Dynamic Mechanial Properties of Sulfonated Cyclized *cis*-1,4-Polyisoprene

ZHENG LONG ZHOU* and A. EISENBERG, *Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6*

Synopsis

Acetyl sulfate was used as sulfonating agent for the sulfonation of *cis*-1,4-polyisoprene. IR and NMR spectra showed that the sulfonation was accompanied by extensive cyclization. A series of DSC and loss tangent studies of both the sodium salts and the methyl esters was undertaken. It was found that cyclization exerts a profound influence on the microbrownian segmental motion of the hydrocarbon matrix and is the dominant factor in raising the glass transition temperatures. However, the differences in the mechanical properties between salts and esters suggest that the presence of ions does influence the melt viscosities and shear moduli of the sulfonated cyclized rubbers; this influence can be minimized by esterification or water absorption. It is seen that the ionic effects in these materials are quite typical of those encountered in a wide range of other ionomers.

INTRODUCTION

Over the past few decades, extensive studies have been performed on a wide range of ion-containing polymers. The literature on these ion-containing polymers is now quite extensive, four review articles[1-4] and two books[5,6] having been devoted to the field. Accordingly, only those aspects which are of direct relevance to the present investigation will be discussed here.

Ionomeric elastomers have been the subject of a number of studies, most of them involving anions based on the carboxylate group, with only very few concentrating on pendent anions of the sulfonate type. The preparation of elastomeric hydrocarbon polymers containing low levels of sulfonic acid is a relatively recent development. Makowski et al. incorporated zinc sulfonate groups into ethylene–propylene rubbers (EPDM).[7] Through the proper selection of the EPDM backbone, the molecular weight, and the sulfonate content, and through the use of the zinc cation along with zinc stearate as plasticizer, it was possible to prepare EPDM-based ionomers that were thermoplastic elastomers with excellent mechanical properties and with very low melt viscosities.

In another system, selective plasticization of either the ionic regions or of the neutral hydrocarbon backbone was effected. This was achieved by the differing plasticizing behaviors of glycerol and dioctyl phthalate in sulfonated polystyrene salts, where the dual plasticization yielded a material similar to plasticized poly(vinyl chloride).[8] In still another investigation, Rahrig and MacKnight studied a series of sulfonated polypentenamers containing different concentrations of pendant groups. The dynamic mechanical and DSC results for sulfonated polypentenamers combine to give evidence for the existence of ionic clusters in these materials.[9]

* On leave from the East China Institute of Textile Science and Technology, Shanghai, China.

Lunberg et al. made a comparison of sulfonated and carboxylated ionomers.[10] The softening behavior of the metal sulfonate ionomer suggests that strong ionic association persists to temperatures 50–100°C above those of the corresponding carboxylate ionomer. Similarly, the melt viscosities of the sulfonate ionomers at a given functionality at the same temperature and molecular weight are two to three orders of magnitude greater than those of the carboxylate analogs. Rigdahl and Eisenberg[11] compared the properties of copolymers of styrene with styrene–p-sodium sulfonate with the corresponding properties of copolymers of styrene and sodium methacrylate (S-NaMA) as determined by Navratil and Eisenberg.[12] They found that the viscoelastic behavior in the primary transition region of these two ionomers was very similar, although the high-temperature dynamic mechanical peak (due to the glass transition of the ionic regions) occurs at a considerably higher temperature in the sulfonates than in the carboxylates.

Since sulfonated rubbers are of great interest, we intended to study the properties of sulfonated polyisoprene (S-PIP) as a low-T_g noncrystalline system. Although the SO_3 complexes of triethyl phosphate, dioxane, and tetrahydrofuran are effective in introducing sulfonic acid groups into unsaturated double bonds in rubber,[13] some previous studies utilized acetyl sulfate (which was generated most conveniently from acetic anhydride and concentrated sulfuric acid) as the sulfonating reagent for the sulfonation of olefins and EPDM.[7,14–16] This method was also chosen as the sulfonating reagent for the sulfonation of polyisoprene in this work. Natural rubber, balata, and synthetic polyisoprene of predominantly 1,4-configuration were reported to be easily cyclized with strong acids (e.g., H_2SO_4), with organic acids, with Lewis acids (e.g., $SnCl_4$, $TiCl_4$, BF_3, $FeCl_3$), or with other catalysts of an acidic character.[17]

Therefore, the question arose whether the dual effects of sulfonation and cyclization in natural rubber could be separated, and what effects each would have in the presence of the other. This article reports the results of that study. Specifically, we discuss the synthesis of sulfonated polyisoprene using acetyl sulfate; the characterization in regard to simultaneous sulfonation and cyclization; the glass transition behavior of cyclized sulfonated products in their salt and ester forms utilizing DSC and dynamic mechanical methods; and, finally, the dynamic mechanical properties themselves.

EXPERIMENTAL

Synthesis

Starting Materials. The starting cis-1,4-polyisoprene, Natsyn 2200, was kindly provided by the Goodyear Tire and Rubber Company, through the courtesy of Dr. K. W. Scott and Mr. D. W. Stiff. The molecular weight average was reported to be in the range 140,000–160,000.

Sulfonation Reagents. All the sulfonations reported here were performed with acetyl sulfates, using a modification of the procedure described by Makowski et al.[7,15] The sulfate reagent for the synthesis was generated at a ratio of 1.6 mol acetic anhydride per mol concentrated sulfuric acid (96.4 wt %). Acetic anhydride and concentrated sulfuric acid were mixed at a temperature below 0°C (usually −5 to 0°C), and the thick solution was brought to room temperature and diluted using 2 volumes of chloroform.

Sulfonation of *cis*-Polyisoprene. Polyisoprene was dissolved in chloroform at a concentration of 2 g/L. The sulfonation reagent was added to the vigorously stirred polymer solution drop by drop within 30 min at 0–5°C. After addition, the temperature of the reactant mixture was raised to 20°C and kept at that temperature for varying periods depending on the desired degree of sulfonation of the product. The polymeric sulfonic acid was then isolated through solvent flashing of the resultant cement in boiling water (steam stripping). The resultant polymeric material was washed with distilled water repeatedly until no trace of acid was detected. The polymer was filtered and then dried under vacuum at room temperature for 24 h. The sulfonated PIP was stored in a refrigerator until use because of the instability of some sulfonic acid polymers.

