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Dielectric Properties of a Model Cationic Ionomer

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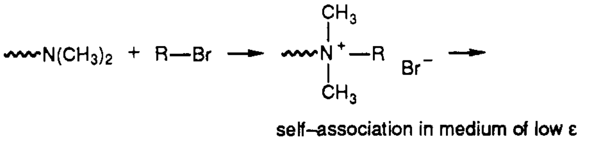
ABSTRACT: An α,ω-bis(dimethylamino)polyisoprene ($\bar{M}_n$ = 5000) has been quaternized by α,α'-dibromo-*p*-xylene with formation of a model cationic ionomer. Dielectric spectroscopy has shown an α relaxation which corresponds to the micro-Brownian motion of chain segments directly attached to the quaternary ammonium dipoles. A shoulder on the low-temperature side of the α relaxation has been assigned to the contribution of the polymer segments, the mobility of which is not restricted by the multiplets. That situation is in full agreement with the multiplet-cluster concept recently revisited by Eisenberg et al.[28]

Introduction

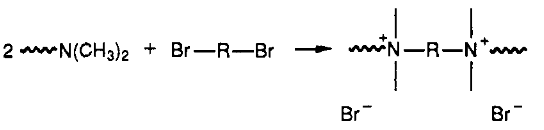
In recent years, self-association has received a growing interest in the field of polymeric materials. Ionomers are an example of the unique properties which can be imparted to a hydrophobic polymer when it is modified by a few percent of dipoles such as metal carboxylates and metal sulfonates.[1] In addition to dipole–dipole interactions, self-association can be promoted by several other mechanisms, e.g., hydrogen bonding,[2] charge-transfer complexes,[3] acid–base interactions,[4–6] and coordinative interactions.[7,8] That approach is fruitful not only in increasing the range of applications of homopolymers but also in achieving compatibility of otherwise immiscible macromolecules.

Amine groups, and particularly tertiary amines, are well suited to promote intra- and/or intermolecular interactions when randomly distributed along a polymeric backbone or selectively attached at the ends of linear chains. Tertiary amines can indeed be quaternized and generate ionomers or halatotelechelic polymers of the cationic type. In this regard, terminal tertiary amine groups have been converted to sulfopropyl betaines (or sulfozwitterions) by treatment with cyclopropane sultone, and they have proved to be strongly associated in aliphatic hydrocarbons.[9] Ionomers of a carboxylato-betaine type have also been considered[10] as well as quarternized α,ω-bis(dimethylamino)polydienes[11] and vinylpyridinium ionomers.[12] Coordination of tertiary amino groups of a telechelic polymer[13,14] or a random copolymer[15,16] to transition-metal salts is another effective way to cross-link the polymer thermoreversibly and to affect deeply both the solution and the viscoelastic properties of the material. Acid–base and coordinative interactions are also very instrumental either in promoting compatibility[4,5] or in controlling phase separation of immiscible polymers.[6–8,17,18]

When quaternization of tertiary amino groups is carried out, the functionality of the alkyl or aromatic halide used as a reagent should have a great impact on the final properties of the modified polymer. Indeed, monohalides convert amino groups to ion pairs which might mutually interact in a medium of low dielectric constant (ϵ) (eq 1). The situation is expected to be still more deeply modified when a dihalide is used since a chain extension is then promoted by covalent bonding (eq 2).



$$\sim\!N(CH_3)_2 + R{-}Br \rightarrow \sim\!\overset{CH_3}{\underset{CH_3}{N^+}}{-}R \quad Br^- \rightarrow \text{self–association in medium of low } \epsilon \qquad (1)$$



$$2 \sim\!N(CH_3)_2 + Br{-}R{-}Br \rightarrow \sim\!\underset{Br^-}{\overset{|}{\overset{+}{N}}}{-}R{-}\underset{Br^-}{\overset{|}{N^+}}\!\sim \qquad (2)$$

When α,ω-bis(dimethylamino) polymers are considered, the pathway schematized by eq 2 is of a greater interest since the chain extension is stable up to the thermal decomposition of the quaternary ammonium groups (>200 °C), which is definitely higher than the temperature at which the dipolar interactions are observed to relax (90 °C when methyl iodide is the quaternizing agent).[19] This paper aims at investigating an α,ω-bis(dimethylamino)polyisoprene of low molecular weight ($\bar{M}_n$ = 5000) quaternized by α,α'-dibromo-*p*-xylene. Dielectric spectroscopy has been selected as a method for probing the quaternary ammonium dipoles by reference to the precursor tertiary amino groups.

