Scheme I. The reactions are systematically explained as initiated by the VCZ cation radical intermediate (I) formed by the photochemical electron transfer from VCZ to the electron acceptor, the direct evidence of which has been obtained by means of flash spectroscopy.[9,10] The present results concerning the correlation between the reaction course in basic solvents and the strength of the solvent basicity are consistent with the mechanism shown in Scheme I. That is, cation solvation toward I in the basic solvents leads to the formation of II by the radical reaction of I with the VCZ monomer and then the electron back-transfer to II and the cyclization produces the cyclodimer.[2] When the solvent basicity becomes very strong, the electron back-transfer to II comes to be impeded due to the very strong cation solvation; hence subsequent radical additions of the VCZ monomer occur leading to the formation of the polymer. In the previous paper[2] we have shown that whether I shows cationic or radical reactivity is mainly determined by the strength of the solvent basicity. In addition, the present study shows that the direction of the succeeding reaction following the initial radical reaction of I, *i.e.*, cyclodimerization or radical polymerization (?), is also determined by the strength of the solvent basicity most probably at the stage of II. Thus, photosensitized reactions of VCZ in the presence of the electron acceptor are entirely regulated by the solvent basicity.

References and Notes

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A Resolution of the State of Association of Poly(dienyl)lithium Chain Ends in Hydrocarbon Solvents

Lewis J. Fetters* and Maurice Morton

Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

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ABSTRACT: The association states of the poly(dienyl)lithium species in cyclohexane have been reexamined. This study was undertaken in view of a recent report which purports to show that, in cyclohexane solution, poly(butadienyl)lithium is associated as a tetramer while poly(isoprenyl)lithium possesses average degrees of association ranging from 3 to 4. It is shown here that these conclusions are in error and result from artifacts arising from faulty experimental procedures. The errors in the above-mentioned report are discussed and new data presented which confirm the fact that the poly(dienyl)lithium chains are associated *in pairs* at concentrations appropriate for polymerization. These results are derived, in part, from concentrated solution viscosity measurements of the polydiene solutions before and after linking with $(CH_3)_2Si(Cl)_2$, $(CH_3)Si(Cl)_3$, and $SiCl_4$. The use of the latter two chlorosilanes brought about the nearly quantitative formation of "star" branched polymers and a concurrent *increase* in solution viscosity whereas the use of $(CH_3)_2Si(Cl)_2$ brought about virtually *no* change in viscosity. This behavior is consistent with an association state of two for the poly(dienyl)lithium chains.

The degree of association of the chain ends of poly(styryl)-, poly(isoprenyl)-, and poly(butadienyl)lithium was originally determined[1-4] from measurements of the viscosity of concentrated solutions, using the well-known equation

$$\eta = KM^{3.4} \tag{1}$$

which relates the viscosity to the molecular weight in the "entanglement region." These measurements consistently and reproducibly showed that all of the above polymeric species are associated *in pairs*. Such results, though, have apparently met with dismay or have been ignored on the part of those[5-13] who wished to ascribe much higher states of association to the poly(dienyl)lithium chain ends (up to 4 or 6), based purely on considerations of polymerization kinetics, rather than on direct molecular weight measurements. More recently, a publication[14] has appeared which purported to present direct evidence for the tetrameric state of association of poly(dienyl)lithium.

The motivation behind assigning an association number of 4 or higher to the poly(dienyl)lithium chain ends results from the observed ¼–⅙ dependency of polymerization rate on chain end concentration and the acceptance of the proposition that only unassociated chain ends are reactive toward monomer. However, the convenient concept that only unassociated organolithium compounds are the reactive species in initiation and propagation reactions need not, necessarily, be correct. In fact, quite plausible mechanisms have been presented[15-25] which show that the fractional orders of these reactions can be accounted for quite satisfactorily by involving associated organolithium species (hexamer, tetramer, dimer) as reactive entities. The vast majority of the balanced appraisals and observations reveal that one must consider a wide range of possibilities in defining the active participant *or* participants in any organolithium reaction and that the establishment of any reaction order with respect to each participant is by no means a trivial operation.

The purpose of this article is to offer a critique of the publication[14] mentioned above and to present new data which support the original findings[1-4,25] that the poly(dienyl)lithium species are associated in dimers, in hydrocarbon solvents, at the low concentrations appropriate to polymerization reactions. The evidence presented in the above paper[14] in support of the higher states of association consisted of the following.

(1) A presumed demonstration of the inapplicability of eq 1 above to these polymers because the 3.4 power dependency on molecular weight is allegedly invalid in the region of molecular weights (8×10^4 to 4×10^5 g/mol) studied at the concentration used.[14] This invalidity is claimed to be due to an extended *gradual* curvature (instead of a relatively sharp transition) in the viscosity *vs.* molecular weight plot in the region where the dependency changes from 1st power to 3.4 power. As a result, for example, these investigators[14] obtained *low* ratios of the viscosity of *active vs. terminated* polystyrene chains (ranging from 4.2 to 9.2 with increasing molecular weight, instead of the value of 10, consistently reported elsewhere,[1-4] as expected for dimeric association).

(2) Light scattering measurements on poly(styryl)lithium itself or after "capping"[26] with isoprene or butadiene to create poly(isoprenyl)lithium and poly(butadienyl)lithium chain ends. These results purported to show that while polystyrene chain ends were associated in pairs, polybutadiene chain ends were associated as tetramers and the polyisoprene chain ends showed a range of association values, from tetrameric at higher concentrations (*ca.* 10^{-3} *M*) to less than trimeric at the lowest concentration (*ca.* 10^{-6} *M*).

It will be shown that the conclusions reached[14] on the basis of the above two lines of investigation are invalid, not only because the experimental approach was faulty, but also because of incorrectly plotted data, both original and quoted.

