in question involves a six-membered ring as in polystyrene. In spite of their assertion that the displayed spectra were Lorentzian, the actual picture shows considerably asymmetry to the main peak and a long tail at lower frequencies. In principle, the spectra could be fitted to a sum of peaks and a central Lorentzian line width could be extracted, but this was not done. Instead the spectra were recorded on chart paper and analyzed by hand. Choosing the value of the base line for the observed spectra was not an easy task, nor could the peak height be determined with high precision. Thus, the half-height could only be determined (even in the best cases) to ±10%. After a half-height was arbitrarily chosen, further uncertainty was introduced in the measurement of the full-width by the noisy spectra. Given the quality of the Raman spectra of polymers in solution when the slits were narrow enough to yield reliable line shapes, the half-width at half-height could not have been determined with a precision better than ±10%.

The full-widths of the 1002-cm^{-1} Raman band of polystyrene in solution were reported to be approximately 4 cm^{-1}. Thus, $2\Gamma_{\mathrm{or}}$ could be determined with a precision of ±0.8 cm^{-1} since each observed line had a precision of ±0.4 cm^{-1} due to the 10% uncertainty in the absolute line width. The Japanese authors in their first paper reported line widths with a precision of ±0.01 cm^{-1}. This claimed precision is not valid. A corresponding relaxation time can be obtained from the half-width at half-height according to

$$\tau_{\mathrm{or}} = 1/2\pi\Gamma_{\mathrm{or}} \qquad (3)$$

for Γ measured in hertz. The longest relaxation time that could be determined with 100% uncertainty when the precision of Γ_{or} was 0.4 cm^{-1} is thus 13 ps. Raman line shape analysis is usually applied[7] to the study of small molecules where the characteristic orientational relaxation times are a few picoseconds. The Japanese authors reported relaxation times near 1000 ps. Also, the figures in the paper in *Macromolecules* show beautiful smooth curves with every point on the line for relaxation times far beyond the valid limit of 13 ps.

Since the characteristic relaxation times associated with local conformational motions in polymers are in fact in the nanosecond time range, it becomes immediately apparent that Raman line shape analysis should never have been applied to such systems. For small oligomers, the reorientational motion is dominated by overall molecular reorientation.[8] But even in these cases the times usually substantially exceed 13 ps. There are many theoretical and experimental reasons given above why Raman line shape analysis should not be applied to the study of reorientational motions in polymers. But the crucial point is that the time scale is clearly in the wrong range.

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Comments on the Measurement of the Active Center Association of Living Polymers via Concentrated Solution Viscosity Measurements

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A recently published note[1] questions (a) findings of ours[2,3] pertaining to the mean degree of association of the (2,4-hexadienyl)lithium active center in benzene (prepared, for example, by reacting 2,4-hexadiene with polystyryllithium) and (b) our preliminary statement[3] that asserted that diphenyl ether will alter the dimeric association state of polystyryllithium in benzene. We wish to present our case that the evidence offered[1] for these claims is invalid.

There is general agreement that in hydrocarbon solvents, the active centers of some polymers derived from organolithium initiators are associated—often as dimers.[3-13] A survey of the literature shows that a convenient route to determining the mean degree of association of these active centers is to measure the flow times of concentrated solutions in an evacuated low-shear viscometer of the Ubbelohde type. Such solutions conform to the equation

$$\eta = K\bar{M}_{\mathrm{w}}^{3.4} \qquad (1)$$

where η is the viscosity, $\bar{M}_{\mathrm{w}}$ the weight-average molecular weight, and K a constant, provided that

$$v_2\bar{M}_{\mathrm{w}} > 2M_{\mathrm{e}} \qquad (2)$$

where v_2 is the polymer volume fraction and M_{e} is the molecular weight between entanglement points. If the flow times are designated as t_{a} and t_{t} for the active and terminated solutions, respectively, the weight-average degree of association, N_{w}, is given by

$$t_{\mathrm{a}}/t_{\mathrm{t}} = (M_{\mathrm{a}}/M_{\mathrm{t}})^{3.4} = N_{\mathrm{w}}^{3.4} \qquad (3)$$

This procedure has been successfully used[3-7] where the degree of association is 2. It is important, however, to recognize that there are limits to the situations where the measurement of viscosity can provide useful information or be considered a viable technique.