Neutralization. The S-PIP was redissolved in a mixture of 90/10 (v/v) benzene–methanol at a concentration of 5 g/L. The polymer was titrated to the phenolphthalein endpoint under nitrogen, with a $0.1N$ sodium hydroxide solution in methanol. The neutralized polymer was recovered by freeze drying.

Esterification. The sulfonated PIP was redissolved in a mixed solvent of benzene–methanol using a smaller amount of methanol than in the neutralization procedure. The esterified polymer was obtained by reaction with diazomethane. This reagent was prepared using a diazomethane generator (Diazald Kit, Aldrich Co.) by the reaction of Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) and potassium hydroxide solution.[18] The resultant esters of the sulfonic acids were also recovered by freeze drying.

Characterization

Chemical Analysis. The sulfonated polymers were analyzed for carbon, hydrogen, sulfur, and oxygen by the M-H-W Laboratories (Phoenix, AZ, USA) and the Guelph Chemical Laboratories (Guelph Canada). The sulfonic acid contents were also determined by titration to the phenolphthalein endpoint under nitrogen, with $0.01N$ sodium hydroxide solution in methanol.

Infrared Analysis. Infrared spectra were taken on a Perkin–Elmer 297 instrument in the range 600–4000 cm^{-1} on film samples produced by evaporation from chloroform.

Nuclear Magnetic Resonance. NMR measurements were carried out on a Varian T-60A instrument. A $CDCl_3/CD_3OD$ mixture was used as the solvent.

DSC. The glass transition temperatures (T_g) of the samples were determined under nitrogen partly on a Perkin–Elmer DSC-2C and partly on a DSC-1B instrument. Heating rates were 20°C/min.

Sample Molding. The samples used for the torsion pendulum measurements were prepared by compression molding. Prior to molding, the polymers were dried under vacuum for two days. The polymers with T_g values above room temperature were then heated in the mold to 20–50° above T_g under an applied load of 1000–1500 lb for ca. 1 hr; they were then cooled down slowly to room temperature. Typical dimensions of the specimens used were 2.5 × 5.5 × 50 mm. Samples with T_g values below room temperature were molded at 50°C.

Water Uptake. Water-soked samples were prepared by storing a compression-molded specimen in distilled water at room temperature. After a certain time period, the sample was removed from the water and the weight gain was
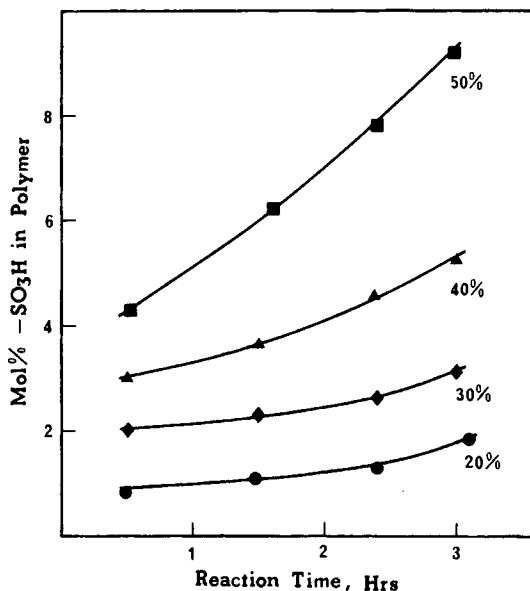
Fig. 1. Degree of sulfonation of cis-PIP with acetyl sulfate in chloroform (acetic anhydride to sulfuric acid ratio = 1.6; polymer concentration = 2 g/100 ml; temperature = 20°C) for various reaction times. The percentage figures give the amount of H_2SO_4 per repeat unit.

determined. Thereafter, the sample was replaced in the water for another period of time, and so on. The weighting procedure was completed in less than 15 s.

Dynamic Mechanical Measurements. Dynamic mechanical studies were performed using a torsional pendulum described elsewhere.[19] The frequencies varied between ca. 4 Hz in the glassy region to ca. 0.1 Hz in the low-modulus region. The heating rates were 0.5–1°C/min.

RESULTS

Sulfonation

The degrees of sulfonation as a function of reaction time and concentration of sulfonating reagent for cis-PIP are shown in Figure 1. Comparisons of the titration results with the sulfur values from microanalysis are listed in Table I. The results show that each sulfur atom corresponds to a sulfonic acid moiety and that the neutralization is essentially complete. Table II shows the results of esterification by diazomethane. It is clear that the methylation is nearly complete.

TABLE I
Titration and Organic Microanalysis Results for S-PIP Acids

SO$_3$H, mol %	Titration[a]				Organic microanalysis			
	S, wt %	O, wt %	C, wt %	H, wt %	S, wt %	O, wt %	C, wt %	H, wt %
1.8	0.84	1.26	86.31	11.59	0.81	1.32	85.49	12.37
4.3	1.91	2.86	83.90	11.27	1.96	—	80.11	10.98
6.2	2.73	4.08	82.16	11.03	2.64	5.31	81.83	10.21
9.3	3.95	5.91	79.47	10.67	3.59	8.42	77.56	10.48

[a] Calculated from SO$_3$H mol % as determined by titration.

TABLE II
Degree of Esterification of Sulfonated Polyisoprenes

Sulfonation content of S-PIP, %	Degree of esterification,[a] %
1.8	98.1%
4.3	91.5%
6.2	97.6%
9.3	98.4%

[a] Measured by titrating the residual SO_3H groups using $0.01N$ NaOH–methanol solutions.

