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Viscoelastic Properties of Telechelic Ionomers. 2. Quaternized α,ω-Bis(dimethylamino)polyisoprene

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ABSTRACT: A short-length polyisoprene ($\bar{M}_n$ = 5000) was selectively end-capped at both ends by a dimethylamino group. Quaternization of these end groups by a series of *n*-alkyl iodides deeply affected the dynamic mechanical behavior. The glass transition temperature (T_g) of polyisoprene and the storage modulus (G') in the glassy state were found to be largely dependent on the length of the *n*-alkyl group of the quaternization agent: both of these properties increased as the *n*-alkyl group was shortened. Furthermore, as a result of the quaternization of the tertiary amine end groups a rubbery plateau emerged in the isochronous curves of G' vs temperature. An ionic relaxation peak was also displayed by the thermal dependence of the loss modulus (G''), in a range depending on the length of the *n*-alkyl group and on the functionality of the quaternization agent.

1. Introduction

Thirty years ago, E. I. du Pont de Nemours & Co. launched the first ionomer on the market under the trade name Surlyn. This material is made of polyethylene containing a few percent of sodium or zinc carboxylate groups which are distributed at random along the polymer backbone. In a medium of low dielectric constant, the ionic groups associate by dipole–dipole interactions and cause physical cross-linking of the polymer.[1-5] Since the ionic aggregates are thermoreversible, the ionomer can be processed by traditional techniques. Generally, Surlyn offers improved properties as compared to those of the parent polyolefin. Although the ionomer concept has been extended to various polymer backbones and ionic groups, the structure of the ionic aggregates is still a pending question. In order to establish the fundamental "structure–property" relationships, model ionomers and especially halato-telechelic polymers (HTP's) have been synthesized.[6-19] In HTP's an ionic group is selectively attached at both ends of the linear chains. Most of these polymers have been prepared by living anionic polymerization by using an electrophilic deactivating agent as a precursor of the end groups. So the nature, the length, i.e., the distance between the ionic groups, and the molecular weight distribution of the polymer as well as the nature of the ionic end groups (metal carboxylate,[6-19] metal sulfonate,[20] quaternized tertiary amine[21-25]) can be largely controlled. A number of papers have reported on the morphology and properties of HTP's.[26-34]

An extensive study of carboxylato-telechelic polymers has shown that, in a solvent of low dielectric constant, gelation can take place at a polymer concentration as low as 1 or 2 wt %. However, gelation depends on temperature, on the dielectric constant of the solvent, and on the size and charge of the cation.[6,9]

Dynamic mechanical measurements have been performed on gels of α,ω-dicarboxylatopolyisoprene and -polybutadiene. They show a relaxation process which has been attributed to the ionic aggregates. This relaxation is responsible for the occurrence of the viscous flow, and it shows an Arrhenius-type of temperature dependence. The activation energy decreases as the size of the alkaline-earth cation increases, i.e., as the dipole–dipole interactions are weakened.[11] The ionic aggregates have also been characterized in the bulk. They exhibit the same overall behavior as in solution. It is however clear that the solvent leads to a decrease in the bulk activation energy which tends to be more pronounced whenever the cation size increases. From the modulus of the rubbery plateau it can be inferred that the mean association degree increases with the cation radius, i.e., as the strength of the mutual interactions of dipoles decreases. This means that the extension of the ion-pair association is mainly controlled by steric effects rather than by the strength of electrostatic interactions. In the alkaline cation series, the effect of cation size is different since the mean association degree goes through a maximum when the cation radius increases from Li to Cs,[19] which might indicate that the cation charge also affects the ion-pair association. These results motivate an investigation of HTP's as models for the more complex ionomers.

This paper considers extending the study of HTP's to linear chains end-capped by quaternary ammonium groups. It focuses on the dynamic mechanical behavior of α,ω-bis(dimethylamino) polymers quaternized with a series of *n*-alkyl iodides and 1,5-diiodopentane. The research aims at determining how the electrostatic association of quaternary ammonium pairs can be compared to that of metal carboxylates and to what extent the length of the *n*-alkyl group affects the dipole–dipole interactions of ammonium iodide end groups. Whenever the *n*-alkyl iodide is difunctional (1,5-diiodopentane), two chain ends are covalently bonded together as shown in Chart I. This structural modification is liable to perturb the mutual electrostatic interactions of ion pairs now joined two by two and separated from each other by five carbon atoms.

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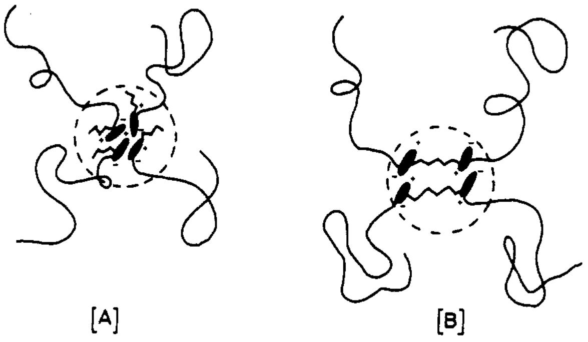
Chart I
Schematic Representation of the Association of the Quaternary Ammonium Ion Pairs: Quaternization of the Tertiary Amine End Groups with (A) an *n*-Alkyl Iodide and (B) 1,5-Diiodopentane[a]



[a] + ● – stands for the ion pair; ﹏ stands for the alkyl chain of the iodide.

2. Experimental Section

2.1. Sample Preparation. The anionic polymerization of isoprene was performed in a previously flamed and nitrogen-purged glass reactor equipped with rubber septums. Hypodermic syringes and stainless steel capillaries were used to handle liquid products under a nitrogen atmosphere.

Tetrahydrofuran (THF; pure grade) was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. Isoprene (pure grade) was dried over calcium hydride at room temperature and distilled under reduced pressure. It was finally mixed with *n*-BuLi and distilled just before polymerization.