Experimental Section

The methods of purification of solvents and monomers have been presented elsewhere.[27,28] One modification that was used for the purification of styrene was the use of the hydrocarbon-soluble dibutylmagnesium.[29] This organometallic compound does not rapidly initiate or polymerize styrene but does serve to purge this monomer of reactive impurities. Its use has already facilitated preparation[30,31] of polystyrene with weight-average molecular weights of up to 43.7×10^6 g/mol.

The monomer and final solvent purifications were conducted on a high vacuum line equipped with Teflon Rotaflow stopcocks. The polymerization reactors, including the viscometers, were evacuated on this vacuum line prior to their final purging by low molecular weight poly(styryl)lithium. Phillips high purity (>99.5%) butadiene and isoprene and Eastman styrene were the monomers used.

Polymer solutions in benzene or cyclohexane were filtered twice without applying pressure through 0.45-μ filters[32] prior to placement in the light-scattering cells. The light-scattering photometer was a commercial instrument[33] and was calibrated for absolute scattering intensity against benzene. The Rayleigh ratio of benzene adopted for our measurements was 15.8×10^{-6} cm^{-1} at 546 nm.[34] Unpolarized light was used for all measurements, while the scattered intensity was measured at 11 angles over the angular range of 30–150°. Optical alignment was verified by observing the scattering envelope for pure benzene and by carrying out measurements on the National Bureau of Standards 705 and 706 polystyrene samples. The measurement temperatures were 30° for benzene and 35° for cyclohexane. The values of d*n*/d*c* used were those given elsewhere.[35,36]

Number-average molecular weights were measured with the aid of commercial high-speed membrane servo-osmometers.[37] Gel-cellophane 600 membranes were used. All measurements were conducted in toluene solutions at 37°. The number-average molecular weights were determined by the usual $(\pi/C)^{0.5}$ *vs.* *C* plots. Prior to any measurements, the osmometers were checked with the use of solutions of the National Bureau of Standards 705 polystyrene standard.

Intrinsic viscosity measurements were performed using a Cannon-Ubbelohde low shear viscometer. Benzene and cyclohexane were the solvents used at 30 and 35°, respectively. The viscometer had shear rates in the range of 50–240 sec.$^{-1}$ Viscosity measurements on the concentrated polymer solutions followed the procedures described elsewhere.[3,4]

A commercial[38] gel permeation chromatograph was used to gain additional insight into the molecular weight distributions of the polymers synthesized in this study. Tetrahydrofuran was the carrier solvent at a temperature of 25°. Solution concentrations were 0.25% (w/v). A differential refractive index detector was used with the following seven Styragel columns: $2–5 \times 10^3$ Å, two columns with $5–15 \times 10^3$ Å, $1.5–5 \times 10^4$ Å, $5–15 \times 10^4$ Å, $1.5–7 \times 10^5$ Å, and $7–50 \times 10^5$ Å. A flow rate of 0.25 ml min^{-1} was used. At this flow rate the seven column set had a plate count of 950 ppf. The plate count was determined in the usual fashion[39] as were the number- and weight-average molecular weights.[40] The columns were calibrated using 19 polystyrene standards[41] of both narrow and broad molecular weight distributions. A linear calibration was obtained between the molecular weights of 4×10^3 and 2.1×10^6 g/mol. The instrument was equipped with a 5-ml syphon. Solution injection times were 20 min in all cases.

The polyisoprene samples were isolated by coagulation in methanol. The polystyrene samples were isolated by freeze drying for 72 hr. For the polystyrene samples prepared in cyclohexane, the solutions were diluted with 0.2 to 0.3 l. of benzene prior to freeze drying.

Commercial solutions[42] of *sec*-butyllithium and *tert*-butyllithium were used. The initiators were purified *via* a short path distillation under high vacuum.[43,44] Colorless solutions were obtained in all cases. It is interesting to note that analyses,[45] *via* gas chromatography, of the commercial *sec*- and *tert*-butyl chloride used in the preparation of the initiators revealed that these materials contained a small amount (0.2–0.3%) of *n*-butyl chloride. Hence, the commercial *sec*- and *tert*-butyllithium would be expected to contain a corresponding amount of *n*-butyllithium. This has been verified by analysis in these laboratories of purified solutions of both the *sec*- and *tert*-butyllithium initiators.

Results and Discussion

I. Viscosity Studies. The results obtained by the above authors[14] with regard to the viscosity of concentrated polystyrene solutions are in error, as a proper understanding of the available evidence pertaining to the flow properties of concentrated polymer solutions reveals. Their results are vitiated on at least three counts, as follows: (a) the misplotting of viscosity data in an attempt to demonstrate the purported failure of the relation shown in eq 1 above; (b) the use of the slow[46-48] initiator *tert*-butyllithium for styrene polymerization, leading to a marked broadening of the molecular weight distribution of the samples as well as variations in polydispersity with molecular weight; this renders the use of $\langle M_n \rangle$, instead of $\langle M_w \rangle$, in the log η–log M plot by the same authors[14] invalid; (c) the use of cyclohexane as solvent at 35°, where it shows anomalous results for diene-capped polystyrenes.

In the first place, the above authors[14] base their claim about the inapplicability of eq 1 on their data shown in Table IV and plotted in Figure 3 of ref 14. The latter purports to show a gradual curvature instead of a relatively sharp transition in the log η *vs.* log M plot, as well as failure to attain the 3.4 power relation until a molecular weight of about 4×10^5 g/mol is reached at the concentration of polystyrene used. However, this plot is based on a mixture of experimental points, including selected data points from the work of Graessley, *et al.*,[49] which were obtained both at a different temperature (30° instead of 35°), a slightly different concentration, and even in a different solvent (butylbenzene). It actually turns out that the polystyrene viscosity data in Table IV of ref 14 alone lead to a plot which fails to show the curvature illustrated in Figure 3 of ref 14. In reality, for example, the first seven (out of eight) data points pertaining to the viscosities of the polystyrenes yield a straight line with a slope of about 2.6.