The infrared spectra of the starting material (*cis*-PIP), the 4.3 mol % S-PIP, and the 9.3 mol % S-PIP are given in Figure 2. The presence of the O=S=O symmetrical and asymmetric stretch peaks at 1040 and 1200 cm^{-1}, respectively, in the spectra of the sulfonated PIP confirms the presence of sulfonic acid groups.[20]

Figures 3 and 4 show the NMR spectra of the starting material (*cis*-PIP), the 1.8 mol % S-PIP, the 6.2 mol % S-PIP, and the 9.3 mol % S-PIP, in the acid form and in the ester form, respectively. The breadth and extensive overlapping of resonance peaks in the sulfonated polyisoprene (both in their acid and ester forms) throughout the δ = 0–2.8 region is due to the cyclic structure of these products which contain a variety of nonequivalent methylene groups with different chemical shifts.[21]

Owing to the presence of 1,4-units

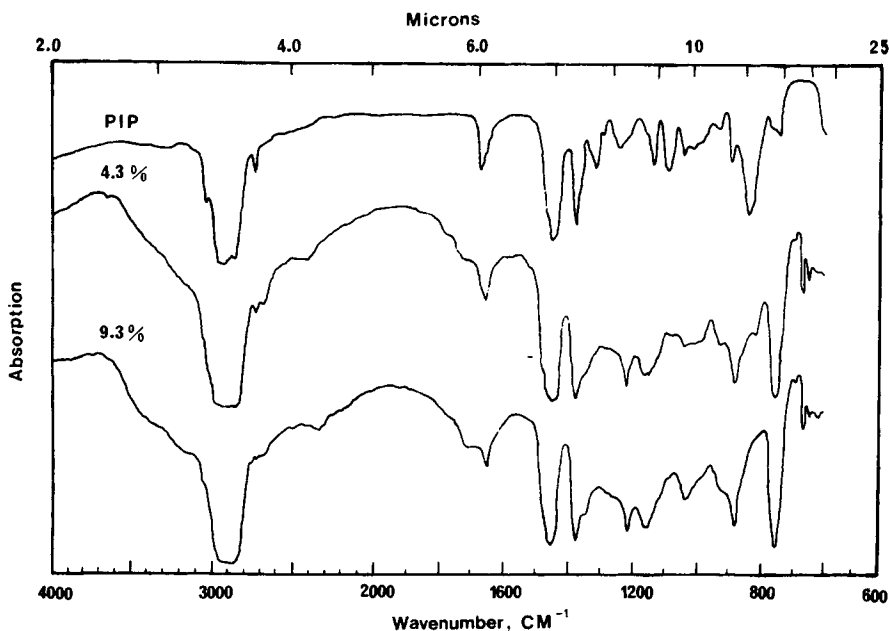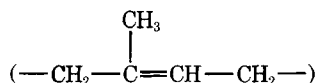$$(-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-)$$

Fig. 2. Infrared spectra of synthetic *cis*-polyisoprene and the 4.3 and 9.3 mol % sulfonated polymers in the acid form.
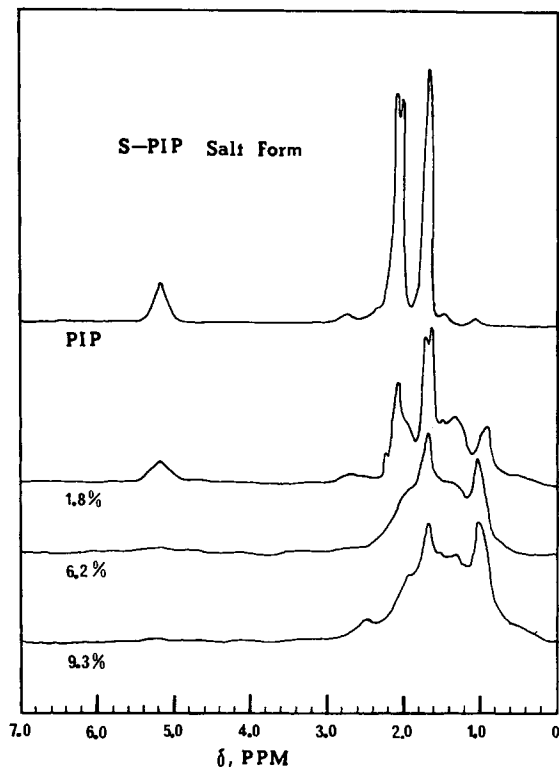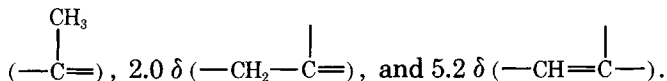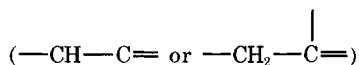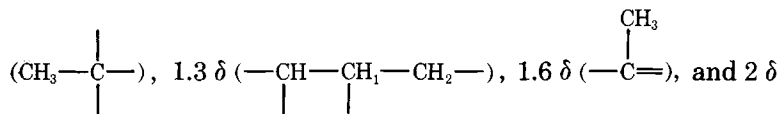
Fig. 3. NMR spectra of sulfonated cyclized rubber and the 1.8, 6.2, and 9.3 mol % salts.

in the initial polymer, the spectrum of cis-PIP displays peaks at 1.6 δ

$$(-\overset{\overset{\displaystyle CH_3}{|}}{C}=)\,,\quad 2.0\ \delta\ (-CH_2-\overset{|}{C}=)\,,\ \text{and}\ 5.2\ \delta\ (-CH=\overset{|}{C}-).$$

