From Figure 14 it can be seen that the retardation times associated with the branches are orders of magnitude larger than those of free polystyrene chains of the same molecular weight. This is reminiscent of the slow processes attributed to dangling ends in networks[30] and block copolymers.[31]

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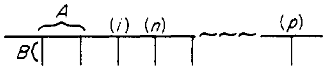
Appendix

A monodisperse backbone with p equidistantly placed monodisperse branches is considered as shown:



The number of branches = p, $A = M_{bb}/(p + 1)$, and $B = M_{br}$.

1. Starting from one end of the backbone

$$M_{EE}' = (p + 1)A + \sum_{i=1}^{i=p}(iA + B)$$
$$= \frac{(p + 1)(p + 2)}{2}A + pB$$

The total for the two backbone ends is

$$2M_{EE}' = (p + 1)(p + 2)A + 2pB \qquad (1')$$

and the number of end-to-end combinations is $2(p + 1)$.

2. Starting from the end of the nth branch

$$M_{EE}'' = (B + nA) + \sum_{i=1}^{n-1}(iA + 2B) + (B + (p - n + 1)A) + \sum_{i=1}^{p-n}(iA + 2B)$$
$$= 2pB + n^2A + (p + 1)[p/2 - n + 1]A$$

which summed over all branches n from 1 to p is

$$pM_{EE}'' = 2p^2B + \frac{p(p + 1)(p + 2)}{3}A \qquad (2')$$

and the number of end-to-end combinations starting from a branch end is $p(p + 1)$. $\bar{M}_{EE}$ is the sum of all molecular weights between each two ends of the comb (1′) + (2′) divided by the total number of end-to-end combinations and is given by eq 10. For $p \gg 3$, eq 10 reduces to

$$\bar{M}_{EE} = 2M_{br} + M_{bb}/3$$

which for a star with many branches becomes $\bar{M}_{EE} = 2M_{br}$.

References and Notes

(1) See, e.g.: Rokudai, M. *J. Appl. Polym. Sci.* **1979**, *23*, 463.
(2) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(3) Kraus, G.; Gruver, J. T. *J. Polym. Sci., Part A* **1965**, *3*, 105.
(4) Meyer, H. H.; Ring, W. *Kautsch. Gummi Kunstst.* **1971**, *24*, 526.
(5) Masuda, T.; Ohta, Y.; Onogi, S. *Macromolecules* **1971**, *4*, 763.
(6) Utracki, L. A.; Roovers, J. *Macromolecules* **1973**, *6*, 366, 371.
(7) Roovers, J.; Hadjichristidis, N. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2521.
(8) Graessley, W. W.; Masuda, T.; Roovers, J.; Hadjichristidis, N. *Macromolecules* **1976**, *9*, 127.
(9) Graessley, W. W.; Roovers, J. *Macromolecules* **1979**, *12*, 959.
(10) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(11) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802. See also: de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(12) Bueche, F. *J. Chem. Phys.* **1964**, *40*, 484.
(13) Ham, J. S. *J. Chem. Phys.* **1957**, *26*, 625.
(14) de Gennes, P. G. *J. Phys. (Paris)* **1975**, *36*, 1199.
(15) Fujimoto, T.; Narukawa, H.; Nagasawa, M. *Macromolecules* **1970**, *3*, 57.
(16) Noda, I.; Horikawa, T.; Kato, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 795.
(17) Fujimoto, T.; Kajiura, H.; Hirose, M.; Nagasawa, M. *Polym. J.* **1972**, *3*, 181.
(18) Pannell, J. *Polymer* **1972**, *13*, 1.
(19) Roovers, J. *Polymer* **1975**, *16*, 827.
(20) Roovers, J. *Polymer* **1979**, *20*, 843.
(21) Long, V. C.; Berry, G. C.; Hobbs, L. M. *Polymer* **1964**, *5*, 517.
(22) Graessley, W. W.; Shinbach, E. S. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2047.
(23) Ferry, J. D. "Viscoelastic Properties of Polymers", 2nd ed.; Wiley: New York, 1970.
(24) Macosko, C. W.; Davis, W. M. *Rheol. Acta* **1974**, *13*, 814.
(25) Casassa, E. F.; Berry, G. C. *J. Polym. Sci., Part A-2* **1966**, *4*, 881.
(26) Pannell, J. *Polymer* **1971**, *12*, 558.
(27) Candau, F.; Rempp, P.; Benoit, H. *Macromolecules* **1972**, *5*, 627.
(28) Pearson, D.; Raju, V., private communication.
(29) Marin, G.; Graessley, W. W. *Rheol. Acta* **1977**, *16*, 527.
(30) Langley, N. R.; Ferry, J. D. *Macromolecules* **1968**, *1*, 353.
(31) Cohen, R. E.; Tschoegl, N. W. *Int. J. Polym. Mater.* **1973**, *2*, 205.