As a matter of record, eq 1 has been amply confirmed by a wealth of experimental data[49-62] and is generally accept-

Table I
The Molecular Weights of Polystyrene Prepared by *tert*-Butyllithium Initiation in Cyclohexane at 35°[a]

Sample	$\langle M_n \rangle\ 10^{-3}$ g mol^{-1}	$\langle M_n \rangle\ 10^{-3}$ g mol^{-1} (gpc)	$\langle M_v \rangle\ 10^{-3}$[b] g mol^{-1}	$\langle M_w \rangle\ 10^{-3}$ g mol^{-1}	$\langle M_w \rangle\ 10^{-3}$ g mol^{-1} (gpc)
S-6	27 ± 1.0	24	42	45 ± 2.0	46
S-3	57 ± 1.5	55	103	120 ± 5.0	113
S-4	90 ± 2.7	90	145	148 ± 6.0	147
S-7[c]	97 ± 2.0	96	97	98 ± 3.0	97
S-1	185 ± 10.0	184	272	320 ± 14.0	318
S-2	190 ± 8.0	195	296	327 ± 12.0	337
S-5	380 ± 20.0	384	550	540 ± 20.0	530

[a] The initial monomer concentration in these polymerizations was 2 *M*. [b] The values of $\langle M_v \rangle$ were derived (T. Altares, Jr., D. P. Wyman, and V. R. Allen, *J. Polym. Sci., Part A-2,* 4533 (1964)) from the equation $[\eta] = 8.5 \times 10^{-5} M^{0.75}$ (C_6H_6). [c] Initiated by *sec*-butyllithium.

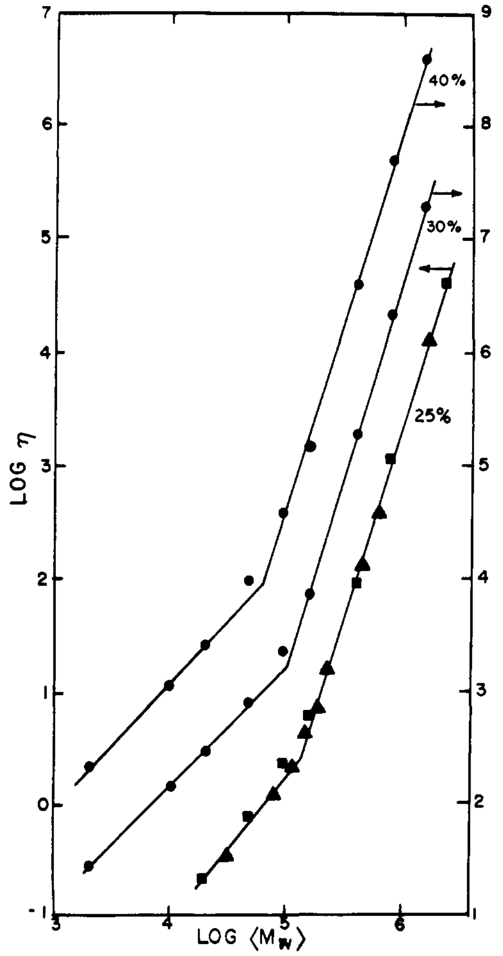

Figure 1. Viscosity-molecular weight relationship for concentrated solutions of near monodisperse polystyrenes. The numbers refer to polystyrene concentrations expressed as volume fraction: (●) ref 59, in di-2-ethylhexyl phthalate at 25°; (■) ref 49, in butylbenzene at 30°; (▲) ref 60 in diethylbenzene at 30°.

ed without question. None of these references reveal the purported extended gradual transition claimed by the above authors.[14] On this occasion we would like to reconfirm its validity in the particular case of polystyrene solutions, using recent data from the literature.[49,59,60] These are shown in Figure 1, where the data from three different groups of investigators are reproduced. It can be seen that the 3.4 power dependency of η on $\langle M_w \rangle$ is valid as long as $vM_w \geq 4 \times 10^4$, where v is the volume fraction of polymer in solution. This contrasts with the alleged value of about 1.2×10^5 found by the above authors.[14] Needless to say, the minimum product quoted above was always applicable in work done in this laboratory.[3,4]

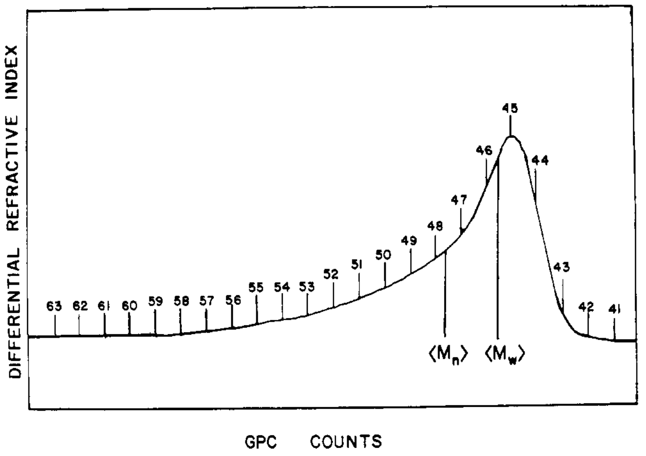

Figure 2. Gel permeation chromatogram of polystyrene S-2.

With regard to this latter point, a check of the validity of eq 1 at the polystyrene concentrations and molecular weights studied by us was reported elsewhere.[4] Unfortunately, the above authors[14] failed to mention this fact in their report.