One significant limitation of the viscometric approach in determining the degree of association of polymers with organolithium chain ends is imposed by the need to use viscometers of the Ubbelohde type, compounded by the necessity to operate these under the rigorous high-vacuum conditions demanded in order to avoid active-center deactivation. Hadjichristidis and Roovers[14] used Ubbelohde viscometers to study concentrated solutions of linear and star-shaped polyisoprenes and concluded that, in practice, the technique is limited to systems having viscosities less than 10^3 P. This opinion is also shared by others.[15]

Our experience[5-7,12,16] also indicated that these viscometers are unsuitable for polymer solutions with viscosities >10^3 P (unless the solutions are driven by an inert gas under pressure). An examination of our previous data[5-7] involving benzene solutions of polystyryllithium reveals that the viscosities encountered ranged from about 20 to 800 P (this assessment is based on the data of ref 17 and 18).

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Table I
Calculated Solution Viscosities

$[M]_0$, mol L^{-1}	$[SiLi]_0$, mol L^{-1}	associated $M_S \times 10^{-5}$ [a]	concn, g/dL	η,[b] P
4.5	1.2	7.8	$50.{}_0$	$\sim 1.6 \times 10^5$
3.5[c]	0.87	8.4	$38.{}_4$	$\sim 2.2 \times 10^4$
3.4	1.5	4.8	$37.{}_2$	$\sim 2.6 \times 10^3$

[a] M_S denotes the stoichiometric number-average molecular weight. [b] These values were calculated for 24 °C, the temperature of measurement of ref 1, from the results of ref 17 (Table II) and ref 18. It is appropriate to mention that solutions having such high viscosities preclude efficient mixing of any additive, i.e., 2,4-hexadiene or diphenyl ether, under the conditions necessary to maintain the active centers. [c] Run in duplicate.

Viscometers employing a capillary have been used by Flory,[19] Fox and Flory,[20–22] Fox and Allen,[23] and Gupta and Forsman[24] to measure either polymer melts or solutions having viscosities as high as 10^8 P. However, these were of an entirely different design than the Ubbelohde type viscometer and involved the application of pressure to drive the fluid.

The data in Tables II and III of the Wang–Szwarc note show that the concentration of the polystyrene in the solutions they studied ranged from about 33 to 50 g/dL for the four measurements they reported (Table I). An inspection of the polystyrene viscosity/concentration data of Graessley and co-workers[17,18] reveals that three of the four systems listed[1] exhibit viscosities (in the associated state) ranging from 2.2×10^4 to about 1.6×10^5 P while the remaining sample would have had a corresponding viscosity of about 2.6×10^3 P[25] (Table I). Similar conclusions follow from the work of Kotaka[26] and Ghandi and Williams.[27,28]

We submit that solutions with viscosities of the magnitudes shown in Table I cannot be measured in a meaningful fashion in the unmodified capillary viscometers used by Wang and Szwarc.[1] We have checked the feasibility of working with solutions with viscosities $>10^3$ P in the following fashion. Benzene solutions of a polystyrene with an $\bar{M}_w$ of 7.9×10^5 ($\bar{M}_z/\bar{M}_w = 1.0$; $\bar{M}_w/\bar{M}_n = 1.0_6$) were prepared under vacuum in a sealed viscometer[29] of the design reported elsewhere.[11] The concentrations were chosen to duplicate those listed in Table I. It proved to be impossible to manipulate in an effective fashion the solutions with viscosities $>2 \times 10^4$ P in the viscometer. The solution with the viscosity of about 2.6×10^3 P did not lend itself to accurate measurement of its flow time due to difficulties in filling the viscometer bulb, the *very* slow rate of flow of the solution between the fiducial marks, and drainage problems, viz., the adherence of the polymer solution to the viscometer interior.[30] These problems were not avoidable by the use of large-diameter (1.5 cm) tubing.

