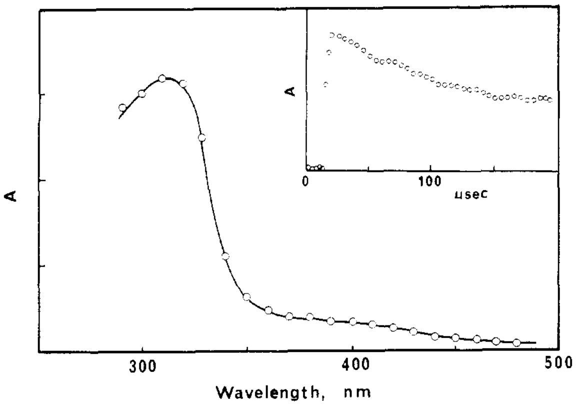

Figure 5. Transient absorption spectrum of MTHF solution containing 1 × 10^{-2} M dimethylphenylchlorosilane. Insert is the absorption profile recorded at 360 nm representing the decay of the transient.

of electron scavenger, *n*-BuCl, the band at 370 nm disappeared. This result confirms that the band is due to the radical anion.

Figure 4 shows the transient absorption spectrum of an *n*-BuCl solution containing polysilastyrene at the end of electron pulse. The inset shows the time dependence of the absorption band at 360 nm. The band at 360 nm is assigned to the radical cation of polysilastyrene on the basis of the spectra at low temperature. The half-life was obtained to be 85 μs. The absorption band at 360 nm also disappeared by the addition of a positive hole scavenger, MTHF.

The absorption spectrum of dimethylphenylsilyl radical was also measured in MTHF solution containing dimethylphenylchlorosilane as shown in Figure 5. As described in the previous section, the radical is produced by the reaction of dimethylphenylchlorosilane with electrons ejected by radiation. The radical has the absorption band at 310 nm. The decay fits well to a reciprocal plot. This means the radicals disappear by a bimolecular reaction.

Registry No. (Dimethyldichlorosilane)(methylphenyldichlorosilane) (copolymer), 70158-17-7.

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Association Behavior in End-Functionalized Polymers. 1. Dilute Solution Properties of Polyisoprenes with Amine and Zwitterion End Groups

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ABSTRACT: The dilute solution properties of linear polyisoprenes with a highly polar sulfo-zwitterion group on one end of the chain were examined in several solvents by osmometry, light scattering, and viscometry. The polymers were prepared by anionic polymerization with initiation by (3-(dimethylamino)propyl)lithium. The terminal tertiary amine groups were converted to zwitterions by treatment with cyclopropane sultone. A few linear and star materials with all ends functionalized were also prepared. The zwitterion-capped polymers were found to associate strongly in aliphatic hydrocarbons. Solutions of monofunctional zwitterion polymers were highly aggregated in cyclohexane. The multifunctional versions (two or more zwitterions per molecule) formed gels which, however, readily dissolved when small amounts of alcohol were added. Considerably less association of the zwitterion-capped chains was found in aromatic or more highly polar solvents. The number of molecules per zwitterion aggregate in cyclohexane decreased with increasing chain length, a characteristic that we have attributed to excluded volume repulsions of the polymeric tails. The aggregates were found to resemble star polymers in behavior. Some tentative conclusions are drawn about aggregate lifetimes, polar core geometry, and the concentration dependence of aggregation in these systems.

Introduction

The dilute solution properties of flexible chain polymers are reasonably well-understood when the interactions between chain units are weak.[2] Progressive dilution below the coil overlap concentration c^* separates the individual chains, and their influence upon one another diminishes rapidly. Extrapolation of osmotic pressure or small angle scattering measurements to infinite dilution provides absolute values of the molecular weight, and similar extrapolation of viscosity or diffusion measurements provides information about the chain dimensions. Initial departures from these various limits yield data about the thermodynamic and hydrodynamic interactions of the chains. The influence of chain length and chain branching on dimen-

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sions and the interaction coefficients has been examined in some detail with model polymers of several species.[3-7] The results are in broad agreement with molecular theories based on the random coil picture with excluded volume and Stokes law descriptions of the interactions between chain units.

The level of understanding is much less satisfactory for associating polymers, i.e., polymers containing a small number of functional groups that attract one another strongly.[8,9] Association can, of course, be brought about in many ways. Of particular interest here are the associations produced by highly polar groups when they are attached to a small fraction of the chain units in a nonpolar polymer.[10-13] These groups, like the polar heads of surfactant molecules, tend to form clusters in the relatively nonpolar solvents for the base polymer. The clusters provide temporary links among the chains and have a strength and lifetime that depend in some complicated way on the nature of the group and its local environment. Sufficiently strong association can, of course, produce gelation: a good solvent for the base polymer in this case acts simply as the swelling solvent for an association-induced network. Association that is too weak to result in gelation can still cause extensive aggregation of the chains. Like the critical micelle concentration in surfactants, the concentration required for dissociation to individual chains is now dictated by association equilibria. Aggregation can thus persist well below c^*, so even in dilute solutions the solute may consist of aggregates.[14,15] The presence of associating substituents, whether distributed along the backbone[10-16] as in the sulfo ionomers or concentrated at the chain ends[17-25] as in the halato telechelics, can change the solution properties dramatically. The systematics of such effects, however, have not been clearly established even in dilute solution.

The behavior of associating polymers is clearly derived from a combination of highly specific local features governing the clusters and intrinsically polymeric features (chain length, location of groups, etc.) about whose effects one might hope to deduce some general conclusions. However, it is difficult to study each in isolation from the other. The size, shape, and lifetime of such clusters are central issues in surfactant systems[26,27] but are also particularly hard to establish if the clusters are interconnected by polymer chains. Base polymer chain length as well as the number and location of associating groups are also important, but determination of base polymer molecular weight is now complicated by aggregation below c^*. Determination of chemical structure is also difficult because the concentration of associating groups is very small.

In the present work we have explored some aspects of polymeric association under the simplifying conditions of chains that contain only one associating group.[28-31] A series of nearly monodisperse linear polyisoprenes with a strongly polar zwitterion group on one end have been prepared by anionic polymerization. These "semitelechelic" polymers are the structural analogues of conventional surfactants except that the hydrocarbon tail is extremely long, ranging from 900 to 11 000 backbone carbons instead of the 15–20 range for typical surfactants. The dilute solution properties of these polymers were examined by a variety of techniques in several solvents of similar "goodness" with respect to conventional polyisoprene but differing considerably in their interaction with polar substituents.

One significant advantage of the monofunctional architecture is avoidance of direct cluster interconnections. Gelation in the conventional sense cannot occur no matter how strong the association, and the number of associating groups per cluster N can be determined directly from measurements of aggregate molecular weight M and the base polymer molecular weight M_o: $N = M/M_o$, where N is the aggregation number. Aggregation of surfactants in organic solvents has been discussed extensively in the literature.[26,27] "Reversed micelles" with fairly well-defined values of aggregation number and critical micelle concentration are found in some systems, but polydisperse aggregates and an average aggregation number $\bar{N}$ that shifts continuously with concentration are also quite common. The polar core regions may be nonspherical and even cylindrical in some surfactant systems. Aggregation number and core geometry change with the addition of polar species to the system: the core regions even in nominally dry systems probably contain some tenaciously bound water. The dynamics of association–dissociation equilibria, like core size and geometry, is locally determined and highly variable: equilibration times for the aggregate structure (following dilution, for example) can apparently range from milliseconds or less to weeks or more, depending on the system. Similar characteristics are found in solutions of block copolymers when one of the blocks is insoluble,[32-35] and they must certainly be anticipated in solutions of end-functionalized polymers as well.