Solubility Behavior of Copolymers of Isoprene and Sodium Styrenesulfonate

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ABSTRACT: Solubility studies were made on poly(isoprene-*co*-sodium styrenesulfonate) ionomers in nonpolar hydrocarbon solvents and in mixed solvents containing a minor amount of alcohol. It was shown that these isoprene-based ionomers were ionically aggregated and that alcohols effectively solvated the ionic associations. The temperature dependence of the solution viscosity of these ionomers was also investigated.

Introduction

Modification of partially unsaturated elastomeric hydrocarbon polymers by sulfonation has been recently reported by several investigators.[1-4] The rheological and tensile properties[5] of these sulfonated elastomers as well as their thermal and dynamic mechanical responses[3] have been characterized and disclosed. We have been able to extend the scope of these ion-containing elastomers by successfully copolymerizing diene monomers with a number of olefinic sulfonic acid salts.[6]

Evidence shown in recent studies[3,7] indicates that pen-

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Table I
Solubility of Isoprene Ionomers at the 1% Level at 25 °C

polymer	% sulfur	mol % NaSS	wt % gel[a]		reduced viscosity,[b] dL/g
			xylene	xylene/MeOH	
A	0.30	0.64	86.3	1.4	3.15
B	0.38	0.81	74.0	1.0	1.57
C	0.71	2.09	87.0	5.0	2.64
D	0.95	3.62	86.0	0.5	3.09
E	1.60	1.54	44.0	2.0	0.65
G	3.50	8.71	76.0	23.0	2.33

[a] Insoluble polymer obtained on attempted dissolution of 1 wt % of polymer in solvent. [b] At 30 °C and 0.2 g/dL, a qualitative measure of true molecular weight.

Table II
Dependence of Ionomer Solubility on the Type and Amount of the Polar Solvent[a]

solvent	vol % alcohol	% insoluble
toluene	0	44
toluene/hexanol	1	29.5
toluene/hexanol	3	27.5
toluene/hexanol	5	25
toluene/hexanol	7	23
toluene/hexanol	10	23
xylene/methanol	5	2

[a] Polymer sample E, containing 3.63 mol % NaSS, was added in the amount of 1 wt % to the indicated solvent at 25 °C.

Table III
Dependence of the Solubility and the Solution Viscosity on Alcohol Content of the Mixed Solvent[a]

solvent	vol % alcohol	insol wt % polymer.	reduced viscosity,[b] dL/g
toluene	0	86.3	
toluene/hexanol	1	3	163
toluene/hexanol	1.5	2	81
toluene/hexanol	2.7	1	14
toluene/hexanol	5	~0	15
toluene/hexanol	7	0.5	10
toluene/hexanol	10	~0	9
xylene/methanol	5	1.4	

[a] Polymer sample A, containing 0.59 mol % NaSS, was added in the amount of 1 wt % to the indicated solvent at 25 °C. [b] At 30 °C and 1 g/dL.

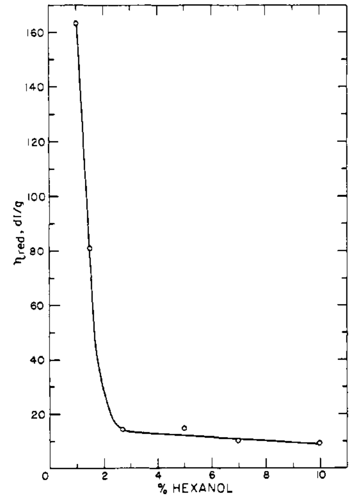

Figure 1. Reduced viscosity of a 1% solution of poly(isoprene-*co*-sodium styrenesulfonate) in toluene/hexanol as a function of hexanol content of the solvent.

dent ionic groups of these elastomers aggregate to form microphase-separated ionic domains which are imbedded in the rubber matrix.

In the present work solubility studies of isoprene ionomers were carried out to assess the extent of ionic cross-linking of the elastomeric network. Another purpose of this study was to understand the interaction of polar functional groups such as alcohols with the ionic groups in solution. One of the motivations for this understanding was ultimately to be able to apply this understanding to the flow behavior of these materials in the bulk polymer.

