actual results fell somewhat short of this optimum scenario, unfortunately.

The effect of melting on the molecular weights of the most easily dequaternized ionenes was followed by monitoring the inherent viscosities of the elastomers. Preliminary experiments revealed that extensive degradation occurred if the elastomers were heated without antioxidants,¹³ or if held in the

TABLE III

	IV (dL/g) in CHCl ₃
Ionene 3	2.37
Melt (145°C, 10 min)	0.88
After 2 h (65°C)	1.26
18 h (65°C)	2.19
42 h (65°C)	2.27
Ionene 7	3.22
Melt (145°C, 7 min)	1.00
After 18 h (65°C)	2.21

melt for any length of time even with antioxidants; such syrups never resolidified. Best results were obtained when a thin film of the ionene was heated at the minimum softening temperature until it would just flow (ca. 10 min) and then cooled rapidly. A small sample was taken and immediately dissolved in chloroform for measurement of inherent viscosity which is reported as melt IV in Table III. The cooled film, which solidified rapidly to an elastomer, was placed in a 65°C oven and samples were cut from it periodically thereafter to follow the progress of the repolymerization. Results are reported in Table III for the ionenes prepared from 8000 molecular weight PTMO diamine and the activated dichloride VI-A (ionene 3) and the 3:1 molar ratio of dichloride VI-A and activated dibromide VI-B (ionene 7).

Although these ionenes depolymerize to lower molecular weight materials on heating and rapidly resolidify on cooling, they are very slow to actually repolymerize to near their original molecular weight in the solid state, even with annealing at 65°C. The presence of the benzyl bromide VI-B in ionene 7 also had no effect on increasing the rate of repolymerization as it had on the rate of polymerization in solution. Reasons for this very slow and incomplete degree of repolymerization of these ionene elastomers observed in the solid state remain a matter of conjecture at this time. It may be that the two-phase morphology⁸ of these polymers is in some way playing a role in inhibiting the recombination reaction. Also, in view of the deleterious effects of prolonged heating, there may be a problem with unidentified irreversible side reactions, or with oxidative decomposition of PTMO chains despite the presence of antioxidants.

Future studies will be investigating the potential of using ionic plasticizers for lowering the softening temperature to allow thermal processability of these ionomer systems. As has been demonstrated by Makowski and Lundberg, zinc stearate can often serve this purpose at least in some ionomer systems.¹⁴

CONCLUSIONS

The course of the reaction of α,ω -bis(dimethylamino) polytetramethylene oxide with dihalides to form ionene elastomers has been demonstrated to be profoundly influenced by the structure of the dihalide employed. The use of benzyl halides with electron donating substituents enhanced the reactivity of

all the halides, but the rate and ultimate degree of polymerization increased most dramatically as the leaving group was varied from Cl to Br to I.

Upon heating, certain ionenes were shown to undergo a depolymerization reaction which was also influenced by the choice of substituents, with chloride being most reactive in this case. Under carefully controlled conditions, the elastomers would repolymerize to close to their original molecular weight. Unfortunately, the elastomers appeared to be quite prone to irreversible degradation during heating, and were very slow to repolymerize so that their utility as a new type of thermoplastic elastomer appears to be quite limited. However, films of these ionenes cast from solution have exhibited excellent elastomeric behavior, which in certain applications may offer advantages over other materials. The structure-property behavior of these ionene elastomers is the subject of the accompanying paper.⁸

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