α,ω-Bis(dimethylamino)polyisoprene was synthesized in THF (3 wt % of monomer) at −78 °C by living anionic polymerization. Sodium naphthalene was used as a difunctional initiator. A dark green sodium naphthalene complex resulted from the reaction between an excess of metallic sodium and naphthalene in dry THF. After 1 h of polymerization, the living macrodianion was deactivated with an excess of 1,3-bis(dimethylamino)propyl chloride (DMAPC). DMAPC was obtained by neutralization of its hydrochloride with sodium hydroxide in water. The DMPAC-rich oil phase was separated by 3-fold extraction with diethyl ether. The ether solution was washed three times with deionized water, and ether was thereafter distilled off. The resulting DMAPC had been dried with anhydrous Na_2SO_4 and then with CaH_2 for at least 3 days and finally distilled just before use.

The α,ω-bis(dimethylamino)polyisoprene was precipitated with a 10-fold excess of methanol, then dissolved in a minimum amount of THF, and, in order to eliminate the impurities (excess DMAPC, naphthalene, and NaCl), reprecipitated twice with methanol.

The obtained polymer contained 65% of 3,4 units, and the rest was composed of 1,2 isomers. The number- and weight-average molecular weights, $\bar{M}_n = 6500$ and $\bar{M}_w = 8500$ (in PS), respectively, were estimated by size exclusion chromatography (SEC) by using a polystyrene calibration. The polydispersity index was thus $\bar{M}_w/\bar{M}_n = 1.3$. The absolute value of $\bar{M}_n = 5200$ was determined by vapor-pressure osmometry. The potentiometric titration of the amino end groups was carried out by using a perchloric acid solution (0.02 mol/L) in a toluene/methanol mixture (90:10 vol %). Considering that the polymer chain should have two amino groups, the molecular weight was calculated as $\bar{M}_t = 5520$. The amino functionality was calculated from the $\bar{M}_n/\bar{M}_t$ ratio and found to be 1.9. In the following text, the α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5200$) is abbreviated to $PIP(NMe_2)_2$ 5K, where Me = CH_3.

The quaternization reactions were carried out by dissolving $PIP(NMe_2)_2$ 5K in a THF/methanol mixture (95:5 vol %) and by adding a 2-fold molar excess of the quaternizing agent. The reaction mixture (5 wt % polymer solution) was refluxed for 4 days; the quaternization was then complete as proved by the absence of any amino groups (titration with $HClO_4$). The *n*-alkyl iodides used in this work are listed in Table I. The reaction product was precipitated in an excess of methanol (in order to eliminate the unreacted alkyl iodide), dried, and then redissolved in THF containing IRGANOX 1010 (antioxidant) in an amount of 1 wt % on polymer. Films of α,ω-bis(dimethylamino)polyisoprene were prepared by THF solution casting and slow evaporation of solvent followed by drying under vacuum at 60–70 °C during more than 1 month.

Table I
List of *n*-Alkyl Iodides Used as Quaternizing Agents

quaternizing agent	formula	code for the quaternized polymer
iodomethane	CH_3I	PIP 5K C1
iodoethane	C_2H_5I	PIP 5K C2
1-iodobutane	C_4H_9I	PIP 5K C4
1-iodooctane	$C_8H_{17}I$	PIP 5K C8
1-iodohexadecane	$C_{16}H_{33}I$	PIP 5K C16
1,5-diiodopentane	$C_5H_{10}I_2$	PIP 5K C5I2

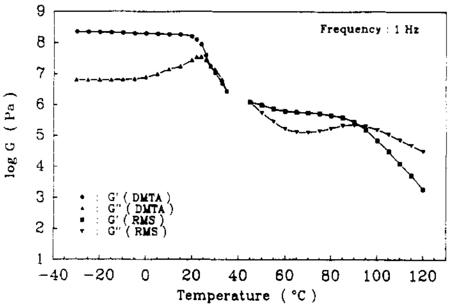


Figure 1. Temperature dependence of the storage (G') and loss (G'') moduli of α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with methyl iodide.

It is worth noting that, in the case of 1,5-diiodopentane as a quaternizin agent, 1 mol of the alkyl diiodide was added per mol of $PIP(NMe_2)_2$. Potentiometric titration of amino groups with $HClO_4$ proved again that the quaternization was quantitative under the reaction conditions described above.

2.2. Measurements. Samples were characterized in the glassy region, i.e., below the glass transition temperature, T_g, using the dynamic mechanical thermal analyzer (DMTA) from Polymer Laboratories. The instrument was operated at a constant frequency in a single cantilever bending mode. The material's behavior at temperatures above T_g was analyzed with the Rheometrics mechanical spectrometer RMS 605 in a dynamic parallel-plate geometry. Two types of viscoelastic data were collected: (1) the constant-frequency temperature scans ($-40\ °C < T < +200\ °C$) and (2) the isothermal frequency scans at $T > T_g$ and frequencies $\nu = 0.016$–16 Hz. In type 1, the data from RMS and DMTA were collected under common conditions: a frequency $\nu = 1$ Hz and a heating rate of 2 °C/min.

Samples had been prepared by compression molding at 2 MPa for 15 min at a temperature approximately 50 °C above T_g. The measurements were carried out within the linear viscoelastic region. The RMS scans were carried out under dry nitrogen on completely relaxed samples. Scans were indeed started when the normal stress was zero, and they were stopped as soon as that condition was no longer observed. Time and strain sweeps were performed in order to determine the limits of the linear response. After being tested at high temperatures, the samples remained soluble in toluene, meaning that no cross-linking took place. Thermogravimetric analysis of the quaternized samples showed that no dequaternization occurred up to 200 °C, i.e., the upper limit for the rheological measurements.

Differential scanning calorimetry (DSC) measurements were carried out by using a Perkin-Elmer DSC-4 under a flow of dry N_2, at a constant heating rate of 20 °C/min in the temperature range from −30 to +120 °C.