Wang and Szwarc reported[1] flow times of polystyryllithium–benzene solutions before and after the addition of diphenyl ether; they then terminated their solutions and again measured the flow times. Table III of their note says that in pure benzene, N_w is 1.96 and 2.0 for two experiments, in apparent agreement with the general belief that polystyryllithium is exclusively dimeric in benzene.

The addition of diphenyl ether to their polystyryllithium–benzene solutions to achieve the specified concentration (0.15 M) prior to termination is accompanied by an increase in volume of ca. 2.4%. The data of Graessley and co-workers[17,18] show that $\eta \propto M^{3.4}c^{7.5}$ (where c denotes polystyrene concentration) for polystyrene in butylbenzene. An examination of the average T_1 and T_2 flow times (before and after the addition of diphenyl ether) reveals that approximately this expected decrease in flow times indeed occurred.

However, the dilution occasioned by the addition of the diphenyl ether ought also to have resulted in apparent values of N_w of about 2.1 (based on the ratio T_1/T_3) unless the initial solution contained some polymer terminated by adventitious impurities. To place this anomaly in sharper perspective, the results of Graessley and co-workers predict that the two average flow times, T_1, in Table III of ref 1 should be about 400 s higher (some 18 and 25% larger) than the values reported, based on the flow times, T_3, of the terminated solutions. If the foregoing assessment is based instead on the initial average flow times, T_1, then the terminated flow times, T_3 (Table III of ref 1), ought to be about 20–15% lower than the values actually listed (again calculating on the basis of exclusive dimerization of the active system).

Since Wang and Szwarc do not provide adequate descriptions of their apparatus and leave uncertain whether or not their procedures involved dilution, further discussion of their work would be mere speculation. It is clear that in the light of this uncertainty their claim that diphenyl ether does not alter the degree of association of polystyryllithium lacks the necessary foundation for serious consideration.

Wang and Szwarc also reported[1] that Van Beylen has independently confirmed that diphenyl ether has no influence upon the association of polystyryllithium. However, the data supplied show that not only did Van Beylen use an ether to active center ratio of only 30 but that his measurements were not even made in the entanglement regime where eq 1 applies. One would not see much change in flow times under such conditions,[31] and hence Van Beylen's work neither confirms nor refutes the observations contained in ref 1.

In conclusion, Wang and Szwarc[1] have criticized us for the divergent N_w values (ca. 1.4[32] and 1.6) we have *independently*[33] reported[2,3,11] for the (2,4-hexadienyl)lithium active center. In 1980 we commented[11] "the cause of the difference between our (Al-Jarrah and Young) value for N for polyhexadienyllithium and that reported by Morton et al.[2] is obscure." Recently, a joint spectroscopic analysis we have commenced[34] has shown that benzene and cyclohexane solutions of hexadienyllithium exhibit the gradual development of a new peak over a period of 2 or 3 days at ambient temperature at about 385 nm; the absorbance at the primary peak at 284 nm simultaneously decreases as does the value of N_w. The origin of this spectral change is unknown, but previous work has shown[2] that there is no loss of chain end activity—at least over a period of 3 days at 30 °C as evidenced by GPC analysis of the polymer formed from such a sample by chain extension by the introduction of additional monomer. Also, the addition of butadiene causes the 385-nm peak to disappear.

Wang and Szwarc also found N_w values significantly below 2.0 (viz., 1.85 and 1.88). They attributed this observation to an undefined chain transfer step!

Acknowledgment. We thank those listed in ref 15 for their most useful comments and assistance.

