at the present time. Preliminary X-ray studies of the triblock polymers under stress indicate very marked changes in all of the scattering peaks. However, the interpretation is no longer as simple as in the above experiments.

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The Association Behavior of Polystyryllithium, Polyisoprenyllithium, and Polybutadienyllithium in Hydrocarbon Solvents[1a]

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ABSTRACT: The states of association of the following polymer–lithium species were determined in various solvents: polystyryllithium in benzene; polyisoprenyllithium in benzene, *n*-hexane and cyclohexane; and polybutadienyllithium in benzene. Both concentrated solution viscosity and light-scattering measurements yielded convincing evidence that all of these polymeric molecules are associated *in pairs* in these hydrocarbon solvents. As indicated in previous studies, the effect of ethers, such a tetrahydrofuran, is to break up these dimeric associated species, presumably by means of a solvation equilibrium. These results appear to vitiate the postulate, which has been advanced at various times, that the isoprene and butadiene systems must have higher states of association in order to explain the low kinetic order of the propagation reaction in hydrocarbon media.

It has been long recognized on the basis of experimental evidence that organolithium compounds are associated to various extents in hydrocarbon media. Thus ethyllithium has been found to be a hexamer in both benzene[2] and cyclohexane[3] but a tetramer in the vapor state.[2] In these solvents *n*-butyllithium[4] also is a hexamer. This aggregation of organolithium species is the result of multicenter bonding, *i.e.*, the number of atomic orbitals available for bonding exceeds the number of electrons which are available to occupy them with the result that the available atomic orbitals are combined to form molecular orbitals which extend over more than two atoms but which can only accommodate one electron pair.

The variation in the degree of association between the straight and branched chain organolithiums has been discussed by Brown.[2] He noted that in any proposed structures for ethyllithium, the distance between adjacent alkyl groups was much greater in the tetramer than in the hexamer. Thus, in those instances in which there is little interaction between the alkyl groups, the hexamer would be the preferred structure. However, in *sec*-butyllithium and *t*-butyllithium the comparatively bulky branched chains will interact with its neighbors in the hexamer structure. Thus these organoliths would be expected to accept the next most favorable association state, the tetramer, and this has actually been found to be the case for *sec*-butyllithium on benzene[5] and for *t*-butyllithium in both benzene and hexane.[6]

On steric grounds, one might also anticipate low states of association for long chain organolithiums, *e.g.*, *n*-dodecyllithium is reported to be a tetramer in benzene.[7] The polymerization of styrene, butadiene, and isoprene by organolithium initiation in hydrocarbon solvents has brought to light the fact that these polymer–lithium species are also associated even at very low lithium concentration (10^{-3} to 10^{-4} M, as contrasted with 0.2–3 M for the alkyllithiums). The state of association of polystyryllithium and polyisoprenyllithium was actually first[8,9] determined by precise molecular weight measurements, using the concentrated solution viscosity method. These results showed that these polymeric species were associated *in pairs*, the degree of association being about 98–99% at 10^{-3} to 10^{-4} M concentrations of lithium. As might be expected, in such polymerization systems, the polymer–lithium species might cross-associate with any unreacted alkyllithium initiator, and evidence for this has also been found.[8]

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[1] (a) Portions of this paper were presented at the International Symposium on Macromolecular Chemistry Tokyo-Kyoto, Japan, 1966; (b) to whom all correspondence should be addressed.

[2] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, **84**, 1371 (1962).

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[8] M. Morton, E. E. Bostick, and R. A. Livigni, *Rubber Plastics Age*, **42**, 397 (1961).

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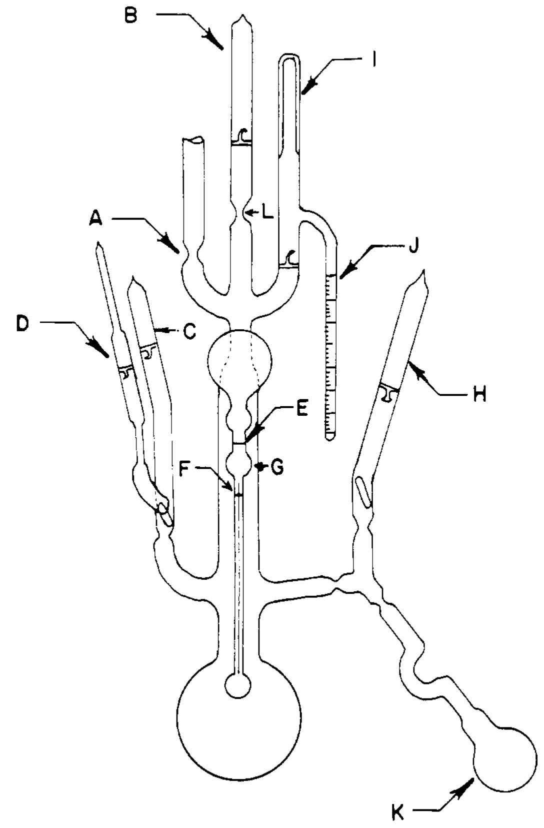

