Macromolecules 1988, 21, 1644–1653

Association Behavior of End-Functionalized Polymers. 2. Melt Rheology of Polyisoprenes with Carboxylate, Amine, and Zwitterion End Groups

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ABSTRACT: Viscoelastic behavior in the melt state was investigated for polyisoprenes with associating groups on the ends of the chain and compared with the behavior of their nonfunctionalized counterparts. Narrow distribution samples were prepared with a range of molecular weights by anionic polymerization; functional groups such as tertiary amine, zwitterion, carboxylic acid, and sodium carboxylate were introduced through the initiator as well as by appropriate postpolymerization reactions. Melt viscosities of the monofunctional samples were examined for evidence of end group clustering. The polymeric star model gave an excellent account of results for the sodium carboxylate series, indicating long-lived spherical clusters in the melt. Strong association was also evident in the zwitterion series, but the viscosities were much too large to explain by a simple star model, suggesting the possibility of extended aggregate structures. Judged by rheological evidence, the polymers capped by amine and carboxylic acid groups were only weakly associated. However, nearly complete dimerization of the carboxylic acid is expected for the experimental conditions used, suggesting a highly labile monomer–dimer equilibrium. Multifunctional versions of the zwitterion-capped polymers behaved like networks at room temperature but relaxed in the experimental time scales (~minutes) above 100 °C.

Introduction

In the first paper of this series,[2] we reported a study of the dilute solution properties of linear polyisoprenes with the highly polar sulfo-zwitterion group attached to one end of the chain. These polymers were found to associate strongly in aliphatic hydrocarbon solvents. Aggregation numbers (molecules per cluster) in cyclohexane and in cyclohexane–heptanol mixtures were obtained by osmotic pressure and light-scattering intensity measurements. Diffusion and viscometric data were interpreted by assuming that the aggregates would behave like polymeric stars (spherical clustering); aggregation numbers similar to those from light scattering were obtained. Some tentative conclusions were drawn about the influence of excluded volume repulsion of the polymeric tails on the chain length dependence of aggregation number. Aggregate lifetimes, likely geometries of the polar cores, the concentration dependence of aggregation, and effects of the solvent medium were also discussed.

Viscoelastic behavior in the melt state for these polymers and their amine-capped precursors are presented here. We also describe the preparation, dilute solution characterization, and melt properties of polyisoprenes with carboxylic acid and sodium carboxylate groups on one end. The rheological results are compared with predictions based on a polymeric star model for the aggregates. Finally, melt-state measurements on linear and star polyisoprenes with zwitterions on all chain ends (telechelic polymers) are presented and discussed briefly.

The structure and solid-state properties of polymers with associating groups randomly distributed along the backbone, primarily of the ionomer type, have received considerable attention.[3-8] Their viscoelastic properties in the melt state and in solution have been studied extensively by Lundberg and co-workers.[9-15] Sulfo ionomers with polystyrene and ethylene–propylene copolymer backbones were used to explore the influence of substitution level, counterion, and the solvent medium. It was shown that the rheological response could be manipulated over wide ranges through these variables and that properties could be obtained that are not achievable with nonassociating polymers. It seems reasonable to conclude from their work that viscoelasticity in such systems depends on the structure and relaxation of an association-induced network as determined by the arrangement and lifetimes of clusters formed by the associating groups. Theoretical work relating structure and properties in associating polymers is being developed but is still at an early stage.[16-22]

The literature on end-functionalized associating polymers is quite modest compared with that for the randomly functionalized species. Teyssie and co-workers have made an extensive study of viscoelasticity in α,ω-dicarboxylic acid salts with a variety of chain backbones and counterions.[23-28] Earlier work on acid and salt forms of α,ω-poly(butadiene)carboxylates suggested the possible influences of cluster lifetime and ring formation on rheological behavior.[29,30] More recent work has dealt with both linear and star polyisobutylenes[31,32] and linear polystyrenes capped with sulfonate salts[33] and with polystyrenes capped with sulfate salts.[34] For the most part, these studies were concerned with telechelic materials. Some rheological work has also been reported for polymers with only one functionalized chain end.[30-39] The monofunctional materials are structurally analogous to surfactants[40,41] and also to diblock copolymers (in the limit of a very short but highly incompatible second segment).[42-46] Comparisons of properties for random functionalization and chain end (block) functionalization have been made recently.[47,48] Theoretical work on the structure and rheological properties of monofunctional associating polymers has also begun.[49,50]

Experimental Section

Synthesis of Poly(isoprene)carboxylates. Anionic polymerizations of isoprene were conducted under vacuum-line conditions and ambient temperature in 9:1 cyclohexane–benzene mixtures.[51] Polymerization was initiated by *sec*-butyllithium with the monomer–initiator mole ratio r chosen to provide polyisoprenyl anions with the desired stoichiometric molecular weight $M_s = rm_0$, where m_0 is the monomer molecular weight. After polymerization, an aliquot was withdrawn and terminated with degassed methanol to provide several grams of a nonfunctionalized polyisoprene reference sample. An excess of tetrahydrofuran (~25% by volume) was then added to the remainder, gaseous CO_2 was admitted, and the carboxylated product was isolated by precipitation with methanol. This procedure has been found to reduce the formation of coupled byproducts to the level of only a few percent.[52]

Eight samples of lithium poly(isoprene)carboxylate (30–50 g each) were prepared with M_s ranging from 3.6×10^3 to 6.0×10^4.

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Table I
Molecular Weights for Poly(isoprene)carboxylates and Their Base Polymer Precursors

sample	$10^{-4}M_s$	$10^{-4}M_o$	sample	$10^{-4}M_s$	$10^{-4}M_o$
VII	0.40	0.36_5	III	2.3	2.1_5
VIII	1.0	1.1_5	IV	2.8	3.1_0
VI	1.5	1.3_5	I	4.9	5.2_2
V	1.5	1.4_0	II	5.7	6.2_0

They were dissolved in tetrahydrofuran and converted to the acid form by treatment with aqueous HCl. The product was precipitated with methanol, washed to remove LiCl, and dried thoroughly. Approximately half of each sample was then redissolved to form a 10% solution in 10:1 toluene–ethanol and titrated to an alizarin–thymolphthalein end point with enthanolic NaOH, the end point being tested by removal of small portions of the solution and adding a few drops of the indicator. The amount of NaOH consumed was about 5–10% less than predicted from M_s. A 20% excess of NaOH was then added, and the solution was stirred for 10–30 h. The sodium poly(isoprene)carboxylate product was precipitated with methanol, washed thoroughly to remove excess NaOH, and dried to constant weight under vacuum.

Three versions of each polymer with the same chain microstructure and base polymer molecular weight M_0 were thus made available for study—a nonfunctionalized polyisoprene, a polyisoprene capped on one end by a carboxylic acid group, and a polyisoprene capped on one end by a sodium carboxylate group. The products are specified by Roman numerals. The suffixes -COOH and -COONa denote the acid and salt versions.

Molecular Characterization of Poly(isoprene)carboxylates. Proton NMR measurements confirmed the expected microstructure for polyisoprene formed by anionic polymerization in hydrocarbon media[51]—~70% cis 1,4-addition, ~20% trans 1,4-addition, and ~8% 3,4-addition with no observable amount of 1,2-addition and insignificant variations of microstructure with molecular weight. A fairly prominent carbonyl stretch absorption was observed at 5.84 μm in the infrared spectrum for the low molecular weight carboxylated products, fading into the noise as the molecular weight increased. Size exclusion chromatography (SEC; Waters 150 °C with μ-styragel columns) in tetrahydrofuran was used to determine the base polymer molecular weight M_0. Calibration was established with a set of polyisoprene standards. All nonfunctionalized samples had the expected narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.1$ without correction for column spreading). Comparison of M_0 ($\bar{M}_w$ from SEC) with M_s is shown in Table I.