As a result of the cyclization, the olefinic proton peaks are greatly diminished[22] in the S-PIP acid, and the important peaks which appear are those at 0.95 δ

$$(CH_3-\overset{|}{\underset{|}{C}}-)\,,\ 1.3\ \delta\ (-\overset{|}{CH}-\overset{|}{CH_1}-CH_2-)\,,\ 1.6\ \delta\ (-\overset{\overset{\displaystyle CH_3}{|}}{C}=),\ \text{and}\ 2\ \delta$$

$$(-CH-C=\ \text{or}\ -CH_2-\overset{|}{C}=)$$

superimposed on a very broad resonance in the 0–2.8 δ region. By comparing the spectra of the acid and ester forms of the sulfonated material, it is seen that for the same mole percentage of sulfonation there is no distinct difference between acid form and ester form in the 0–2.8 δ region. By contrast, a new peak appears at 3.9 δ. Since it is known that for methyl protons in $RCOOCH_3$ the chemical shift is in the region δ 3.7–4.1, it seems that the new δ 3.9 peak is due to the methyl protons which are introduced in the methylation of the sulfonic acid.
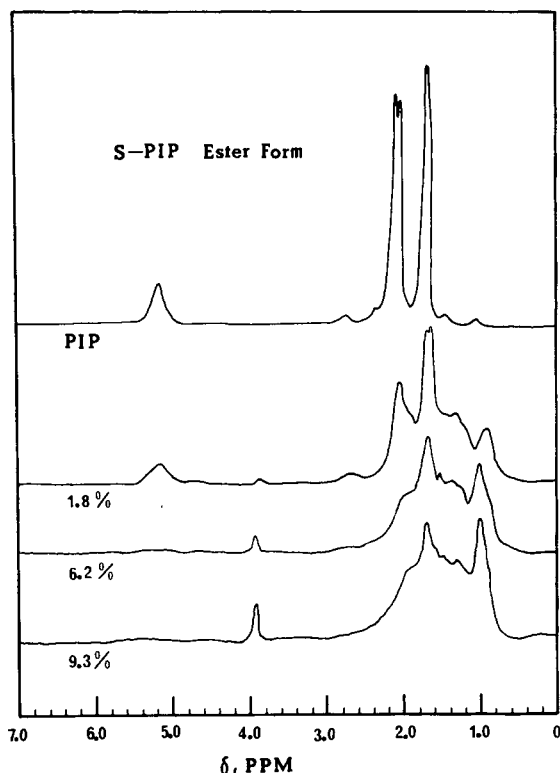
Fig. 4. NMR spectra of sulfonated cyclized rubber and the 1.8, 6.2, and 9.3 mol % esters.

Glass Transitions

The DSC results for *cis*-PIP and for 1.0, 1.8, 4.3, 6.2, and 9.3 mol % S-PIP, in both the salt and ester forms, are given in Table III. These results can also be compared with those obtained by dynamic mechanical techniques.

In Table III, it can be seen that the T_g values of sulfonated polyisoprenes increase as the degree of sulfonation increases. It should also be pointed out that the glass transition detected by DSC for the 1.0 and 1.8% S-PIP salts exhibit readily observable transitions (a sharper shift of the baseline within a narrower temperature range), while for the 4.3% salt the glass transition becomes broadened and is spread over a range of ca. 25°c, centered at 53°C. It is worth noting that for the 6.2 and 9.3% salts no glass transition can be seen, the DSC traces merely showing sloping lines; while for the 6.2 and 9.3% ester forms the DSC curves again show typical glass transition behavior. This can be attributed to

TABLE III
Glass Transition Temperatures (T_g) and Temperature Differences (ΔT_g) between S-PIP Salts
and Esters

| Sulfonic acid, mol % | T_g salt, °C | | T_g ester, °C | | ΔT_g |
	DSC[a]	tan δ_{max}	DSC[a]	tan δ_{max}	tan δ_{max}
0	−64–−66 (−62)	−60	—	—	—
1.0	−55–−49 (−52)	−50	—	—	—
1.8	−7–3 (−2)	0	−8–1 (−4)	−2	2
4.3	40–65 (53)	57	45–55 (47)	48	9
6.2	no transition visible	120	100–115 (107)	100	20
9.3	no transition visible	—	115–130 (122)	—	—

[a] Entire range is given, with the midpoint in parentheses.

the fact that the esterification destroys the strong coulombic interactions and reestablishes "normal" behavior, i.e., sharp transitions in the DSC.

The changes of the glass transition temperatures of the S-PIP salts with degree of sulfonation are shown in Figure 5; Figure 6 shows the glass transition differences between S-PIP salts and esters. All these data come from the peak maxima of tan δ (see below).

Mechanical Properties

The loss tangent (tan δ) of *cis*-PIP as well as the 1.0, 1.8, 4.3, and 6.2 mol % S-PIP salts and the 1.8, 4.3, and 6.2 mol % S-PIP esters are shown as a function of temperature in Figures 7 and 8. The tan δ curves of the S-PIP salts show two
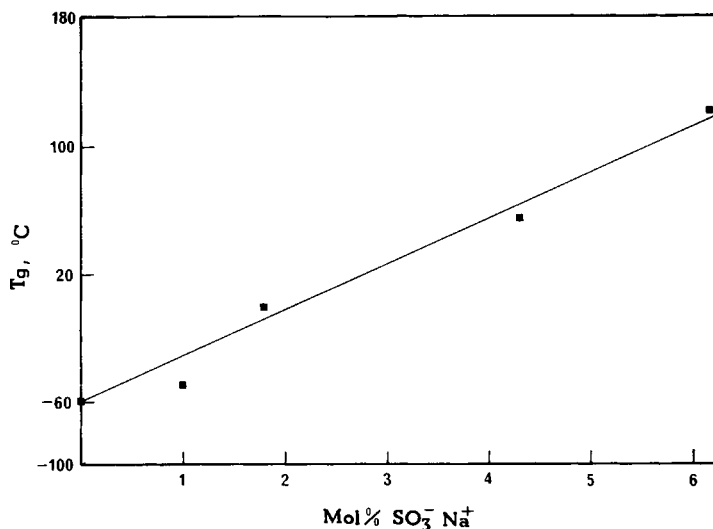

