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Influence of the functionality of the quaternizing agent and the polymer molecular weight on the viscoelastic behaviour of α,ω-(dimethylamino)polyisoprenes

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Quaternization of the end-groups of α,ω-(dimethylamino)polyisoprenes with monofunctional, difunctional and trifunctional halides (iodides and bromides) has been undertaken on polymers of different molecular weights ($\bar{M}_n = 6000$ and 38 000 g mol^{-1}). The thermal stability of the ammonium end-groups is somewhat better when iodide counteranions are present. Quaternization increases the T_g of the material. This effect is more pronounced for low molecular weight chains, especially when a short alkyl group quaternizing agent is used. However, the size of the alkyl or aryl radical has a minor effect on polymer T_g when difunctional quaternizing agents are used. Nevertheless, the modulus of the rubber-like plateau of materials with difunctional agents is higher than with monofunctional quaternizing agents, owing to coupling reactions between the chain-ends. Rheological measurements indicate that the quaternized low molecular weight polyisoprenes exhibit an Arrhenius-type temperature dependence characterized by activation energies which vary between 121 and 146 kJ mol^{-1} and suggest that the relaxations attributed to dipole–dipole interactions dominate over long chain entanglements.

(Keywords: polyisoprene; telechelic polymers; coupled and entangled chains)

INTRODUCTION

In a medium of low dielectric constant, randomly distributed ionic groups in ionomers associate by dipole–dipole interactions and promote the physical crosslinking of the chains[1–5]. The resulting ionic aggregates are thermoreversible and ionomers can be processed by conventional techniques such as injection moulding and extrusion. Although the ionomer concept has been extended to various polymer backbones and ionic groups, the structure of the ionic aggregates is still debated. Eisenberg *et al.* have recently reviewed the subject and proposed an interesting approach to the conventional multiplet cluster model conjectured to be prevailing in these systems[6]. In order to establish the fundamental structure–property relationships, model ionomers such as halato-telechelic polymers (HTPs) have been synthesized on purpose[7]. In HTPs, dipoles are selectively attached at both ends of linear chains of a desired architecture. Such polymers have been prepared by living anionic or cationic polymerization. Thus, structure and molecular weight, i.e. the distance between the ionic groups and the molecular weight distribution, and the nature of the ionic end-groups, for example metal carboxylates, metal sulfonates, and quaternized and complexed amines, are fairly well controlled. A large number of papers have reported on the morphology and properties of HTPs. Recently, growing attention has been paid to the blending of HTPs based on the mutual interactions of the functional end-groups[8–11].

Dynamic mechanical measurements are currently used in order to draw relationships between the ion pair association (stability and extent) and the structure of the ionic groups, particularly of the metal carboxylate type[12–14]. In α,ω-metal carboxylatopolyisoprene and carboxylatopolybutadiene of low molecular weight, the ion pair association is responsible for a new relaxation process that corresponds to the occurrence of the viscous flow and obeys an Arrhenius-type temperature dependence.

For high molecular weight telechelic carboxylato-polyisoprenes, the relaxation mechanism is no longer in agreement with an Arrhenius law, but the shift factors a_T correspond to a WLF-type dependence, suggesting

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that the relaxation responsible for the occurrence of the flow is controlled by free volume aspects. For polymers of intermediate molecular weights, approximately between 7000 and 20 000 g mol^{-1}, two different relaxation mechanisms are observed. One is attributed to the thermoreversible (de)aggregation of the ion pairs, and the other to the chain (dis)entanglement process. This situation results in thermorheologically complex systems, since the conventional viscoelastic master curves cannot be drawn.

Complexation of the amino end-groups of telechelic polydienes with transition metal salts is another way to promote associative interactions[15,16]. The rubber-like plateau, which goes unnoticed for the uncomplexed polymers, is highly dependent on the nature of the transition metal cation and the metal to end-group molar ratio. In such systems, the strength of the coordinative association apparently matches the metal–amine complexation constant. The best thermal and mechanical properties are found when the metal to amino end-group molar ratio is unity. A recent investigation[17] of α,ω-(dimethylamino)polyisoprene quaternized with a series of n-alkyl iodides has shown that the relaxations attributed to the quaternary ammonium aggregates strongly depend on the length of the n-alkyl radical. As a rule, the modulus in the glassy plateau, the T_g and the temperature at which viscous flow of the polymer takes place all decrease as the length of the n-alkyl radical increases. Similar to low molecular weight telechelic carboxylatopolybutadienes, quaternized polyisoprenes ($M_n = 5000$ g mol^{-1}) exhibit an Arrhenius-type temperature dependence. The activation energy of flow decreases as the length of the n-alkyl radical increases, which suggests that the ion pair association is perturbed by steric effects. The activation energy levels off when the alkyl radical contains more than four methylene units.

The aim of this paper is to extend the above study to the dynamic viscoelastic properties of quaternized α,ω-(dimethylamino)polyisoprenes. Part of the present work focuses on the influence of molecular weight on the polymer rheology. The specific question is addressed of how the length of the alkyl radical affects relaxations within the polyisoprene matrix, particularly for samples quaternized with α,ω-n-alkyl dihalides, i.e. when the chain-ends are covalently bonded together through ammonium entities. Preliminary data with 1,5-diiodopentane as a quaternizing agent have indeed shown that a difunctional reagent has a comparatively much stronger effect on the viscoelasticity than a monofunctional one.