Figure 1. Vacuum viscometer.

The existence of this association in the polymer–lithium species has been used to account for the kinetic order of the propagation step in these polymerizations. Thus the observed *half-order dependence*[10] of the styrene propagation rate on lithium concentration could conveniently be explained by a kinetic scheme in which only the *dissociated chain ends* are capable of propagating. However, in the case of the dienes, isoprene and butadiene, the kinetic order of the propagation rate with respect to lithium concentration was subsequently found to be much lower than one-half. In fact these orders were reported to be as low as *one-fourth* for isoprene[11] and *one-sixth* for butadiene.[12] Unfortunately, these kinetic orders have actually been used[12,13] to infer correspondingly higher states of association for these polymer lithium species, without any reliable experimental evidence for the existence of such states. Thus polyisoprenyllithium was *assumed* to be associated as a tetramer[11,13] while polybutadienyllithium was proposed as a hexamer[12,14] based on the same kinetic scheme as for styrene, *i.e.*, where only the dissociated chain ends are assumed to propagate.

The above assumed high values of association for polyisoprenyllithium, based purely on kinetic considerations, were at variance with the only reliable direct measurements,[8,9] which showed these species to be associated in pairs. However, the latter measurements had been made in *n*-hexane solution while the kinetic data were obtained from cyclohexane solutions. As for butadiene, the only physical measurements[8,9] of association led to values somewhat higher than 2, and this was ascribed to the presence of some branched polyfunctional lithium species.

In view of the above contradictions and uncertainties, it was thought advisable to obtain additional information on the states of association of these two dienes in organolithium polymerization systems in several hydrocarbon solvents, using both concentrated solution viscosity and light scattering methods.

Experimental Section

The purification of solvents and monomers, and the preparation of ethyllithium are presented elsewhere.[15,16] All experimental manipulations were accomplished on a high-vacuum system or in closed, evacuated flasks. The general techniques used have been described previously.[16]

Preparation of Polymeric "Seeds." Low molecular weight (*ca.* 2000) isoprenyl- or styryllithium was prepared by reacting in bulk at 0° ethyllithium and the appropriate monomer. This "seed" was then diluted with solvent and used to actuate the polymerization of the appropriate monomer. *sec*-Butyllithium (Lithium Corp.) was also used as an initiator. The *sec*-butyllithium was purified by following the distillation procedure of Worsfold.[5]

Viscometric Measurement of Association Number. In concentrated polymer solutions the viscosity relationship; $\eta = KM^{3.4}$ has been found[17,18] to hold in the region where $cM \gg 2M_e$. In these equations c is the volume fraction of polymer, M is the polymer molecular weight, M_e is the well-known "molecular weight between entanglements," and the polymer concentration is included in K (the constant of proportionality). Since one is measuring flow times in a viscometer, the above viscosity equation can be rewritten as

$$t = K^1M^{3.4}$$

where t denotes the solution flow time. Hence

$$\frac{t_a}{t_t} = \left(\frac{M_a}{M_t}\right)^{3.4}$$

where the subscript a refers to the active (associated) solution while t refers to the terminated solution. The ratio of M_a/M_t can be defined as the association number (N). The apparatus shown in Figure 1 was used for viscometry. The viscometer was sealed onto the grease trap (Figure 2) at tube A. After the viscometer had been flamed, about 50 ml of benzene was distilled in, and the viscometer sealed off from the vacuum line at the constriction on tube A. The purge, consisting of a mixture of *n*-butyllithium and styryllithium was enclosed in ampoule B. The viscometer was washed and the purge solution collected in the side flask K. Solvent was then distilled back into the viscometer several times in order to remove all traces of active lithium compounds. The solution was frozen in liquid nitrogen and the purge flask removed. The reactor was then reattached to the grease trap *via* tube B. After evacuation of the grease trap, the break-seal in tube C was shattered. The seed solution in ampoule D

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(15) M. Morton, A. A. Rembaum, and J. L. Hall, *ibid.*, *Part A*, **1**, 461 (1963).

