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(29) The viscometer design used is that shown in Figure 1 of ref 11. The measurement capillary had a diameter of 0.3 cm and a length of ca. 18 cm. The filling tube was made of 1.5-cm tubing and was ca. 35 cm in length. The main reservoir was a 250-mL round-bottom flask. The bulb between the fiducial marks had a capacity of approximately 8 cm^3.
(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 ~3.4, in experiment 1 from 1585 to ~472 s, whereas our observed flow time was 1372 s, and in experiment 2 from 2248 to ~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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1.6, and only a 2.5-fold reduction should be observed for $N_w = 1.3$. After we pointed out this discrepancy,[3] Fetters and Young provided for it an explanation in their present comment.[5] They report some destruction of lithium poly(2,4-hexadienyl) after aging its solution for a few days. Does this mean that an aged and partially decomposed solution was used in the 1972 study? This information is important since it has been repeatedly stressed[9] that freshly prepared solutions are required in any reliable work.

Deviation of N_w of lithium poly(2,4-hexadienyl) from 2 is puzzling since Fetters et al.[1,13] have reported that $N_w = 2$ for lithium salts of polymers derived from vinylbiphenyl, styrene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, etc. The exceptional behavior of the polymer derived from 2,4-hexadiene is attributed by Fetters[8] to delocalization of the charge. Surely the delocalization is greater for the polymers derived from vinylbiphenyl or styrene, and hence neither the delocalization nor a steric hindrance could explain this anomaly.

The viscosity studies of Fetters were performed in the entanglement region and some of the results critically depend on the *exact* value of the exponent α relating the viscosity to weight-average molecular weight of investigated polymers, $\eta \sim M^{\alpha}$. For example, the heat of dissociation of the dimeric lithium polyisoprenyl, ΔH, is stated by Morton and Fetters[10] to be 37.4 ± 0.8 kcal/mol; the derivation requires α to be 3.40. *The same data* give $\Delta H \sim 50$ kcal/mol for $\alpha = 3.42$ and ~ 25 kcal/mol for $\alpha = 3.37$.[11] The above two values of α were determined by Fetters and reported in the same paper.[10] Fetters drew our attention[14] to his later paper,[12] reporting a more refined determination of α, namely, 3.41 and 3.39—close to the required value of 3.40. However, the true values of α deduced from his data listed in Table II of that paper[12] are 3.48 and 3.36, respectively (see Table II below).

Table II, from Morton, Fetters, et al. (*Macromolecules* 1970, *3*, 330)

$M_V \times 10^{-4}$	vol fraction of polymer	flow time, min	α	true α
9.8	40	58	3.41	ln (147/58)/ln (12.8/9.8) = 3.48
12.8	40	147		
7.7	50	51.5	3.39	ln (284/51.5)/ln (12.8/7.7) = 3.36
12.8	50	284.0		

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$[M]_0$, mol L^{-1}	$[SLi]_0$, mol L^{-1}	$M_S \times 10^{-5}$	concn, g/dL	η, P
3.5	1.2	6.0	36	1×10^4