Table 1 Molecular characteristics of synthesized polyisoprenes

Polymer	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	$\bar{M}_t$ (g mol^{-1})	f^a
PIP(NMe$_2$)$_2$ 5K	5 500	1.4	5 500	2
PIP(NMe$_2$)$_2$ 5K	6 000	1.1	6 500	1.84
PIP(NMe$_2$)$_2$ 38K	38 500	1.3	41 500	1.86

$^a f = 2\bar{M}_n/\bar{M}_t$, the average number of functionalized end-groups per chain

EXPERIMENTAL

Polymer synthesis and characterization

Three α,ω-(dimethylamino)polyisoprene samples of different molecular weights (*Table 1*) were synthesized by anionic polymerization as detailed elsewhere[17]. The polyisoprene (PIP) microstructure consisted of 65 and 35% of 3,4 and 1,2 units, respectively, as measured by conventional spectroscopic techniques. The molecular weight was controlled by the monomer to initiator molar ratio and measured by osmometry and size exclusion chromatography using a polystyrene standard. The living macrodianions were deactivated with an excess of 1,3-bis(dimethylamino)propyl chloride. The amino end-groups were titrated with a perchloric acid solution in a toluene/methanol mixture (90/10 vol%).

On the assumption that each polyisoprene chain was end-capped with two amino groups, titration data allowed an ideal molecular weight ($\bar{M}_t$) to be calculated. The chain functionality was then calculated from the $\bar{M}_n/\bar{M}_t$ ratio. Values of $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, $\bar{M}_t$ and functionality are reported in *Table 1*, where samples are quoted by the abbreviation for the polymer (PIP), followed by the amino end-group (where Me is methyl) and the polymer molecular weight (5K stands for 5000 g mol^{-1}).

Quaternization of the amino end-groups was carried out in a THF/methanol mixture using a two-fold molar excess of the alkyl or aryl halides listed in *Table 2*. Details are also available elsewhere[17]. Polyfunctional halides were used in a 1/1 amine/halide molar ratio and the potentiometric titration of the amino end-groups confirmed that quaternization was complete. Since 1,3,5-tri(bromomethyl)benzene was not commercially available, it was synthesized by bromination of mesitylene with

Table 2 Samples and identification codes

Sample code	PIP M_n (g mol^{-1})	Name of quaternizing agent	Formula of quaternizing agent
K38NQ	38K		
K38C1	38K	Iodomethane	MeI
K38C8	38K	1-Iodooctane	$C_8H_{17}I$
K5C1	5K	Iodomethane	MeI
K5C8	5K	1-Iodooctane	$C_8H_{17}I$
K6C3I2	6K	1,3-Diiodopropane	$I(CH_2)_3I$
K6C8I2	6K	1,8-Diiodooctane	$I(CH_2)_8I$
K6C10I2	6K	1,10-Diiododecane	$I(CH_2)_{10}I$
K6φBr1	6K	Bromomethylbenzene	$C_6H_5CH_2Br$
K6φBr2	6K	1,4-Di(bromomethyl)benzene	$BrCH_2C_6H_4CH_2Br$
K6φBr3	6K	1,3,5-Tri(bromomethyl)benzene	$C_6H_3(CH_2Br)_3$

N-bromosuccinimide under u.v. irradiation[18]. It was purified by recrystallization, and the sharp melting point at 92°C confirmed the purity of the tribromide.

Measurements

Samples were compression moulded under a 2 MPa pressure and at a temperature between 60 and 100°C depending on the functionality of the halide. Differential scanning calorimetry (d.s.c.) was carried out using a Perkin–Elmer DSC-4 under a nitrogen flow at a constant heating rate of 20°C min^{-1} in the temperature range from −30 to 120°C. Thermogravimetric analysis (t.g.a.) was performed on a Perkin–Elmer thermobalance using samples of 5–10 mg. Weight losses were measured as a function of temperature at a heating rate of 5°C min^{-1} under a nitrogen atmosphere. After testing, the furnace was heated up to 800°C for a few minutes under an oxygen stream in order to remove any trace of residual material.

Viscoelastic characterization of samples was done above the glass transition temperature (T_g) with a Rheometrics RMS 800 using a parallel plate geometry. Data for two types of operating conditions were collected. Firstly, non-isothermal scans were performed in the temperature range $T_g < T < T_{flow}$. These were done by accumulating G' and G'' data at a constant frequency of 1 Hz at each desired temperature; the average heating rate was 2°C min^{-1}. Secondly, isothermal frequency scans of G' and G'' were performed in the range 0.016–16 Hz. Measurements were carried out under dry nitrogen and within the limits of the linear viscoelastic region. The latter was previously ascertained by strain and time sweeps. After testing at high temperatures, the samples remained soluble in toluene, confirming that no crosslinking had occurred.