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(17) V. R. Allen and T. G Fox, *J. Chem. Phys.*, **41**, 337 (1964).

(18) T. G Fox and V. R. Allen, *ibid.*, **41**, 344 (1964).

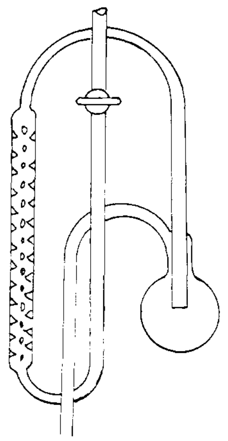

Figure 2. Grease trap.

was then admitted by shattering its break-seal, and complete transfer assured by refluxing solvent into the ampoule. This ampoule was then removed by sealing off from the rest of the reactor after the seed solution was frozen with liquid nitrogen. Following this, the desired amounts of solvent and monomer were distilled into the viscometer, chilled to −78°, and the viscometer removed from the vacuum line by sealing off at L. After the reaction mixture was warmed to room temperature, the contents were mixed well, and the viscometer was clamped in a constant-temperature bath at 30°. Polymerization was allowed to proceed for a minimum of 12 hr before flow times were determined.

Filling the viscometer was accomplished by bringing the viscometer to a horizontal position in a constant-temperature tank and then tilting the viscometer slightly so that the polymer solution flowed into bulb G. The tank was set at the same temperature as the bath in which the viscometer was immersed when it was in the vertical position. Once again, the apparatus was clamped in the vertical position in a constant-temperature bath, and the time required for solution to flow between lines F and E was recorded. Since the solution must be mixed well, the viscometer was rotated while in the horizontal tank before each filling cycle.

Use of both the horizontal tank and the vertical constant temperature bath was found to be necessary to eliminate errors due to distillation of solvent from the polymer solution to any surface which might be slightly cooler. The time during which the viscometer was out of a constant-temperature bath was kept to less than 3 sec per filling cycle.

After the active flow time had been determined, about 0.1 ml of methanol was added from ampoule H to terminate the polymer. The flow time of the terminated polymer solution was then determined.

Light-Scattering Procedure. The apparatus used to prepare the active polymer lithium solutions for measurement of the state of aggregation by light scattering is shown in Figure 3. Attachment to the vacuum line was done at outlets V. Ampoule A contained the purge solution, and ampoule B contained the seed solution. The polymerization solution was prepared in bulb D and the required amount transferred to ampoule C. After polymerization was complete, the ampoules C were sealed off from the reactor at E and stored at −20° until use.

The actual apparatus used for the light-scattering measurements is shown in Figure 4. Ampoule A contained the purge solution, ampoule B contained the polyisoprenyllithium, and ampoule C had the methanol terminator. The glass frit at D prevented fragments of the break-seals from entering the light-scattering cell E. In practice, the solvent (*n*-hexane) used in the purging process was reserved and used for diluting the polymer lithium solution from ampoule B. This prevented introduction of possible terminating impurities with the dilution solvent. All of the solution was poured into the cell E and any residual polymer–lithium solution was rinsed into cell E by distilling hexane throughout the reactor. The polymer concentration in the cell was controllably changed by distilling hexane back into the measuring section G and noting the volume distilled out. Since the volume of solvent which had to be removed to double the concentration in the cell decreased as the volume of solution in cell E decreased, bulb F was made to contain the volume removed from the first change in concentration and subsequent changes were read as increases in section G (part of a 25 ml graduated cyclinder). Attachment to the vacuum line was done at tube V of the apparatus.