3. Results

Examples of experimental results are shown in Figures 1 and 2 for mono- and difunctional *n*-alkyl iodides, respectively, as a plot of the storage, G', and loss, G'', shear

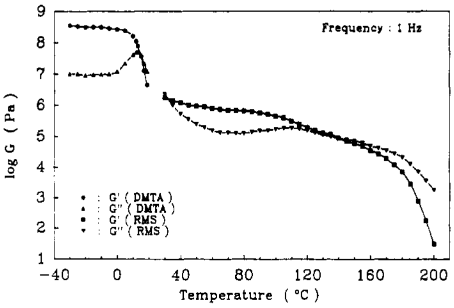


Figure 2. Temperature dependence of the storage (G') and loss (G'') moduli of α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with 1,5-diiodopentane.

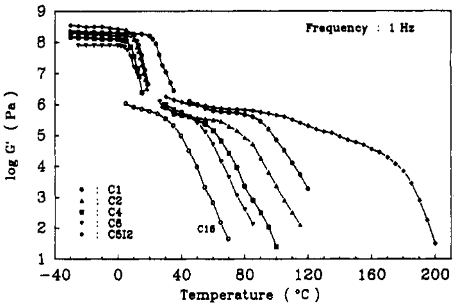


Figure 3. Storage modulus vs temperature for α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with a series of n-alkyl iodides. The n-alkyl group is designated by the number of carbon atoms; C_5I_2 stands for 1,5-diiodopentane.

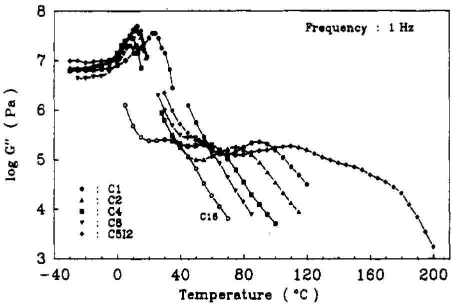


Figure 4. Loss modulus vs temperature for α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with a series of n-alkyl iodides. The n-alkyl group is designated by the number of carbon atoms; C_5I_2 stands for 1,5-diiodopentane.

moduli vs temperature. The low-temperature data (the left upper corner) have been measured by DMTA and those at higher temperatures, $T > T_g$, by RMS. Since the DMTA results are usually expressed in terms of the tensile (Young's) modulus (E), here the values are plotted as $G' = E'/3$ and $G'' = E''/3$ in order to be compared with RMS data.

A comparative summary of the results for quaternized samples is presented in Figures 3 and 4 as G' vs T and G'' vs T curves, respectively. At room temperature, PIP 5K C16 (i.e., PIP 5K quaternized with 1-iodohexadecane; C16 actually indicates the number of carbon atoms of the alkyl iodide) had the consistency of a soft chewing gum, while at $T < T_g = -8$ °C, it was extremely brittle. For these reasons, that sample could not be tested with DMTA.

The DSC results are summarized in Table II where glass transitions, T_g(DSC), of the quaternized $PIP(NMe_2)_2$ 5K samples are listed for the five monoiodo and the one diiodo derivatives. The transition temperatures at $\nu = 1$ Hz provided by the viscoelastic tests are also given for comparison; the T_i under the heading *a* is the dynamic glass transition temperature that corresponds to the peak position of the log E'' vs T curve. The T_i under the heading *d* is the position of the first peak observed above T_g in the log G'' vs T curve. The T_i under the heading *d* refers to the temperature at which the ionic aggregates disintegrate.

Table II
Transition Temperatures of the Quaternized $PIP(NMe_2)_2$ 5K (in °C)

sample	T_g(DSC)	T_i *a*	*b*	*c*	*d*
unquaternized	1				
PIP 5K C1	38	24	28	30	89
PIP 5K C2	17	12	18	18	74
PIP 5K C4	13	8	13	11	56
PIP 5K C8	13	8	11	10	50
PIP 5K C16	-8			6[e]	29
PIP 5K C5I2	15	13	17	19	108

[a] Temperature at the maximum of the log E'' vs T curve (DMTA). [b] Temperature at half-height between the glassy and rubbery plateaux. [c] Temperature corresponding to $G' = 10$ MPa. [d] Ionic transition: temperature at the maximum of the log G'' vs T curve (RMS). [e] Value obtained by extrapolating to $G' = 10$ MPa.

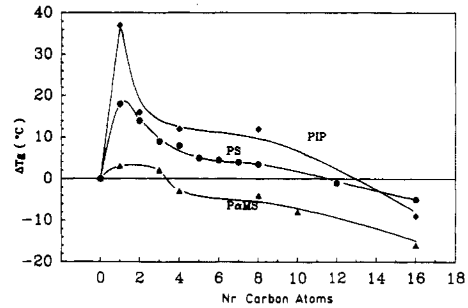


Figure 5. Change in T_g (ΔT_g) as promoted by the quaternization of α,ω-bis(dimethylamino) polymers with n-alkyl iodides. The length of the n-alkyl group is indicated by the number of carbon atoms. Polymers are polyisoprene (PIP), polystyrene (PS), and poly(α-methylstyrene) (PαMS).

Figure 5 illustrates the effect of quaternization on glass transition temperature as ΔT_g vs the number of carbon atoms in the iodide alkyl chain. ΔT_g is defined as the difference between the DSC-measured T_g of the quaternized sample and the T_g of the unquaternized material. Data for $PIP(NMe_2)_2$ 5K and for two other series of telechelic ionomers (to be discussed in the following publications of this series) are mentioned as well. "PS" and "PαMS" stand for polystyrene (PS; $\bar{M}_n = 5700$) and poly(α-methylstyrene) (PαMS; $\bar{M}_n = 7000$), respectively. These polyvinyl aromatics are, of course, end-capped with dimethylamino groups quaternized with n-alkyl iodides. The unquaternized polymers are referred to as the zero-carbon atom (Figure 5). T_g of the unquaternized PIP, PS, and PαMS samples are 1, 92, and 167 °C, respectively.