RESULTS AND DISCUSSION

Prior to the investigation of their viscoelastic behaviour, the quaternized α,ω-(dimethylamino)PIPs were analysed by thermogravimetry in order to assess the thermal stability of the quaternary ammonium end-groups. Some of us have recently reported that α,ω-(dimethylamino)-polystyrene 5K quaternized with n-alkyl iodides experiences an irreversible degradation above 200°C[19]. Dequaternization occurs according to the following scheme

$$\sim CH_2CH_2CH_2-\underset{\underset{Me}{|}}{\overset{Me}{\overset{|}{N}}}-RI^- \rightarrow$$

$$\sim CH_2-CH=CH_2 + HI + RNMe_2$$

This implies that these telechelic polymers lose their ion pairs above a critical temperature. The effect is obviously expected to modify and alter significantly both the physical and mechanical properties of the model ionomers, particularly when the amino end-groups of telechelic PIP chains have been covalently bonded to each other through difunctional and trifunctional halides.

Figures 1a–c illustrate the thermogravimetric behaviour of some of the samples listed in *Table 2*. The data show that polymers quaternized with alkyl iodides are stable below 200°C. A small weight loss observed around 120°C

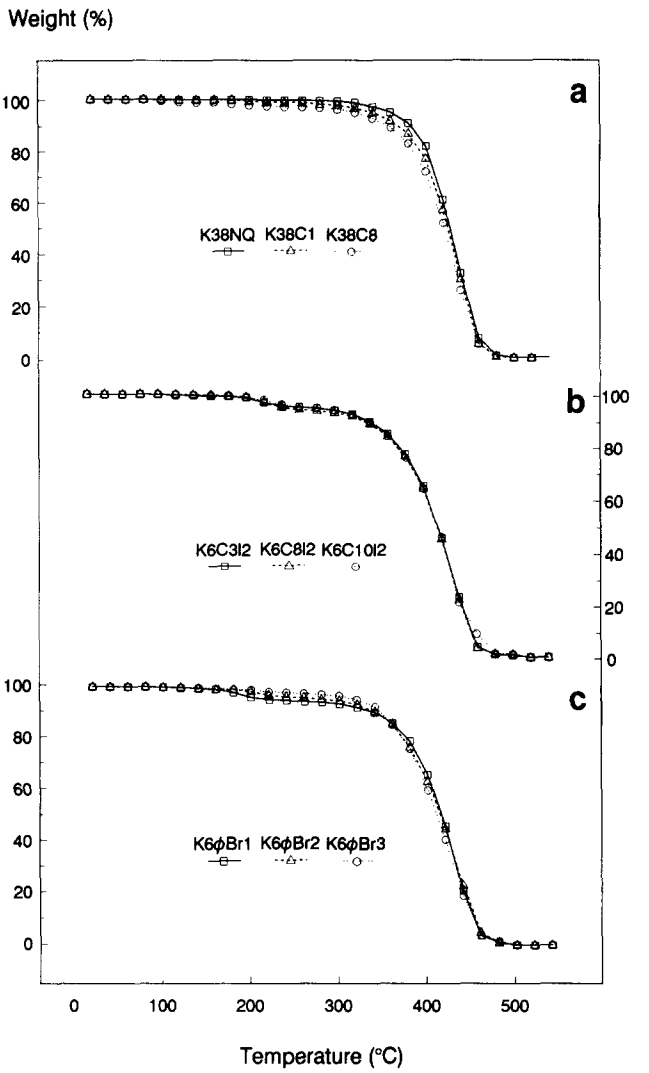

Figure 1 Weight loss as a function of temperature for α,ω-(dimethylamino)polyisoprenes with 6000 and 38 000 g mol^{-1} molecular weights, unquaternized and quaternized with various alkyl iodides and aryl bromides

is due to the loss of residual solvent. Quaternary ammonium bromide ion pairs appear to be somewhat less stable (*Figure 1c*) as compared to the ammonium iodide ion pairs, since they show some degradation near 180°C. Bearing these results in mind, the polymers were tested below their degradation temperatures.

Effect of molecular weight

As briefly mentioned earlier, quaternization of the dimethylamino end-groups of $PIP(NMe_2)_2$ 5K with n-alkyl iodides has been proven to modify significantly the physical and mechanical properties of PIP. In this respect, the T_g values of all the samples used in this study appear in *Table 3*. Whatever the molecular weight of the base polyisoprene (5K or 38K), the T_g increases upon quaternization of the amino end-group with methyl iodide (C_1) and then decreases when the methyl radical (C_1) is substituted by an octyl one (C_8). For the low molecular weight PIP (5K), variations in T_g are much more significant, since from K5C1 to K5C8 (*Table 3*) T_g drops by 25°C, whereas in the high molecular weight series (K38C1 to K38C8) it drops by only 5°C from 22 to 17°C. These results are in qualitative agreement with a T_g dependence on the end-group concentration. Indeed,

Table 3 Main physical and viscoelastic properties of quaternized α,ω-(dimethylamino)polyisoprenes

Sample code	T_g (°C)	T_i(°C) (at G''_{max})	$\tan\delta_{min}$	M/M_c	M_{app} (g mol^{-1})	E_a (kJ mol^{-1})	C_1	C_2
K38NQ	17	64	0.50	2.50	38400		5.26	102
K38C1	22	145	0.18	8.96	138000		11.9	325
K38C8	17	98	0.20	7.85	121000		8.6	196.5
K5NQ	1							
K5C1	38	89	0.23	6.59	101000	146		
K5C8	13	50	0.59	2.03	31000	121		
K6C3I2	18	108	0.15	11.25	173000			
K6C8I2	19	94	0.22	6.97	107000			
K6C10I2	19	99	0.11	16.58	255000			
K6φBr1	16	67	0.39	3.41	52000			
K6φBr2	19	144	0.14	12.26	188000			
K6φBr3	14	98	0.25	5.94	91000			

on a molar basis, the 5000 g mol^{-1} molecular weight PIP contains about seven times more end-groups than PIP 38K. It is therefore expected that the effect of the alkyl radical length of the quaternizing agent is less critical for the T_g of the PIP 38K.