Chromatograms for the carboxylated polymers were indistinguishable from those for the corresponding precursors except for a small peak on the high molecular weight side, indicating ~2–3% of coupled product. We regard that level as acceptably small for our purposes and used the samples without fractionation.

Carboxylic acids are known to dimerize in aliphatic hydrocarbon solvents, but the equilibrium ($K_{eq} \sim 2.5 \times 10^3$ L mol^{-1}, see below) favors the dissociated state at the concentrations used for SEC measurements (~1 g L^{-1} of polymer or $<10^{-4}$ mol L^{-1} of acid groups). The equilibrium constant is smaller in aromatic solvents and probably also in polar solvents such as tetrahydrofuran.[39] Thus, as expected, no SEC evidence for association of the acid versions was found. However, we were surprised also to find no indication of association from SEC for the carboxylate salt versions. The instrument was changed over to toluene as elution solvent in hopes that a lower dielectric constant ($\epsilon = 2.4$, compared with $\epsilon = 7.4$ for tetrahydrofuran) would strengthen that association and produce some visible evidence of it. We obtained the results shown in Figure 1.

The THF elution curves for sample VIII in its nonfunctionalized, acid, and sodium salt forms are shown in Figure 1, top. The coupled product peak is too small to show up on this scale. The toluene elution curve for the nonfunctionalized version was practically unchanged (toluene and THF are both good solvents for polyisoprene), but the result for the salt version, shown in Figure 1, middle, was clearly different. Two peaks were obtained—one that eluted at the same time as the nonfunctionalized polymer, comprising about 20% of the sample, and one that eluted at a later time. The later peak is broad with a long trailing edge, and it varied in shape from scan to scan. Nothing eluted faster than the nonfunctionalized polymer, i.e., no evidence of high molecular weight clusters were found. We believe the slower peak is caused by adsorption on the columns, perhaps a result of association between sodium carboxylate groups and adventitious polar impurities attached to the gel particles.

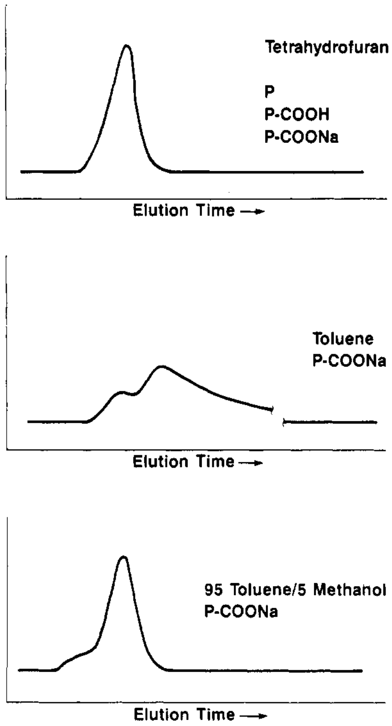


Figure 1. Size exclusion chromatographs for polyisoprene samples VIII, VIII-COOH, and VIII-COONa for various elution solvents.

The elution curve in Figure 1, bottom, was obtained for the carboxylate salt by using a mixed elution solvent, 95% toluene and 5% methanol. Methanol was added in the hope of avoiding column adsorption, and in this case we indeed found no evidence of adsorption. The main peak corresponds to the nonfunctional precursor; the shoulder at earlier times can only indicate the presence of species that are larger than the precursor. From this result we conclude that association of carboxylate salt groups occurs in toluene but that it was obscured by SEC column adsorption. With alcohol present, the adsorption is suppressed, and the effect of salt group association becomes visible, albeit in some presumably attenuated form because alcohol would tend also to reduce polar association. Tetrahydrofuran appears to be polar enough to suppress both column adsorption and association.

Dilute solution osmotic pressure in toluene, small-angle light-scattering intensity in cyclohexane, and viscosity in both cyclohexane and toluene were measured for selected samples of the nonfunctionalized precursors by using procedures that are described elsewhere.[2,53] Values of number-average molecular weight $\bar{M}_n$ and weight-average molecular weight $\bar{M}_w$, intrinsic viscosity $[\eta]$, second virial coefficient A_2, and Huggins coefficient k_H were obtained and found to be in excellent agreement with expectations based on the M_0 values and previous results for similar polyisoprenes.[53]

A few measurements were also made on the acid versions; no significant differences from the results for the nonfunctionalized precursors were found. The dilute solution behavior of the salt versions is decidedly different, however, but also discouragingly complicated. Solution viscosities, for example, were found to drift downward with time and required a few days to several weeks for stabilization, depending on the polymer concentration. Rigorous exclusion of moisture from the system seemed to have little effect on that behavior. We assume it reflects a very slow dissociation of the carboxylate salt clusters that had been formed in the melt prior to dissolution. Intrinsic viscosities determined with freshly prepared solutions were considerably larger than those determined with equilibrated solutions (Figure 2, right). Intrinsic viscosities from equilibrated solutions were the same as or slightly

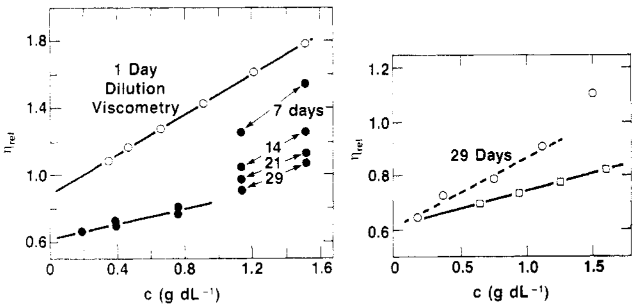


Figure 2. Dilution solution viscosities for polyisoprene samples II and II-COONa in toluene at 25 °C. The figure on the left shows relative viscosity $\eta_{rel} = (\eta - \eta_s)/\eta_s c$ versus c for sample II-COONa measured at various times after stock solution preparation. The figure on the right compares η_{rel} versus c for the nonfunctionalized sample II (□) and sample II-COONa after the individual solutions had been allowed to equilibrate for about 1 month (○).

larger than the values for the nonfunctionalized precursors. The Huggins coefficients were always larger, as observed for zwitterion-capped polyisoprenes.[2]

Light-scattering intensity was also larger for freshly prepared solutions of the carboxylate salt samples and drifted downward over a period of several days. More surprisingly, however, the scattering intensity drifted downward for several hours after injection into the scattering cell even for solutions that had been prepared several weeks earlier. We were led to conclude that aggregation is somehow induced by flow—an effect that presumably would influence our viscosity results as well. Molecular weights were obtained for two samples from equilibrated scattering data (several weeks in solution and ~10 h after injection into the scattering cell). Weight-average aggregation number $N_w = \bar{M}_w/M_o$ was 6.8 for sample III-COONa and 1.8 for sample II-COONa, indicating significant association for the salt-capped polyisoprenes in cyclohexane and a decrease in association with increasing base polymer molecular weight, as also found for the zwitterion-capped polyisoprenes.[2]

Osmotic pressures were measured for solutions of sample II-COONa in both cyclohexane and toluene. In this case, however, no drifts with time were observed, and the values of $\bar{M}_n$ and A_2 gave no indication of association. Work on dilute solutions of the salt-capped polymers was abandoned for the present time in view of their complicated and seemingly contradictory behavior.

Rheological Measurements. Linear viscoelastic response of end-functionalized polymers was examined in the melt state over a wide frequency range and at a number of temperatures. Several groups of narrow distribution ($\bar{M}_w/\bar{M}_n < 1.1$) samples were studied:

(a) Polyisoprenes with carboxylic acid and sodium carboxylate groups on one end of the chain.[2] Base polymer molecular weights are given in Table I.