Table I
Selected Dilute Solution Properties of Linear and Star Polyisoprenes in Toluene

no. of arms	k_H	$A_2M/[\eta]$	$[\eta]/[\eta]_{arm}$
1 (linear)	0.27	1.15	1.00
2 (linear)	0.27	1.15	1.67
3	0.30	1.35	1.90
4	0.34	1.55	2.04
6	0.37	1.71	2.17
8	0.52	1.65	2.34
12	0.69	1.93	2.12
18	0.74	2.12	1.87

We have used the extensive dilute solution data available for polymeric stars[36,37] as a framework for interpreting our results. Some relevant properties of linear and star polyisoprenes are given in Table I. Those measurements were made on toluene solutions, but the values should also be applicable for the other good solvents used in this study.[37] The star structure should be a reasonable model for the aggregates if the chains are long enough and aggregation numbers are moderate even when the cores are not precisely spherical. We compare the aggregation numbers obtained by equilibrium methods and dynamic methods on the same samples, and we deduce information about cluster polydispersity and the effects of polar cosolvents. We also report some observations on specific solvent effects and gelation in the multifunctional (telechelic) versions of the same polymers. Some tentative conclusions are offered about the effect of excluded volume on the chain length dependence of average cluster size[30] and about the shift of $\bar{N}$ with concentration in the range of our measurements.

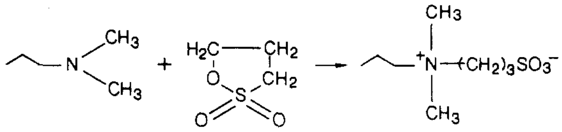
Experimental Section

A. Synthesis. Isoprene was polymerized anionically under vacuum line conditions in a 9:1 mixture of cyclohexane and benzene at ambient temperatures.[38,39] Polymerization was initiated by (3-(dimethylamino)propyl)lithium,[30] resulting in a terminal tertiary amine group on each polyisoprenyl anion. The synthesis of (3-(dimethylamino)propyl)lithium was carried out in n-pentane at reflux temperature from the corresponding chloride and a lithium dispersion which contained about 2 wt % sodium.[40] The conditions of synthesis were chosen so as to minimize the potential for Wurtz coupling. According to gas chromatography the anticipated product of such a reaction, bis(tetramethylhexylene)diamine, is not present in the initiator solution. Its absence is imperative if the influence of such species on diene microstructure[39] is to be avoided. The organolithium concentration was determined by acid–base titration. Care was taken to ensure that the hydrolysis product, dimethylpropylamine, was eliminated by distillation prior to the titration.

The monomer–initiator ratio r was chosen to provide the desired molecular weight: $M_s = m_0 r$, where M_s is the stoichiometric (predicted) molecular weight of the polymer and $m_0 = 68$ is the molecular weight of isoprene monomer. Linear polyisoprenes with the tertiary amine group on one end were obtained by deactivation of the poly(isoprenyllithium) anions with degassed methanol. Linear polyisoprenes with tertiary amine on both ends were obtained by coupling the anions with dichlorodimethylsilane. Star polymers (3-arm and 12-arm) with tertiary amine groups on all ends were obtained by an appropriate silane-linking chemistry.[41] A slight excess of anions was employed in the coupling and linking reactions to avoid the presence of chlorosilane groups in the product.

The polymers were recovered by precipitation with methanol; the chlorosilane-derived products were fractionated to remove unlinked species. The amine-capped polymers tend to form fine dispersions when an excess of polar nonsolvent is added. As a result, purification and fractionation were generally more difficult and required more care in execution than needed for conventional polyisoprenes. All samples were dried under vacuum and stored in a refrigerator.

The tertiary amine groups were converted to sulfo zwitterions by reaction with cyclopropane sultone (eq 1).[42,43] Solutions of the amine-capped polymers (2% concentration in tetrahydrofuran) were reacted for several days at 70 °C with a 5:1 excess of sultone to amine (10:1 in some cases) and then isolated by precipitation with acetone. Partial evaporation yielded a gelatinous precipitate that was washed repeatedly with acetone to remove unreacted sultone, then evaporated to dryness, and stored under vacuum. Direct contact with alcohols and water was avoided to minimize opportunities to hydrogen-bond complexation by the zwitterions. Separate experiments showed no change in properties when conventional polyisoprenes were treated with cyclopropane sultone.



(1)

The reaction with tertiary amine appears to be relatively free of side reactions;[44] ring-opening polymerization of the sultone can apparently take place, but only at much higher concentrations than those used here.[45] We have, however, found some differences in properties when different sultone-to-amine ratios were used. The extent of association (as determined by the aggregation number in cyclohexane, see below) varied somewhat from batch to batch. We are currently exploring the problem by spectroscopic techniques with polyisoprenes of low molecular weight. For now, the precise variation of aggregation number with chain length remains somewhat uncertain. However, our other conclusions about cosolvent effects, cluster size polydispersity, concentration dependence of aggregation, and equilibrium vs dynamic measurements of aggregation number should be unaffected.

In the tables the amine-capped polymers are designated alphabetically (in the order of their preparation). A numberical prefix indicates those samples with more than one amine group per molecule. Thus, sample D has just one amine group per molecule, and sample 3A is a three-arm star with amine groups on all three chain ends. Zwitterion polymers are designated by adding Zw to the name of its amine precursor; samples D-Zw and 3A-Zw were derived from samples D and 3A by the sultone treatment.

B. Chain Microstructure. Proton NMR was used to determine frequencies for the various modes of isoprene enchainment in the amine-capped polymers. The results, together with the stoichiometric molecular weight M_s and the number-average molecular weight $\bar{M}_n$ from osmometry for some samples, are given in Table II. No evidence of 1,2 enchainment was found, but there is an increase in the 3,4 content with decreasing chain length. This trend is reasonable in view of the increased initiator concentration used to prepare samples of lower molecular weight and the known modifying activity of tertiary amines on diene microstructure.[39] As M_0 approaches 10^5, the microstructure becomes indistinguishable from the microstructure of polyisoprenes made with conventional organolithiums in hydrocarbon solvents. The variations in 3,4 content are too small to affect the dilute solution properties in any significant way. Changes in contour length and characteristic ratio are nearly offsetting;[46] the intrinsic viscosity, for example, changes by only a few percent between 8% and 50% 3,4 content for polyisoprenes of the same molecular weight. The glass transition temperature was found to be unchanged by the sultone reaction. Its value is dictated by 3,4 content alone.[47]

Table II
Molecular Weights and Microstructures of Amine-Capped Polyisoprenes

sample	$10^{-4}M_s$	$10^{-4}\bar{M}_n$[a]	% 1,4 cis	% 1,4 trans	% 3,4
G	1.5		52	28	20
E	1.6	1.6_7	53	27	20
C	2.2	2.0_8	53	29	18
A	4.3	4.5_2	56	29	15
H	4.8		64	25	11
B	7.5	7.4_0	63	25	12
D	7.9	8.5_6	65	27	8
I	10.4		68	23	9
F	10.8	9.7_5	74	18	8
J	18.5		71	22	7
2A	13.6	$12._9$			
3A	7.5	$6._6$[b]			
12A	30	$24._5$[c]			

[a] Obtained by membrane osmometry in toluene. [b] Arm molecular weight $\bar{M}_n = 2.5_1 \times 10^4$ from osmometry in toluene. [c] Arm molecular weight $\bar{M}_n = 2.5_5 \times 10^4$ from osmometry in toluene.