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(30) Flory[19] has commented on this problem.
(31) For measurements done in the entanglement regime we found a value for N_w of 1.89 for a diphenyl ether to active center ratio of 30. Our findings on this topic are published in *ACS Symp. Ser.* **1981**, *No. 166*, 95.
(32) Wang and Szwarc asserted that the values of N_w reported in Table I of ref 2 were "1.3–1.45". In reality, the values listed were 1.36, 1.39, and 1.35!
(33) Wang and Szwarc stated that our results were from the same laboratory ("the Akron team" and "the Akron group"). An examination of ref 2, 3, and 11 reveals their statement to be a misrepresentation.
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Comments on the Preceding Note of Fetters and Young

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The kinetics of 1,1-diphenylethylene addition to lithium poly(2,4-hexadienyl) were reported by Fetters et al.[1] in 1979. The results, for which they had no explanation,[2] puzzled us. We reexamined this system and found that our results,[3] different from those reported by Fetters et al.,[1] fitted a mechanism that accounts for the behavior of similar systems.[4] Our kinetic findings are *not disputed* by Fetters and Young, who contest in the preceding note[5] only the viscosity measurements reported in the last part of our paper.[3]

Briefly, Fetters and Young claim[5] (1) that capillary viscometers cannot be used when a solution has a viscosity $\eta > 10^3$ P and (2) that in our work the 2.4% dilution arising from the addition of 0.15 M diphenyl ether did not affect the viscosity of the investigated solution.

To take the last point first, Fetters and Young state[5] that our flow time data fail to reflect the concentration change occasioned by the addition of diphenyl ether. Although we did not consider this point, nevertheless the predicted effect of the dilution is clearly revealed by our results. Since the viscosity increases with the 7.5 power of polymer concentration, the 2.4% dilution should reduce it by a factor of $1.19 = (1.024)^{7.5}$. The results reported in Table III of our paper[3] show that in experiment 1 the flow time before dilution is 1585 s and after dilution is 1372 s. This corresponds to a factor of 1.16. In experiment 2 the flow time before dilution is 2248 s and after dilution is 2037 s, leading to a factor of 1.10. These reductions in the flow times strengthen the confidence in their reliability.

Since the viscosity of the dead polymer solution was measured after the 2.4% dilution, we should not have listed the values of "N before" in Table III. On the other hand, Fetters et al.[1] claim that 60% of the dimeric polystyrene is dissociated by the addition of 0.15 M diphenyl ether. In such a case, the flow times should decrease by a factor of $\sim$3.4, in experiment 1 from 1585 to $\sim$472 s, whereas our observed flow time was 1372 s, and in experiment 2 from 2248 to $\sim$669 s, compared with our observed flow time of 2037 s. Our observed decrease in flow time approximately accounts for the dilution effect. Hence, our measurements indicate an insignificant degree of dissociation in the presence of 0.15 M diphenyl ether.

It should be recalled that Worsfold and Bywater[6] found that the square root dependence of the rate of lithium polystyryl polymerization on its concentration is still valid, in the concentration range 10^{-4}–10^{-3} M, even in the presence of 10^{-3} M THF. This implies that less than 10% dissociation is caused by THF at the lowest polystyrene concentration, i.e.

$$(\text{polystyryl-Li})_2 + 2\text{THF} \rightleftarrows 2(\text{polystyryl-Li,THF}) \qquad K \sim 1$$

Using the viscometric technique, Morton and Fetters[7] found $K = 200$, a value which is much too large—again overestimating the effect of ether.

In regard to the first objection of Fetters and Young, we calculate the viscosities of our solution to be in the range of 10^3–10^4 P. The concentration of styrene was 3.4–3.5 M, although due to a typographical mistake in one footnote, it was given as 4.5 M.[15] By using a 2-cm-long tube of 0.4-cm radius as our "capillary", we had no difficulties in measuring the flow time with an accuracy of 5%, which was sufficient for our needs.

The following scientific problem is raised by the work of Fetters and Young.[1,13] Does lithium poly(2,4-hexadienyl) exist in benzene solution as a dimer; i.e., is the $N_w = 2$, or is its degree of association 1.6, as reported by them in 1979[1] and again by Young et al.[13] in 1980? Significantly, the value 1.3 reported for *the same solution at the same concentration* by Morton and Fetters[8] in 1972 was not mentioned in ref 1. To place this anomaly in sharper perspective: an approximately 10-fold reduction of flow time is expected on termination of dimeric living polymers ($N_w = 2$), a 5-fold reduction should be observed for $N_w =$

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