4. Discussion

It is interesting to discuss the experimental results presented in Figures 1–4 in relation to the four viscoelastic regions which are usually identified for homopolymers: glassy state, transition zone, rubbery plateau, and terminal zone. These regions are distinguished from each other by the chain mobility, i.e., the modulus. In the glassy region, the macromolecules are in a random-coil conformation with chain mobility limited to short-chain segments. The glassy modulus, $E_G \simeq 3G_G \simeq 0.1$–$5$ GPa, depends on the inherent rigidity of the system but not on molecular weight. The transition zone is characterized by a rapid change of physical properties according to temperature. Here, as the temperature increases, so does the chain mobility: from the level characteristic of a glass to that of a rubber. Properties of material within this zone are sometimes

Table III
Physicomechanical Properties of the Quaternized PIP$(NMe_2)_2$ 5K[a]

sample	T_g (DSC), K	T_G, K	T_R, K	T_i K	E'_G, MPa	log G'_R, Pa	log G'_m, Pa	$\bar{n}$
unquaternized	274							
PIP 5K C1	311	271	342	362	617	5.8	5.8	5.2
PIP 5K C2	290	253	319	347	575	5.6	5.6	3.5
PIP 5K C4	286	250	315	329	407	5.5	5.6	2.8
PIP 5K C8	286	250	315	323	229	5.7	5.6	4.5
PIP 5K C16	265		292	302		5.8	5.7	6.1
PIP 5K C5I2	288	251	317	381	1023	6.0	5.9	8.9

[a] T_G/T_g(DSC) = 0.872. T_R/T_g(DSC) = 1.1. $T_i = T$ at the maximum of G'' vs T (rubbery plateau). $E'_G = E'$ at $T = T_G$. $G'_R = G'$ at $T = T_R$. $G'_m = G'$ at the minimum of G'' vs T (rubbery plateau).

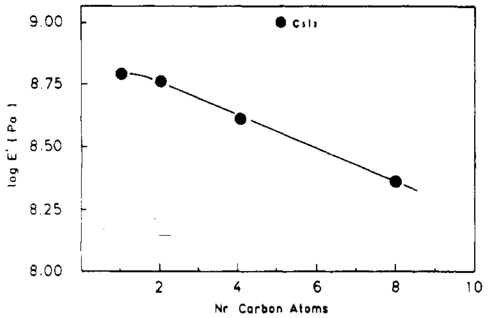


Figure 6. Storage modulus in the glassy state for α,ω-bis(dimethylamino) polyisoprene ($\bar{M}_n = 5000$) quaternized with a series of n-alkyl iodides. Effect of the length (number of carbon atoms) of the n-alkyl group.

described as leathery. Within the next rubbery plateau region the modulus remains relatively constant; $E_R \simeq 3G_R \simeq$ 10–1000 kPa. The magnitude of E_R depends on the chain entanglement (cross-link) density whereas the size of the plateau depends on the molecular weight. For molecular weight below the critical value for entanglements ($\bar{M}_C$), network formation is impossible and the transition zone merges with the terminal one. As a reminder $\bar{M}_C = 2\bar{M}_e$, where $\bar{M}_e$ is the average molecular weight between entanglements. On the other hand, for permanently cross-linked systems, the rubbery plateau stretches up to the thermal decomposition temperature and the molecular terminal region is absent.

There are numerous variations of the simple image described above. The advantage of viscoelastic analysis lies in its ability to propose a mechanism responsible for the changes. Let us discuss now the behavior of the quaternized PIP$(NMe_2)_2$ 5K materials in the glassy, transition, rubbery, and terminal zones under separate headings.

Glassy State. As shown in Figure 3, the storage modulus depends on composition and on the distance from the transition zone. Values E'_G listed in Table III have thus been taken at a temperature T_G which is in a T_G/T_g(DSC) ratio of 0.872.

E'_G decreases as the length of the alkyl radical of the monoiodide, i.e., the number of C atoms in the n-alkyl chain, increases (Figure 6). As a second marked effect, E'_G is definitely larger when a difunctional quaternizing agent (1,5-diiodopentane) is used (PIP 5K C5I2) instead of a monofunctional one of the same length.

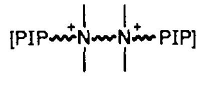
Although experimental changes in E'_G are not important, they are meaningful since they refer to polymeric samples which are identical except for the alkyl group of the terminal quaternary ammonium ion pairs. When the length of the alkyl radical (associated with the ion pairs) changes from C_1 to C_{16} compared to a PIP backbone of a constant length ($\bar{M}_n = 5000$), the ion-pair content is not significantly modified and cannot account for the experimental data. The argument is still more convincing if a difunctional iodide (C_5) and the monofunctional counterpart (C_2, although ideally $C_{2.5}$) are being compared, since the ion content is then the same and E'_G is different by 2 (Table III). Instead of the ion content, the density of the samples can be considered in relation to the structure of the quaternary ammonium ion pairs. Samples have been treated on purpose as two-component materials (PIP matrix filled with tetraalkylammonium iodides), and density has been expressed as

$$\rho = (\sum W_i/\rho_i)^{-1} \qquad (1)$$

where W_i and ρ_i represent the weight fraction and density of each component. ρ does not change by more than 0.5% in the series which are being considered. That conclusion agrees with the thermodynamics of the corresponding states principle, since the ionomer density in the glassy state at a reduced temperature, T_G, is the same for all quaternized polymers. A similar behavior has been reported for a series of poly(n-alkyl methacrylates),[35] for polystyrene ionomers containing carboxylic acid groups neutralized by n-alkylamines of various length,[36] for poly(styrene-*co*-vinylpyridine) quaternized with a series of n-alkyl iodides,[37] and for styrene/methacrylic acid ionomers, the styrene units of which have been grafted with various amounts of 1-decene.[38]

Since in homogeneous systems the modulus would be a reflection of the free-volume fraction as expressed, e.g., by the material density, the observed constancy of that property (906 ± 4 kg/m^3) paralleled by variation of E'_G can only be interpreted by the multiphase nature of the quaternized ionomers. On the basis of a two-phase model, Utracki has calculated E'_G from the Kerner equation[39] and found that it coincided with experimental values as will be reported later on.[40] The results give credit to a model for the quaternized PIP ionomers in the glassy state consisting of spherical inclusions distributed at random throughout a polymeric matrix with good adhesion between the phases.