An additional point to be made is that the above authors[14] took their results to mean that eq 1 was also invalid for polyisoprene solutions. Thus, our previous data[1–4] pertaining to poly(isoprenyl)lithium chain ends was considered to be in error as a result of this alleged failure of eq 1. This conclusion was reached[14] even though we had presented data[3,62] which verified the applicability of this equation to the polyisoprene system. As was the case for the polystyrene system, these results[3,62] were not mentioned in the paper by the above authors.[14]

The question, naturally, therefore arises as to the possible reasons for the failure of the above authors[14] to attain the expected 3.4 power dependency. The most logical explanation lies in their unfortunate use of *tert*-butyllithium as the initiator for the polymerization of styrene. This initiator is known[46–48] to be a relatively slow initiator for styrene in both benzene and cyclohexane. It should be noted that the above authors[14] used *sec*-butyllithium for all polymerizations reported in their paper except for the polymerization (in cyclohexane) of the polystyrene used in their viscosity studies. Furthermore, these authors[14] were apparently aware of the differences in the reactivities of *sec*- and *tert*-butyllithium in the initiation of styrene since Hsieh's work[46] has been cited by them in the past (*e.g.*, see ref 8, 9, and 12 in ref 10, 63, and 64, respectively, of this paper).

In view of this slow reaction between *tert*-butyllithium and styrene, this initiator can be expected to lead to an undesirable broadening of the molecular weight distribution (MWD) of polystyrene; as was in fact reported by Hsieh

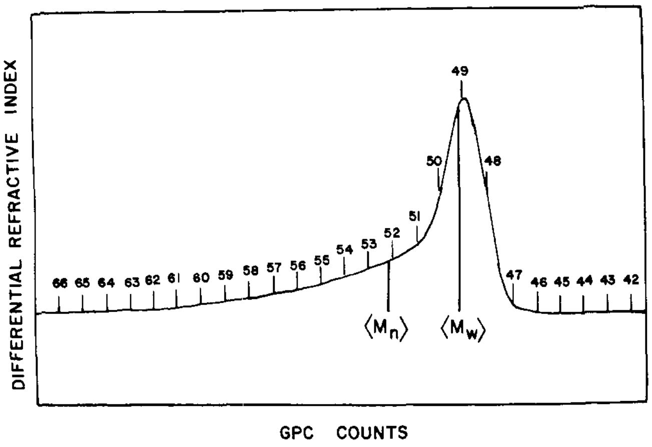

Figure 3. Gel permeation chromatogram of polystyrene S-3.

and McKinney.[47,48] Some recent experiments in our laboratories have verified those results very convincingly, and these are shown in Table I. It should also be noted that similar results have been found for polystyrenes prepared in benzene.[65]

The broadened molecular weight distributions of samples S-1 through S-6 are clearly evident and may be compared with the narrow MWD of sample S-7 prepared under the same conditions but with the use of the more efficient initiator *sec*-butyllithium. Furthermore, the dependence of the MWD on molecular weight can be seen; *i.e.*, the MWD's of these samples narrow as the molecular weights increase. In this work it was also noted that all of the gel permeation chromatograms of the polystyrenes prepared *via tert*-butyllithium showed a pronounced low molecular weight *tail,* leading to unexpectedly low $\langle M_n \rangle$ values. Hence, the use of these $\langle M_n \rangle$ values (instead of $\langle M_w \rangle$) by the above authors[14] in their log η *vs.* log M plot is invalid and led to the erroneously low and allegedly variable values which they obtained for the exponent of M.

In this connection, it is interesting to note that if the $\langle M_n \rangle$ values shown in Table IV of ref 14 are converted to $\langle M_w \rangle$ values, using the appropriate factors taken from Table I above, then the η values show very good dependence on the 3.4 power of the $\langle M_w \rangle$ values. This correction also takes into account the narrowing of the molecular weight distributions that occurs when these polydisperse polystyrenes are associated in the dimeric state.

A better insight into the MWD's of the polystyrenes can be obtained from the gel permeation chromatograms shown for samples S-2, S-3, and S-7 in Figures 2, 3, and 4, respectively. The existence of the low molecular weight tails in the samples prepared by *tert*-butyllithium initiation is evident, and this may be contrasted to the complete lack of any such tail in the sample (S-7) prepared *via sec*-butyllithium initiation. The low reactivity of *tert*-butyllithium with styrene was originally thought[46] to be due to steric hinderance existing between initiator and monomer. We have, however, noted that there is an initial, relatively rapid reaction between styrene and a fraction of the added *tert*-butyllithium. The observed rate of initiation then rapidly decreases. Examination of the chromatograms in Figures 2 and 3 lends support to these observations. It can be seen that the molecular weight distributions of samples S-2 and S-3 both show a low molecular weight tail while neither shows an analogous high molecular weight tail. These asymmetrical distributions seemingly demonstrate that a fraction of the *tert*-butyllithium initiator reacts relatively rapidly with styrene while the remaining initiator reacts at a markedly decreased rate of initiation. This retardation of the initiation step is most probably a reflection of the formation of a less reactive form of *tert*-butyllithium. It has been known[1,64,66,67] for some time that the organolithium initiators can cross-associate with the chain ends of the organolithium polymer. It may very well be that the *tert*-butyllithium which is cross-associated with poly(styryl)lithium is less reactive in initiation than is the self-associated initiator. Obviously, a quantitative resolution and explanation of this particular initiation reaction will require additional work. Along this line, it is pertinent to note that it has been suggested[68] that the *sec*-butyllithium existing in the cross-associated complex with poly(butadienyl)lithium reacts directly with additional butadiene in the initiation reaction of this particular system.