Experimental Section

Polymerization. Copolymers of isoprene and sodium *p*-vinylbenzenesulfonate (NaSS) were prepared by emulsion polymerization technique. The reaction conditions and recipes were the same as those reported by Siadat, Oster, and Lenz.[6]

Procedure. Determination of Insoluble Content. To determine the solubility of the copolymer in various solvents, it was mixed at a level of 1% by weight with the desired solvent and was rotated on a Staudinger wheel for 1–2 days. The gel portion was centrifuged out, dried, and weighed to determine the insoluble content of the copolymer in the solvent.

Viscosity Determination. Reduced viscosities in toluene, xylene, and a 95/5 volumetric mixture of xylene/methanol were measured in an Ubbeholde dilution viscometer at 30 °C. Shear viscosities were measured on a Rheomat-15 concentric cylinder rheometer under couette flow conditions.

Discussion and Results

Copolymers of isoprene and sodium *p*-vinylbenzenesulfonate (NaSS) were essentially insoluble in those hydrocarbon solvents that ordinarily dissolve the isoprene homopolymer. Apparently, in these solvents substantial ionic association existed due to the metal–sulfonate interaction. Table I indicates that only a small fraction of the emulsion copolymerization product was soluble in xylene. Addition of small amounts of methanol to the mixture improved the solubility of all polymers and resulted in almost complete solubilization of these ionomers. Presumably, the alcohols preferentially solvated the strongly polar, associating sulfonate groups and thereby broke up the ionic aggregates. Table I compares the solubility of these ionomers in a straight hydrocarbon solvent and a mixed solvent containing 5% (on a volume basis) methanol.

The influence of the amount and type of the alcohol on the solubility of isoprene ionomers is shown in Table II. The soluble fraction of the polymer increased as the level of alcohol in the mixed solvent increased; that is, higher levels of alcohol resulted in a higher extent of preferential solvation of the ionic cross-links.

Some alcohols were more efficient than others; for example, methanol was a much more efficient preferential solvating agent for ionic domains than hexanol. This observation is important because the maximum level of the polar cosolvent was limited by the solubility of the polyisoprene backbone. The data of Table II are based on an ionomer that contained 3.63 mol% sulfonate groups; if the ionic content was progressively lowered to 0.6 mol% sulfonate content, a product was obtained that was almost completely soluble in a mixed solvent containing 1% hexanol. Under these conditions, at these lower sulfonate levels, the isoprene ionomer tended to behave as if it were

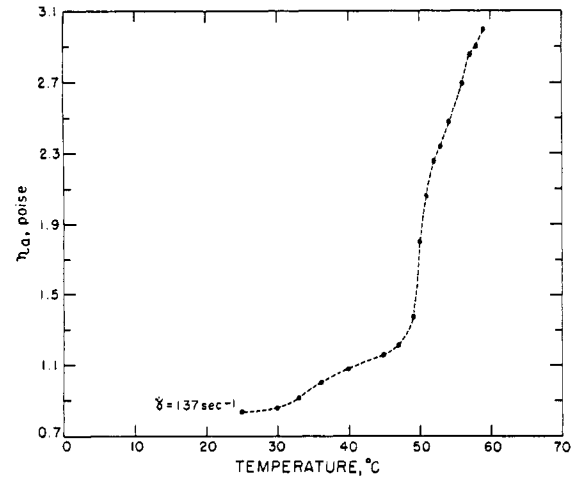

Figure 2. Temperature–viscosity relationship of polymer sample E in a 98/2 mixture of xylene/methanol at 137-s^{-1} shear rate.

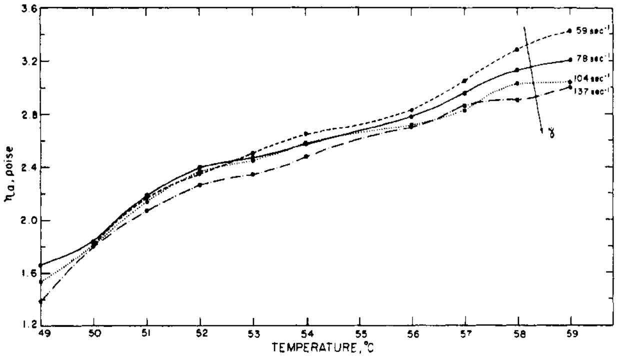

Figure 3. Effect of temperature and shear rate on the apparent viscosity of a 10% solution of polymer sample E in a 98/2 mixture of xylene/methanol.

a much higher molecular weight polyisoprene. The data in Table III and Figure 1 show that as the hexanol content was increased, the viscosity decreased markedly, especially at the level near 3% hexanol. These results can be interpreted as simply a change in the apparent polymer molecular weight, which was strongly dependent on the alcohol concentration.