The temperature dependence of the dynamic moduli of PIP(NMe$_2$)$_2$ quaternized with iodomethane and 1-iodooctane is shown in *Figure 2* for a molecular weight of 38000 g mol^{-1}. Data characteristic of the low molecular weight PIP (5K) have been illustrated elsewhere[17]. Above T_g, the unquaternized PIP 5K, being a viscous fluid, does not exhibit any rubbery plateau as is observed for the higher molecular weight polyisoprene PIP 38K (*Figure 2a*). The critical molecular weight (M_e) at which polyisoprene chains start to be entangled[20] is about 14000 g mol^{-1}. After quaternization of PIP 38K, the extent of the rubbery plateau greatly increases, although as a function of the n-alkyl radical size. *Table 3* indicates that T_i, noted as the temperature at which G'' is a maximum, jumps from 64 up to 145°C upon quaternization by MeI. A perceptible flow starts, however, to dominate at 98°C (T_i) when the radical size is increased from C_1 to C_8. A similar trend is observed for the low molecular weight PIP as well (*Table 3*).

The relaxation observed at the G'' maximum for the low molecular weight quaternized PIP precursor (PIP 5K) has been previously attributed to relaxation of the ion pair interactions, in agreement with an Arrhenius-type temperature dependence[17]. Furthermore, the viscoelastic data relevant to the rubbery plateaus of these quaternized α,ω-(dimethylamino)PIPs have been discussed on the basis of rubbery elasticity. The average number of amino end-groups per crosslink has been accordingly calculated and found to be close to 4.5 (±1.5), whatever the length of the n-alkyl radical. This value is in good agreement with an estimate of 3.5 ion pairs per ionic domain as calculated from small angle X-ray scattering (SAXS)[21,22]. Actually, the association degree (n) of the quaternized amino groups as approximated from the rubbery theory is very small ($n=4.5$) compared to that of metal carboxylates ($n=29.5$ and 16.5 for Na and K carboxylato end-groups, respectively, attached to a 4600 g mol^{-1} polybutadiene chain)[13]. It must, however, be stressed that trapped entanglements have been found to contribute appreciably to the small strain tensile moduli of some neutralized telechelic carboxylatoPIPs (PIP 8K)[22]. Since this effect has been ignored in the calculation of n, it is clear that the average number of ammonium ion pairs per aggregate is smaller than 4.5, in qualitative agreement with the bulkiness of this type of ion pair. It is also worth pointing out that quaternized α,ω-(dimethylamino)PIPs do not promote the gelation of hydrocarbon solutions, in sharp contrast to the metal carboxylate counterparts[21]. So it might be argued that the main effect of the ion pair association in quaternized α,ω-(dimethylamino)PIPs is to increase the apparent molecular weight (M_{app}), so that initially short and viscous PIP chains ($\bar{M}_n < \bar{M}_e$) become long enough to be entangled upon quaternization of the amino end-groups ($M_{app} > M_e$) and exhibit a rubbery behaviour. Thus, these polyisoprene ionomers might be analysed as essentially entangled chains of an appropriate apparent molecular weight, rather than as three-dimensional network stabilized by ionic aggregates acting as physical crosslinks. The lower limit for M_{app} would be the $\bar{M}_n$ of the precursor PIP, and M_∞ would be the upper limit. M_e for an uncrosslinked polymer of molecular weight M can be calculated from the minimum of $\tan\delta$, which is usually observed in the rubbery plateau region[24]

$$\frac{M}{M_e} = \left(\frac{\tan\delta}{1.04}\right)^{-5/4} \quad (1)$$

The M/M_e ratio has been calculated for all the investigated samples and the results are reported in *Table 3*. From the M/M_e value for the unquaternized α,ω-(dimethylamino)PIP with a 38000 g mol^{-1} molecular weight (M), M_e is found to be 15500 g mol^{-1}, in fairly good agreement with the previously mentioned value (14000 g mol^{-1})[20]. Since M_e is a characteristic value for a PIP of constant microstructure, equation (1) allows M (i.e. M_{app}) to be calculated for the quaternized samples (*Table 3*).