Kerner's model has however failed in predicting E'_G if the quaternizing agent is difunctional. Chart IB shows that 1,5-diiodopentane is a chain extender which incorporates pairs of dipoles



$$[PIP\sim\overset{+}{N}\sim N\overset{+}{\sim}PIP]$$

into the main backbone through C–N covalent bonds. The main effect of these pairs of dipoles is to decrease the mobility of chain segments. Indeed, chains are extended through rigid moieties, i.e., two dipoles separated by only five methylene groups. Furthermore, the "ionic extenders" which are regularly spaced along the backbone tend to associate as in traditional ionomers. The combination of these two effects is a specific characteristic imparted by a difunctional quaternizing agent, since monofunctional agents cannot promote a chain extension by covalent

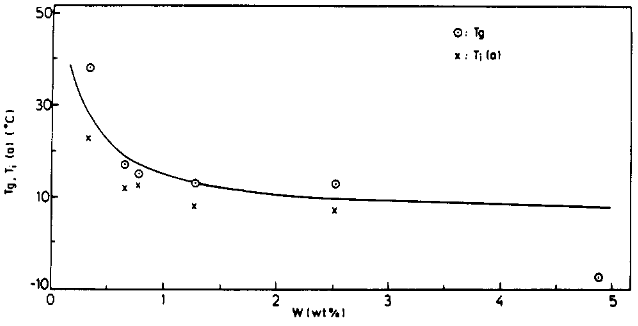


Figure 7. DSC-measured glass transition temperature, T_g, and the viscoelastic inflection temperature (see text), T_i, vs n-paraffin content in quaternized PIP(NR_2)$_2$ 5K ionomers.

bonding but only by temporary dipolar interactions. Clearly, the functionality of the iodide has an effect on the molecular structure of the chains and on their organization in the two-phase system. This is reflected by a higher modulus E'_G in the glassy state and a departure from the Kerner model when a monoiodide is replaced by its difunctional counterpart.

Chart IA illustrates the electrostatic association of the terminal ammonium end groups when the quaternization agent is monofunctional. E'_G is then mainly affected by the characteristic features of the association which are controlled by the steric effect and the strength of mutual interactions, i.e., by the structure of the homologous series of ammonium iodide ion pairs. The interplay of several mechanisms contributes to the dependence of E'_G, and thus of segmental rigidity, on the length of the alkyl radical. The bulkiness of the ion pairs is undoubtedly related to the length of that radical and is unfavorable to both the extent and strength of ion-pair interactions. Moreover, the alkyl radicals are expected to relax at temperatures lower than −30 °C, i.e., the lower limit of the investigated temperature range. The extent of that relaxation and the perturbing effect on the ionic association might also depend on the length of the alkyl radical and also affect E'_G as was experimentally observed.

Transition Zone (Glass Temperature T_g). Although T_g has been measured by DSC (Table II), the transition zone has also been described by the inflection temperature T_i. Several measurements of T_i have been carried out, e.g., (a) the maximum of the log E'' vs T curve (DMTA), (b) the temperature at half-height between the glassy and rubbery plateaux, and (c) the temperature at which $G' = 10$ MPa. T_i values are reported in Table II and show that definition a gives rise to temperatures systematically lower by 3–6 °C than those obtained by definitions b and c. Within the range of experimental error, the latter ones are equal and close to T_g as measured by DSC. T_g and T_i values have been plotted vs the content of the n-alkyl chains associated with the quaternary ammonium ion pairs (Figure 7). The thermal, T_g, and the mechanical, T_i, transitions are similar although T_i seems to be less sensitive to the length of the alkyl group than T_g. It is important to recall that T_g depends on domain size, in contrast to T_i which results from a macroscopic answer. Figure 7 interestingly shows that T_g and T_i values for the diiodopentane-quaternized PIP fall on the curve defined by mono-n-alkyl iodides provided that the total number of C atoms (five) is assumed to be shared by two PIP molecules.

In addition to Figure 7, Figure 5 shows that the length of the alkyl radical has an effect on T_g of the matrix whatever its chemical nature might be. Except for the methyl group and in contrast with it, n-alkyl groups of increasing length are responsible for a nonlinear decrease in T_g. A similar behavior has already been reported (i) whenever carboxylic or sulfonic acid end groups have been neutralized by n-alkylamines[36,41] and (ii) for ionomers containing vinylpyridine units quaternized with n-alkyl halides.[37] The less bulky ammonium ion pairs are responsible for an increase in T_g as a result of their mutual dipolar interactions which are a restriction to the chain mobility. Whenever the length of the alkyl radical of these ion pairs increases, some steric effect is expected to occur at the expense of the interaction and association of the ammonium end groups. The loss of segmental mobility, and thus the increase in T_g, should be accordingly less important. If the n-alkyl group is long enough, not only does it perturb the ion-pair association but it also plasticizes the polymeric matrix since T_g of the quaternized polymer is then lower than T_g of the unquaternized material.

When PIP, PS, and PαMS are compared with each other, the increase in T_g as promoted by methyl iodide is all the less pronounced since T_g of the unmodified polymer increases, i.e., from PIP to PS and finally to PαMS (Figure 5). Another sign of the same effect is that the n-alkyl group has to contain more than 12 C atoms to plasticize the unquaternized PIP, although an n-propyl radical is enough to induce the same effect on the PαMS matrix (Figure 5). Finally, plasticization by the n-alkyl radicals is the most important for PIP since, by reference to methyl iodide, T_g decreases by 46 °C when 1-iodohexadecane is used (C16), although the effect is comparatively smaller for PS (13 °C) and PαMS (19 °C). The effect of the matrix might be accounted for by the phase separation of the ammonium ion pairs from the polymeric material. The two-phase character of the investigated halato-telechelic polymers has already been put forward in the previous section. Moreover, it has been corroborated by SAXS measurements at 25 °C. Indeed, a diffraction peak has been systematically observed which is the counterpart of the "ionic peak" exhibited by ionomers as a result of their multiphase morphology.[21]

For thermodynamic and kinetic reasons, it may be understood that the sharpness of phase separation is all the more limited since the matrix becomes glassy at a higher temperature. This can explain why ΔT_g is highest for PIP matrix whenever methyl iodide is the quaternization agent. Furthermore, PIP and alkyl paraffins are aliphatic compounds in contrast to polyvinyl aromatics. Energetic reasons could then be at the origin of the much more effective plasticization of PIP by n-alkyl radicals.