Experimental Section

α,ω-Bis(dimethylamino)polyisoprene (DMA-TPI) of 5000 molecular weight was synthesized in THF (5 wt % of monomer) at −78 °C by living anionic polymerization using sodium naphthalene as a difunctional initiator. The living macrodianion was deactivated with an excess of 1,3-bis(dimethylamino)propyl chloride (DMAPC) after a 1-h polymerization time. DMAPC was obtained by neutralization of the hydrochloride with sodium hydroxide in water. The DMAPC-rich oil phase was separated by repeated extractions with diethyl ether. The ether solution was washed 3 times with deionized water, and ether was then distilled off. The resulting DMAPC was dried with anhydrous Na_2SO_4 and then with CaH_2 and finally distilled just before use. The final polymer was precipitated from THF into a tenfold excess of methanol. It was purified by repeated dissolution in THF and precipitation into methanol (3 times).

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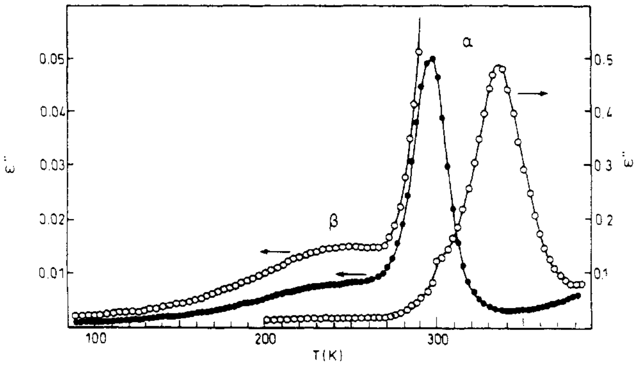

Figure 1. Temperature dependence of the dielectric loss, ϵ'', at 1 kHz for DMA-TPI (●) and the quaternized counterpart (○).

The polyisoprene consisted of 65% of 3,4 units and 35% of 1,2 units. The polydispersity index ($\bar{M}_w/\bar{M}_n$) was 1.15 as determined by GPC, the molecular weight ($\bar{M}_n$) was 5000 as measured by vapor-pressure osmometry, and the functionality was found to be 1.9 amino groups per chain (potentiometric titration of the end groups with perchloric acid in a 90:10 toluene/methanol mixture).

The α,ω-bis(dimethylamino)polyisoprene was dissolved in a THF:methanol (95:5 vol %) mixture and added with the stoichiometric amount of α,α'-dibromo-p-xylene. The reaction mixture (5 wt % polymer solution) was refluxed for 10 days; the quaternization was then complete as supported by the absence of unreacted amino groups (titration with perchloric acid). The reaction product was precipitated in an excess of heptane, stabilized with 1 wt % of Irganox 1010, and finally dried at 50 °C.

Dielectric measurements were carried out with a multifrequency LCR meter (Hewlett-Packard, Type 4274A) equipped with a personal computer in a temperature range 85–390 K at several frequencies between 100 Hz and 100 kHz. A three-terminal electrode system was used as described previously.[20,21] For the dielectric measurements, the DMA-TPI sample, which is a sticky liquid at room temperature, was cast from benzene solution onto the surface of the guarded plate electrode at room temperature. After drying in vacuo at 340 K for 3 h, the polymer lying on the guarded plate electrode was lightly pressed to the thickness of a Teflon spacer (about 0.1 mm thick) at 390 K under a dry nitrogen atmosphere by the spring-loaded unguarded electrode.[20] The sample was cooled from 390 K at a rate of about 0.2 K min^{-1}, and the data were collected during that cooling process. The quaternized counterpart was compression molded into a sheet of ca. 1.9 mm thick at 410 K. The sheet was carefully surface coated in vacuo by aluminum to ensure electrical contact between electrode and sample. The same three-terminal electrode cell as reported previously[21] was used for the dielectric measurements.