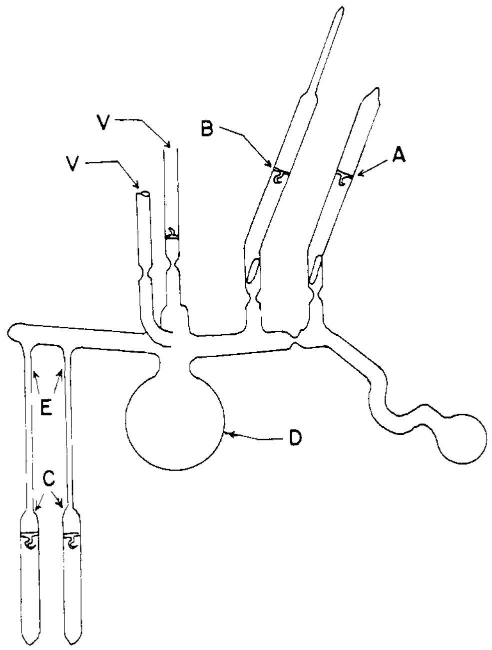

Figure 3. Reactor for the preparation of polyisoprenyllithium used for the light-scattering experiments.

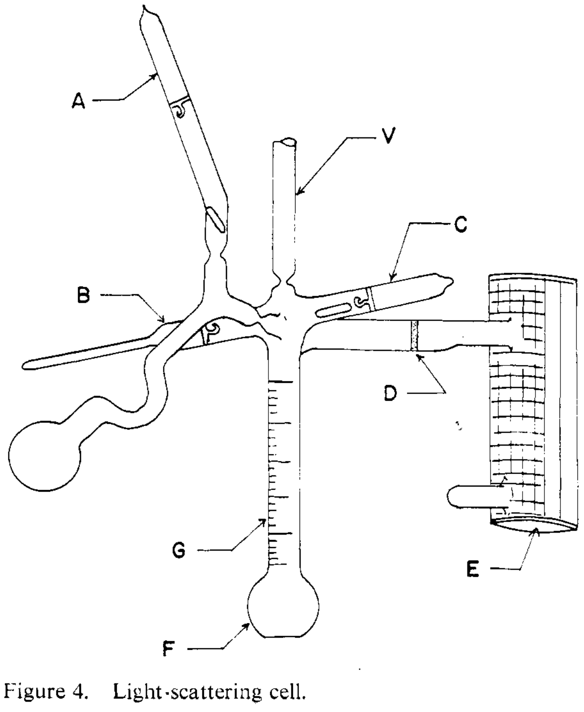

Figure 4. Light-scattering cell.

Light-scattering data were taken as usual with a Brice-Phoenix light-scattering photometer. Unpolarized light of 5461 Å was used. Since small temperature differences are sufficient to cause distillation of the hexane under vacuum, care was taken that the apparatus was at thermal equilibrium with the instrument before the volume of solvent was read from G or light-scattering measurements taken.

"Capping" Procedure. Following the conventional polymerization of styrene in the vacuum viscometer (Figure 1), the styryllithium chain ends were allowed to react with a small amount of diene monomer. A hammer was introduced through the heavy wall tubing I and the reactor sealed onto the grease trap at I. The desired amount of diene was distilled into the measuring tube J (a section of a 1-ml graduated pipet) and frozen with liquid nitrogen. The viscometer was then sealed off from the line at I. Butadiene was warmed to −78° and its volume checked while isoprene was warmed to 20° for its volume check. At the desired time, the break-seal was shattered and the monomer distilled into the reactor.

Results

Association of Polystyryllithium. The change in "molecular weight" of polymer–lithium chains in going from the active-associated state to the terminated-unassociated state will manifest itself by a change in solution viscosity and in the intensity of scattered light. Hence, both techniques lend themselves to a quantitative determination of the degree of association. Although both methods reflect the weight-average molecular weight, while the number-average value is desired for association measurements, the virtually monodisperse nature[10,19] of these samples means that the weight- and number-average values should be identical.

Table I presents the association data for polystyryllithium in benzene. The value of the association number, N, confirms earlier results obtained by this method.[8,9] Hence the evidence shows that polystyryllithium in benzene is a dimeric chain.