Clearly quaternization of α,ω-bis(dimethylamino)polyisoprene by n-alkyl iodides is an effective way of adjusting the T_g of the matrix with a wide range of temperatures from 38 °C for methyl iodide to −8 °C for 1-iodohexadecane.

Rubbery Plateau. As shown in Figure 1, quaternization of the amino end groups seriously modifies the viscoelastic properties of polyisoprene. Indeed a rubberlike behavior is observed above T_g although the unquaternized polymer is a very sticky viscous material at room temperature. In the log G'' vs T plot, each sample exhibits a well-defined maximum above T_g (Figure 4), which must be attributed to the relaxation of the ionic end groups. The temperature at which this relaxation occurs and flow is observed (T_i) (Figure 3) decreases as the length of the alkyl radical increases (Table III).

In order to estimate the cross-linking density of the quaternized samples, the equilibrium modulus (G'_e) has been approximated by G'_R (the value of G' at $T_R = 1.1T_g$ (DSC)) and G'_m (the minimum G' value in the G'' vs T curve). G'_R

and G'_m are quoted in Table III and have roughly the same value which is mainly independent of the length of the *n*-alkyl group, i.e., log $G' \simeq 5.7$ Pa. It means that the cross-link density and accordingly the number of end groups per ionic aggregate does not change very much. The main difference between the investigated samples (C1 to C16) is T_i, i.e., the thermal energy required to disintegrate the ionic aggregates.

According to the Rouse theory of rubber elasticity, the equilibrium modulus (G'_e) is a function of the molecular weight between cross-links, M_e. For the investigated samples, M_e can be approximated to $\bar{M}_n$ of the short polyisoprene chains, and the functionality of the cross-links is not 4 as in the Rouse model but $\bar{n}$, i.e., the number of the amino end groups per cross-link. $\bar{n}$ can thus be written as[12]

$$\bar{n} = 4\bar{M}_nG_e/\rho_eRT_e \qquad (2)$$

where ρ_e is the polymer density at T_e and R is the gas constant. $\bar{n}$ values have been calculated, assuming that ρ_e is constant in the temperature range from 292 to 342 K (Table III).

In the limits of validity of eq 2, it appears that the degree of association ($\bar{n}$) of the dimethylalkylammonium ion pairs does not depend significantly on the length of the alkyl group, at least in the range from C1 to C16. An average value of 4.5 is quite consistent with the estimation of 3.5 ion pairs per ionic domain as results from application of the Porod law to SAXS profiles.[21] In the light of these results, it means that an increase in size of the ion pairs does not deeply affect their ability to associate but rather the strength of their mutual interactions as reflected, for instance, by changes in E'_G.

As already mentioned for the two previously discussed viscoelastic regions, a difunctional quaternizing agent has a general reinforcing effect (Figures 2–4). Indeed, the rubberlike plateau of the PIP 5K C5I2 sample extends over the largest temperature range (at least 100 °C). Furthermore, T_i has the highest value, and G' in the rubbery plateau is approximately 2 times greater than that reported for the monofunctional quaternization agents. Moreover, the general shape of the G' and G'' curves changes when a α,ω-alkyl diiodide is used instead of an ω-alkyl iodide in the quaternization reaction. In the latter case, the occurrence of the flow process promotes a continuous decrease in G', whereas it is observed as an inflection in the log G' curve (Figure 3) and as an intermediate maximum in the log G'' curve (Figure 4) when the quaternizing agent is difunctional. This behavior indicates that above T_i, when the ion pairs are no longer associated, the PIP chains are still interconnected to each other by the α,ω-alkyl diiodide [N^+–C_5–N^+] into chains long enough to be entangled up to ca. 443 K, i.e., 60 K higher than T_i.

Terminal Zone (Ionic Transition). Above T_g, the short-length α,ω-bis(dimethylamino)polyisoprene is a viscous material, in contrast to the quaternized counterpart. The association of the ionic end groups is responsible for the rubbery plateau as discussed in the preceding section. Such a plateau is also observed when amino end groups of polydienes are coordinated to transition-metal salts.[23] The relaxation of the dipolar interactions, observed as a maximum in the log G'' vs temperature curve on the high-temperature side, limits the extent of that plateau and allows the PIP chains to flow.

In order to throw light on the relaxation mechanism, samples have been studied by frequency sweeps at different temperatures. The log G' (log G'') vs frequency isotherms have been reported for each sample. Master curves have been built up by horizontally shifting successive isotherms with respect to a reference curve, and the shift factors, a_T, have been determined. T_i has been chosen as the reference temperature, and a very good superposition is generally observed (Figure 8). Figure 8 clearly shows that the extent of the rubbery plateau decreases when the length of the alkyl radical increases from methyl to octyl. It becomes however more extended when the octyl group is substituted by the C16 radical. Master curves of PIP 5K C4 and C16 are actually quite comparable (Figure 8).