Although the stabilizer (a hindered phenol) might have an effect on the dielectric properties, no blank was run because of the poor thermal stability of polyisoprene in relation to the high temperature required by the sample preparation. Since all the samples contain the same percentage of stabilizer, the comparison of their dielectric properties is expected to be reliable.

Results and Discussion

The temperature dependence of the dielectric constant, ϵ', and the loss factor, ϵ'', was measured in the temperature range 85–390 K at several frequencies between 100 Hz and 100 kHz. Figure 1 illustrates the ϵ'' vs temperature curve at 1 kHz for both the α,ω-bis(dimethylamino)polyisoprene (DMA-TPI) and the quaternized material. Two relaxations are clearly observed whatever the sample, and they are designated as α for the relaxation at the highest temperature and β for the second one. The α relaxation for the quaternized DMA-TPI sample is shifted toward higher temperatures, it extends over a larger temperature range, and its amplitude is an order of magnitude higher. Moreover, a faint shoulder is observed on the low-temperature side which is located roughly at the same temperature as the α peak of the nonionic material.

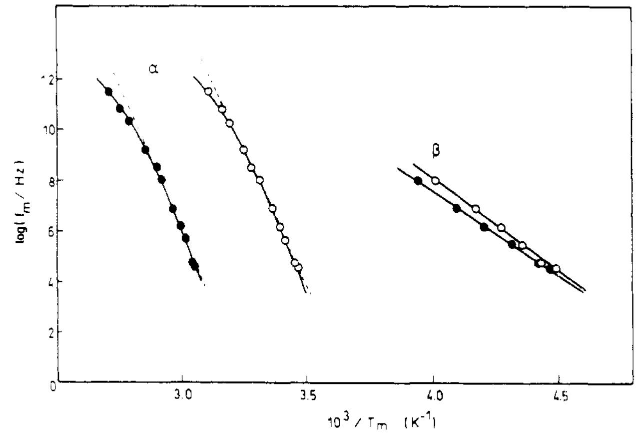

Figure 2. Arrhenius plots for α and β relaxations of DMA-TPI (○) and the quaternized counterpart (●).

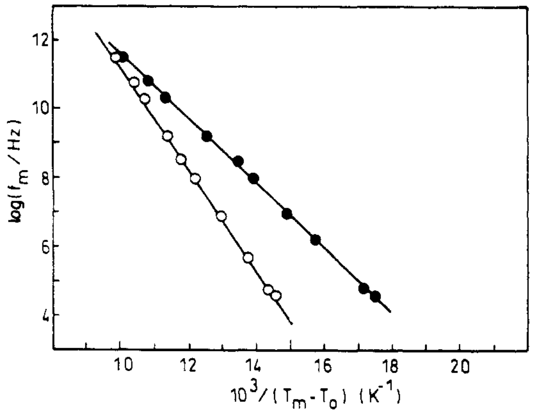

Figure 3. Plots of $\log f_m$ versus $1/(T_m - T_0)$ for DMA-TPI (○) and the quaternized counterpart (●).

Figure 2 shows the Arrhenius plots for the two relaxations of each sample, i.e., $\log f_m$ vs $1/T_m$, where f_m and T_m are the frequency and the temperature at the maximum (for the relevant relaxation) of the ϵ'' vs temperature curve, respectively. The α relaxation does not fit properly an Arrhenius equation, particularly on the high-temperature side. This is the reason the underlying process has been analyzed on the basis of the Vogel–Tamman equation (eq 3). A, B, and T_0 are parameters determined by trial and

$$\log f_m = A - B/(T_m - T_0) \tag{3}$$

error so as to obtain the best fit with the experimental curve. They are related to the WLF parameters C_{1g}, C_{2g}, and T_g as follows:

$$A = C_1 + \log f_{mg} \tag{4}$$

$$B = C_{1g}C_{2g} \tag{5}$$

$$T_0 = T_g - C_{2g} \tag{6}$$

$\log f_m$ has been plotted vs $1/(T_m - T_0)$ for the α relaxation. A straight line is obtained as shown in Figure 3, and the related values of A, B, and T_0 are reported in Table I.

T_g is 272 K as measured by DSC for both DMA-TPI and the quaternized sample. C_{1g} and C_{2g} were calculated from eqs 5 and 6 and found to be 13 and 52, respectively, for DMA-TPI and 205 and 2, respectively, for the quaternized material.