Since the evaluation of N is dependent upon the applicability of the 3.4 exponent, it was thought to be worthwhile to verify this viscosity–molecular weight relation for this system. Three polystyrenes of varying molecular weights were prepared for this purpose, their molecular weights ($\overline{M}_v$) being determined from their intrinsic viscosities in benzene using the equation of Altares.[20] The relation between flow time and molecular weight is shown in Table II, where it can be seen that the two values of the exponent are very close to the expected value of 3.4. Far more substantial and sophisticated verification of the validity of the 3.4 power is available elsewhere.[17,18] The entanglement molecular weight of polystyrene was taken as 18,000.[18]

TABLE I
ASSOCIATION OF POLYSTYRYLLITHIUM IN BENZENE AT 30°

$[RM_jLi] \times 10^3$	Flow time, sec t_a	t_t	M	N
0.5	2060	209.5	1.2	1.96
1.0	2273	230.2	1.7	1.96
1.1	1501	152.4	1.8	1.96
1.2	1577	160.0	1.9	1.96
1.2	1363	135.0	1.8	1.98
1.4	1960	195.8	1.8	1.97

TABLE II
VERIFICATION OF a IN THE RELATION $\eta = KM^a$ FOR POLYSTYRENE IN BENZENE AT 40°

$M_v \times 10^{-4}$, g mol^{-1}	Volume fraction of polystyrene	Flow time, min	a
9.8	40	58.0	3.41
12.8	40	147.0	
7.7	50	51.5	3.39
12.8	50	284.0	

TABLE III
THE EFFECT OF TETRAHYDROFURAN ON POLYSTYRYLLITHIUM ASSOCIATION IN BENZENE AT 30°[a]

$[RM_jLi]_0 \times 10^3$	$[THF]/[RM_jLi]_0$	—Flow time, sec— t_a	t_t	N	$K \times 10^{-2}$
1.2	2.6	347.5	86.0	1.51	1.8
1.2	3.1	514.4	129.3	1.50	1.3
0.87	3.2	208.0	56.0	1.47	1.9
0.62	4.3	200.0	62.6	1.41	2.0
0.73	5.2	386.7	127.3	1.39	1.2
3.8	7.4	242.0	179.6	1.09	1.1

[a] $K = [RM_jLi \cdot THF]^2/[(RM_jLi)_2][THF]^2$.

With polystyryllithium definitely established as being dimeric in hydrocarbon solution, the influence of tetrahydrofuran on the state of association was examined. It can be seen from the results in Table III that only trace amounts of tetrahydrofuran are sufficient to disrupt completely the associated polystyryllithium. Hence polystyryllithium self-association is virtually absent when the tetrahydrofuran reaches a concentration ten times greater than the lithium chain-end concentration. This may be contrasted with the previous observation[9] that polyisoprenyllithium requires a tetrahydrofuran–lithium ratio of about 2600 in order to eliminate completely all associated species. As was the case for polyisoprenyllithium, the tetrahydrofuran does not seem to coordinate with the polystyryllithium in a stoichiometric fashion, but seemingly participates in an equilibrium reaction. Thus, the following equilibrium system can be proposed[9]

$$(RM_jLi)_2 + 2n\text{THF} \underset{}{\overset{K}{\rightleftarrows}} 2RM_jLi \cdot n\text{THF} \qquad (1)$$

The concentration of the solvated species $RM_jLi \cdot n$THF can be calculated from the N values in a fashion analogous to the procedure presented elsewhere.[9] When this is done, values of K can be calculated by assigning various values to n in eq 1. As was the case for the polyisoprenyllithium complex, the only consistent values of K are obtained when n is unity.

It should be noted that the measurements listed in Table III were completed within 1 hr or less after adding the ether to the solution. This was done in order to circumvent the occurrence of the well-known reactions between organolithiums and tetrahydrofuran.[21,22]

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(19) M. Morton, E. E. Bostick, and R. G. Clarke, *J. Polym. Sci., Part A*, **1**, 475 (1963).

(20) T. Altares, Jr., D. P. Wyman, and V. R. Allen, *ibid., Part A*, **2**, 4533 (1964).

(21) A. A. Rembaum, S.-P. S. Yen, and N. Indictor, *ibid.*, **56**, S17 (1962).

(22) L. J. Fetters, *ibid., Part B*, **2**, 425 (1964).