The excellent agreement between M_s and $\bar{M}_n$ is in contrast to earlier reports about amine-containing initiators.[48] Side reactions leading to premature termination are effectively absent for the initiator used here.

C. Size Exclusion Chromatography. All polymers were routinely examined by size exclusion chromatography (SEC, Waters 150-C with μ-Styragel packing and with tetrahydrofuran as elution solvent at 25 °C). Injection concentrations of 0.1–0.5 g dL^{-1} were used. Some evidence of adsorption of functional groups on the SEC columns was found, mild and barely detectable for the amine-capped samples but more obvious for the zwitterions. Thus, the chromatographs were typical of narrow distribution samples ($\bar{M}_w/\bar{M}_n < 1.1$) except for slight tails or shoulders on the high elution volume side of the peak. Peak molecular weight M_p, obtained from a calibration curve established with polyisoprene standards, was always in good agreement with M_s from stoichiometry. No indication of aggregates (tails, shoulders, or peaks on the low elution volume side) was found. The polarity of tetrahydrofuran (dielectric constant $\epsilon = 7.4$) is apparently sufficient to suppress any amine or zwitterion group association.

D. Dilute Solution Measurements. Dilute solution properties were determined by membrane osmometry (MO) at 34 °C with a Wescan 231 osmometer and RC-51 or RC-52 membranes, by low angle laser light scattering (LALLS) at 23 °C with a Chromatix KMX-6 photometer for wavelength $\lambda = 633$ nm, by quasi-elastic light scattering (QELS) at 25 °C with a Brookhaven Instruments photometer and correlator for wavelength $\lambda = 633$ nm and by capillary viscometry at 27 °C with Cannon-Ubbelohde viscometers.

The solvents used were toluene, tetrahydrofuran, and cyclohexane, all good solvents for conventional polyisoprene and, judged by values of intrinsic viscosity $[\eta]$ and second virial coefficient A_2, rather similar in thermodynamic interaction with that polymer.[7,37,49,50] Some experiments on the zwitterion-capped polymers were also conducted in cyclohexane to which small amounts of alcohol were added to disrupt association. 1-Heptanol was used because its refractive index nearly matches that of polyisoprene. The value of A_2 for a nonfunctionalized polyisoprene in cyclohexane was only slightly reduced with the addition of 5 wt % 1-heptanol, showing that solvent "goodness" was hardly changed. All solvents were of reagent grade purity or better; results were found to be insensitive to additional purification steps such as

Table III
Dilute Solution Properties of Amine-Capped Polyisoprenes in Toluene and Tetrahydrofuran

	toluene		tetrahydrofuran		toluene		
sample	$10^{-4}\bar{M}_n$	$10^4 A_2$, mL g^{-1}	$10^{-4}\bar{M}_w$	$10^4 A_2$, mL g^{-1}	$[\eta]$, dL g^{-1}	k_H	$A_2M/[\eta]$
E	1.6_7	$27._1$	1.7_7	$13._4$	0.23_7	0.38	1.91
C	2.0_8	$20._8$	2.4_6	$10._5$	0.28_5	0.39	1.52
A	4.5_3	$14._1$	4.5_6	$11._0$	0.53_9	0.36	1.19
B	7.4_0	$11._8$	7.4_1	$9._9$	0.73_4	0.33	1.19
D	8.5_6	$12._0$	8.6_8	$9._4$	0.77_9	0.32	1.32
F	9.7_5	$10._9$			0.89_4	0.31	1.19
2A	$12._9$	$8._2$	14.3	$8._5$	1.25	0.45	0.85
3A	6.6	9.5	7.2	$9._6$	0.64_3	0.59	0.98
12A	$24._5$	$6._2$	$22._7$	$5._4$	0.70_6	0.73	2.15

Table IV
Dilute Solution Properties of Amine-Capped Polyisoprenes in Cyclohexane

sample	$10^{-4}\bar{M}_n$	$10^4 A_2$, mL g^{-1}	$10^{-4}\bar{M}_w$	$10^4 A_2$, mL g^{-1}	$[\eta]$, dL g^{-1}	k_H	$A_2M/[\eta]$[a]
G	1.6_5	25			0.25_0	0.38	1.65
E	1.8	18	4.1_4	0.9	0.27_3	0.46	1.19
C	2.8	13	$15._1$	~0	0.36_1	0.49	1.01
A	$5._1$	14	$10._2$	$3._2$	0.57_8	0.35	1.24
H	5.3_1	$13._3$					
B	7.6_5	$11._2$	9.0	$8._6$	0.75_7	0.35	1.13
D	$10._5$	$10._3$	$14._0$	$6._2$	0.99	0.43	1.09
I	$10._7$	$10._6$			0.98_8	0.33	1.15
J	$17._6$	$8._9$			1.53	0.34	1.02
2A	$21._4$	$8._5$	60	$2._9$	1.44	0.57	1.27
3A	9.0	$9._7$	23	4.0	0.71_1	0.44	1.23
12A	$24._3$	$6._2$	34	3.0	0.74_0	0.63	2.04

[a] Values calculated with $\bar{M}_n$ and A_2 from osmometry.

Table V
Dilute Solution Properties of Zwitterion-Capped Polyisoprenes in Cyclohexane and Cyclohexane–Heptanol Mixtures

sample	$10^{-4}\bar{M}_n$	$10^4 A_2$, mL g^{-1}	$10^{-4}M_w$	$10^4 A_2$, mL g^{-1}	$[\eta]$, dL g^{-1}	k_H	$A_2M/[\eta]$[a]
Cyclohexane							
G-Zw	$35._8$	$4._7$	$71._7$	$3._4$	0.42_9	0.82	3.91
E-Zw	21	$4._0$	$28._6$	$2._6$	0.44_1	1.0_3	1.91
C-Zw	65	$2._1$	91	~0	0.48_5	1.1_4	2.81
A-Zw	66	$2._4$	130	~0.3	0.78	1.0_5	2.03
B-Zw	36	$5._3$	87	$2._6$	1.22	1.3_1	1.56
D-Zw	34	$4._2$	240	~0	1.22	1.0_3	1.57
F-Zw	$11._2$	$7._7$	15	~0	1.08	1.1_1	1.17
I-Zw	$35._5$	$6._0$	116	$2._8$	1.7_9	0.67	0.80
J-Zw	25.1	$7._6$	$81._3$	$3._6$	2.0_0	0.37	0.95
1% 1-Heptanal in Cyclohexane							
C-Zw	$19._2$	$2._3$	84	0.5	0.49_7	0.88	0.89
A-Zw	9.1_5	$4._7$	$53._5$	~0	0.71	1.2_4	0.61
B-Zw	$10._4$	$7._5$	46	$2._8$	0.98_4	1.0_8	0.79
F-Zw	$9._4$	$9._6$	$15._7$	$5._4$	1.0_1	0.57	0.89
5% 1-Heptanol in Cyclohexane							
C-Zw	4.3_3	1.0	40.5	$-1._3$	0.34_4	1.6_0	0.13
A-Zw	5.6_8	$6._0$	$38._6$	~0	0.56	0.75	0.61
B-Zw	7.5_0	$9._6$	$25._8$	$3._4$	0.79	0.57	0.91
F-Zw	8.5_0	$9._8$	$15._1$	$4._3$	0.92_2	0.65	0.90
3A-Zw	$10._1$	$3._3$	$25._7$	$2._6$	0.56_2	4.4_5	0.59
12A-Zw	$27._3$	$2._9$	$67._2$	$1._8$	0.62_9	3.5_7	1.26

[a] Values calculated with $\bar{M}_n$ and A_2 from osmometry.

distillation after drying over CaH_2.