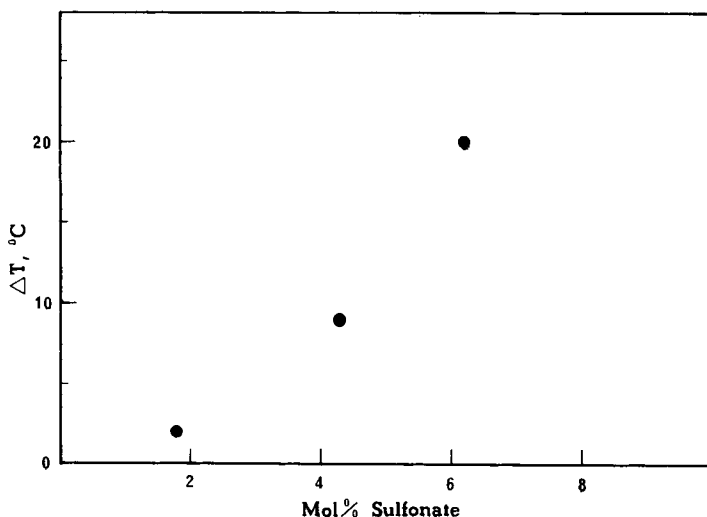Fig. 5. Glass transition temperatures vs. sulfonate content for S-PIP salts.

Fig. 6. Differences in the glass transition temperatures, ΔT_g, between S-PIP salts and esters vs. the sulfonate content of S-PIP.

peaks, labeled α and β; the α peak positions move to higher temperature as the degree of sulfonation and cyclization increases.

Figure 9 compares the tan δ curves of the 6.2% S-PIP salt and ester forms. The differences in the tan δ peak positions for the 1.8, 4.3, and 6.2% samples in their salt and ester forms are ca. 2, 9, and 20°C, respectively.

The storage and loss moduli for the 6.2% salt and ester samples are plotted semilogarithmically in Figure 10. The difference of the maxima in G'' between salt and ester is 20°C, just as for the tan δ curve (Fig. 9). Above the glass transition, the values of both G' and G'' for the ester are much lower than those for the salt.

The storage modulus G' as a function of temperature for the *cis*-PIP and the 1.0, 1.8, 4.3, and 6.2 mol % salts as well as the 1.8, 4.3, and 6.2 mol % esters are
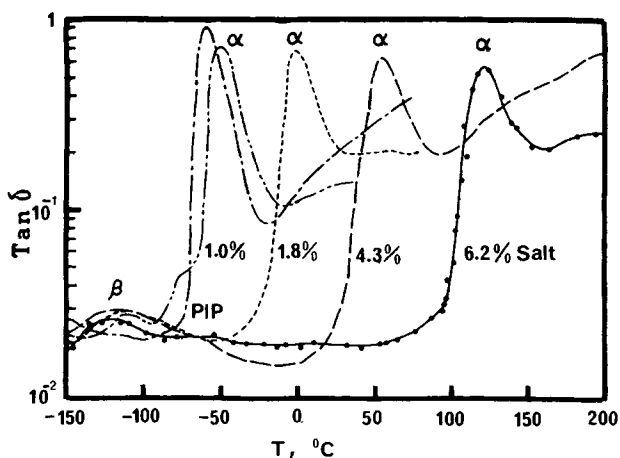

Fig. 7. Loss tangent vs. temperature for *cis*-PIP and the sulfonated cyclized polyisoprene salts of different ion concentrations. For the sake of clarity, the experimental points are only shown for one curve.
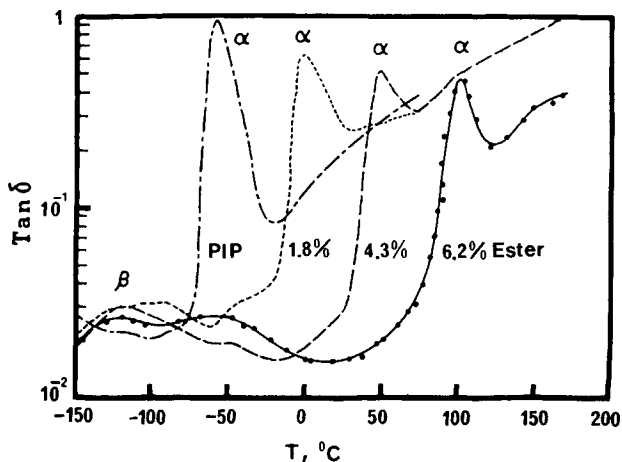
Fig. 8. Loss tangent vs. temperature for *cis*-PIP and sulfonated cyclized polyisoprene esters of different ion concentrations. For the sake of clarity, the experimental points are only shown for one curve.

shown in Figures 11 and 12. It can be seen that for both salts and esters, the glass transition regions move to higher temperatures and the slopes of the curves in those regions decrease as the degree of sulfonation and cyclization increases. Furthermore, it is worth noting that there is no distinct difference in the slopes in the transition region between the salts and esters at the same degree of sulfonation.

Finally, in order to ascertain the effect of water absorption on the dynamic mechanical properties, a sample of the 4.3% S-PIP salt was stored in water at room temperature. The amount of water absorbed kept increasing over a period of 70 days without attainment of equilibrium. The total water content at that point was 12.5% of the dry weight. The loss tangent plot for this sample is given in Figure 13. It is clear that the peak position (ca. 50°C) is close to the peak
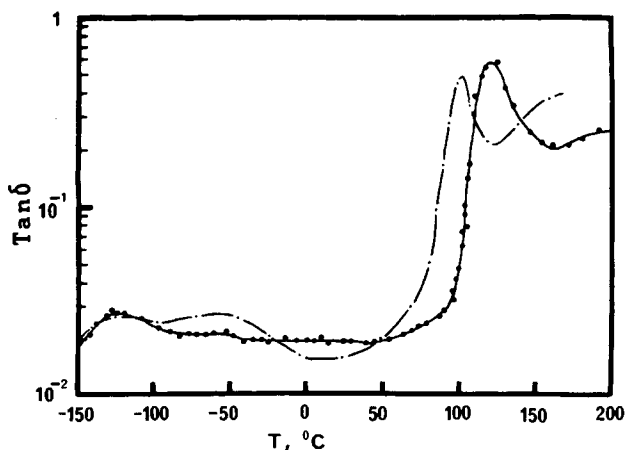