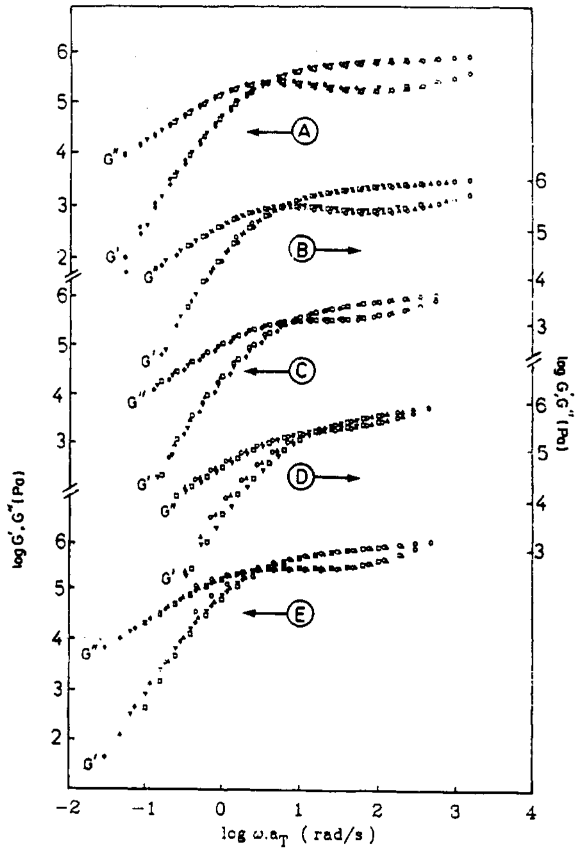


Figure 8. Shear moduli vs reduced frequency for α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n$ = 5000) quaternized with the following. [A] Methyl iodide; (○) 70 °C; (△) 77 °C; (□) 83 °C; (▽) 89 °C (T_i); (◇) 95 °C; (●) 102 °C. [B] Ethyl iodide; (○) 55 °C; (△) 59 °C; (□) 64 °C; (▽) 69 °C; (◇) 74 °C (T_i). [C] *n*-Butyl iodide; (○) 40 °C; (△) 51 °C; (□) 56 °C (T_i); (▽) 61 °C; (◇) 66 °C. [D] *n*-Octyl iodide; (○) 40 °C; (△) 45 °C; (□) 50 °C (T_i); (▽) 55 °C. [E] *n*-Hexadecyl iodide; (○) 19 °C; (△) 24 °C; (□) 29 °C (T_i); (▽) 34 °C; (◇) 39 °C.

By reference to ionomers, the good superposition of the isotherms could mean that the ion pairs are associated into multiplets and that no clustering occurs.[1–5] It is however worth noting that no clustering has been reported so far for ionomers containing quaternary ammonium units.[42,43] As a rule, the ion-pair content (3 mol %) of the investigated telechelic polyisoprene is far below the critical value for cluster formation.[44]

The temperature dependence of the shift factor, a_T, is dictated by the relaxation mechanism. The plot of ln a_T vs the reciprocal temperature is linear (Figure 9), which means that the relaxation of all the samples under investigation obeys an Arrhenius equation. The slope of these plots provides the activation energy (ΔH_a) of the relaxation process

$$\ln a_T = \frac{\Delta H_a}{R}(1/T - 1/T_0)$$

where R is the gas constant and T_0 the reference tem-

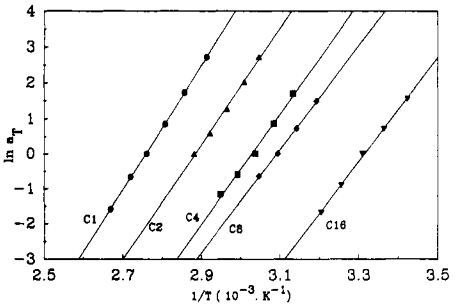


Figure 9. Plots of shift factors vs $1/T$ for α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with a series of n-alkyl iodides. The number of carbon atoms refers to the length of the n-alkyl group.

Table IV
Energetic Properties of the Relaxation Mechanism of the Quaternized PIP(NMe$_2$)$_2$ 5K in the Terminal Zone

sample	ΔH_a, kJ/mol	RT_i, kJ/mol	$\Delta H_a/RT_i$
PIP 5K C1	146	3.01	48.5
PIP 5K C2	136	2.88	47.1
PIP 5K C4	129	2.74	47.2
PIP 5K C8	121	2.69	45.1
PIP 5K C16	122	2.51	48.6

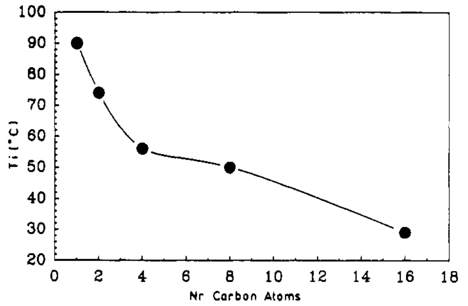


Figure 10. Temperature at the maximum of G'' in the terminal zone for α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n = 5000$) quaternized with a series of n-alkyl iodides. The number of carbon atoms refers to the length of the n-alkyl group.

perature (chosen as T_i).

According to Table IV, ΔH_a decreases as the length of the R alkyl radical increases but levels off when R is an octyl or a longer radical. Values of ΔH_a and their dependence on the number of C atoms of the alkyl group could be rationalized as follows. For very short alkyl radicals of increasing length (C1 to C5), the ion pairs suffer from increasing steric hindrance in their tendency to associate. This effect results in less stable aggregates which require less energy to dissociate. When the alkyl radical contains more than five carbons, the stability of the ionic aggregates would become independent of the length of the alkyl radical, as supported by the apparent constancy of ΔH_a. Furthermore, T_i also decreases upon an increase in the length of the R radical, first rapidly (C1 to C4) and then more slowly from C4 to C16 (Figure 10). As a first approximation, the thermal energy ($E = RT_i$) required to break the ionic aggregates depends on the number of C atoms of the alkyl radical in the same way as ΔH_a values. Table IV illustrates the relative proportionality between ΔH_a and RT_i: $\Delta H_a/RT_i = 47.3 \pm 1.8$.