Solutions for the light scattering experiments were clarified by filtration with Alpha Metricel or Fluoropore filters and also by centrifugation in the case of the zwitterion-capped polymers. Reasonable care was taken to minimize contact of the solutions with moisture. Repeated measurements obtained with the same carefully dried and stoppered stock solutions of the zwitterion polymers were found to change slowly (over a period of several weeks) in some cases. All results reported here were obtained with freshly prepared solutions (<1 week). Measurements were made in the dilute range, from near the coil overlap concentration,[51] $c^* = [\eta]^{-1}$, down to $0.1c^*$ and even well below that level in some cases.

Number-average molecular weight and second virial coefficient were obtained from the dependence of osmotic pressure π on the polymer concentration c (wt/v) in toluene, cyclohexane, and 1-heptanol–cyclohexane mixtures

$$\frac{\pi}{cRT} = \frac{1}{\bar{M}_n} + A_2c + ... \qquad (2)$$

where R is the gas constant and T is the temperature. Data for several concentrations were analyzed by square root plots[52] ($(\pi/c)^{1/2}$ vs c), but results from linear plots (π/c vs c) were not significantly different. Readings were stable, and data collection was uneventful whether strong association was present or not. Example plots for samples B and B-Zw are shown in Figure 1. The results are given in Tables III–VI.

Weight-average molecular weight and second virial coefficient were obtained from the concentration dependence of excess

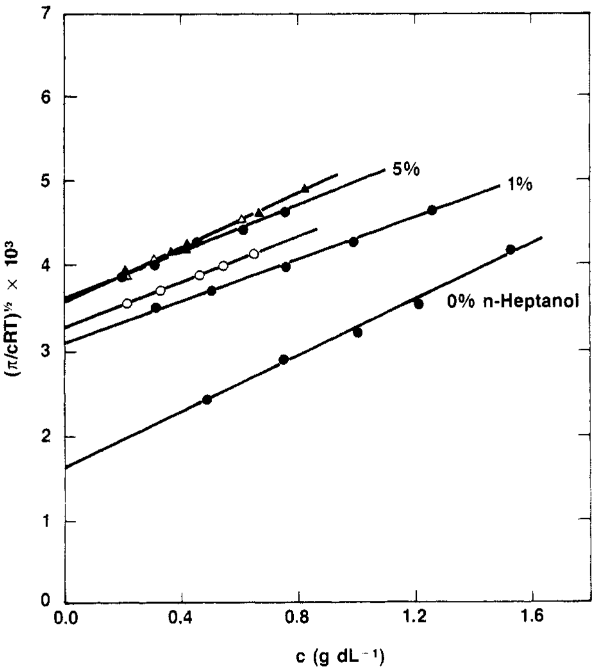


Figure 1. Osmotic pressure measurements for samples B and B-Zw in several solvents. The symbols denote sample B in toluene (△), sample B in cyclohexane (▲), sample B-Zw in toluene (○), and sample B-Zw in 1-heptanol–cyclohexane mixtures (●).

Table VI
Dilute Solution Results for Zwitterion-Capped Polyisoprenes in Toluene

sample	$10^{-4}\bar{M}_n$	10^4A_2, mL g^{-1}	$[\eta]$, dL g^{-1}	k_H
A-Zw	4.8_3	2.9		
B-Zw	8.8_3	$10._4$		
D-Zw			0.77_5	0.32
F-Zw[a]	8.3_4	$10._8$		
3A-Zw			0.62	8.2

[a] $\bar{M}_w = 14.4 \times 10^4$ and $A_2 = 6.3 \times 10^{-4}$ dL g^{-1} were obtained for this polymer by light-scattering measurements in tetrahydrofuran.

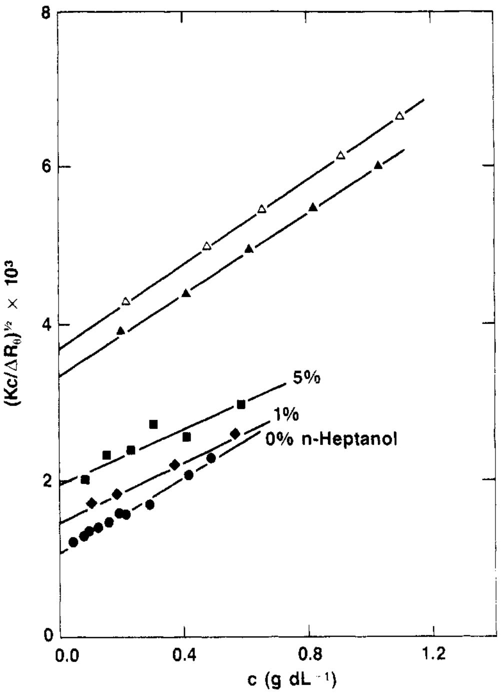


Figure 2. Light scattering intensity measurements for samples B and B-Zw in several solvents. The symbols denote sample B in tetrahydrofuran (△), sample B in cyclohexane (▲), and sample B-Zw in 1-heptanol–cyclohexane mixtures (●, ♦, ■).

Table VII
Quasi-Elastic Light Scattering Results for Zwitterion-Capped Polyisoprenes in Cyclohexane

sample	10^7D_0, cm^2 s^{-1}	k_D, mL g^{-1}	R_H, nm
E-Zw	1.7_8	45	$13._7$
C-Zw	1.3_4	~0	$18._1$
A-Zw	0.80	−75	$30._4$
B-Zw	1.3_5	49	$18._0$
D-Zw	0.58	−32	$41._7$
F-Zw	2.1_8	−12	$11._2$

Rayleigh ratio at small scattering angles in tetrahydrofuran, cyclohexane, and 1-heptanol–cyclohexane mixtures

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{\bar{M}_w} + 2A_2c + ... \tag{3}$$

where K is a combination of known optical parameters (including the refractive index increment dn/dc which has been determined for polyisoprene in all solvents used here[53]). (The value of dn/dc for polyisoprene in toluene is too small for light scattering work.) Square-root plots were used[52] ($(c/\Delta R_\theta)^{1/2}$ vs c), but again the values obtained from linear plots were similar. We found an unusually large amount of fluctuation in the photomultiplier output for the functionalized polymers in cyclohexane. Excursions on time scales of the order of seconds were much more common than for the solutions of ordinary polymers and were larger for the zwitterion-capped polymers than for the amine-capped polymers. The same solutions were difficult to filter, and plugging was a frequent problem with either Alpha Metricel and Fluoropore filters. In general the fluctuation and filtration problems increased with the number of functional groups per molecule and with decreasing molecular weight of the base polymer. Surprisingly, those problems also increased with the addition of alcohol to the cyclohexane solutions. The base-line intensities were quite stable in all cases, however. Example plots for samples B and B-Zw are shown in Figure 2. The results are given in Tables III–V.

Diffusion coefficients were determined for several zwitterion-capped polymers in cyclohexane from the QELS intensity autocorrelation function. The same procedures applied earlier for conventional polyisoprenes were used.[7] Mean decay rate $\bar{\Gamma}$ and variance from the single exponential form $\mu_2/\bar{\Gamma}^{-2}$ were obtained by a second cumulant fit of the field correlation function. Diffusion coefficients were calculated from $\bar{\Gamma}$ and the scattering angle θ

$$D = \bar{\Gamma}/q^2 = \bar{\Gamma}\Big/\left(\frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)^2 \tag{4}$$

then extrapolated to zero concentration according to

$$D = D_0(1 + k_Dc + ...) \tag{5}$$

The average hydrodynamic radius was calculated from

$$R_H = kT/6\pi\eta_sD_0 \tag{6}$$

where k is Boltzmann's constant and η_s is the solvent viscosity.