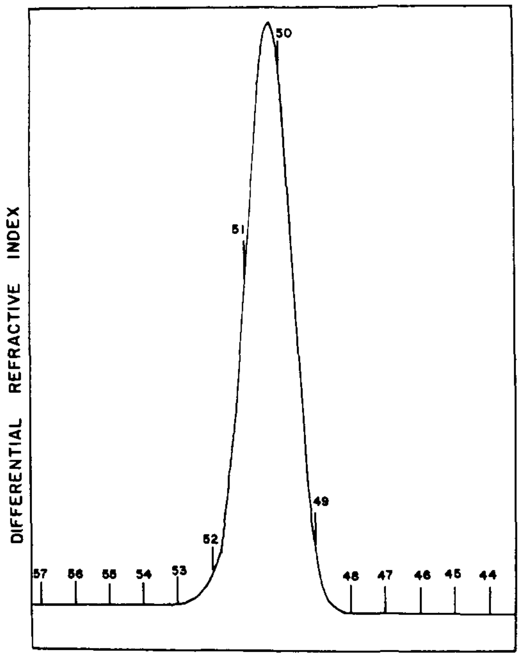

Figure 4. Gel permeation chromatogram of polystyrene S-7.

An additional consequence of the slow reaction of *tert*-butyllithium with styrene is that under the conditions used by the above authors,[14] unreacted initiator may have been present at the completion of the styrene polymerization.[46,47] This conclusion is fortified by the fact that the number-average molecular weights of samples S-1 to S-4 and S-6 were found to be higher than the values predicted based on the ratio of monomer to *tert*-butyllithium. Thus, due to the expected cross-association of initiator with poly(styryl)lithium, the viscosity of at least sample 1 in Table IV of ref 14 would be influenced by the presence of residual initiator.

Finally, one additional mystifying factor was the use by the above authors[14] of cyclohexane as the solvent for their viscosity studies. Obviously such a θ solvent would give lower and *less sensitive* viscosity values than a good solvent and is thus a poor choice for such purposes. Furthermore, although the use of cyclohexane can at least be grudgingly accepted for polystyrene, it is unacceptable in the case of the diene-capped polystyrene, as will be shown later, since anomalous behavior is observed in that case. Thus, the observed rise in viscosity of poly(styryl)lithium after capping with isoprene, which the above authors[14] claim as evidence for a rise in association number, is clearly vitiated on the grounds of this anomalous behavior.

II. Light-Scattering Studies. The above authors[14] also used light-scattering measurements to demonstrate the

Table II
Molecular Constants of Poly(styrene-*b*-butadiene-*b*-styrene)

Sample	$\langle M_w \rangle$ 10^{-4} g mol^{-1}	$\langle M_v \rangle$ 10^{-4a} g mol^{-1}	$\langle M_w \rangle$ 10^{-4b} g mol^{-1}	$[\eta]$ dl g^{-1} (C_6H_{12}) Predicted[c]	Found
1	3.0 ± 0.2	3.0	3.1	0.15	0.19
2	10.0 ± 0.5	10.0	10.2	0.27	0.47
3	14.8 ± 0.5	15.0	15.0	0.33	0.45
4	24.0 ± 0.7	25.0	25.0	0.425	0.63

[a] The values of $\langle M_v \rangle$ were derived (T. Altares, Jr., D. P. Wyman, and V. R. Allen, *J. Polym. Sci., Part A-2*, 4533 (1964)) from the equation for polystyrene in benzene, $[\eta] = 8.5 \times 10^{-5} M^{0.75}$. [b] *Via* gel permeation chromatography. The values of $\langle M_w \rangle$ obtained from light scattering in benzene were within ±5% of the gpc values. [c] From the equation for polystyrene in cyclohexane (Altares, Wyman, and Allen, footnote *a*), $[\eta]_\theta = 8.5 \times 10^{-4} M_w^{0.5}$.

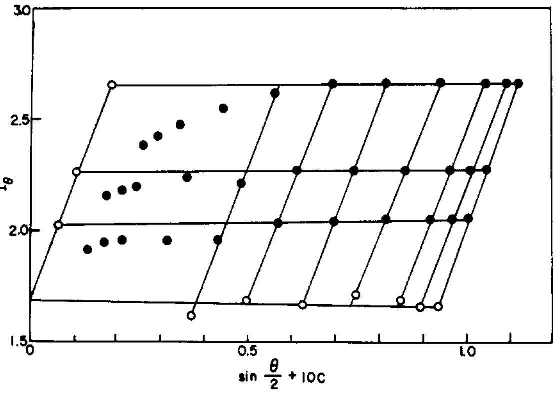

Figure 5. Zimm plot of a poly(styrene-*b*-butadiene-*b*-styrene) copolymer (sample 1) with 1 wt % butadiene. The apparent $\langle M_w \rangle$ is 4.4×10^4 g/mol.

purported association of butadiene-capped poly(styryl)lithium as tetramers and isoprene-capped poly(styryl)lithium as tetramers at high chain end concentrations (*ca.* 10^{-3} *M*) and trimers at lower concentrations (*ca.* 10^{-6} *M*). Here again, the unfortunate choice of cyclohexane as solvent at 35° serves to vitiate the results, as will be shown later.

It is significant that the above authors[14] complained of "anomalous scattering" at low angles (below 75°), which they attributed to the possible presence of glass particles from the breakseals used in their high vacuum reactors. This particular rationale was presented without any apparent attempt to verify this thesis independently. Actually, such reasoning can only be considered to be in error, since it would require the presence of micelle-sized glass fragments (larger particles would be expected to settle out in a short time) and since such a "dispersion" of particulate matter should lead to fluctuations in scattered light intensity at virtually all angles, and molecular weights determined under these conditions would be of dubious value. Unfortunately, the above authors[14] have yet again[10,69] omitted showing representative Zimm plots, making it impossible to examine this light-scattering behavior in detail.