TABLE IV
ASSOCIATION OF POLYISOPRENYLLITHIUM IN HYDROCARBON SOLVENTS AT 30°

$[RM_jLi]_0$ × 10^3	Flow times, sec t_a	t_t	M	Solvent	N
1.8	1268	126.0	3.4	Benzene	1.97
1.9	1006	103.6	3.4	Benzene	1.95
3.2	5855	449.5	3.6	Benzene	2.13
1.40	690	67.5	3.4	*n*-Hexane	1.98
1.42	544	53.3	3.4	*n*-Hexane	1.98
1.42	436	43.1	3.4	*n*-Hexane	1.98
0.7	3080	290	2.9	0.03[a,b]	2.00
1.0	412	72	3.0	0.26[b]	1.99
1.2	1190	114	3.2	0.40[b]	1.99
1.5	3060	290	3.4	0.03[b]	1.99
0.9	169	16.6	2.9	Cyclohexane	1.98

[a] Volume fraction of benzene. [b] Solvent *n*-hexane-benzene.

TABLE V
LIGHT SCATTERING OF POLYISOPRENYLLITHIUM IN *n*-HEXANE AT 27°

Polymer no.[a]	Zimm plots intercept $c/(\Delta I \times \phi)$ Active	Terminated	$M_w \times 10^{-5}$, g mol^{-1} Active	Terminated
1	4.3	8.5	3.0	1.5
2a	4.95	9.45	2.6	1.4
2b	5.1	9.60	2.6	1.3

[a] Polymers **2a** and **2b** were duplicate samples taken from the same polymer solution d*n*/d*c* = 0.1802 ml g^{-1}: K. Altgelt and G. V. Schulz, *Makromol. Chem.*, **36**, 209 (1960).

Over this time interval, the flow times of the active solutions were constant.

Association of Polyisoprenyllithium. Using vacuum viscometry, values of N for polyisoprenyllithium in several hydrocarbon solvents and solvent mixtures were obtained. For these measurements, a value of 7000[23] was used for M_e. The data are presented in Table IV, where it can be seen that a value of 2 was obtained for N, as was the case for the previous investigation.[8,9] Thus the active chains appear to be associated in pairs in these hydrocarbon solvents, regardless of the solvent used.

This conclusion also receives substantial support from light-scattering measurements of the molecular weights of polyisoprenyllithium in *n*-hexane. These results are shown in Table V, based on values obtained from measurements taken between 35 and 135°. Two of the Zimm plots are shown in Figures 5 and 6. Thus both the viscosity and light-scattering techniques yield identical values for N, *i.e.*, an association number of two for polyisoprenyllithium, within the concentration range of 10^{-3} to 10^{-5} M.

Association of "Capped" Polymers. In order to obtain a more unequivocal resolution of this problem, these association studies were extended by introducing a new technique, *viz.*, the "capping" of a fully polymerized chain by the addition of another monomer, in order to note any changes in the solution viscosity. Such a change, if observed, would of course reflect an alteration in the state of association. Since polystyryllithium has been shown to be associated in dimers, both in benzene and cyclohexane, by viscometric and light-scattering methods,[12] it was thought best to use it as the base polymer. Thus, to the completely polymerized polystyryllithium was added a small amount of either isoprene or butadiene. Since it is known that this "cross-over" reaction is very rapid,[14,24,25] any marked changes in viscosity should be easily noticeable.

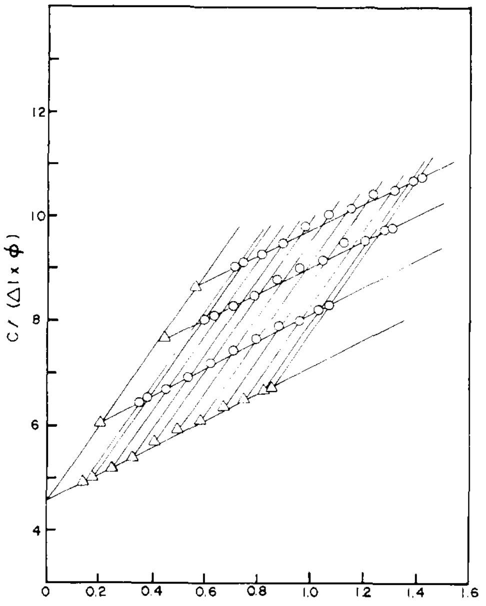

Figure 5. Zimm plot of polymer **1**, unterminated.