Whatever the molecular weight of the PIP precursor (5K or 38K), M_{app} is higher for samples quaternized with methyl iodide (C_1) compared to octyl iodide (C_8). This means that the ion pair association is more effective for shorter n-alkyl radicals. This observation is in qualitative

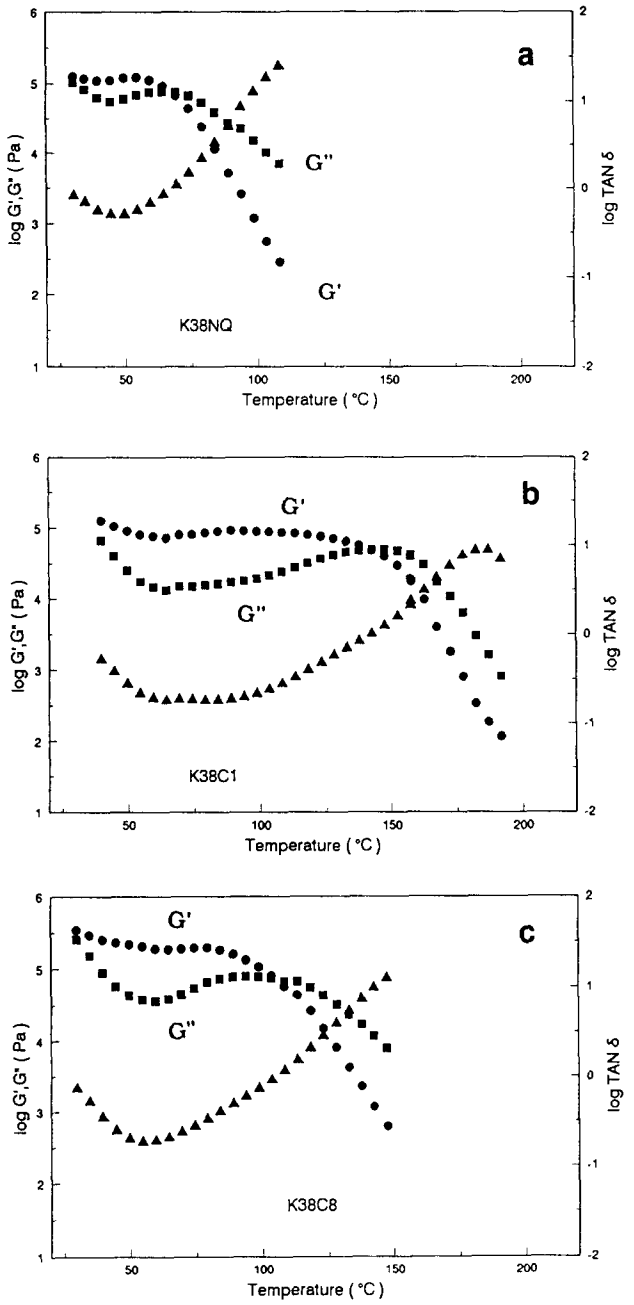

Figure 2 Temperature dependence of the storage (G') and loss (G'') moduli and $\tan\delta$ for an α,ω-(dimethylamino)polyisoprene ($\bar{M}_n = 38\,000\,g\,mol^{-1}$): (a) unquaternized; (b) quaternized with iodomethane; (c) quaternized with 1-iodooctane

agreement with the T_g and T_i data, which increase as the length of the n-alkyl radical decreases. That T_i is higher for C_1 compared to C_8 indicates a higher thermal stability for the mutual interactions of the less-crowded ion pairs. It is also clear that upon quaternization, the $\tan\delta$ response of PIP 5K is quite similar to that of the unquaternized PIP 38K sample, which gives some credit to the model used in this discussion. This model appears to be more realistic than the previous one, which did not reflect the effect of the n-alkyl radical on the ion pair association. In sharp contrast to M_{app}, n was indeed found to be independent of that structural parameter[17].

For the low molecular weight PIP (5K) at the temperature at which the ion pairs are no longer associated (T_i), the material flows since the shorter polymer chains which are released are not entangled. For high molecular weight PIP (38K) samples, constitutive chains are long enough to be still entangled at comparatively high temperatures, all other conditions being the same. For instance, T_i is 145°C for K38C1 compared to 89°C for K5C1 (*Table 3*).

The effect of molecular weight for a constant n-alkyl radical can be appraised from the ratio of the M_{app} values for the 38K and 5K samples. This ratio is 1.4 for the shortest n-alkyl radical (C_1) and it increases up to 3.9 for the n-octyl radical (C_8). It is now clear that when the ion pair interactions are strong enough (the case of C_1), the molecular weight of the PIP precursor has no decisive effect on the viscoelastic behaviour, at least in the rubbery plateau. When the dipolar interactions are weaker (C_8), the chain length of the constitutive PIP chains is of major importance. This trend makes sense since in the extreme of covalent interchain bonding, M_{app} would be infinite irrespective of the precursor molecular weight and the aforementioned ratio would be unity.

From isothermal frequency scans of the shear modulus, master curves were built up, and the reference temperature was chosen so as to approximate to the temperature at which G'' exhibits a maximum. The reference temperatures are reported in *Table 3* as T_i values. No vertical shift was required to superimpose the curves for the isotherms of the low molecular weight materials (PIP 5K), in agreement with previous observations[17]. However, a small vertical correction was applied to the PIP 38K samples in order to obtain smooth master curves of G' and G'' (*Figure 3*). In spite of these vertical shifts, superimposition of the $\tan\delta$ curves, particularly for the Me-quaternized PIP$(NMe_2)_2$ 38K sample, is not satisfactory. At low frequencies the high temperature data exhibit a significant scattering. This is believed to be at least partly due to the sensitivity limits of the instrument and expansion of the sample during measurements.

The temperature dependence of the horizontal shift factor a_T was assessed using the Arrhenius and WLF relationships.

$$\log a_T = \frac{E_a}{2.303R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{2}$$

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \tag{3}$$

where T_0 is the reference temperature chosen at G''_{max} (T_i in *Table 3*).