It is worth noting that the activation energy characteristic of the ion-pair relaxation is greater for the quaternized amino groups compared to the metal carboxylato ones.[12,19] It is observed that metal carboxylato telechelic polymers[6,9] can promote the gelation of hydrocarbon solutions in contrast to the quaternized amino counterparts.[21] It might be concluded that the association of the quaternized amino groups is less extended (for steric reasons) but stronger (for electrostatic reasons) than that of metal carboxylato groups.

5. Conclusions

Just like complexation,[23] quaternization of the amino end groups of a low-T_g (1 °C) α,ω-bis(dimethylamino) polymer promotes the occurrence of a rubberlike plateau which is not observed for the unquaternized material. The length of n-alkyl iodides used as quaternizing agents has a pronounced effect on the modulus in the glassy plateau and on the T_g as well as on the temperature at which the ionic relaxation occurs (T_i). As a rule the value of these properties decreases as the length of the n-alkyl radical increases. Moreover, the ionic relaxation obeys an Arrhenius type of temperature dependence, the activation energy of which also depends on the length of the n-alkyl radical. Compared to metal carboxylato telechelic polymers, the association of the ammonium iodide end groups is more restricted by the steric hindrance of the ion pairs, although the activation energy is higher.

The use of a difunctional quaternizing agent has a strong effect on the viscoelastic behavior of the polymer; it particularly increases the extent of the rubbery plateau.

It is worth noting that the electrostatic interactions of the ammonium end groups deeply change the viscoelastic properties of the base polymer although the content of the terminal ion pairs does not exceed 3 mol %.

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References and Notes

(1) Eisenberg, A.; King, M. *Polymer Physics*; Stein, R. S., Ed.; Academic Press: New York, 1977; Vol. 2.
(2) Holiday, L., Ed. *Ionic Polymers*; Applied Science Publishers: London, 1975.
(3) MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(4) Longworth, R. *Developments in Ionic Polymers*; Wilson, A. D., Prosser, H. J., Eds.; Applied Science Pulishers: London, 1983; p 53.
(5) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28* (1), 1.
(6) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 224.
(7) Broze, G.; Jérôme, R.; Teyssié, Ph. *Polym. Bull.* **1981**, *4*, 241.
(8) Broze, G.; Jérôme, R.; Teyssié, Ph.; Gallot, B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 415.
(9) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(10) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 1300.
(11) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1983**, *16*, 996.
(12) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2205.
(13) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Macromolecules* **1983**, *16*, 1771.
(14) Broze, G.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 237.

(15) Jérôme, R.; Vlaic, G.; Williams, C. E. *J. Phys., Lett.* **1983**, *44*, L717.

(16) Jérôme, R.; Horrion, J.; Fayt, R.; Teyssié, Ph. *Macromolecules* **1984**, *18*, 2447.

(17) Jérôme, R.; Broze, G. *Rubber Chem. Technol.* **1985**, *58*, 223.

(18) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Macromolecules* **1985**, *18*, 1376.

(19) Horrion, J.; Jérôme, R.; Teyssié, Ph.; Marco, C.; Williams, C. E. *Polymer* **1988**, *29*, 1203.

(20) Foucart, M. Ph.D. Thesis, University of Liège, 1988.

(21) Charlier, P. Ph.D. Thesis, University of Liège, 1990.

(22) Charlier, P.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 1831.

(23) Charlier, P.; Jérôme, R.; Teyssié, Ph.; Utracki, L. A. *Macromolecules* **1990**, *23*, 3313.

(24) Granville, M.; Jérôme, R.; Teyssié, Ph.; De Schryver, F. C. *Macromolecules* **1988**, *21*, 2894.

(25) Hara, M.; Wu, J. L.; Jérôme, R.; Granville, M. *Macromolecules* **1988**, *21*, 3330.

(26) Jérôme, R. *Telechelic Polymers: Synthesis and Applications*; Goethals, E., Ed.; CRC Press, Inc.: Boca Raton, FL, 1989; Chapter 11.

(27) Kennedy, J. P.; Ross, L. R.; Lackey, J. E.; Nuyken, O. *Polym. Bull.* **1981**, *4*, 67.

(28) Percec, V.; Guhaniyogi, S. C.; Kennedy, J. P. *Polym. Bull.* **1983**, *9*, 27.

(29) Mohajer, Y.; Bagrodia, S.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *J. Appl. Polym. Sci.* **1984**, *29*, 1943.

(30) Bagrodia, S.; Tant, M. R.; Wilkes, G. L.; Kennedy, J. P. *Polym. Eng. Sci.* **1986**, *26*, 662; *Polymer* **1987**, *28*, 2207.

(31) Laleg, M.; Pascault, J. P.; Boiteux, G. *J. Macromol. Sci., Phys.* **1987**, *B26* (4), 389.

(32) Register, R. A.; Foucart, M.; Jérôme, R.; Ding, Y. S.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1009.

(33) Tant, M. R.; Song, J. H.; Wilkes, G. L.; Horrion, J.; Jérôme, R. *Polymer* **1986**, *27*, 1815.

(34) Tant, M. R.; Venkateshwaran, L. N.; Song, J. H.; Subramanian, R.; Wilkes, G. L.; Charlier, P.; Jérôme, R., submitted for publication in *Polymer*.

(35) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1980; Chapters 12 and 15.

(36) Smith, P.; Eisenberg, A. *J. Polym. Sci., Part B* **1988**, *26*, 569.

(37) Wollman, D.; Gauthier, S.; Eisenberg, A. *Polym. Eng. Sci.* **1986**, *26*, 1451.

(38) Gauthier, M.; Eisenberg, A. *Macromolecules* **1989**, *22*, 3751.

(39) Kerner, E. H. *Proc. Phys. Soc.* **1956**, *69B*, 808.

(40) Utracki, L. A., to be published.

(41) Weiss, R. A.; Agarwal, P. K.; Lundberg, R. D. *J. Appl. Polym. Sci.* **1984**, *29*, 2719.

(42) Gauthier, S.; Duchesne, D.; Eisenberg, A. *Macromolecules* **1987**, *20*, 753.

(43) Bazuin, C. G.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1121.

(44) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.