Interpretation of the QELS data for the zwitterion-capped polymers was not as straightforward as for nearly monodisperse conventional polyisoprene.[7] It was difficult to obtain unambiguous values of $\bar{\Gamma}$ and $\mu_2/\bar{\Gamma}^2$, and neither $\bar{\Gamma}/q^2$ nor $\mu_2/\bar{\Gamma}^2$ was independent of the scattering angle ($30° < \theta < 90°$). Fortunately, these complications diminished considerably as the concentration decreased. We regard the values of D_0 as quite reasonable estimates, but the values of k_D as questionable. Even at the lowest concentrations, however, the departure from single exponential decay was clearly much larger ($\mu_2/\bar{\Gamma}^2 > 0.2$) than obtained for nearly monodisperse conventional polyisoprenes[7] of similar R_H ($\mu_2/\bar{\Gamma}^2 < 0.1$). This is a natural result of aggregate polydispersity (see below). An example plot of D vs c for sample B-Zw is shown in Figure 3. The results are given in Table VII.

Intrinsic viscosity and Huggins coefficient were obtained from the concentration dependence of viscosity

$$\frac{\eta_r - 1}{c} = [\eta] + k_H[\eta]^2c + ... \tag{7}$$

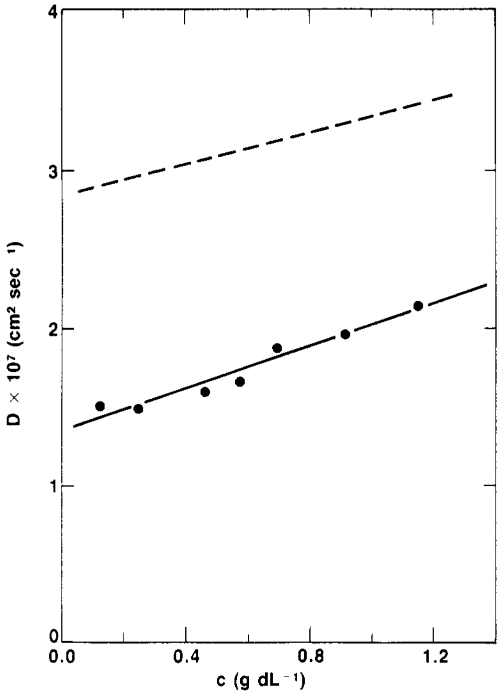


Figure 3. Diffusion coefficient measurements for sample B-Zw in cyclohexane. The dashed line indicates the results expected for a conventional polyisoprene with $M = 7.4 \times 10^4$, the base polymer molecular weight for this sample.

where the relative viscosity η_r is the ratio of solution to solvent flow times. The shear rate rannge, $\dot{\gamma} \approx 5 \times 10^2\ s^{-1}$, was well below that expected to produce non-Newtonian effects in conventional polymers with the same intrinsic viscosities. Results obtained from Huggins plots ($(\eta_r - 1)/c$ vs c) and Kraemer plots ($\ln \eta_r/c$ vs c) were similar except when k_H was unusually large; the reported values were obtained from the Kraemer plots in those cases since their curvatures were less. The average viscometric radius was calculated from[7]

$$R_V = 5.41 \times 10^{-9}\ ([\eta]M)^{1/3} \tag{8}$$

with $\bar{M}_w$ from light scattering as the molecular weight. Example plots for samples B and B-Zw are shown in Figure 4. The results are given in Tables III–VI.

Results

A. Solubility and Gelation. All amine-capped polymers were readily dissolved by solvents for conventional polyisoprene—a wide range of aliphatic, olefinic, and aromatic hydrocarbons as well as esters, ketones, and ethers. These solvents also dissolved the polymers containing one zwitterion per molecule. However, the behavior was different for polymers containing two or more zwitterions per molecule. Although still soluble in aromatic hydrocarbons (toluene, xylene) and in solvents with polar groups (tetrahydrofuran, amyl acetate, 2-pentanone), the multifunctional zwitterion polymers formed only swollen gels in aliphatic and olefinic solvents (hexane, decane, cyclohexane, and squalene). The gels were stable over periods of many weeks but dissolved quickly when a small amount of alcohol (~2% 1-heptanol) was added.

Gel formation indicates strong association. It also means that there is an average of more than two zwitterions per cluster: two groups per cluster or less would produce chain extension but not gelation in the difunctional (linear telechelic) polymers. Weakened association of zwitterions would be expected in more polar solvents such as tetrahydrofuran. However, we were somewhat surprised by the large difference in behavior between aliphatic and aromatic solvents. The dielectric constants differ hardly at all ($\epsilon = 2.2$ for cyclohexane and 2.4 for toluene), so we assume

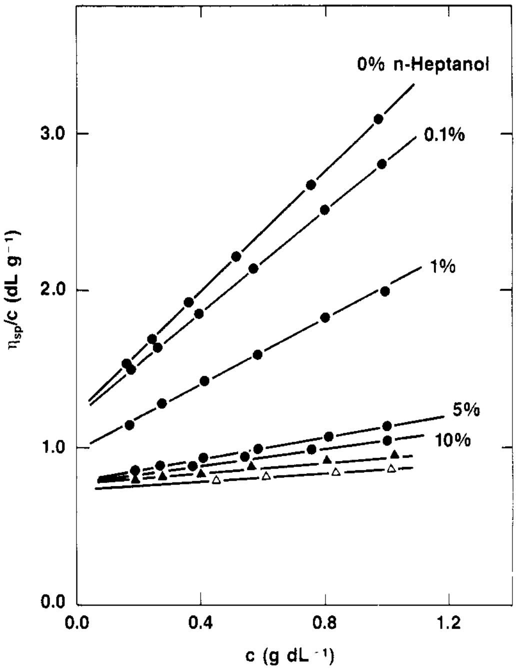


Figure 4. Viscosity measurements for samples B and B-Zw in several solvents. The symbols denote sample B in toluene (△), sample B in cyclohexane (▲), and sample B-Zw in 1-heptanol–cyclohexane mixtures (●).

the greater polarizability of aromatic rings is somehow responsible. Parallel effects were seen in the solubility of Ralufon DS (stearyl(dimethylamino)-3-sulfopropylbetaine), a commercial surfactant with the same zwitterion head group as the polymers. Ralufon DS was found to be soluble up to 0.5% in both tetrahydrofuran and toluene but virtually insoluble in cyclohexane.

Some crude estimates were made of gel fraction w and gel swelling ratio Q = swollen volume/dry volume for the two-star samples, 12A-Zw and 3A-Zw, in cyclohexane. Five specimens of 12A-Zw were added to large excesses of cyclohexane; after 1 week w ranged from 0.67 to 0.98 and Q ranged from 24 to 28. The 3A-Zw gels were mechanically weaker and changed slowly over time: $w \approx 0.5$ and $Q \approx 38$ after 1 week and $w \approx 0.3$ and $Q \approx 55$ after 5 weeks. We found that literature data on swelling ratio for model polyisoprene networks in cyclohexane[54] could be expressed by

$$Q = 0.15M_c^{0.525} \tag{9}$$

where M_c is the molecular weight of the network strands. With this equation we obtained $M_c \approx 1.8 \times 10^4$ for 12A-Zw ($Q \approx 26$) and $M_c \approx 3.8 \times 10^4$ for 3A-Zw ($Q \approx 38$), values which agree at least roughly with the arm molecular weights ($M_c \approx 2.5 \times 10^4$ for both samples).