Fig. 9. Comparison of the loss tangents vs. temperature plot for the 6.2% S-PIP salt (——) and ester (–·–). The experimental points are only shown for one curve.
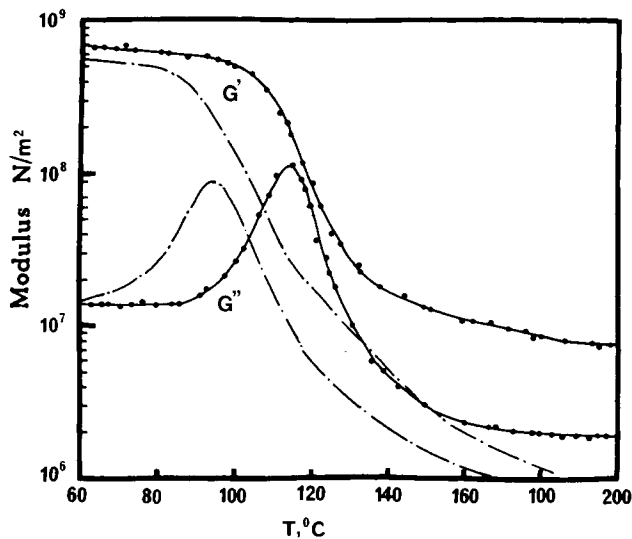
Fig. 10. Storage modulus and loss modulus vs. temperature for the 6.2% S-PIP salt (——) and ester (–·–). The experimental points are only shown for set of curves.

position of the ester form (of the same degree of sulfonation, i.e., 4.3 mol %). This suggests that the water molecules weaken the ionic interactions in the material and lower the T_g of the 4.3% S-PIP salt by the same amount as the esterification,
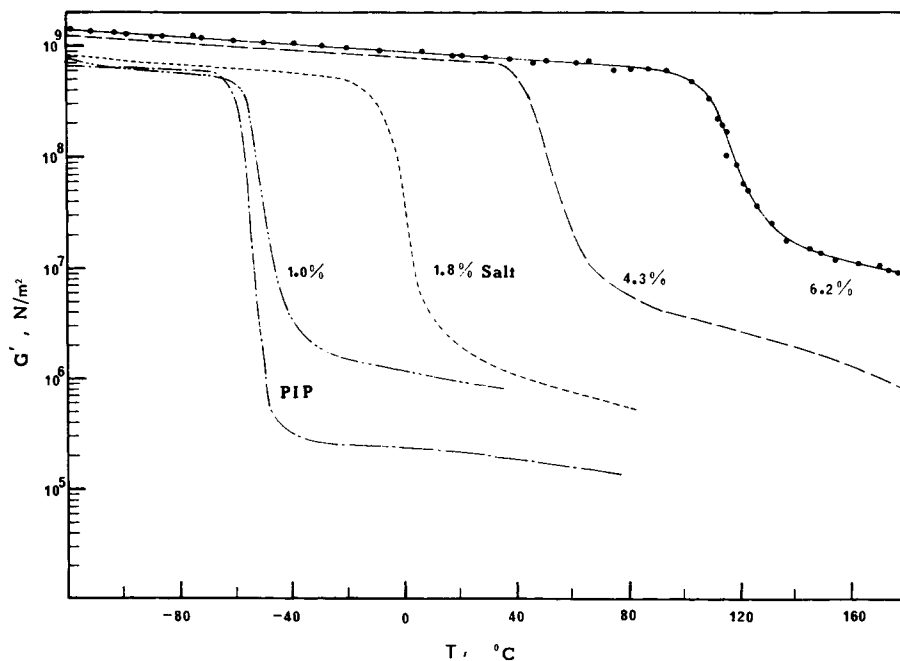

Fig. 11. Storage modulus vs. temperature for the *cis*-PIP and the sulfonated cyclized polyisoprene salts. The experimental points are only shown for one curve.
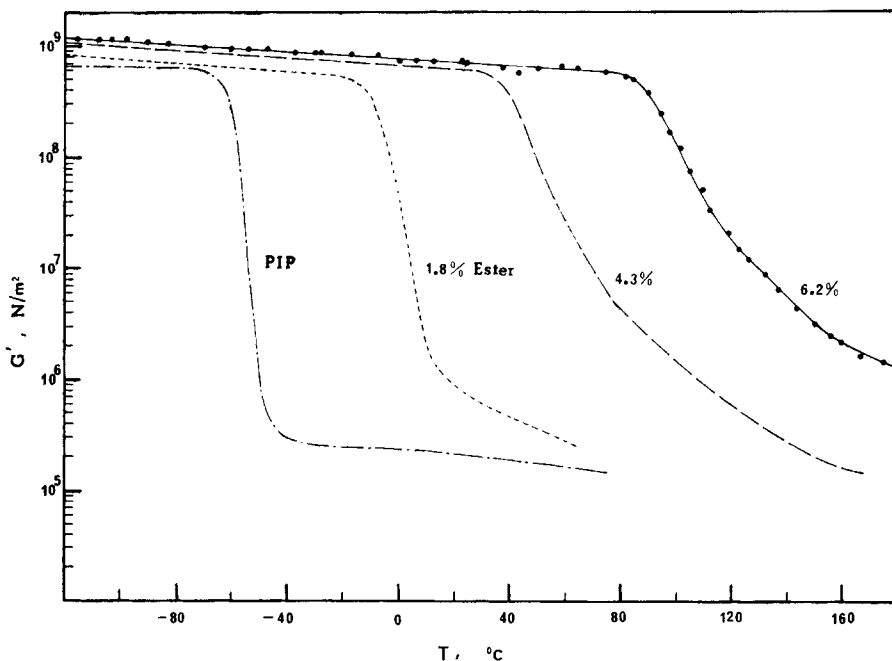
Fig. 12. Storage modulus vs. temperature for the *cis*-PIP and the sulfonated cyclized polyisoprene esters. The experimental points are only shown for one curve.

i.e., by 5–7°C. It is also seen that a new peak appears at ca. −85°C, as well as a very small one at ca. 0°C.