However, it is possible to draw some conclusions about the behavior in cyclohexane solution of polystyrene containing a short center "block" of polybutadiene from some recent experimental observations in this laboratory. Thus, we recently prepared some poly(styrene-*b*-butadiene-*b*-styrene) in which the butadiene content was about 1% by weight or slightly less. Such a molecular structure would, of course, be analogous to the dimerized state of a butadiene-capped polystyrene although we do not know with certainty whether this butadiene content is comparable to that used in the capping reaction by the above authors,[14] since they did not state how much of either diene they used for this purpose.

Light-scattering measurements on these "triblock" polymers in cyclohexane at 35° led to curved Zimm plots and to erroneously high molecular weights, as is shown in Figure 5. No such behavior was observed for these polymers in the "good" solvent benzene. Nor was it observed in cyclohexane solutions of a "diblock" polymer (S-7) consisting of a polystyrene having a short polybutadiene segment at one end only. It is evident that some kind of aggregation of these "triblock" polymer molecules occurs in cyclohexane, giving the anomalously high molecular weights. In this connection it was also observed that cyclohexane solutions of such "triblock" copolymers exhibited quite noticeable turbidities at 25°, while corresponding, *i.e.*, molecular weights and concentrations, polystyrene solutions remained clear. The formation of such aggregates probably originates from the incompatibility of the two components of the polymer chain and the fact that the major component is under *θ* conditions.

These results confirm some previous observations[70] that the presence of even a very small segment of a comonomer in a polymer chain can profoundly alter the solution behavior of the chain, when the polymer is under *θ* conditions for the principal component. Hence it becomes obvious why cyclohexane was such a poor and unfortunate choice for the type of polymers used by the above authors.[14]

At this point some additional comment is in order concerning the viscosity of these solutions. Thus intrinsic viscosity measurements of the above "triblock" copolymers in cyclohexane at 35° yielded values which were markedly higher than expected (for polystyrene). This effect can be seen in the data presented in Table II. These anomalously high viscosity values offer a ready explanation of the increase in viscosity which the above authors[14] observed after capping poly(styryl)lithium with isoprene and which they erroneously ascribed to a rise in the state of association of the active chain ends. These capping procedures, which we had previously originated,[4] have clearly shown that, in benzene, the association states of the poly(styryl)- and poly(dienyl)lithium chain ends are identical, *i.e.*, dimeric.

III. Direct Confirmation of the Dimeric State of Association. Even though the dimeric state of association of poly(dienyl)lithium in nonpolar solvents at concentrations appropriate for these polymerizations has already been very convincingly confirmed in a recent publication,[71] some additional experiments were carried out in these laboratories to provide additional direct evidence on the state of association of these chain ends. These consisted of measurements of the concentrated solution viscosity of these chains before and after linking the active ends by means of $SiCl_4$, CH_3SiCl_3, or $(CH_3)_2SiCl_2$. These reagents can lead to virtually complete linking of poly(butadienyl)lithium.[52,72,73] Obviously, if association numbers greater than two exist, the reaction of a tri- or tetrafunctional linking agent should not cause any change in viscosity, while a difunctional linking agent should lead to a viscosity drop.

The results of our experiments can be examined in Table

Table III
Viscosities of Associated and Linked Polydiene Chains in Cyclohexane at 25°

		Flow times,[a] sec			Number-average molecular weights			
Polymer	Linking agent	Active	Linked	Terminated[b]	Primary M_s,[c] 10^{-5} g/mol	Primary $\langle M_n \rangle$, 10^{-5} g/mol	Linked $\langle M_n \rangle$, 10^{-5} g/mol	Wt % of unlinked polyisoprene[d]
Polyisoprene-1[e]	$SiCl_4$	1320	2340	2280	1.2	1.2 ± 0.1	3.35 ± 0.2	5
Polyisoprene-2 capped with butadiene	$SiCl_4$	2480	4800	4770	1.5	1.6 ± 0.1	6.0 ± 0.4	3
Polyisoprene-3	CH_3SiCl_3	500	825	820	1.3	1.35 ± 0.1	3.6 ± 0.3	5
Polyisoprene-4	$(CH_3)_2Si(Cl)_2$	235	229	229	0.81	0.85 ± 0.04	1.6 ± 0.1	<2

[a] The flow times recorded are average values from at least five determinations. Polymer concentrations were 18–20 vol %. [b] The terminated flow times are those recorded after the addition of a trace amount of methanol to the solution after the linking reaction was complete. These results indicate that virtually no active chain ends remained at the completion of the linking reaction. [c] M_s denotes the predicted stoichiometric molecular weight and is based on the ratio of monomer to initiator. [d] *Via* gel permeation chromatography measurements. [e] $[SiCl_4]/[s\text{-}C_4H_9Li] = 0.33$.

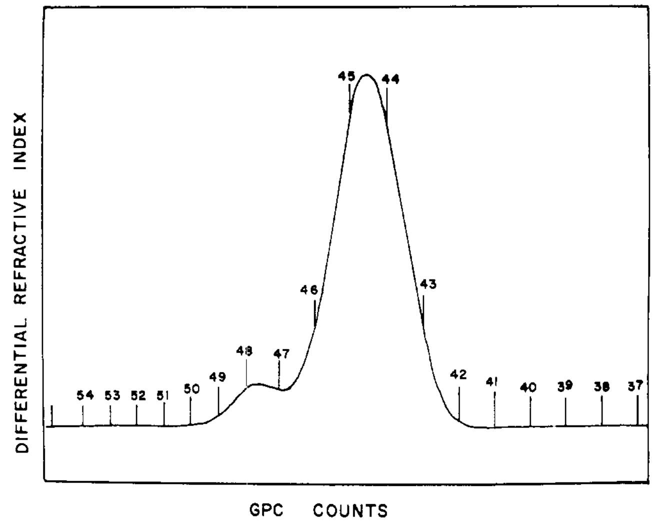

Figure 6. Gel permeation chromatogram of polyisoprene-1.