B. Dilute Solution Behavior of the Amine-Capped Species. Results obtained for amine-capped polymers by osmometry, light scattering, and viscometry in toluene and tetrahydrofuran are given in Table III. These results provide little evidence of association. The values of $\bar{M}_n$ and $\bar{M}_w$ are nearly the same and in good agreement with M_s (Table I) and with the SEC results. Viscosity-average molecular weight $\bar{M}_v$ calculated from[55]

$$[\eta] = 1.72 \times 10^{-4}\ M^{0.74}\ \text{(toluene)} \tag{10}$$

is also in good agreement with M_s (an adjustment for branching is necessary for samples 3A and 12A). The Huggins coefficients are marginally elevated (k_H = 0.27, 0.30, and 0.69 are expected for linear, 3-arm star, and 12-arm star polyisoprenes from Table I), and the second virial coefficients are slightly unusual for some samples ($A_2M/[\eta]$ = 1.15, 1.35, and 1.93 are expected for linear, 3-arm star, and 12-arm star polyisoprenes from Table I). Most of these differences, however, might simply be caused by small systematic departures at lower molecular weights from the values in Table I, the latter having been established with samples of much higher molecular weight.[37] We do not regard the differences to be significant.

Similar conclusions can be drawn from results obtained by osmometry and viscometry in cyclohexane (Table IV). Thus, values of $\bar{M}_n$ and values of $\bar{M}_v$ calculated from[7]

$$[\eta] = 2.05 \times 10^{-4} M^{0.73} \text{ (cyclohexane)} \qquad (11)$$

are mostly consistent with M_s although running somewhat larger than expected in a few samples. Second virial coefficients from osmometry are in the conventional polymer range as judged by the values of $A_2M/[\eta]$. The slight elevation of k_H is similar to the result found in toluene.

The light scattering behavior in cyclohexane (Table IV) is different, however. The values of $\bar{M}_w$ are significantly elevated, and the values of $A_2\bar{M}_w/[\eta]$ are substantially depressed. The effects are generally larger for short chains and those containing more than one amine group. It is clear that association occurs in cyclohexane even for the weakly polar tertiary amine substituent. Apparently the tertiary amine clusters in cyclohexane are fairly large but few in number because $\bar{M}_w$ is affected so strongly and $\bar{M}_n$ hardly at all. Compared with the zwitterion-capped species, however, the effects of association in the amine polymers are still relatively weak.

C. Dilute Solution Behavior of the Zwitterion-Capped Species. Results obtained for several of the zwitterion-capped polymers by osmometry, light scattering (LALLS), and viscometry in cyclohexane and in 1% and 5% (w/v) solutions of 1-heptanol in cyclohexane are given in Table V; results from quasi-elastic light scattering in cyclohexane are given in Table VII. Strong association is clearly indicated for the zwitterion polymers in cyclohexane. Both $\bar{M}_n$ and $\bar{M}_w$ are much larger than those of the base polymer. The number-average aggregation number, $\bar{N}_n = \bar{M}_n/M_o$, increases systematically with decreasing base polymer molecular weight M_o. The values of $\bar{M}_n$ for some of the short chain samples are in fact near the upper limit obtainable by osmometry: the true values for those polymers might be even larger. The intrinsic viscosities are elevated, and both R_V and R_H are larger than the values calculated from eq 8 and[7]

$$R_H = 1.23 \times 10^{-2} M^{0.584} \text{ (nm)} \qquad (12)$$

for the base polymers. The values of k_H and $A_2M/[\eta]$ (based on the somewhat more reliable osmometry measurements) are larger than obtained for linear polyisoprenes. The values of k_D are erratic (and probably unreliable, as discussed earlier), behaving in a manner quite unlike the smooth increase with molecular weight found in conventional polyisoprene.[7]

The effect of alcohol in weakening the association is similar to that found in solutions of sulfoionomers.[10] The values of $\bar{M}_n$, $\bar{M}_w$, and $[\eta]$ decrease with increasing concentration of 1-heptanol; k_H remains relatively large, but $A_2M/[\eta]$ is now somewhat depressed even in relation to the value for linear chains (Table I). The zwitterion stars 3A-Zw and 12A-Zw are soluble in the 5% 1-heptanol solutions. Their elevated values of $\bar{M}_n$ and $\bar{M}_w$ indicate some aggregation, but, unlike the monofunctional polymer behavior, $[\eta]$ is now somewhat smaller than the base polymer value $[\eta]_o$ and k_H is extremely large. Values of $[\eta]/[\eta]_o$ below unity are commonly observed in sulfoionomers, a behavior that has been attributed to a contraction of chain dimensions caused by intramolecular association.[10-12]

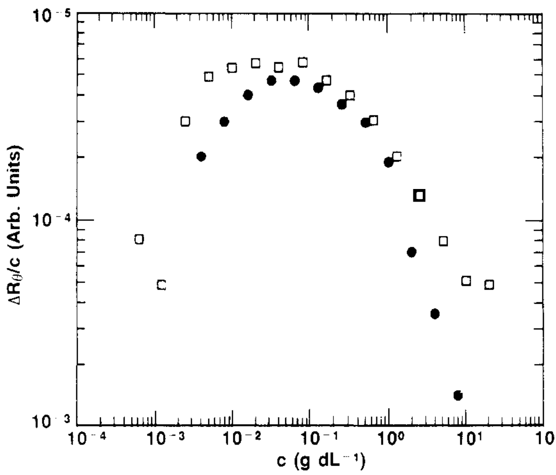


Figure 5. Reduced light scattering intensity at θ = 90° over an extended range of concentration for samples D-Zw and E-Zw in cyclohexane. Intensity units are arbitrary.[56] Overlap concentration, estimated at $[\eta]^{-1}$, are c^* = 0.82 g dL^{-1} for D-Zw (□) and c^* = 2.1 g dL^{-1} for E-Zw (●).

To test reversibility of association a few osmometry measurements were made with cyclohexane solutions to which methanol had first been added to disrupt association and then removed by sparging with dry nitrogen. Reassociation appeared to occur, but the results were somewhat inclusive quantitatively and need further work.

Some results for zwitterion polymers obtained by osmometry and viscometry in toluene are shown in Table VI. The monofunctional polymers show little evidence of association in this solvent. On the other hand, although the intrinsic viscosity of the trifunctional sample 3A-Zw is practically the same as $[\eta]_o$, the value of k_H is extremely large.

Discussion

The aggregate molecular weights reported were obtained by extrapolations to infinite dilution of data obtained at several concentrations in the dilute range, typically $0.1c^* < c < 0.7c^*$. Of course, at the literal limit of zero concentration the aggregates would be completely dissociated, assuming equilibrium is attained, so what we actually obtain here is some measure of aggregate size at concentrations in the vicinity of $0.1c^*$.