The influence of temperature on the solution viscosity of isoprene ionomers is shown in Figures 2 and 3. In these studies a simple coaxial cylinder rheometer was used because it was convenient, rapid, and reliable. For isoprene ionomers the effect of temperature is seen to be quite significant in that at the higher temperature the apparent viscosity was substantially higher than at lower temperature. The data of Figure 2 for a 10% solution of an isoprene ionomer (3.6 mol% sulfonate) in (98/2) xylene/methanol solvent show a marked effect of temperature on apparent viscosity. At first glance, this effect appears to be opposite to what might normally be expected. Investigating the solubility of sulfonated polystyrene and sulfonated ethylene–propylene rubber, Lundberg[8,9] observed similar results and proposed a simplified equilibrium between the alcohol and associated polymer to explain this rather strange temperature dependence of the viscosity. His proposed equilibrium for alcohol–polymer interaction is as follows:

$$\text{alcohol} + (\text{Ⓟ-SO}_3\text{Na})_n \underset{k_2}{\overset{k_1}{\rightleftarrows}} n(\text{alcohol-Ⓟ-SO}_3\text{Na})$$

domain-forming species (favored at high temperature) — solved species (favored at low temperature)

Such an equilibrium scheme suggests that addition of sufficient amounts of alcohol will eventually eliminate ionic aggregation by shifting the equilibrium toward the solvated species. Less alcohol would result in an equilibrium between domain-forming and solvated species, and progressive lowering of the amount of alcohol would cause a continuing increase in the relative amount of the domain-forming species, resulting in a continuous increase in the apparent molecular weight of the ionomer in solution.

The total amount of alcohol necessary to solvate all ionic associations will depend on the strength of the association of the alcohol–ionic association; for strongly solvated species this level may be reasonable, but for weak associations the level of required alcohol may be so high that precipitation of the backbone polymer occurs. This level of alcohol, of course, also depends on the ionic content of the polymer; if the sulfonate level is rather high and strongly associating, the association is not dissipated regardless of how much alcohol is added. Finally, at temperatures below those required for the weakening of the ionic associations, dilute-solution viscosity of the ionomer would increase with temperature by shifting the equilibrium toward the domain-forming species, hence resulting in a higher apparent molecular weight of the polymer in solution.

Such behavior patterns were observed in a number of experiments with isoprene ionomers, indicating that a rather simple equilibrium could satisfactorily interpret the results. However, clearly, expressing these complex interactions in such a simple equilibrium is oversimplifying the situation.

Homogeneity of the Product. Effects on Solubility. From the previous discussion it is apparent that several factors influence the solubility of isoprene ionomers in a solvent system, most important of which are a combination of high molecular weight and high sulfonate level. The present solubility studies showed that as sulfonate level or the backbone molecular weight increased, the copolymers became insoluble in a solvent system unless the amount of alcohol in the solvent system was also increased. However, the increase in the alcohol content of the solvent could result in the precipitation of those ionomer molecules that have a high molecular weight polyisoprene backbone. Therefore, in order to have a completely soluble ionic elastomer, moderate molecular weights (e.g., a reduced viscosity of approximately 2 dL/g at a concentration of 0.2 g/dL) and moderate sulfonate contents (that is, approximately 1 wt% sulfur) were required.

Table I contains data on a series of these ionomers which were substantially insoluble in xylene (due to strong ionic association) but were almost completely soluble in a mixed solvent comprising xylene and methanol. Polymers such as sample G, which had a high sulfonate content, 8.17 mol% in this case, had a higher insoluble fraction content in mixed solvents than those with moderate sulfonate content. The reason is that the level of alcohol required to solvate the ionic associations also resulted in some degree of main-chain precipitation. But, the solubility of the ionomer was increased upon heating, which resulted in better dissolution of the backbone polymer in the mixed solvent.

On the basis of these and related observations,[10] it may be concluded that there are several contributing factors to the increase in dilute-solution viscosity with increasing temperature for these isoprene ionomers. At higher sulfonate contents (~5–10 mol%) these polymers may assume a very compact conformation due to the relatively poor solvation by the mixed solvents for this polymer. Thus, increasing solution temperature results in improved solvation of the polymer chain and expands the conformation. Under these conditions, specific solvation effects are less important in dominating the solution viscosity behavior. At lower ionic contents ($\sim$1 mol%) and low alcohol cosolvent levels, the equilibrium described above becomes more dominant in controlling viscosity and its temperature dependence. Under these conditions rather dramatic changes in the apparent molecular weight of the associated polymer chains can arise as a function of temperature, which are atypical of conventional polymer solutions. These results can be interpreted only as a result of interchain associations of the ionic groups.