(b) Polyisoprenes with dimethylamine and sulfo-zwitterionic groups on one end of the chain. Base polymer molecular weights and chain microstructures are given in Table II. The zwitterion-capped versions were prepared by treating amine-capped precursors with cyclopropanesultone and are designated by the suffix Zw. The amine-capped precursors associate only weakly in aliphatic hydrocarbons. The zwitterion-capped versions associate strongly, and the number of chains per aggregate (Table II) decreases with increasing M_o.[2]

(c) Hydrogenated polyisoprenes with the amine and zwitterion groups on one end of the chain. Samples C and A (Table II) were hydrogenated with a $Pd/CaCO_3$ catalyst[54] to give samples C-H and A-H. Portions of these materials were then treated with cyclopropanesultone to give samples C-H-Zw and A-H-Zw.

(d) Linear and star polyisoprenes with amine or zwitterion groups on all chain ends and with base polymer molecular weights given in Table II. Samples 2A, 2B, and 2C, are linear telechelic polymers, sample 3A is a three-arm star telechelic, and sample 12A is a twelve-arm star telechelic. The zwitterion versions of these polymers form gels in aliphatic hydrocarbons but dissolve readily when a small amount of alcohol (~3%) is added.[2]

Dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured for frequencies in the range $10^{-3} < \omega < 10^{2}$ s^{-1} with a Rheometrics System-Four rheometer. Zero-shear viscosities were obtained wherever possible from the limiting behavior of loss modulus at low frequencies:[55]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \qquad (1)$$

The corresponding limiting behavior for storage modulus ($G'(\omega) \propto \omega^2$)[55] was not in general attained for the functionalized polymers, so the recoverable compliance J_e° could not be determined. Measurements were made on selected samples of the functionalized samples a few weeks after preparation, but the behavior was found to change over a period of a few months under vacuum at room temperature in the melt state, in some cases by a substantial amount. The dynamic moduli changed in shape and the viscosity increased over the period of a few months, probably the result of a slow cluster equilibration. The results reported here were obtained after several months of room-temperature storage under vacuum on what appear to be fully equilibrated melts.

Results at different temperatures were reduced to master curves by using time–temperature superposition:[55]

$$G'(\omega;T) = b_T G'(\omega a_T;T_0) \qquad (2)$$

$$G''(\omega;T) = b_T G''(\omega a_T;T_0) \qquad (3)$$

where a_T and b_T are shift factors for the frequency and modulus scales at temperature T relative to some chosen reference temperature T_0 ($a_T = b_T = 1$ at $T = T_0$). A reference temperature of 25 °C was used for the polyisoprenes and 100 °C for the hydrogenated polyisoprenes to allow direct comparisons with results for the nonfunctionalized species.[54,56] Superposition was found to be reasonably good in all cases, though not quite as precise as obtained for nonassociating polymer melts. Association did affect the shift factors, however. The ratio of viscosities at two temperatures is a useful measure of temperature dependence:

$$\eta(T)/\eta_0(T_0) = a_T b_T \qquad (4)$$

and provides a convenient method for comparing functionalized polymers with their nonfunctionalized counterparts. That measure was used for all except the zwitterion-capped polymers, for which η_0 could not always be obtained. For those, a_T and b_T were established and compared separately.

Results for the carboxylate-capped polymers are given in Table III–V and for the amine- and zwitterion-capped polymers in Tables VI–VIII.

Results and Discussion

Linear chains with an associating group at one end (molecular weight = M_o) become the arms of "star" molecules if the associating groups aggregate into spherical clusters. A melt of such aggregates should then behave

Table II
Molecular Weights, Microstructures, and Aggregation Numbers in Cyclohexane of Amine-Capped and Zwitterion-Capped Polyisoprenes

			$\bar{N}_n$	
sample[a]	$10^{-4}M_o$	% 3,4	amine	zwitterion
G and G-Zw	1.6_5	20		22
E and E-Zw	1.6_7	20	1.0_9	12
C and C-Zw	2.0_8	18	1.3_5	31
A and A-Zw	4.5_3	15	1.1_3	$14._5$
B and B-Zw	7.4_0	12	1.0_3	$4._9$
D and D-Zw	8.5_6	8	1.2_3	$4._0$
I and I-Zw	$10._7$	9		$3._3$
J and J-Zw	$17._6$	7		$1._4$
2B and 2B-Zw	1.8	28		insoluble
2C and 2C-Zw	2.7	22		insoluble
2A and 2A-Zw	$12._9$	13	1.6_5	insoluble
3A and 3A-Zw	$6._6$	18	1.3_7	insoluble
12A and 12A-Zw	$24._5$	17	0.9_9	insoluble

[a] The prefactor 2 designates the difunctional polymers (linear telechelics); 3 and 12 designate the number of arms for the star telechelics, i.e., star polymers with all ends functionalized (see ref 2).

Table III
Temperature Dependence of Melt Viscosity in Poly(isoprene)carboxylates and Nonfunctionalized Precursors

sample	$10^{-4}M_o$	end group	$\eta_0(25)$, P	$\eta_0(50)/\eta_0(25)$	$\eta_0(75)/\eta_0(25)$
VII	0.36_5	H	2.8×10^1	0.23	0.082
		COOH	5.0×10^1	0.21	0.068
		COONa	4.0×10^2	0.19	0.058
VIII	1.1_5	H	3.3×10^2	0.21	
		COOH			
		COONa	3.6×10^3	0.19	0.050
VI	1.3_5	H	4.2×10^2	0.21	
		COOH	5.6×10^2		
		COONa	4.6×10^3	0.15	0.024
V	1.4_0	H	4.5×10^2	0.22	0.073
		COOH	6.2×10^2	0.19	0.065
		COONa	5.0×10^3	0.19	0.056
III	2.1_5	H	1.4×10^3	0.21	0.066
		COOH	2.2×10^3	0.18	0.055
		COONa	2.3×10^4	0.14	0.035
IV	3.1_0	H	4.5×10^3	0.20	0.058
		COOH	5.1×10^3	0.19	0.057
		COONa	1.0×10^5	0.20	0.060
I	5.2_2	H	2.6×10^4	0.21	0.065
		COOH	2.9×10^4	0.20	0.059
		COONa	5.2×10^5	0.18	0.044
II	6.2_0	H	4.0×10^4	0.20	0.065
		COOH	5.2×10^4	0.19	0.058
		COONa	2.2×10^6	0.18	0.044

Table IV
Melt Viscosity Ratios for Poly(isoprene)carboxylates at 25 °C

sample	$10^{-4}M_o$	$\eta_0(\text{COOH})/\eta_0(\text{H})^a$	$\eta_0(\text{COONa})/\eta_0(\text{H})^a$
VII	0.36_5	1.8	14
VIII	1.1_5		11
VI	1.3_5	1.4	11
V	1.4_0	1.4	11
III	2.1_5	1.6	16
IV	3.1_0	1.1	22
I	5.2_2	1.1	20
II	6.2_0	1.3	~55

[a] $\eta_0(\text{H})$ indicates the melt viscosity of the nonfunctionalized precursor.

mechanically as a melt of star polymers with arm molecular weight $M_a = M_o$ if the clusters do not interact and the association lifetimes are sufficiently long. The viscoelastic properties of star polymers in the melt state are insensitive to the number of arms per molecule, but they depend very strongly on arm length.[56,57] In the entanglement region η_0 increases exponentially with M_a. Three-arm stars have viscosities that are about 80% of those for four-arm stars with the same arm length, but with from 4 to 18 arms per molecule the viscosities are independent of branch point functionality.[56] Considerable data are now available on the molecular weight dependence of dynamic response in linear and star polyisoprenes in the melt state,[56] so the possibility that the end groups associate to form long-lived spherical clusters can be tested rather directly.

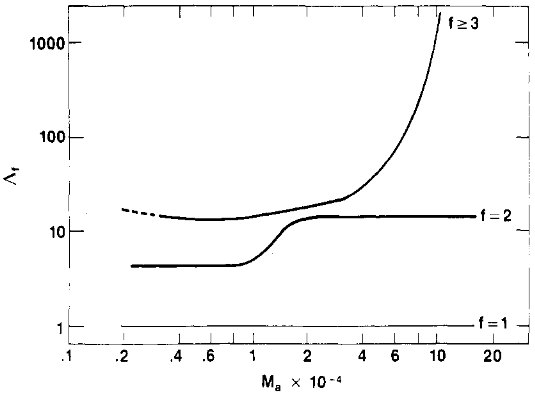


Figure 3. Melt viscosity of *f*-arm star polyisoprenes divided by the melt viscosity of free arm as a function of arm molecular weight. The line for $f = 2$ corresponds to a "two-arm star", i.e., a linear polyisoprene whose molecular weight is twice that of the arm.