To explore the more dilute range, light scattering measurements were repeated and extended to much lower concentrations for two highly aggregated systems, samples D-Zw and E-Zw in cyclohexane.[56] Reduced scattering intensity $\Delta R_\theta/c$ is shown as a function of concentration in Figure 5. For sample D-Zw, a relatively well-defined plateau in $\Delta R_\theta/c$ is found between 10^{-2} and 10^{-1} g dL^{-1}, the concentration range that was used in the experiments to determine $\bar{M}_w$ and A_2. Sample E-Zw shows a broad peak near 3×10^{-2} g dL^{-1} rather than a clear plateau, although $\Delta R_\theta/c$ remains fairly constant up to about 10^{-1} g dL^{-1}. The measurements to determine $\bar{M}_w$ and A_2 for that sample were made between 10^{-1} and 10^{0} g dL^{-1}. The reduced intensity drops rapidly at concentrations below $c \approx 10^{-2}$ g dL^{-1} for both samples, indicating dissociation and perhaps the approach to some "critical micelle concentration" not far below 10^{-3} g dL^{-1}, or 10^{-6}–10^{-7} molar concentration of zwitterions. The results of similar experiments on two 18-arm polyisoprene stars are shown in Figure 6. As expected for those samples, $\Delta R_\theta/c$ in the dilute range remains constant down to the lowest attainable concentrations.

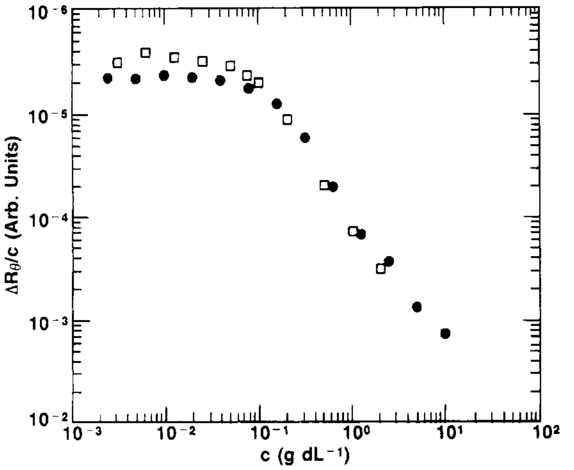


Figure 6. Reduced light scattering intensity over an extended range of concentrations for two 18-arm star polyisoprenes in cyclohexane. Intensity units are arbitrary.[56] The molecular weights are 3.57×10^6 (●) and $6.2_0 \times 10^6$ (○).

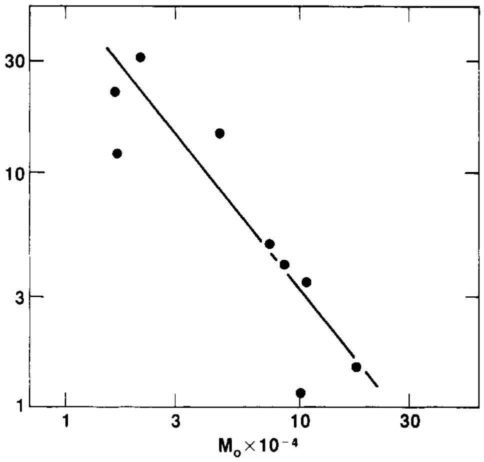


Figure 7. Number-average aggregation number for zwitterion-capped polyisoprenes in cyclohexane vs base polymer molecular weight.

In each sample the molecular weight obtained corresponds to a plateau or near-plateau in reduced intensity, i.e., from data above the critical micelle concentration. The aggregation number for zwitterion-capped polymers is accordingly fairly constant over some dilute range of concentrations in cyclohexane. Aggregation numbers based on osmometry, $\bar{N}_n = \bar{M}_n/M_0$, and light scattering, $\bar{N}_w = \bar{M}_w/M_0$, are given in Table VIII. The zwitterion aggregates are clearly polydisperse, a result which, theoretically at least, rules out a spherical cluster structure based on either the liquid-drop or preferred packing model.[57]

The variation of aggregation number with base polymer molecular weight also supports this conclusion. Figure 7 shows $\bar{N}_n$ vs M_0 for the zwitterion-capped polymers in cyclohexane. A progressive decrease in cluster size with chain length is evident. The problem of reproducibility in the reaction converting amine to zwitterion makes the detailed variation somewhat uncertain, but it nevertheless seems reasonable to conclude that there is an excluded volume interaction causing $\bar{N}_n$ to decrease with increasing M_0. The dependence is neither the sharp cutoff predicted by the preferred-packing model nor the very gradual variation ($N \propto M_0^{-3/10}$) predicted by the liquid-drop model.[57] Both the large polydispersity of cluster size and the intermediate nature of the $\bar{N}$ vs M_0 relationship are more consistent with an extended (cylindrical or stringlike) core morphology.[58]

Table VIII
Aggregation Results for Amine-Capped and Zwitterion-Capped Polyisoprenes in Cyclohexane and Cyclohexane–Heptanol Mixtures

sample	$10^{-4}M_0$[a]	$\bar{N}_n$	$\bar{N}_w$	$[\eta]/[\eta]_0$[b]
		Cyclohexane		
G	1.6_5			1.02
E	1.6_7	1.0_9	2.5	1.16
C	2.0_8	1.3_5	7.3	1.24
A	4.5_3	1.1_3	2.2_5	1.05
B	7.4_0	1.0_3	1.2	1.01
D	8.5_6	1.2_3	1.6_5	1.26
2A	12.9	1.6_5	4.6_5	1.13
3A	6.6_0	1.3_7	3.5	1.08
12A	$24._5$	0.99	1.4	1.03
G-Zw	1.6_5	22	40	1.75
E-Zw	1.6_7	12	17	1.82
C-Zw	2.0_8	31	44	1.64
A-Zw	4.5_3	$14._5$	28	1.42
B-Zw	7.4_0	4.9	12	1.63
D-Zw	8.5_6	4.0	28	1.55
F-Zw	9.7_5	1.1_5	1.5_5	1.18
I-Zw	$10._7$	3.3	10	1.86
J-Zw	$17._6$	1.4	4.2	1.45
		1% 1-Heptanol in Cyclohexane		
C-Zw	1.6_7	9.2	40	1.71
A-Zw	4.5_3	2.0	12	1.29
B-Zw	7.4_0	1.4	6	1.31
F-Zw	9.7_5	0.9_6	1.6	1.10
		5% 1-Heptanol in Cyclohexane		
C-Zw	2.0_8	2.1	$19._5$	1.18
A-Zw	4.5_3	1.2_5	$8._5$	1.02
B-Zw	7.4_0	1.0_1	3.5	1.06
F-Zw	9.7_5	0.87	1.5_5	1.01
3A-Zw	6.6_0	1.5	3.9	0.86
12A-Zw	$24._5$	1.1	2.7_5	0.87

[a] Molecular weight of base polyisoprene, obtained as $\bar{M}_n$ from osmometry for the amine-capped polymer in toluene (except sample G for which $\bar{M}_n$ by osmometry in cyclohexane was used). [b] Values of $[\eta]_0$ were calculated from the base polymer molecular weight M_0 with eq 11. A correction for branching was applied for samples 3A, 12A, 3A-Zw, and 12A-Zw.

The viscosity and diffusion results offer additional means for estimating aggregation number based on the star model. The values obtained from such dynamic measurements, $\bar{N}$(VIS) and $\bar{N}$(DIF), can then be compared with those from the equilibrium measurements ($\bar{N}_w$ is more appropriate in this case, since both dynamic methods weight the larger clusters more strongly). There are two possibilities to consider, depending on the characteristic time associated with any dynamic method compared with the lifetime of the clusters. If the cluster lifetimes are much longer, the value of $\bar{N}$ obtained should agree fairly well with $\bar{N}_w$ from scattering intensity since the latter provides an "instantaneous snapshot" and does not depend on the exchange rate. If the lifetimes are much shorter, however, the value of $\bar{N}$ obtained should be smaller than $\bar{N}_w$ because the higher mobility of dissociated chains will dominate the measurement; $\eta - \eta_s$ would be smaller and D would be larger in this case. The characteristic time for the viscosity measurements is $(\dot{\gamma})^{-1} \approx 2 \times 10^{-3}$ s and for the diffusion measurements is $(Dq^2)^{-1} \approx 2 \times 10^{-4}$ s.