From C_{1g} and C_{2g} the free-volume fraction (f_g) at T_g was calculated as 0.033 and 0.002 for DMA-TPI and the quaternized counterpart, respectively. The very small f_g

Table I
Values of Dielectric Parameters (1 kHz)

	α relaxation				β relaxation	
sample	T_m, K	A	B	T_0, K	T_m, K	AE, kJ/mol
DMA-TPI	297	11.5	650	220	240	61
quaternized DMA-TPI	337	9.2	410	270	244	56

(0.002) for the quaternized sample means that T_g associated with the α relaxation should be higher than 272 K. For information, would T_g be 300 K, f_g would be estimated at 0.032, i.e., very close to the value reported for DMA-TPI. T_g at 272 K might thus be associated with T_g of PIP segments unaffected by the ammonium end groups in the quaternized DMA-TPI, as discussed later.

The α relaxation for both samples is a nonactivated process which has to be assigned to a micro-Brownian molecular motion of chain segments. Two main differences in the α relaxation for the unquaternized and the quaternized samples remain however to be explained: the T_m value and the amplitude of ϵ''. Before considering those pending questions, attention should be paid to the β relaxation. According to Figures 1 and 2, that relaxation is essentially independent of the nature of the polyisoprene end groups and it is typically an activated process. Table I reports indeed that T_m and the activation energy are of the same value within the limits of the experimental errors. Thus the β relaxation has to be attributed to a local molecular motion of short segments below the glass transition temperature.

Figure 4 illustrates the thermal dependence of the dielectric increment, $\Delta\epsilon$, for all the relaxations. $\Delta\epsilon$ and the distribution parameter of the relaxation time, P ($0 \leqslant P \leqslant 1$; $P = 1$ means a single relaxation), have been determined from Cole–Cole plots. Consistent with the previous data, $\Delta\epsilon$ for the β relaxation is not affected by the quaternization of the amino end groups. In contrast, $\Delta\epsilon$ relative to the α relaxation is 5–10 times larger for the quaternized telechelic polyisoprene than for the DMA-TPI precursor. Furthermore, it is independent of the temperature as long as the amino end groups are nonionic, whereas it decreases rapidly at increasing temperature when the end groups have been quaternized. The thermal dependence of P obeys the same scheme; it is mainly independent of temperature (at least in the investigated range), except that it increases (from 0.45 to 0.53) with temperature (from 345 to 357 K) for the α relaxation of the quaternized sample. All in all, the experimental data indicate that the α relaxation is profoundly modified by the conversion of the amino groups to ionic species: it appears at a higher temperature, it is more intense, and it is much more sensitive to temperature. The increased amplitude of the ϵ'' peak characteristic of the α relaxation can only be explained by the increased dipole moment of the amino end groups upon quaternization. These groups participate in the micro-Brownian motion of the chain segments, and they probe it as efficiently as their orientation (dipolar) polarization is high. That T_m of the α relaxation increases from the DMA-TPI sample to the quaternized counterpart has something to do with the electrostatic interactions of the dipoles associated with the quaternized amines. Two ammonium bromide ion pairs are actually coupled by an aromatic bridge (eq 2), and these rigid entities tend to associate into multiplets as usually happens in any halato-telechelic polyisoprene and ionomer of similar ion-pair content.[1,19] The formation of multiplets has been demonstrated by small-angle X-ray scattering, which shows an "ionic peak" at a Bragg distance of 6.95 nm, slightly larger than the value noted for the same DMA-TPI sample quaternized by a monoalkyl iodide (6.30 nm for an n-alkyl group containing 4 or less C atoms).[22] Obviously, the micro-Brownian motion of the chain segments directly adjacent to the associated ion pairs will be detected when the temperature will be high enough to weaken the dipolar interactions in the multiplets and to allow the ion pairs to be oriented by the applied electric field. This explanation is also consistent with the effect of the thermal fluctuations on the $\Delta\epsilon$ and P values of the α relaxation of the quaternized DMA-TPI.