The case of strictly pairwise association is also of interest. Carboxylic acids are known to dimerize in hydrocarbon media,[39,58-60] and the equilibrium (see below) favors dimer formation under our conditions of temperature and acid group concentration (0.015–0.25 mol L^{-1}). The dimer of a polymeric carboxylic acid is a linear polymer with $M = 2M_o$, so dimerization has predictable effects on dynamic response and melt viscosity if the dimer lifetimes are long enough.

Viscosity data for nonfunctionalized linear and star polyisoprenes[56] were used to construct the relationship between M_a and Λ_f, the ratio of melt viscosity for an f-arm star polymer to that for a linear polymer with a molecular weight of M_a. The result is shown in Figure 3. These curves should apply to end-associated semitelechelics if the clusters are spherical (or at least noninteracting) and sufficiently long-lived. Thus, the curve for $F \geqslant 3$ corresponds to sufficiently long-lived spherical aggregates with three or more groups per cluster (the difference between $f = 3$ and $f = 4$ or more is negligible on this scale), and the curve for $f = 2$ corresponds to sufficiently long-lived dimers.

Although the results are based on polyisoprene data at 25 °C, they should also be applicable at other temperatures because a_T values are essentially the same for linear and star polyisoprenes.[54-56] Such curves may possibly be universal if M_a were normalized by M_e, the entanglement molecular weight of the species,[55] but we have not yet tested that possibility with data for other polymers. We will use these curves to examine the validity of the spherical cluster model for monofunctional associating polymers.

Poly(isoprene)carboxylic Acids and Poly(isoprene)carboxylate Salts. Dynamic moduli for the nonfunctionalized carboxylated polymer precursors have shapes that are typical of linear polymers with narrow molecular weight distribution.[61] The values of η_0 at 25 °C (Table III) agree with results for other polyisoprenes with

Table V
Temperature Dependence of Melt Viscosity for Poly(isoprene)carboxylic Acids and Precursors

sample	-40 °C	-25 °C	0 °C	25 °C	50 °C	75 °C
VII-COOH	4.1×10^5	1.9×10^4	5.4×10^2	1.05×10^1	1.05×10^1	3.4×10^0
VII	1.5×10^5	6.8×10^3	2.6×10^2	2.8×10^1	6.4×10^0	2.3×10^0
$\eta_0(\text{COOH})/\eta_0(\text{H})^a$	2.7	2.8	2.1	1.8	1.6	1.5
VI-COOH	7.8×10^6	2.5×10^5	6.6×10^3	5.6×10^2	1.14×10^2	3.5×10^1
VI	3.7×10^6	1.6×10^5	4.2×10^3	4×10^2	8.6×10^1	2.8×10^1
$\eta_0(\text{COOH})/\eta_0(\text{H})^a$	2.1	1.6	1.6	1.4	1.3	1.2_5

[a] $\eta_0(\text{H})$ indicates the melt viscosity of the nonfunctionalized precursor.

Table VI
Melt Viscosity of Amine-Capped and Zwitterion-Capped Polyisoprenes

sample[a]	$10^{-4}M_o$	η_0(25 °C), P	η_0/η_0(ref)
G	1.6_5	$1.5_3 \times 10^3$	1.4
G-Zw		3.1×10^6	2.8×10^3
G-ref		(1.1×10^3)	
E	1.6_7	$1.7_5 \times 10^3$	1.6
E-Zw		1.0×10^5	9.1×10^2
E-ref		(1.1×10^3)	
C	2.0_8	6.1×10^3	3.2
C-Zw		$>2.3 \times 10^6$	$>1.2 \times 10^3$
C-ref		(1.9×10^3)	
A	4.5_3	2.3×10^4	0.77
A-Zw		$>1.0 \times 10^7$	$>3.3 \times 10^2$
A-ref		(3.0×10^4)	
B	7.4_0	1.5×10^5	1.1_5
B-Zw		$>5 \times 10^7$	$>3.8 \times 10^2$
B-ref		(1.3×10^5)	
D	8.5_6	3.7×10^5	2.3
D-Zw		$>5 \times 10^7$	$>3.2 \times 10^2$
D-ref		(1.6×10^5)	
I	$10._7$	4.1×10^5	1.0
I-Zw		6.8×10^7	1.7×10^2
I-ref		(4.0×10^5)	
J	$17._6$	3.6×10^6	1.6
J-Zw		3.8×10^7	1.7×10^1
J-ref		(2.2×10^6)	
2B	1.8	2.3×10^3	0.82
2B-Zw		3.3×10^{10}	1.2×10^7
2B-ref		(2.8×10^3)	
2C	2.7	6.8×10^3	1.1
2C-Zw		7.1×10^9	1.2×10^6
2C-ref		(6.1×10^3)	
2A	$12._9$	3.7×10^6	3.7
2A-Zw		5.1×10^{11}	5.1×10^5
2A-ref		(1.0×10^6)	
3A	6.6_0	1.5×10^5	2.1
3A-Zw		1.4×10^{11}	2.0×10^6
3A-ref		(7.1×10^4)	
12A	$24._5$	1.1×10^5	1.5
12A-Zw		4.2×10^{10}	5.8×10^4
12A-ref		(7.2×10^4)	

[a] The suffix ref indicates a value calculated from literature data for nonfunctionalized polyisoprene as described in the text.

Table VII
Melt Viscosity of Amine-Capped and Zwitterion-Capped Hydrogenated Polyisoprenes

sample[a]	$10^{-4}M_o$	η_0(100 °C), P	η_0/η_0(ref)	η_0/η_0(arm)
C-H	2.0_8	5.2×10^2	1.0	
C-Zw-H		2.0×10^4	40	17[b]
C-H ref		(5.0×10^2)		
A-H	4.5_8	1.1×10^4	1.4	
A-Zw-H		3.6×10^6	450	240[b]
A-H-ref		(8.0×10^3)		

[a] The suffix ref indicates a value calculated from literature data for nonfunctionalized hydrogenated polyisoprene as described in the text. [b] Values for nonfunctionalized hydrogenated polyisoprene stars with $M_a = M_0$, obtained as described in the text.

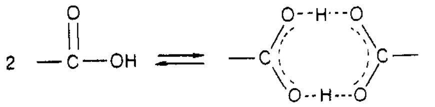
Table VIII
Temperature-Shift Factors for Zwitterion-Capped Polyisoprenes (T_0 = 25 °C) and Hydrogenated Polyisoprenes (T_0 = 100 °C)