The shift factors for the low molecular weight quaternized samples (K5C1 and K5C8) agree with an Arrhenius-type temperature dependence. This behaviour has been recently borne out for a large series of n-alkyl iodides[17], and the activation energy E_a is found to decrease as the size of the n-alkyl group increases. For a molecular weight below M_c, the ion pair relaxation thus governs the relaxation of the entire material. This relaxation being electrostatic in nature, it is not surprising to observe that it follows an Arrhenius law.

For the α,ω-carboxylic acid PIPs neutralized or not, and of a molecular weight higher than M_c, Broze *et al.*[14] have observed a viscoelastic behaviour of the WLF type. The quarternized and unquaternized PIP 38K samples also show a temperature dependence, which indicates that the ionic interactions essentially act as thermoreversible crosslinks and essentially increase the molecular weight of the precursor polymer. Thus, for chains

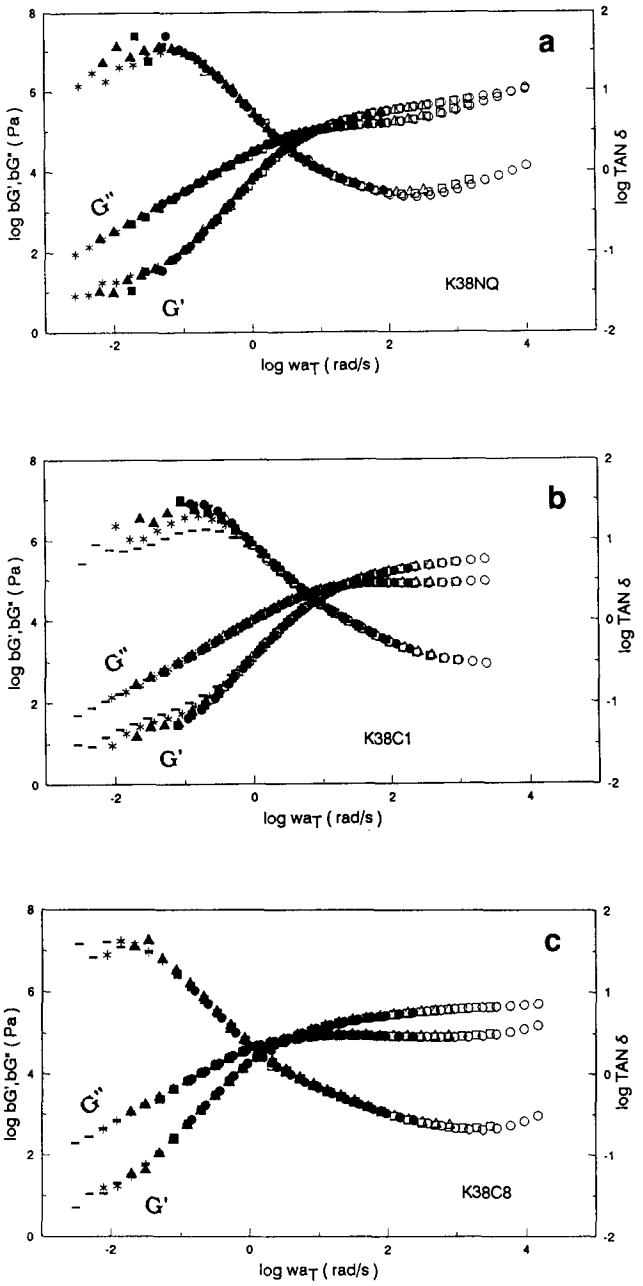

Figure 3 Shear moduli *versus* frequency for an α,ω-(dimethylamino)-polyisoprene ($\bar{M}_n = 38\,000\,g\,mol^{-1}$) ($G'$ and G'' were corrected using the vertical shift factor b). (a) Unquaternized: (○) 40°C; (□) 50°C; (△) 60°C; (●) 70°C; (■) 80°C; (▲) 90°C; (*) 100°C. (b) Quaternized with iodomethane: (○) 110°C; (□) 120°C; (△) 130°C; (●) 140°C; (■) 150°C; (▲) 160°C; (*) 170°C; (−) 180°C. (c) Quaternized with 1-iodooctane: (○) 60°C; (□) 70°C; (△) 80°C; (●) 90°C; (■) 100°C; (▲) 110°C; (*) 120°C; (−) 130°C

with $M_n > M_c$, the concentration of ionic groups is relatively low and the viscoelastic properties in the terminal zone are dominated by the relaxation of the extended chains, in agreement with the WLF theory. The WLF parameters C_1 and C_2 were calculated from a least squares fit and are quoted in *Table 3*.