Clearly, a simple equilibrium describing strictly the ionic associations is not sufficient to describe all the complex ionic interactions but is useful in interpreting the rheology of ionomer solutions.

Conclusion

The insolubility of poly(isoprene-*co*-sodium styrenesulfonate) ionomers in toluene or xylene can be taken as evidence for the presence of ionic association. Solubility behavior of these ionically aggregated elastomers, in common nonpolar solvents of polyisoprene, is similar to that of covalently cross-linked polyisoprene rubber.

Polar cosolvents such as alcohols were believed to preferentially solvate the ionic aggregates, thereby disrupting their association. The extent of ionic association (i.e., degree of physical cross-linking) was shown to be controllable by the amount of polar cosolvents present. This phenomenon can be utilized in practical applications as well as theoretical considerations. For example, polar additives can be applied as processing aids in the fabrication of ionomers, or a controlled degree of cross-linking can be used in verification of various network theories of rubber elasticity.

The solution viscosity of isoprene-based ionomers increased significantly with increasing temperature, providing another potential for these ionomers as viscosity control additives.

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References and Notes

(1) Canter, N. H. U.S. Patent 3 642 728, 1974.
(2) O'Farrell, C. P.; Serniuk, G. E. U.S. Patent 3 836 511, 1974.
(3) Rahrig, D.; MacKnight, W. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *19* (2), 314.
(4) Siadat, B.; Lundberg, R. D.; Lenz, R. W. *Polym. Eng. Sci.* **1980**, *20* (8), 530.
(5) Makowski, H. S.; Lundberg, R. D.; Westerman, L.; Bock, J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (2), 292.
(6) Siadat, B.; Oster, B.; Lenz, R. W. *J. Appl. Polym. Sci.*, in press.
(7) Neumann, R. M.; MacKnight, W. J.; Lundberg, R. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (2), 298.
(8) Lundberg, R. D. U.S. Patents 3 931 021 (Jan 6, 1976) and 4 118 361 (Oct 3, 1978) (assigned to Exxon Research and Engineering Co.).
(9) Lundberg, R. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1978**, *19* (1), 455.
(10) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

Determination of Molecular Weight Distributions of Polyglycol Oligomers by Field Desorption Mass Spectrometry

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ABSTRACT: Field desorption mass spectrometry (FDMS) has been used to analyze three types of polyglycol oligomers—poly(ethylene glycol), poly(propylene glycol), and poly(tetrahydrofuran). Average molecular weight parameters ($\bar{M}_n$ and $\bar{M}_w$) were determined for several low molecular weight batches of these polymers by using either protonated (MH^+) or cation attachment (MNa^+) ions. Despite the fact that these polymers are thermally and structurally fragile, good agreement was found between the FDMS-derived parameters and those derived via classical methods. With these results it appears that average molecular weight determinations can be made by FDMS for a large number of oligomeric systems.

Introduction

Field desorption mass spectrometry (FDMS) has been shown to be a method of choice for determining molecular weights of nonvolatile and higher molecular weight chemicals.[1,2] Numerous reports from several laboratories have shown that FDMS can be used to obtain good qualitative distributions of oligomers for low molecular weight polymers. Oligomeric mixtures examined in this regard include polyesters,[3] poly(pivalolactone),[4,5] poly(2,2,4-trimethyl-1,2-dihydroquinoline),[6,7] polystyrene,[6-8] poly(propylene glycol),[7-10] poly(ethylene glycol),[10] and oligomeric antioxidants.[3]

We have reported the use of FDMS to determine accurate molecular weight averages ($\bar{M}_n$ and $\bar{M}_w$) for a series of low molecular weight polystyrene standards.[11] It was found that FDMS-derived molecular weight parameters compared favorably to values obtained by conventional techniques (vapor pressure osmometry, intrinsic viscosity, kinetic data, and gel permeation chromatography). The polystyrene oligomer molecular weights ranged up to nearly 5300 amu. Polystyrene is a relatively stable polymer in mass spectral analysis and has been used in a number of higher mass studies. Rapid heating of polystyrene has yielded molecular ions up to $\sim$3000 amu (by electron impact or chemical ionization); molecular weight distributions were determined that agreed favorably with standard values.[12] Polystyrene oligomers up to mass $\sim$11 000 have been observed by FDMS.[8] An electrospray ionization

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