sample	$10^{-4}M_o$	T, °C	$\log a_T$	$\Delta \log a_T$[a]	b_T
G-Zw	1.6_5	50	−0.76	0.04	1.20
		75	−1.44	−0.07	1.37
		100	−2.03	−0.25	1.72
E-Zw	1.6_7	0	1.48	0.23	0.78
		50	−0.85	−0.05	1.26
		75	−1.57	−0.20	1.35
C-Zw	2.0_8	0	1.51	0.28	0.74
		50	−0.77	0.00	1.10
A-Zw	4.5_3	50	−0.85	−0.07	1.0
		75	−1.37	−0.04	1.0
B-Zw	7.4_0	0	1.57	0.42	0.89
		50	−0.85	−0.15	1.10
		75	−1.50	−0.29	1.35
D-Zw	8.5_6	50	−0.79	−0.11	0.79
		75	−1.59	−0.42	1.78
		100	−2.22	−0.66	1.78
I-Zw	$10._7$	50	−0.79	−0.11	1.20
		75	−1.41	−0.24	1.43
		125	−2.41	−0.56	1.83
J-Zw	$17._6$	50	−0.71	−0.03	1.10
		75	−1.29	−0.12	1.23
		125	−2.00	−0.15	1.41
2B-Zw	1.8	75	−1.70	−0.09	1.08
		125	−3.75	−1.43	1.14
		150	−4.06	−1.47	1.21
2C-Zw	2.7	75	−2.32	−0.92	1.11
		125	−4.17	−2.07	1.68
		150	−5.04	−2.66	1.59
2A-Zw	$12._9$	75	−2.10	−0.83	1.17
		125	−3.59	−1.67	1.36
3A-Zw	6.6_0	75	−2.43	−1.08	1.35
		125	−4.22	−2.17	1.70
12A-Zw	$24._5$	75	−2.31	−0.96	1.20
		125	−4.46	−2.41	2.00
C-Zw-H	2.0_8	25	2.54	0.45	0.54
		50	1.63	0.41	0.61
		75	0.81	0.28	0.73
A-Zw-H	4.5_3	25	3.28	1.28	0.54
		50	2.01	0.83	0.70
		75	0.97	0.44	0.86
		125	−0.30	0.10	1.09
		175	−1.38	−0.41	1.49

[a] $\Delta \log a_T = \log a_T - \log a_T(\text{ref})$, where a_T(ref) is the shift factor for nonfunctionalized polymer with the same chemical microstructure, calculated from literature data as described in the text.

$\sim$8% 3,4 content and the same molecular weight.[54,56] The temperature dependence of viscosity, $\eta_0(50)/\eta_0(25) \sim 0.21$ and $\eta_0(75)/\eta_0(25) \sim 0.065$, is also similar. Dynamic moduli for the acid form were practically unchanged in shape from the base polymer results, but η_0 at 25 °C is higher than the base polymer value (Table IV) by factors of 1.1–1.8, suggesting some dimer formation by the acid groups. (The presence of 2–3% coupled product is not enough to cause such differences.) The temperature dependence of viscosity is also larger: the viscosity of the acid version divided by the viscosity of the nonfunctionalized version increases with decreasing temperature (Table V). There is a mild trend toward increasing viscosity elevation with decreasing molecular weight, i.e., with increasing acid group concentration in the melt. However, as we discuss now, the elevations are much less than would be expected from the equilibrium extent of acid group dimerization.

The dimerization of carboxylic acids in organic media has been studied extensively:[58,59]



(5)

The equilibrium constant K_{eq} can be expressed in terms of C_0, the molar concentration of acid groups in the liquid, and x, the fraction that are dimerized:[30]

$$K_{eq} = \frac{x}{2(1-x)^2 C_0} \tag{6}$$

The temperature dependence of K_{eq} is governed by the enthalpy of reaction ΔH:

$$\ln K_{eq}(T_2)/K_{eq}(T_1) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

Earnest and MacKnight measured K_{eq} at several temperatures for the carboxylic acid groups in ethylene–methacrylic acid copolymers,[60] obtaining $\Delta H = -12$ kcal mol^{-1} and equilibrium constants that extrapolate (eq 7) to $K_{eq} \sim 2.5 \times 10^3$ L mol^{-1} at 25 °C. Similar values of K_{eq} are obtained for various carboxylic acids in carbon tetrachloride, but smaller values, $K_{eq} \sim 3.7 \times 10^2$ L mol^{-1}, are obtained in benzene and larger values, $K_{eq} \sim 6 \times 10^3$ L mol^{-1}, in heptane (see ref 58 and 62). Norrby[39] obtained $K_{eq} = 2 \times 10^3$ L mol^{-1} for acid-capped polystyrene at Θ conditions in cyclohexane (34.6 °C).

We have used $K_{eq} = 2.5 \times 10^3$ L mol^{-1} to estimate the dimerized fraction in our acid-capped polyisoprenes in the melt at 25 °C. From the results cited above, this is a reasonable but probably minimum value for aliphatic carboxylic acids in an apolar, nonaromatic medium. With $C_0 = \rho/M_0$ and $\rho = 899$ g L^{-1} for polyisoprene at 25 °C,[54] eq 6 becomes

$$x/(1-x)^2 = 4.5 \times 10^6/M_0 \qquad (8)$$

Molecular weights for the acid-capped polyisoprenes range from $M_0 = 0.365 \times 10^4$ to 6.2×10^4, giving fractions of acid groups in dimers from eq 8 that range from $x = 0.97$ to $x = 0.88$. Thus, nearly all the acid groups should be dimerized in the melt at 25 °C, and we would expect linear chains with molecular weights close to $2M_0$ for all samples.

The melt viscosities are much smaller than anticipated from such equilibrium considerations, however. Thus, it is known that η_0 is approximately proportional to $\bar{M}_w^{3.4}$ in binary mixtures of entangled linear chains.[55] The apparent $\bar{M}_w$ of each sample can thus be estimated from data on η_0 versus M for linear polyisoprenes[56] (Figure 3) and used to calculate an apparent x from the easily demonstrated relationship $M_w = M_0(1 + x)$. The values obtained in this way range from $x \sim 0.3$ for small M_0 to $x \sim 0.03$ for large M_0, corresponding to an apparent equilibrium constant that is about 3 orders of magnitude smaller than $K_{eq} = 2.5 \times 10^3$ L mol^{-1} as estimated above.

Otocka et al.[29] noted a similar discrepancy in the values of K_{eq} estimated from the melt viscosity data of Kraus and Gruver[30] for monofunctional poly(butadiene)carboxylic acids. Worsfold[37] has provided an elegant demonstration of the same phenomenon for another dimerizing system. These workers have suggested that the discrepancy is related to the individual rates of association and dissociation. Thus, if these rates are large compared with the testing frequency or shear rate, the chains may indeed spend the majority of time as dimers (consistent with K_{eq}) yet relax mainly during that small fraction of time spent in the more mobile nonassociated state. We have been unable to find any literature estimates of the rate constants for dimerization of carboxylic acids. Theoretical aspects of this potentially crucial feature of relaxation in associating species have recently been addressed.[50]

Dynamic moduli for the sodium carboxylates differ considerably from those for the nonfunctionalized base polymers. The curves are shifted to lower frequencies, and the shapes are broadened in a manner suggesting polydispersity or star-branched structures. The example of IV-COONa ($M_0 = 3.1_0 \times 10^4$) is shown in Figure 4 along with $G'(\omega)$ and $G''(\omega)$ for a four-arm polyisoprene star with an arm molecular weight similar to M_0 ($M_a = 3.67 \times 10^4$). Even allowing for the mismatch in M_0 and M_a, the shapes are clearly different; the star model is evidently too simple to represent the full dynamics. However, it does provide a remarkably good representation of the viscosity, as shown in Figure 5. The data for carboxylates salts, $\Lambda = \eta_0(\mathrm{COONa})/\eta_0(\mathrm{H})$ from Table IV, lie close to the star polymer curve over the entire range of molecular weights. The data for the acid form, shown in the same figure, show very little evidence of association, as discussed earlier.

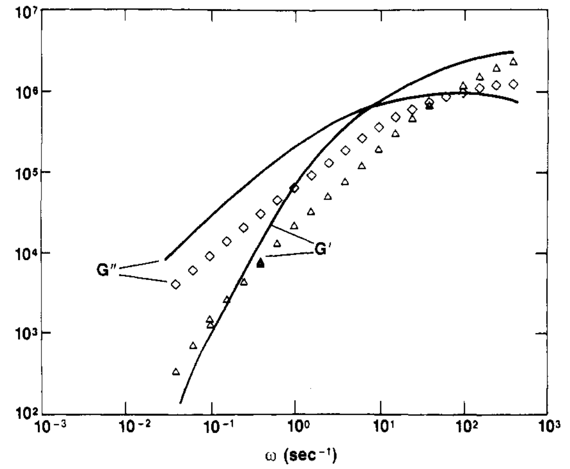


Figure 4. Comparison of dynamic moduli for a four-arm polyisoprene star and a poly(isoprene)carboxylate salt in the melt state at 25 °C. Data for the star ($M_a = 3.7 \times 10^4$) are shown by solid lines; the points are data for sample IV-COONa ($M_0 = 3.1 \times 10^4$).