Effect of functionality of the quaternizing agent

As previously discussed, the size of the n-alkyl radical of monohalides has a significant effect on the T_g of the low molecular weight sample (PIP 5K). When monohalides are substituted by α,ω-dihalides, the quaternization reaction is then a formal coupling reaction

$$n\mathrm{R_2N{-}PIP{-}NR_2} + n\mathrm{I{-}X{-}I} \rightarrow \left[-\mathrm{PIP}-\overset{\overset{\mathrm{I}}{|}}{\underset{|}{\mathrm{N^+}}}-\mathrm{X}-\overset{\overset{\mathrm{I}}{|}}{\underset{|}{\mathrm{N^+}}}- \right]_n \quad (4)$$

Table 3 shows that the T_g of PIP 6K is independent of the length of the n-alkyl radical (X in equation (4)) of diiodides (K6C3I2, K6C8I2 and K6C10I2), in contrast to what happens for monoiodides (K5C1 and K5C8). It is thus obvious that when the alkyl group (X) is covalently bonded to two adjacent ammonium ion pairs (equation (4)), it does not interfere in the PIP chain mobility, because either the ion pair association is independent of X or X has no opportunity to penetrate, and thus plasticize, the PIP matrix. The use of an aryl-containing radical in the K6ϕBrx ($x = 1$–3) series instead of an alkyl radical has no particular effect on T_g, whatever the functionality of the quaternizing agent. Results for the K6ϕBr3 sample should, however, be considered cautiously, since the completeness of the reaction of three amino end-groups with one 1,3,5-tri(bromomethyl)benzene molecule is questionable for steric reasons. Clearly, quaternization of an α,ω-(dimethylamino)PIP of a constant molecular weight (6K) by a difunctional reagent leads to a T_g of ca. 18°C, independent of the nature (alkyl or aryl, bromide or iodide) and size of the dihalide (*Table 3*). This might indicate that 'twin' ammonium ion pairs ($\rangle\mathrm{N^+{-}X{-}N^+}\langle$) are so crowded that their association is very restricted and mainly independent of structural details. The T_g would then be controlled by the chain extension process together with some constraint on chain segment mobility from the 'twin' ion pairs and their limited association.

The rheological behaviour of samples of the K6CiI2 ($i = 3, 8, 10$) and K6ϕBrx series was assessed, as illustrated by *Figure 4* for the temperature scan of the K6C10I2 sample. The temperature at which G'' shows a maximum (T_i) is reported in *Table 3*. These data provide an estimate of the temperature at which PIP starts to flow. Like T_g, T_i is an indicator of the role played by the ammonium ion pairs. Although T_i decreases as the length of the n-alkyl group increases, it is essentially independent of the size of the α,ω-alkyl diiodides. This is consistent with control of the viscous flow by a (dis)association equilibrium of single ion pairs in the K5C1 sample with release

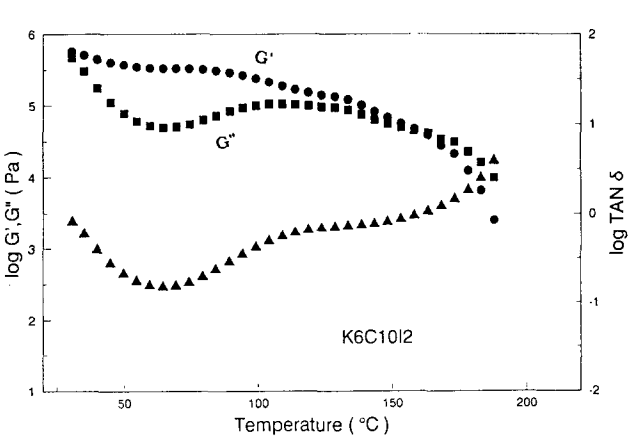

Figure 4 Temperature dependence of the storage (G') and loss (G'') moduli and tanδ for an α,ω-(dimethylamino)polyisoprene ($\bar{M}_n = 6000\,g\,mol^{-1}$) quaternized with 1,10-diiododecane

of the short constitutive PIP chains (5K). For steric reasons, the n-alkyl radical plays an important role in the stability of the ion pair association which decreases (as does T_i) as the n-alkyl radical length increases. In contrast, the extension of the 'twin' ion pair associations in the K6CiI2 series has been assumed to be restricted and independent of the alkyl radical (X). As a result, at a nearly constant T_i extended chains are released, in agreement with a much slower decrease in G' above T_i (*Figure 4*) as compared to samples such as K5C1[17]. The same explanation holds when the monofunctional benzyl bromide (K6ϕBr1) is replaced by the difunctional counterpart (K6ϕBr2), except for a more dramatic effect on T_i compared to the alkyl series (e.g. K5C8 and K6C8I2).

Frequency sweeps for the last six samples in *Table 3* are shown in *Figures 5* and *6*. A common reference temperature of 110°C was selected and a vertical shift was necessary for smooth master curves to be obtained. Thus, these samples do not comply with the equivalence of time and temperature effects. The apparent molecular weight (M_{app}) was calculated as before. The high values of M_{app} ($M_{app} > 10^5$ g mol^{-1}) in the K6CiI2 series emphasize the dramatic effect that the formal coupling reaction (equation (4)) has on the viscoelastic behaviour of a low molecular weight polyisoprene (PIP 6K). Some fluctuations in the M_{app} values of this series more likely reflect some scattering in the completeness of the quaternization reaction (equation (4)), which is a typical step growth process. It is indeed well known that a very small departure from stoichiometry or complete conversion in a polycondensation reaction is responsible for a rapid decrease in molecular weight. This problem is essentially irrelevant for quaternization with a monohalide. Inspection of M_{app} for K6ϕBr2 is illustrative of the effect that the functionality of aryl-containing bromides can have. The same remark as before holds for the K6ϕBr3 sample.