DISCUSSION

Sulfonation of *cis*-Polyisoprene

It is evident that the sulfonation of PIP by acetylsulfate is accompanied by considerable cyclization of the rubber. Sulfonation obviously takes place, and every sulfur atom incorporated into the material is present in the sulfonate form.
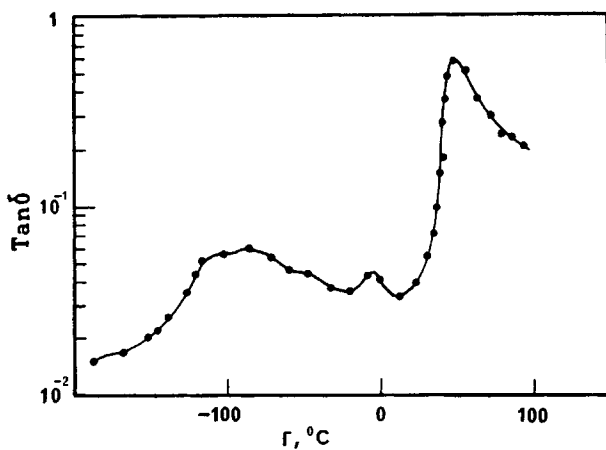

Fig. 13. Loss tangent vs. temperature for the 4.3% S-PIP salt with 12.5 wt % water.

The infrared and NMR spectra of these products confirm that the products were cyclized at the time of sulfonation.

The detailed structure of the cyclized rubber molecule has been the subject of considerable controversy over the years.[23-35] One of the authors[23] discussed typical spectra of cyclized rubbers obtained by $TiCl_4$ catalysis of synthetic cis and natural transpolyisoprenes. The features of the IR spectra are similar to the present IR results except for the presence of peaks due to sulfonic acid groups at 1040 and 1200 cm^{-1}. In Figure 2, the most important spectroscopic changes resulting from cyclization are the disappearance of the 12-μ band (C—H out-of-plane deformation of the cis —C(CH$_3$)=CH— units), and the decrease in the 6.0-μ band (C=C stretching vibration of an internal double band).

The NMR spectra in Figures 3 and 4 give further evidence that the cyclization occurred simultaneously with sulfonation. Figure 1, along with the glass transition temperatures of the products listed in Table III, indicates that the reaction conditions involving less concentrated sulfonating reagent and shorter reaction times produce products of a lower degree of cyclization, since the dominant factor in raising the T_g is cyclization. For instance, samples of 1.0 and 1.8% S-PIP were produced with an amount of sulfuric acid corresponding to 20% of the number of moles of polyisoprene, the reaction times being 1.5 and 3 h, respectively. As a result, these two samples have low glass transition temperatures, i.e., −50 and 0°C. On the other hand, samples 4.3, 6.2, and 9.3% have higher T_gs values, as the sulfonating reagent was more concentrated. From the point of view of the cyclization mechanism by H$^+$ catalysis,[35] it would be expected that the more concentrated the acetyl sulfate (acetic acid and H$^+$ are produced by the reaction of acetic anhydride and sulfuric acid) and the longer the reaction time, the more —C(CH$_3$)=CH— units will be consumed in the cyclization reaction. This is also confirmed from a careful examination of the NMR spectra. For the 9.3% S-PIP, the 5.2 δ peak

$$(\text{—CH}=\overset{|}{\text{C}}\text{—})$$
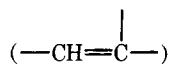
has almost disappeared, while the 0.9 δ peak

$$(\text{CH}_3\text{—}\overset{|}{\underset{|}{\text{C}}}\text{—})$$
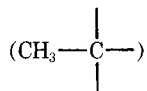
has become dominant when compared with the 1.8 and 6.2% S-PIP samples.

Glass Transitions of S-PIP

The sulfonated polyisoprenes, both in the salt and ester forms, have higher glass transitions than that of *cis*-PIP, as is shown in Table III and Figures 7 and 8. In Figure 5, the average slope (dT_g/dc) is approximately 30°C/mol %, while in other systems, such as sulfonated polystyrene and styrene–sodium methacrylate copolymers, the dT_g/dc values were ca. 2–4°C/mol %.[6] In the sulfonated polypentenamer, it was ca. 2°C/mol % (below ca. 10 mol % sulfonation).[10] This shows that cyclization exerts a profound influence on the microbrownian segmental motion of the hydrocarbon matrix. As previous studies pointed out,

cyclized rubber does not have a unique structure but consists of an assortment of mono- and polycyclic groups such that the average size of the condensed ring system is of the order of 2–4.[21-35] Obviously, the fused rings influence the properties of the resulting materials to the point where they cease to be rubbers at all and become resinous materials. However, if one looks at the effect of coulombic interactions on the glass transition, i.e., by determining the T_g drop during esterification, it is seen that the ionic effects in these materials are quite typical of those encountered in a wide range of other ionomers.

Mechanical Properties

In Figures 7 and 8 it is seen that the α peak positions move to higher temperatures as the degrees of sulfonation and cyclization increase. By comparing the peak positions with the DSC results, it is clear the α relaxation is due to the glass transition of the cyclized and sulfonated polymer. The β peak observed at ca. $-120°C$ has been seen in many other hydrocarbon materials, including the sulfonated polypentenamers.[10]

In Figures 6 and 9, the tan δ peak position differences between salts and esters for the 1.8, 4.3, and 6.2% samples are only 2, 9, and 20°C, which again confirms that the factor dominating the glass transition behavior for sulfonated and cyclized PIP is the cyclization. The influence of ionic interactions in raising the T_g between sats and esters with different functional group contents are only in the region of ca. 2°C (for 1.8%) to ca. 20°C (for 6.2%). The large difference in G' and G'' between the 6.2% salt and ester above T_g, as shown in Figure 10, indicates that ionic group association imparts higher moduli and higher melt viscosities to the sulfonated rubber salts. The higher modulus and melt viscosity of 6.2% S-PIP salt were also observed qualitatively when the specimens were compression-molded. The 9.3% S-PIP salt could not even be molded above 200°C due to the high melt viscosity.