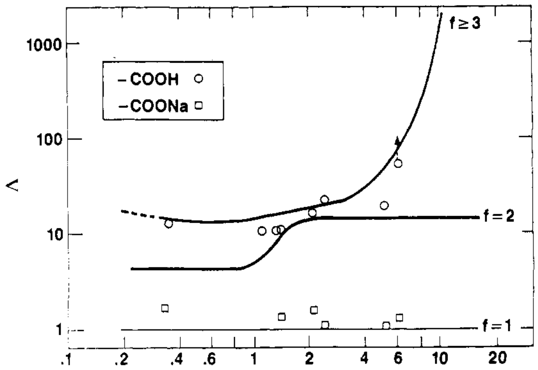


Figure 5. Comparison of melt viscosities for the poly(isoprene)carboxylate salts and poly(isoprene)carboxylic acids with nonfunctionalized linear and star polyisoprenes at 25 °C. The solid lines are taken from Figure 3; the points are viscosities for the acid (□) and sodium salt (○) versions divided by the corresponding viscosities for the nonfunctionalized versions.

The temperature dependence of viscosity for the carboxylate salt polymers is unremarkable. The values of $\eta_0(50)/\eta_0(25)$ in Table III are essentially the same as the base polymer values, and $\eta_0(75)/\eta_0(25)$, though more erratic and generally smaller on average than base polymer values, are still not very different. The carboxylate salt polyisoprenes would be difficult to distinguish from nonfunctionalized polyisoprenes on the basis of thermal response alone.

Polyisoprene and Hydrogenated Polyisoprene Amines and Zwitterions. 1. Polymers with One End Functionalized. The dynamic moduli, temperature coefficients, and viscosity of the amine-capped polymers were changed little if at all from those for nonfunctionalized polyisoprenes of the same molecular weight and 3,4 content. The comparisons are not as direct as in the carboxylate series because nonfunctionalized precursors are not available (the tertiary amine function was introduced through the initiator, not by postpolymerization chemistry). Values of η_0 at 25 °C for polyisoprenes of ~8% 3,4 content were estimated for the M_0 values in Table II with the correlations in ref 56 and then corrected for the effect of 3,4 content with the results in ref 54. The results, designated as η_0(ref), are given in Table VI. Similar procedures were used to estimate η_0(ref) for hydrogenated polyisoprenes (Table VII). In all cases η_0/η_0(ref) for the

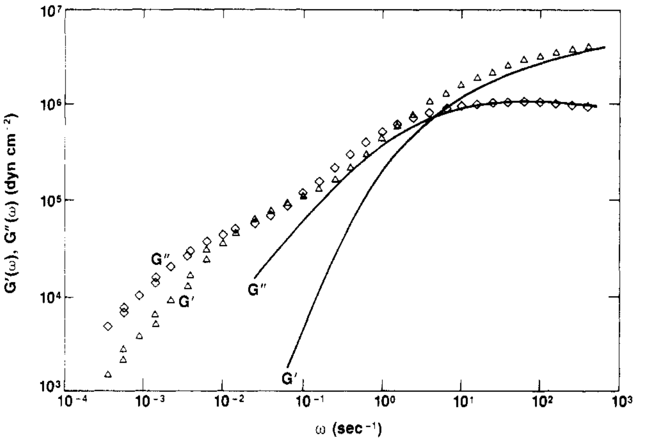


Figure 6. Comparison of dynamic moduli for a four-arm polyisoprene star and a monofunctional zwitterion polyisoprene in the melt state at 25 °C. Data for the star ($M_a = 4.4 \times 10^4$) are shown by the solid lines; the points are data for sample A-Zw ($M_o = 4.61 \times 10^4$).

amine-capped polymers does not depart appreciably from unity. The temperature dependence of viscosity (Table VIII) increases in the expected way with 3,4 content,[54] but no indication of unusual behavior that could be attributed to the amine groups is found.

The zwitterion polymers behave very differently. The dynamic moduli are broadened and shifted to much lower frequencies, but, unlike the carboxylate salt behavior, the temperature coefficients are also changed significantly (Table VIII). Moreover, the shapes of $G'(\omega)$ and $G''(\omega)$ are not merely broadened. A second regime of relaxation appears at very low frequencies in some of the samples, and the response in this regime was found to be unusually sensitive to the imposed strain.

The anomalous response at low frequencies is illustrated in Figure 6 with the data for sample A-Zw ($M_o = 4.6_1 \times 10^4$). The multiple points at each frequency in the low-frequency range are measurements for different strain amplitudes. The dynamic moduli for a four-arm star polyisoprene with arm molecular weight closely matched to M_o ($M_a = 4.4 \times 10^4$) are shown for comparison. There is some resemblance between the zwitterion and star polymers at intermediate and high frequencies (not greatly different from the star versus carboxylate salt comparison in Figure 4). Roughly speaking, the anomalous response of the zwitterion polymer at low frequencies corresponds to a shift of contributions from the longest few relaxation times for either a star polymer or a carboxylate salt. The response in that regime, however, remains nonlinear even at the lowest strain amplitudes we could impose and still obtain a measurable torque signal. The structures responsible for the low-frequency response are evidently very delicate and easily disrupted. Only lower bounds for η_0 could be obtained for some samples because of this nonlinearity.

Low-frequency anomalies were observed only in samples of low and intermediate molecular weights. At high molecular weights the response more closely resembles the behavior of conventional star polymers. The moduli for sample I-Zw ($M_o = 10.7 \times 10^4$) and the corresponding star ($M_a = 10.5 \times 10^4$) are compared in Figure 7. The value of η_0 for the star is larger by a factor of 5, but, with data for the star shifted along the frequency axis to compensate for that difference, the shapes are seen to be rather similar.

Modulus master curves for the monofunctional zwitterion series are shown in Figures 8 and 9. Relaxation is generally slower for samples with larger base polymer molecular weights, but the trends are not systematic.

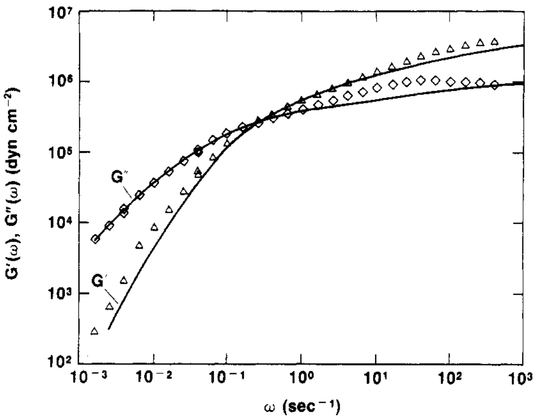


Figure 7. Comparison of dynamic moduli for a four-arm polyisoprene star and a monofunctional zwitterion polyisoprene in the melt state at 25 °C. Data for the star ($M_a = 10.5 \times 10^4$) are shown by the solid lines; the points are data for sample I-Zw ($M_o = 10.7 \times 10^4$).

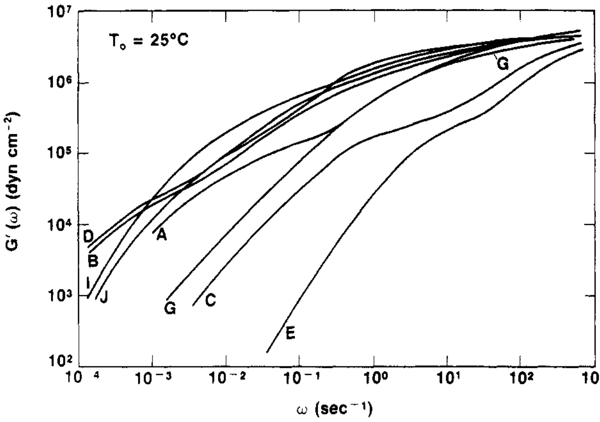


Figure 8. Storage modulus master curves for the monofunctional zwitterion polyisoprenes.