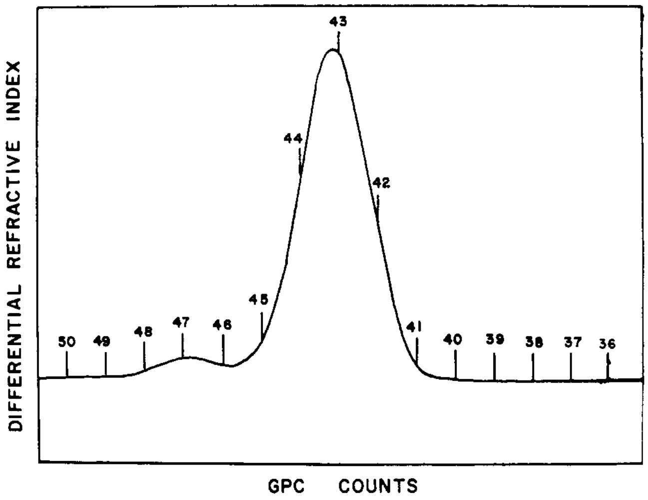

Figure 7. Gel permeation chromatogram of polyisoprene-2.

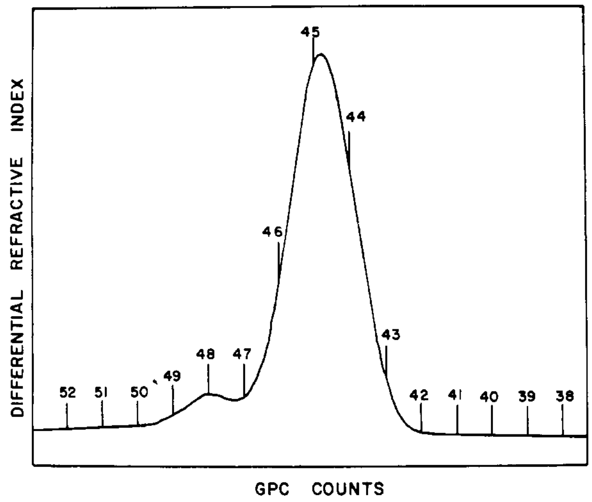

Figure 8. Gel permeation chromatogram of polyisoprene-3.

III, where it can be seen that the difunctional linking agent $(CH_3)_2SiCl_2$ causes no noticeable change in viscosity while both the tri- and tetrafunctional silanes cause a substantial increase, compatible with a dimeric state of association of the chain ends. Similar results have been observed[74] in the preparation of four-armed "star" poly(styrene-*b*-diene) copolymers. It can also be noted, parenthetically, that poly(isoprenyl)lithium does not react completely with $SiCl_4$ when the two species are present in stoichiometric amounts, a trichain polyisoprene being obtained as the predominant species. Polybutadiene chain ends, on the other hand, seem to react quantitatively with $SiCl_4$. It appears that the methyl group in the 4,1 chain end[75] of poly(isoprenyl)lithium may very well inhibit, on steric grounds, a complete reaction with the $SiCl_4$. It does not apparently interfere with the virtually complete reaction with CH_3SiCl_3. Gel permeation chromatograms of the linked polyisoprenes are shown in Figures 6–8. The near quantitative nature of this linking reaction leading to the formation of the "star" polyisoprenes is evident. Figure 9 demonstrates that the unlinked polyisoprenes possessed a narrow distribution of molecular weights. This figure is a gel permeation chromatogram of the precursor of the triarmed polyisoprene formed *via* $CH_3Si(Cl)_3$.

With regard to the viscosity of poly(isoprenyl)lithium solutions, the above authors[14] have presented data resulting from an undefined number of measurements on one sample. The ratio, 15.1 of the active and terminated solution viscosities was taken to demonstrate a degree of association greater than 2. This ratio is in contrast to those previously reported[1-4] which supported the dimeric association state. We have reexamined the poly(isoprenyl)lithium system and these results are presented in Table IV. At the same polymer concentration used by the above authors,[14] the ratio of the active to terminated solution viscosities was found to be 10.5, which is consistent with the dimeric association state. It should be emphasized that due to the rela-

Table IV
Poly(isoprenyl)lithium Association at 25° in Cyclohexane[a]

$[RM_jLi]_0$ 10^3	Flow times, sec[b] Active (t_a)	Terminated (t_t)	Volume fraction of polymer	t_a/t_t	N[c]	$M_s \times 10^{-5}$ g mol^{-1}	$\langle M_n \rangle \times 10^{-5}$[d] g mol^{-1}
2.4	6840	688	0.26	10.5	2.0	1.1	1.1 ± 0.1
2.3	7000	664	0.26	10.5	2.0	1.2	1.2 ± 0.07
2.3	2380	227	0.23	10.5	2.0	0.9	0.9 ± 0.05

[a] The molecular weight between entanglements is reported[62] (J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci., Part A-2*, **6**, 967 (1968); G. V. Vingradov, A. Ya. Malkin, Yu. G. Yanovski, E. K. Borisenkova, B. V. Yarlykov, and G. Berezhnaya, *ibid.*, **10**, 1061 (1972); N. Nemoto, H. Odani, and M. Kurata, *Macromolecules*, **5**, 531 (1972); N. Nemoto, T. Ogawa, H. Odani, and M. Kurata, *ibid.*, **5**, 641 (1972)) to be between 5 × 10^3 and 7 × 10^3 g mol^{-1}. [b] The flow times are the average of at least five determinations. [c] N represents the association state. [d] Measurements *via* gel permeation chromatography revealed that all three samples possessed very narrow molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle < 1.1$).