Values of $\bar{N}$(DIF) and $\bar{N}$(VIS) were determined as follows. Hydrodynamic and viscometric radii for the associating polymers, obtained from eq 6 and eq 8, were divided by $(R_H)_0$ and $(R_V)_0$ values for conventional linear polyisoprenes with the same base polymer molecular weight.[7] Equation 12 and $(R_V)_0/(R_H)_0 = 1.11$ for linear polyisoprene in cyclohexane[7] were used. Those ratios, $R_H/(R_H)_0$ and $R_V/(R_V)_0$, depend only on the number of arms for polymeric stars in good solvents.[37] The results

Table IX
Aggregation Numbers of Zwitterion-Capped Polyisoprenes in Cyclohexane and Cyclohexane–Heptanol Mixtures Obtained by Dynamic Measurements

sample	$10^{-4}M_0$	$R_H/(R_H)_0$	$R_v/(R_V)_0$	$\bar{N}$(DIF)	$\bar{N}$(VIS)
			Cyclohexane		
G-Zw	1.6_5		4.2		43
E-Zw	1.6_7	3.8	3.1	30	15
C-Zw	2.0_8	4.4	4.1	48	40
A-Zw	4.5_3	4.7	3.5	63	22
B-Zw	7.4_0	2.1	2.7	4.2	9
D-Zw	8.5_6	4.5	3.5	51	21
F-Zw	9.7_5	1.1	1.2	1.2	1.3
I-Zw	10.7		2.7		9
J-Zw	17.6		1.9		3.2
			1% 1-Heptanol in Cyclohexane		
C-Zw	2.8_8		1.0		38
A-Zw	4.5_3		2.5		7
B-Zw	7.4_0		2.0		3.7
F-Zw	9.7_5		1.2		1.3
			5% 1-Heptanol in Cyclohexane		
C-Zw	2.0_8		2.8		10
A-Zw	4.5_3		2.1		4.2
B-Zw	7.4_0		1.9		3.2
F-Zw	9.7_5		1.1_5		1.2

for polyisoprene stars in good solvents reported in ref 37 were thus used to obtain the values of $\bar{N}$(DIF) and $\bar{N}$(VIS) given in Table IX.

Agreement between $\bar{N}$(DIF) and $\bar{N}$(VIS) is not precise by any means, but their magnitudes and trends are at least reasonably consistent. Correspondence with $\bar{N}_w$ (Table VIII) is about the same. There seems to be no systematic depression of the values obtained from dynamic measurements compared with those from static measurements. The cluster lifetimes in pure cyclohexane are thus presumed to be longer than 10^{-3} s.

Some information about shifts in aggregation number with concentration can be inferred from the values of k_H and $A_2M/[\eta]$. As shown in Table I, both parameters increase with the number of arms per molecule in star polymers. Thus, their elevated values for the zwitterion-capped polymers in cyclohexane (Table V) are consistent with the expected starlike structure of the aggregates. On the other hand, when alcohol is added, the value of k_H remains elevated, but $A_2M/[\eta]$ is now depressed. This combination of results implies that the aggregation number shifts with concentration in the region of the measurements. Thus, k_H should be enhanced if $\bar{N}$ grows with increasing concentration simply because the viscosity will then increase more rapidly than otherwise,[16,17] but A_2 should be depressed because the aggregates will appear to repel one another less than otherwise in a good solvent.[2] Addition of alcohol seems therefore not only to reduce $\bar{N}$ but also to make it more sensitive to concentration in the dilute range. Judged by k_H values, that effect is especially prominent for the multifunctional zwitterions in alcohol–cyclohexane mixtures and is presumably also acting in the case of 3A-Zw in toluene (Table VI).

Conclusions

Sulfo zwitterions, formed by the reaction of terminal tertiary amine groups on polyisoprene with cyclic sultone, associate strongly in aliphatic hydrocarbons. Polymers that contain one zwitterion per molecule form large aggregates in cyclohexane and those containing two or more zwitterions per molecule form gels. The strength of association is greatly reduced in not only solvents of higher dielectric constant than aliphatics, such as tetrahydrofuran, but also aromatic solvents of similar dielectric constant such as toluene. Gelation does not occur in these cases, and aggregation in dilute solutions appears to be negligible. Aggregation size in cyclohexane is greatly reduced when alcohol is added in low concentration (1–5% 1-heptanol).

For the monofunctional polymers in cyclohexane the number of molecules per aggregate $\bar{N}$ decreases with increasing base polymer molecular weight ($1.5 \times 10^4 < M_0 < 1.7 \times 10^5$). We attribute this to an excluded volume repulsion of the polyisoprene tails. The aggregation number appears to be relatively constant over some finite range of concentrations below c^* and then decreases at still lower concentrations. Our values of $\bar{N}$ correspond to that plateau region. The aggregates exhibit some of the characteristics of conventional starlike structures such as increased values of both the Huggins coefficient k_H and the excluded volume parameter $A_2M/[\eta]$. The aggregates are clearly polydisperse, however, and that property together with the nature of the relationship between $\bar{N}$ and M_0 suggests a stringlike rather than spherical geometry for the polar cores. Reasonable agreement between aggregation numbers from static measurements such as light scattering intensity and dynamic measurements such as diffusion indicate that the cluster lifetimes lie well above the millisecond range.

There is some evidence of a shifting association number with concentration when alcohol is present because in this case k_H is increased but $A_2M/[\eta]$ is reduced. The elevation of k_H is especially pronounced for the multifunctional polymers in 1-heptanol–cyclohexane and also in toluene.

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References and Notes

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Macromolecules 1988, *21*, 121-126 121

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Association Phenomena in Macromolecular Systems—Influence of Macromolecular Constraints on the Complex Formation

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ABSTRACT: A theoretical model is presented to describe the association behavior of interacting units attached to a polymer chain. A polymer chain of i functional groups distributed statistically along the chain is considered. A mean field approach is used to derive the probability that the kth functional group forms a complex, if $k - 1$ groups are already complexed. As a result of the fact that the associating units are linked to the polymer chain, the fraction of complexed units is reduced compared to the corresponding association behavior of low molecular weight compounds. The magnitude of these topological restrictions depends on the molecular weight, the concentration of the functional groups, the equilibrium constant for the "free" association, and the conformational properties of the chain.

Introduction

Since the pioneering work of Lundberg et al.[1-3] there has been increased interest in the structure-property relationships of ionomers. Strong physical associations between ion pairs lead to gel formation which is strongly dependent on dilution and temperature. Several theoretical approaches are reported in the literature to give a more general description of these systems.[4-6] One essential problem is the characterization of the ionic interactions. These may be ionic aggregates of different order (doublets, quadruplets, up to highly ordered clusters). Only few experimental results on ionomeric model systems, in order to characterize the cluster structure in detail, have been reported so far.[7,8] In most of the theoretical approaches[5,6] only the simplest case of two interacting sites is considered. Such types of noncovalent interactions also are observed in biopolymers, where hydrogen bonds are partly responsible for the formation of physical gels.[9,10] Corresponding theoretical work to describe the gel formation has been developed either on the basis of percolation theory[11,12] or