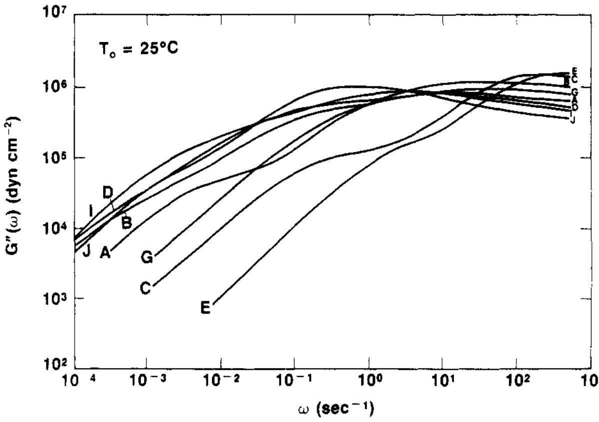


Figure 9. Loss modulus master curves for the monofunctional zwitterion polyisoprenes.

Thus, samples C-Zw, E-Zw, and G-Zw have similar values of M_o, yet they differ considerably in response. Also, sample G-Zw relaxes conventionally, but samples with similar and larger M_o show the anomalous low-frequency behavior; samples B-Zw and D-Zw relax more slowly than samples I-Zw and J-Zw, although the latter have larger M_o. Similar irregularities are observed in dilute solution association (Table II). The temperature-shift factors obtained in constructing the master curves are listed in Table VIII. The values of both a_T and b_T shift somewhat more rapidly than those for nonfunctional polyisoprenes of the same microstructure. No systematic pattern of dependence on M_o is evident.

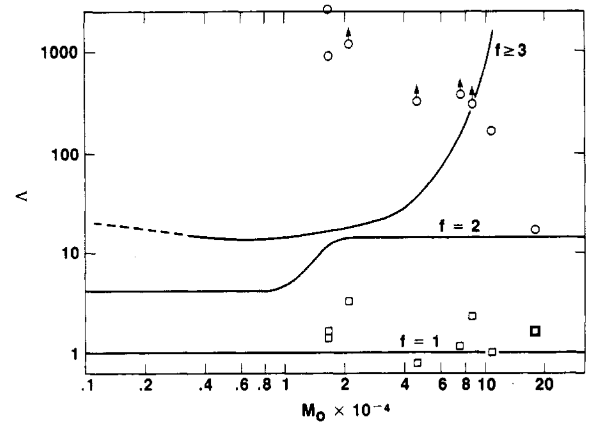


Figure 10. Comparison of melt viscosities for the monofunctional polyisoprene zwitterion and amines with nonfunctionalized linear and star polyisoprenes at 25 °C. The solid lines are taken from Figure 3. The points are viscosities for the amine (□) and zwitterion (○) versions divided by viscosities for nonfunctionalized linear polyisoprenes of the same molecular weight and microstructure.

Viscosities for the amine and zwitterion polyisoprenes at 25 °C are compared with the predictions for long-lived spherical clustering (starlike structures) in Figure 10, where $\Lambda = \eta_0/\eta_0(\text{ref})$ from Table VI are plotted as a function of M_0. The amine polymers, like the carboxylic acids, show little evidence of association in the melt state. At low and intermediate molecular weights the viscosities of the zwitterion polymers are much too large to be accounted for by simple starlike structures alone. In dilute solutions there is a systematic reduction in aggregation number N with increasing M_0.[2] That is consistent with the reduced values of $\eta_0/\eta_0(\text{ref})$ in the high molecular weight samples. However, in dilute solution the reduction in N with M_0 was attributed to an excluded volume repulsion of the polymeric tails, and that interaction should be screened out in the melt. Moreover, the zwitterion concentration in the melt is larger by factors of 10^2–10^4 than that used for the dilute solution measurements. Thus, one would think that even mild association in dilute solution would result in large aggregates in the melt. One possibility that should be considered is that the zwitterion aggregates formed over long times in the melt state are so long-lived that they persist for long times after the melt has been diluted with an inert solvent. The aggregation numbers obtained by dilute solution measurements would in that case reflect the clustering that exists in the melt, a frozen equilibrium rather than a mobile equilibrium of aggregates in solution.

Apart from questions about equilibrium, however, there is still the anomalous response and high viscosities at low and moderate M_0 to explain. We considered the possibility that some side reaction during the sultone treatment might have altered the polyisoprene structure but found no significant change in the melt rheology of a nonfunctionalized polyisoprene after it had received the same treatment. We also considered the possibility of weak association between zwitterion groups and the polyisoprene double bonds, but that seems ruled out by the observation of similar effects in the hydrogenated polyisoprene zwitterions. Thus, sample C-Zw-H shows the anomalous response at low frequencies, and the values of $\eta_0/\eta_0(\text{ref})$ for C-Zw-H and A-Zw-H are somewhat larger than the corresponding Λ for hydrogenated polyisoprene stars with the same microstructure and arm molecular weight (Table VII). *We assume that both these effects are related to some larger scale interaction of zwitterion groups in the melt state.*

The ordering of clusters and tendency of associating groups to form extended morphologies (lamellae, strings, etc.) are well-known in surfactant systems[40] and also in microphase-separated block copolymer.[42] It is, therefore, conceivable that the zwitterion groups in our polymers produce similar structures. Indeed, recent theoretical work in our laboratory has shown that a disklike or tubelike microphase of zwitterions is energetically preferred over spherical clusters,[63] and earlier work on randomly functionalized polysiloxane zwitterionomers has presented rather convincing evidence in favor of a lamellar morphology.[64] Cluster ordering or extension would result in a larger scale organization of the melt than that produced by simple spherical clustering without intercluster interactions, and the melt viscosities might then easily exceed the star polymer values. Moreover, such extended structures would likely be very delicate in a mechanical sense because they are held together only by association forces. That would account for the remarkable strain sensitivity found at low frequencies. Indeed, anomalous strain sensitivity has already been observed in block copolymer melts[44] and in telechelic polymers[26] where some large-scale ordering is known to occur.

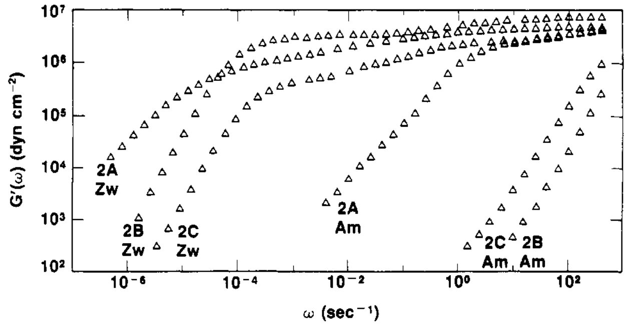


Figure 11. Comparison of storage modulus master curves for linear telechelic amine and zwitterion polyisoprenes samples (T_0 = 25 °C).

2. Polymers with All Ends Functionalized. Viscosities of the amine-capped telechelic polymers are only slightly elevated relative to nonfunctionalized polyisoprenes with the same microstructure and chain architecture (Table VI). Time–temperature superposition is obeyed, and the shift factors are essentially identical with those for nonfunctional polyisoprene (Table VIII). As in the case of monofunctional amine polymers, little indication of association is found.