As a last piece of information, samples which have been formally chain extended with a difunctional halide show a second, although less-pronounced, relaxation on the low ωa_T side (*Figure 5*, except for K6C8I2, and *Figure 6b*). The same observation has already been reported in the temperature scan of a similar sample[17]. This additional relaxation above T_i might be assigned to a relaxation of the entangled chains of a high enough M_{app} value. It is the reason why the less-extended K6C8I2 sample would only show the ionic relaxation at T_i.

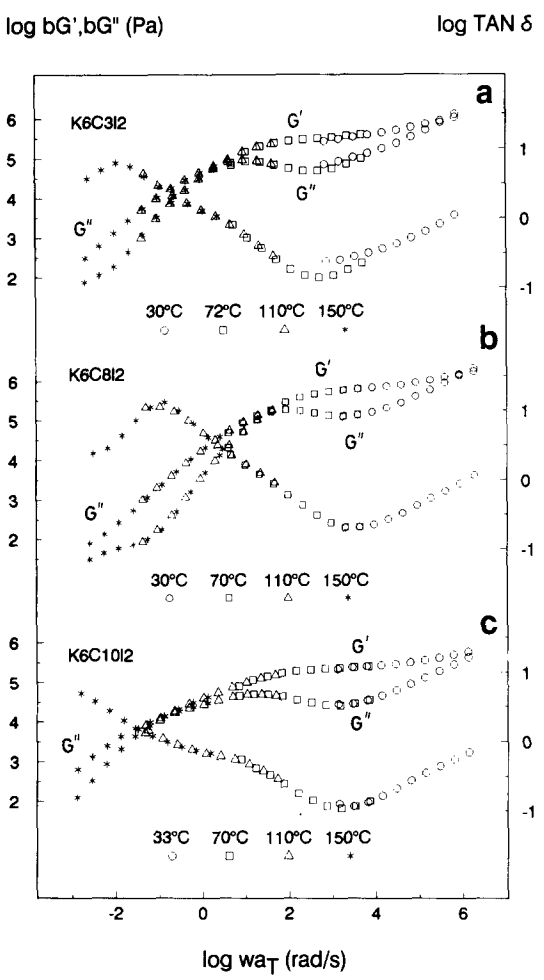

Figure 5 Shear moduli *versus* frequency (reference temperature 110°C) for an α,ω-(dimethylamino)polyisoprene ($\bar{M}_n = 6000$ g mol^{-1}) (G' and G'' were corrected using the vertical shift factor b). (a) Quaternized with 1,3-diiodopropane: (○) 30°C; (□) 72°C; (△) 110°C; (*) 150°C. (b) Quaternized with 1,8-diiodooctane: (○) 30°C; (□) 70°C; (△) 110°C; (*) 150°C. (c) Quaternized with 1,10-diiododecane: (○) 33°C; (□) 70°C; (△) 110°C; (*) 150°C

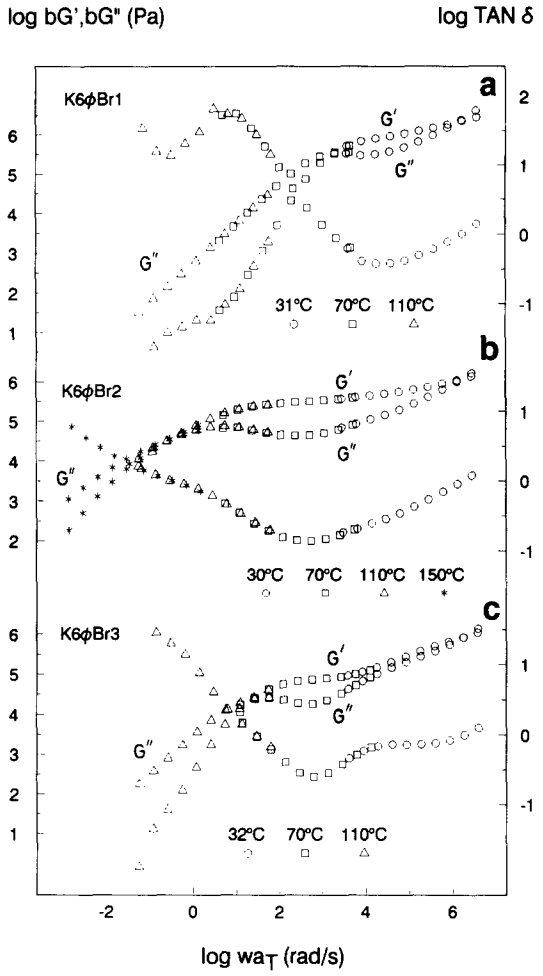

Figure 6 Shear moduli *versus* frequency (reference temperature 110°C) for an α,ω-(dimethylamino)polyisoprene ($\bar{M}_n = 6000$ g mol^{-1}) (G' and G'' were corrected using the vertical shift factor b). (a) Quaternized with bromomethylbenzene: (○) 31°C; (□) 70°C; (△) 110°C. (b) Quaternized with 1,4-di(bromomethyl)benzene: (○) 30°C; (□) 70°C; (△) 110°C; (*) 150°C. (c) Quaternized with 1,3,5-tri(bromomethyl)benzene: (○) 32°C; (□) 70°C; (△) 110°C

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