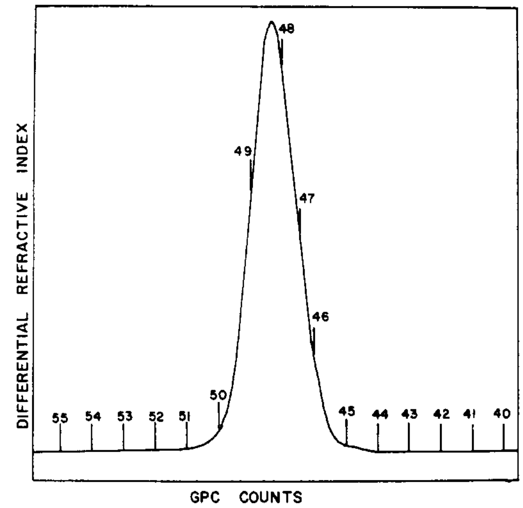

Figure 9. Gel permeation chromatogram of unlinked precursor to polyisoprene-3.

tively high concentrations of polymer chosen by the above authors,[14] care must be exercised in order to maintain a system uniform in concentration under high vacuum. Failure to do so can lead to erratic results.

Further direct confirmation of the dimeric state of association of poly(butadienyl)lithium at chain end concentrations of about 0.05 *m* and less is offered by the work of Glaze, *et al.*[71] They used cryoscopy to study the states of association of 3-neopentylallyllithium, the product formed from the addition of *tert*-butyllithium to one unit of butadiene. They found that at concentrations of 0.33 *m* these chain ends were associated in the tetrameric state. However, a progressive decrease in concentration caused a concurrent decrease in the degree of association. Hence, for the concentration of 0.0495 *m*, the favored state of association was dimeric. The dependence of association state on organolithium concentration has also been observed elsewhere.[76]

The above results also serve to vitiate the approach taken in a recent paper[77] where ultraviolet absorption spectra were used to calculate dissociation constants for a tetramer–dimer equilibrium involving poly(isoprenyl)lithium. It is interesting to note that dissociation constants for a dimer–monomer equilibrium can be estimated from the same data and that these values are in agreement with those presented previously by us,[3] based on viscosity measurements.

It appears, therefore, that the overwhelming experimental evidence still points to a dimeric state of association for these poly(dienyl)lithium chains. The dimerized association state is supported by the results from (a) light-scattering measurements[4] done with *n*-hexane as the solvent, (b) viscosity studies on both high[1–4] and low[25] molecular weight poly(dienyl)lithium chains, (c) cyroscopic measurements[71] on 3-neopentylallyllithium solutions, and (d) the results from the comparison of the concentrated solution viscosities before and after the linking of poly(dienyl)lithium chains into star shaped chains. Thus, in our opinion, there does not currently exist any valid evidence which can be interpreted, in a serious fashion, as indicating the existence of higher degrees of association than the dimeric state for the poly(dienyl)lithium chains at concentrations appropriate for polymerization.

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Construction of Nonequivalent Hybrids in Hydrocarbon Polymers: Polybutadiene, Polyisoprene, and Related Systems

Milan Randić*[1a] and J. W. H. Sutherland[1b]

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received October 11, 1973

ABSTRACT: Nonequivalent hybrid orbitals are constructed for a series of hydrocarbon polymers using bond overlaps as a criterion for the estimate of the relative contributions of s and p orbitals. A suitably weighted sum of bond overlaps is maximized according to the procedure initially developed by, Coulson, Randić, and others.[2] The following systems have been investigated: polyethylene (I), 1,4-polybutadiene (II), 2-methyl-1,4-polybutadiene (III), 2,3-dimethyl-1,4-polybutadiene (IV), polypropylene (V), 1,4-polyisoprene (VI), 1,2-polyisoprene (VII), and 3,4-polyisoprene (VIII). It is found that for a given carbon atom small deviations from the idealized hybrid forms sp^3, sp^2, and sp exist. The magnitude of these deviations is determined by the structural groups bonding to the carbon atom in question. It is shown that although only small changes accompany similar structural groups, such changes correspond to known variations in bond properties. Taken cumulatively these small variations may become important in long-chain systems. The problems associated with orientational isomerization are considered in polypropylene where the calculations have been performed for a head to tail and head to head-tail to tail sequences of the repeating monomer unit. An interesting correlation between the calculated hybrid forms and spin-spin coupling constants is discussed.

The application of theoretical methods to studies of hybridization in macromolecules is a subject which has received relatively little attention by comparison with efforts directed at smaller molecules. The reason is that most quantum chemical methods are laborious and expensive when applied to a relatively large system—if such an application indeed is possible. In this paper we consider hybridization in some common hydrocarbon polymers by a simple and reliable method which has already found widespread application in smaller systems[2f] but which has not previously been applied to polymers. The model abandons the usual description of carbon atoms bonding in terms of sets of equivalent hybrids: tetrahedral sp^3, trigonal sp^2, and digonal sp. It considers more general hybrids of an sp^n type, where n is not restricted to integers and may take any positive value. The particular values reported here are based on a criterion of maximum overlapping,[3] modified in order to take into account differences in various bond types.[4] It is important to recognize that the usual description in terms of sp^3, sp^2, or sp hybrids implies that the carbon atom in question is substituted by four, three, or two *equivalent* groups—a condition which is not generally realized in real hydrocarbon molecules. It has been demonstrated[2f] that the hybrids constructed by the method adopted here provide surprisingly precise and accurate predictions regarding bond properties. The quantitative agreement between various calculated quantities and correlated experimental data justifies a further extension and application of the model. Here we apply the method to polymers.

The purpose of the calculation is to provide a description of the differences between similar bonds in related compounds. The description may not only be qualitatively correct but also quantitative. One may at first be sur-