Very large changes in melt theology are produced upon conversion to the zwitterion form. The products are rubbery solids at room temperature, but flow does occur at elevated temperatures. The viscosities reported for the zwitterion telechelics in Table VI were obtained by extrapolating results from higher temperatures to 25 °C by using time–temperature superposition. Superposition of the modulus data worked fairly well, although the temperature dependence of a_T was much larger than obtained for nonfunctionalized polyisoprene and even for the monofunctional zwitterion polymers (Table VIII). Storage modulus master curves for the amine and zwitterion versions are compared in Figure 11 for the linear telechelics, in Figure 12 for the 3-arm telechelic star, and in Figure 13 for the 12-arm telechelic star. In all cases the shift in terminal relaxation time with the conversion to zwitterion ends is very large, with factors ranging from of 10^5 to 10^7 at 25 °C.

Master curves for both G' and G'' are shown in Figure 14 for sample 3A-Zw, demonstrating not only an essentially flat $G'(\omega)$ over a very wide range of frequencies but also an unusually low loss character in the rubbery response so obtained. The loss tangent, $G''(\omega)/G'(\omega)$, is less than

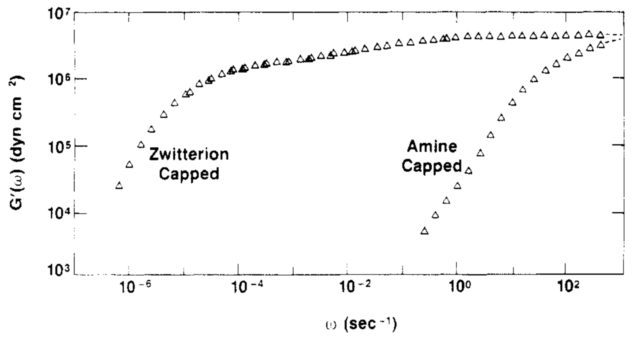


Figure 12. Comparison of storage modulus master curves for the three-arm star telechelic amine and zwitterion polyisoprene (T_0 = 25 °C).

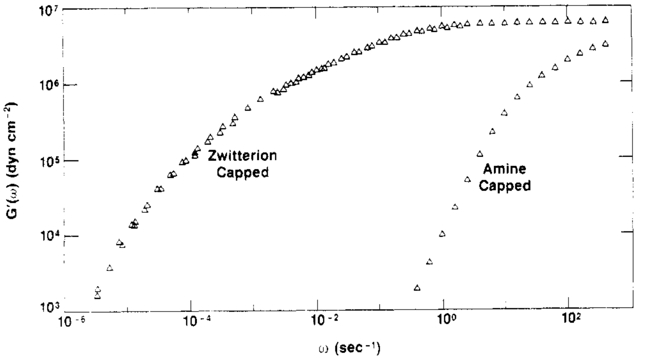


Figure 13. Comparison of storage modulus master curves for the 12-arm star telechelic amine and zwitterion polyisoprene (T_0 = 25 °C).

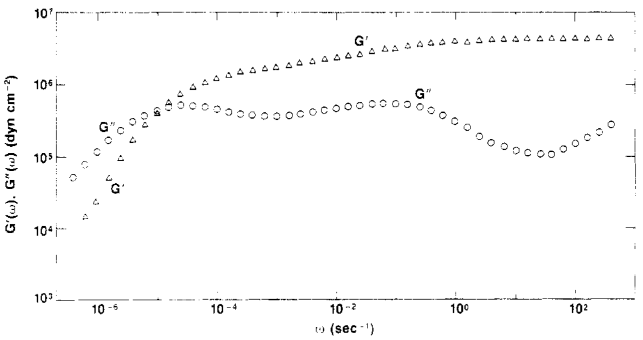


Figure 14. Dynamic modulus master curves for the three-arm star telechelic zwitterion polyisoprene (T_0 = 25 °C).

0.1 for much of the range and falls below 0.03 at high frequencies. This relatively "lossless" network response is quite unusual in conventionally cross-linked systems, although it is seen occasionally in strongly associating polymers.[12,25] Judged by the association-induced insolubility of the telechelic species in aliphatic hydrocarbons,[2] it is not very surprising to find them behaving as networks in the melt state. The fact that the networks eventually relax completely reflects the finite lifetime of association. We plan eventually to extract information on association–dissociation dynamics from such data. Valuable information on the energetics of association may be available here (see ref 24), but our own telechelic data base is still too limited to analyze meaningfully.

Conclusions

On the basis of results for monofunctional polyisoprenes and hydrogenated polyisoprenes, the rheological effects of association are largest for zwitterion groups, somewhat less but still important for sodium carboxylate, and rather small for carboxylic acid and amine groups. This ordering is consistent with dilute solution behavior, presented here for the carboxylates and in our earlier study on the zwitterion and tertiary amine species.[2] Viscosity enhancement for the sodium carboxylates is consistent with starlike structures, as would be produced by the association of end groups to form noninteracting spherical clusters. Viscosity enhancement for the zwitterion polymers is much larger than can be accounted for by such simple starlike structures. The anomalous strain dependence at low frequencies suggests a mechanically weak, spatially extended morphology for the zwitterion phase, either ordering of spherical clusters or the formation of lamellae or strings as found in surfactant or block copolymer systems. Small-angle X-ray scattering measurements are planned to test this possibility. The apparent weakness of association by carboxylic acid groups is contrary to expectations based on known values of the equilibrium constant for dimerization in nonpolar solvents. The lifetime of association must be important here; experimental data on association and dissociation rates and theoretical work to predict the influence of association dynamics on viscoelastic behavior are needed.

The telechelic polymer with zwitterion ends shows networklike properties at ambient temperatures. The large temperature coefficient for telechelic polymer relaxation may be related to the energy and dynamics of association. Future work will address this question.

Acknowledgment. We thank N. S. Davidson and W. Funk for their help on molecular characterization and A. Bug, R. R. Chance, J. Gethner, S. Safran, and T. A. Witten for discussions on various aspects of the work.

References and Notes

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Temperature Dependence of the Crystal Lattice Modulus and the Young's Modulus of Polyethylene

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ABSTRACT: The temperature dependence of the crystal lattice modulus of polyethylene was measured by X-ray diffraction with use of ultradrawn films produced by gelation/crystallization from dilute solution. Measurements were carried out in the temperature range 20–150 °C for specimens with draw ratios >300. The measured crystal lattice modulus was in the range 211–222 GPa, and the values were independent of temperature. In contrast, the storage modulus of an ultradrawn film with a draw ratio of 400, 216 GPa at 20 °C, decreased to 130 GPa at 140 °C. This discrepancy was related to an increase in the amorphous content and a decrease of the amorphous modulus with increasing temperature.

Introduction

In crystalline polymers, the crystal lattice modulus in the molecular chain axis direction is equivalent to the theoretical value of Young's modulus. Extensive work has been reported by X-ray diffraction,[1–4] Raman spectroscopy,[5] and inelastic neutron scattering.[6] The Raman and neutron-scattering methods, however, involve an unfavorable assumption[5,6] concerning the frequency of the absorption bands in a polymeric system, in addition to the difficulty in estimating the lamellar thickness parameter by small-angle X-ray scattering. In contrast, X-ray diffraction measurements have the advantage of estimating the crystal lattice modulus directly from the stress–strain relationship. This method was used by Sakurada et al.[1,2] for many polymers, and a detailed analysis for polyethylene was reported by using oriented specimens with different molecular weights and crystallinities. It was concluded that the values of the crystal lattice modulus are independent of the above factors.

Recently, Matsuo et al. have studied the crystal lattice modulus of polyethylene to determine whether the stress within a specimen is the same as the external applied stress.[3] The measurements were carried out at 20 °C with ultradrawn films produced by gelation/crystallization from dilute solutions according to the method of Smith and Lemstra.[7,8] The measured crystal lattice modulus was in the range 213–229 GPa, which is lower than the value reported by Sakurada et al.[1,2] The observed values were independent of the elongation ratios from 50 to 300 within experimental error.[3] This independence supports the assumption that the homogeneous stress hypothesis is valid, and the concept of independence was confirmed by a linear elastic theory[9] using a composite model of crystalline and amorphous phases.

However, there has been no report concerning a change in the crystal lattice modulus at elevated temperatures.

0024-9297/88/2221-1653$01.50/0