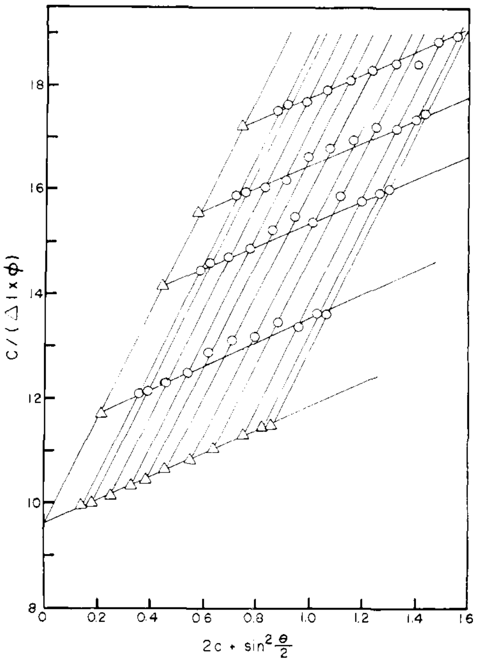

Figure 6. Zimm plot of polymer **1**, terminated.

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(23) L. J. Fetters, *J. Res. Nat. Bur. Stand.*, **69A**, 33 (1965).

(24) M. Morton and F. R. Ells, *J. Polym. Sci.*, **61**, 25 (1962).

(25) A. F. Johnson and P. J. Worsfold, *Makromol. Chem.*, **85**, 273 (1965).

TABLE VI
ASSOCIATION OF CAPPED POLYSTYRYLLITHIUM CHAINS AT 30°

$[RM_jLi]_0$ × 10^3	t_a,[a] sec	t_a/t_t[b]	M	Solvent	Diene monomer	Polydiene, M_s[c] × 10^{-3}, g mol^{-1}	N
0.60		398.8/38.4	1.5	Benzene	Butadiene	2	1.99
0.63		268.9/26.2	1.5	Benzene	Butadiene	2	1.98
2.40	1899	1974/187.5	3.2	Benzene	Isoprene	2	1.98
2.40	1567	1591/158.4	3.0	Cyclohexane[d]	Isoprene	2	1.96

[a] Flow time of polystyryllithium solution prior to capping with the diene. [b] Ratio of the flow times of the capped polymer to the terminated polymer solution. [c] Stoichiometric number-average molecular weight of the polydiene block based on the amount of monomer added and the total lithium concentration. [d] Temperature of 40°.

It should be noted that any change in the association number from 2 to 4 or 6 would be expected to be accompanied by a marked increase in viscosity. At any rate, following the complete polymerization of the small amount of added diene, the viscometric measurements were carried out, as previously described, before and after chain termination.

The results of these experiments are shown in Table VI. It can be seen that all systems correspond to an association number of 2, with the usual allowances for some dissociation. Thus, the flow times of the polystyryllithium solutions before and after capping are nearly the same. This, of course, shows that the polystyryllithium and the polydienyllithium chains possess the same association number. Of interest is the case of the butadiene-capped polymers, since these are the first measurements of the association of polybutadienyllithium uncomplicated by possibilities of crosslinking.[9] Unlike previous results,[9] these polybutadienyllithium species fail to show N values greater than 2.

From the foregoing, it would seem that the state of association of these polymer–lithiums is the same, independent of the type of monomer or hydrocarbon solvent. Furthermore, in the data reported herein, there exists no indication that any of the polymer chains exist in an association state containing more than two active polymer–lithium species.

In conclusion, it can be stated that the results reported herein, based on concentrated solution viscosity and light-scattering measurements, demonstrate unequivocally that polystyryllithium, polyisoprenyllithium, and polybutadienyllithium are all associated *in pairs* in hydrocarbon solvents. In this respect there seems to be general agreement by other investigators[12] as regards the state of association of polystyryllithium. However, some isolated published data on polyisoprenyllithium[11] using light-scattering techniques have been used to propose an association number of four. A closer examination of this claim,[11] however, reveals the fact that it is based on only three measurements of association, leading to values of 1.6, 2.4, and 3.7 instead of the proposed value of 4.0. Furthermore, no details were furnished about these light-scattering measurements and no primary data were shown. It would therefore seem that these reported association numbers of 4 and 6 for polyisoprene and polybutadiene,[14] respectively, can only be considered as the result of wishful thinking under the pressure of puzzling kinetic data.[11,13]

It may, of course, be argued that the value of 2 represents an average of a distribution of states of association, but it would be most fortuitous that such an average should be so close to the value of 2 for the different polymers examined in the different solvents. Hence it can only be concluded that this association number represents the state of the overwhelmingly predominant species.