By comparing Figures 11 and 12, it can be seen that the slopes of the salts and the esters for the same degree of sulfonation show no distinct difference, i.e.,

$$\frac{d \log G'(\text{ester})}{dT} \simeq \frac{d \log G'(\text{salt})}{dT}$$

indicating that the dramatic broadening of the log G' vs. T plot with increasing ion content does not occur here, in contrast to other ionomer systems. In general, in many other ionomer systems, it has been found that the broadening can be attributed to the ionic interactions, especially when clustering is present, as indicated by the decrease of the slope in the curves of storage modulus vs. temperature.[6,11,12] In this cyclized and sulfonated PIP rubber system, the slopes of the esters and the ionomers are practically identical. Thus, it appears that clustering or microphase separation probably does not take place to the extent found in other systems, at least as it is reflected in the broadening of the G' vs. T slope. Instead of ion clustering, cyclization becomes the dominant factor. On the other hand, ions do aggregate in sulfonated PIP salts, probably in the form of multiplets, which can be seen by the differences in the T_g values between salts and esters (from 2 to 20°C), as well as the higher G' values of the salts.

References

1. A. Eisenberg, *Adv. Polym. Sci.*, **5**, 59 (1967).

2. E. P. Otocka, *J. Macromol. Sci., Rev. Macromol. Chem.*, **5**, 275 (1971).

3. W. J. MacKnight and T. R. Earnest, Jr., *J. Polymer Sci., Macromol. Revs.* **16**, 41 (1981).

4. C. G. Bazuin and A. Eisenberg, *Ind. Eng. Chem., Prod. Research and Devel.* **20**, 271 (1981).

5. L. Holliday, Ed., *Ionic Polymers*, Applied Science, New York, 1975.

6. A. Eisenberg and M. King, *Ion-containing Polymers—Physical Properties and Structure*, Academic, New York, 1977.

7. H. S. Makoswki, R. D. Lundberg, L. Westerman, and J. Bock, in *Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series 187, Washington, D.C., 1980, Chap. 1.

8. R. D. Lundberg, H. S. Makowski, and L. Westerman, in *Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series 187, Washington, D.C., 1980, Chap. 5.

9. D. Rahrig and W. J. MacKnight, in *Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series 187, Washington, D.C., 1980, Chap. 6.

10. R. D. Lundberg and H. S. Makowski, in *Ions in Polymers*, A. Eisenberg, Ed., Advances in Chemistry Series 187, Washington, D.C., 1980, Chap. 2.

11. M. Rigdahl and A. Eisenberg, *J. Polym. Sci., Polym. Phys.*, to appear.

12. A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).

13. N. H. Canter, (to Esso Research & Engineering Company), U.S. Pat. 3,642,728 (1972).

14. C. P. O'Farrell and G. E. Serniuk (to Esso Research & Engineering Company), U.S. Pat. 3,836,511 (1974).

15. H. S. Makowski, R. D. Lundberg, and G. H.Singhal, U.S. Pat. 3,870,841 (1975).

16. E. E. Gilbert, *Sulfonation and Related Reactions*, Interscience, New York, 1965.

17. M. A. Golub, in *Polymer Chemistry of Synthetic Elastomers*, Part II, *High Polymers*, Vol. 23, J. P. Kennedy and E. G. M. Törnquist, Eds., 1969, p. 939.

18. A. I. Vogel, *Practical Organic Chemistry*, Longmans, 1966, p. 973.

19. B. Cayrol, Ph.D. thesis, McGill University, Montreal, 1972.

20. *The Sandler Handbook of Infrared Spectra*, 1978, p. 377.

21. M. A. Golub and J. Heller, *Tetrahedron Lett.*, 2137 (1963).

22. R. J. Angelo, *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.*, **4**, 32 (1963); *Chem. Abstr.*, **62**, 645g (1965); *Chem. Eng. News*, Dec. 16, 1963, p. 43.

23. M. A. Golub and J. Heller, *Can. J. Chem.*, **41**, 937 (1963).

24. J. D. D'Ianni, F. J. Naples, J. W. Marsh, and J. L. Zarney, *Ind. Eng. Chem.*, **38**, 1171 (1946).

25. M. Gordon, *Ind. Eng. Chem.*, **43**, 386 (1951); *Rubber Chem. Technol.*, **24**, 940 (1951).

26. M. Gordon, *Proc. Roy. Soc.* (London), **A204**, 569 (1951); *Rubber Chem. Technol.*, **24**, 924 (1951).

27. M. Gordon and T. S. Taylor, *J. Appl. Chem.*, **3**, 537 (1953); *Rubber Chem. Technol.*, **28**, 297 (1955).

28. N. V. C. Rao, *Makromol. Chem.*, **16**, 198 (1955).

29. C. S. Ramakrishnan, S. Dasgupta, and N. V. C. Rao, *Makromol. Chem.*, **20**, 46 (1956).

30. P. J. Flory, *J. Am. Chem. Soc.*, **61**, 1518 (1939).

31. H. L. Fisher and E. M. McColm, *Ind. Eng. Chem.*, **19**, 1325, 1328 (1927).

32. G. J. Van Veersen, *Rec. Trav. Chim.*, **69**, 1365 (1950); *Rubber Chem. Technol.*, **24**, 957 (1951).

33. F. T. Wallenberger, *Monatsh. Chem.*, **93**, 74 (1962); *Rubber Chem. Technol.*, **36**, 558 (1963).

34. D. F. Lee, J. Scanlan, and W. F. Watson, *Proc. Roy. Soc.* (London), **A273**, 345 (1963); *Rubber Chem. Techol.*, **36**, 1005 (1963); *Chem. Eng. News*, June 17, 1963, p. 44.

35. G. F. Bloomfield, *J. Chem. Soc.*, 289 (1943).