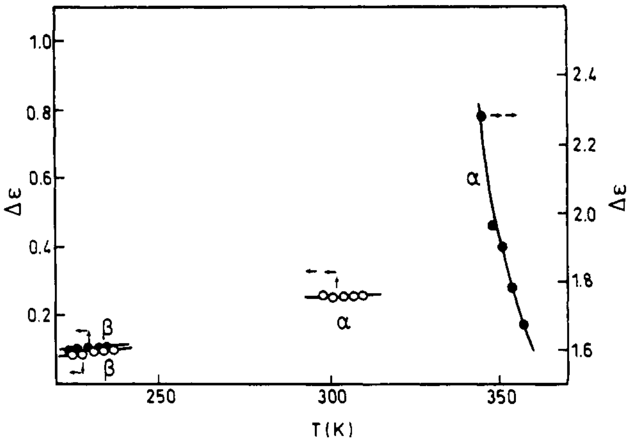

Figure 4. Plots of the dielectric strength ($\Delta\epsilon$) versus temperature for DMA-TPI (○) and the quaternized counterpart (●).

Interestingly enough, the dielectric properties of various ionomers have been reported in the scientific literature.[23-27] Salts of ethylene–(methacrylic acid) copolymers[23-25] exhibited dielectric peaks (α' and β') which correlated with the mechanical results and were therefore assigned to the same molecular mechanism. The β' relaxation was considered to be associated with glass transition in the amorphous polyethylene phase; it would actually reflect the reorientation of unassociated ionic groups in relation to the micro-Brownian motion of chain segments. The α' mechanism was assigned to the glass transition in the ionic regions, in agreement with a high magnitude of the dielectric peak. According to Eisenberg and colleagues,[26,27] who studied styrene–(methacrylic acid) copolymers neutralized with sodium, the higher temperature relaxation (α') is only observed when the ion content is high enough for ionic clusters to be formed. As will be discussed now, there might be a parallelism between the dielectric results previously published on ionomers and the DMA-TPI systems. Indeed, the last question to be addressed is the meaning of the shoulder observed on the low-temperature side of the α relaxation (Figure 1). Clearly, the α relaxation in the quaternized DMA-TPI is a nonactivated process which does not accordingly reflect the dissociation mechanism of the multiplets but which corresponds to the micro-Brownian motion of chain segments directly attached to the ion pairs. This situation is in full agreement with the multiplet-cluster concept recently revisited by Eisenberg et al.[28] According to these authors, multiplets are surrounded by a layer of restricted mobility, the thickness of which might extend over the persistence length of the polymer. Within such a model, T_g of the rest of the polymer should remain unaffected. The shoulder might be nothing but the unmodified T_g of the PIP segments, the mobility of which is not restricted by the multiplets. It is indeed worth noting that, taking into account the peak-overlapping effect, both the position and the amplitude of the relaxation responsible for the shoulder match closely those

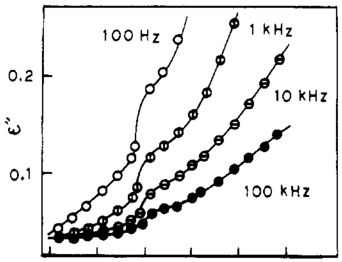

Figure 5. Temperature dependence of the dielectric loss, ε'', at various frequencies for the quaternized DMA-TPI.

for the α relaxation of the nonquaternized material. To substantiate that observation, data taken at other frequencies are reported in Figure 5. Although dielectric results and their interpretation should be sustained by additional and cross-checking data, they are in contrast to DSC measurements which exhibit only one T_g whatever the sample: these T_g's do not differ from each other by more than 10 °C.

In light of these results, it is worth recalling that the analysis of α,ω-bis(metal carboxylato)polybutadienes of a comparable molecular weight (Hycar from Goodrich; $\bar{M}_n$ = 4600) by thermally stimulated (de)polarization current methods[29] and dielectric spectroscopy[30] have revealed an α region consisting of two overlapping peaks. That complex structure has been tentatively attributed to the effect of the polybutadiene polydispersity on the dipole association resulting in a heterogeneous morphology, i.e., multiplets of various size and symmetry and thus resultant dipolar moment. Another explanation might be found in the presence of regions of restricted mobility surrounding each multiplet.

In conclusion, the experimental results reported in this paper emphasize the superiority of dielectric spectroscopy over methods such as DSC and also dynamic mechanical measurements (only one T_g for the quaternized DMA-TPI[22]) in probing a difference in mobility of the chain segments depending on whether they are constrained by the multiplets or not.

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