Table I
Viscosity of BzPVP in Me_2SO-H_2O at 25 °C[a]

	Me_2SO, (v/v) %				
	0	12.5	25	37.5	50
η_{sp}/c,[b] dL g^{-1}	0.84	0.94	0.95	0.78	0.41
$[\eta]$, dL g^{-1}	0.64		0.90		0.37

[a] In pH 8.48 borate buffer. [b] [BzPVP] = 12.0 g L^{-1}.

increase the nucleophilicity of L-Phe. This is because Me_2SO solvates the polyions with its oxygen atom directed to the polyions. Thus, the unfavorable factor (weaker solvation of L-Phe by Me_2SO in the reaction site) suppresses the favorable one (accumulation of reactants).

In binary mixtures of Me_2SO and H_2O, selective solvation of cationic small ions was observed,[7] that is, Me_2SO was preferred and H_2O was rejected by the ions. Selective solvation of Me_2SO to the cationic polyelectrolyte was qualitatively confirmed by the viscosity measurement (Table I). Both η_{sp}/c and $[\eta]$ increased and then decreased by the addition of Me_2SO. The initial increase may be attributed to the expansion of the polymer chain by the solvation of Me_2SO and the following decrease would be due to the shrinkage of the polymer chain by the increase of electrostatic interaction between the polyions and gegenions, because the bulk dielectric constant of the solvent was decreased.

In the pH 8.48 buffer, the reaction rate was unaffected by the polyions because L-Phe exists as a zwitterion. In the 50(v/v)% pH 8.48 buffer-Me_2SO, however, the reaction was *retarded* by the addition of BzPVP ($k_2/k_2^* < 1$). This can be accounted for as follows. As was suggested by Friedman et al. from the observed pH shift, all compounds of pK_2 of 9 or less would be completely ionized (the amino group is deprotonated) in the 50% pH 8.48 buffer-Me_2SO. Therefore L-Phe ($pK_2 = 9.0$) and acrylonitrile must be accumulated in the polymer domain. Nevertheless, the unfavorable selective solvation (BzPVP was solvated by Me_2SO and L-Phe cannot be solvated as a consequence of the specific orientation of the Me_2SO molecule) might overwhelm the accumulation effect of the reactants. As the acceleration effect by Me_2SO was larger at pH 8.48 than at pH 10.06 (compare k_2^* values given above), desolvation of the Me_2SO from the reactants should give larger decrease in the acceleration effect by Me_2SO at pH 8.48 than at pH 10.06, causing $k_2/k_2^* < 1$. Though Friedman did not definitely confirm, Me_2SO seems to stabilize the transition state by the hydrogen bonding effect (eq 3). If so, the addition of polyelectrolyte might diminish this hydrogen bonding effect by the induction of the specific orientation of the Me_2SO molecule. Our results obtained here do not exclude this possibility.

In the case of NaPSt, on the other hand, no influence on rate was observed except small decreases in the 50(v/v)% pH 8.48 buffer-Me_2SO which may be due to the enhanced viscosity of the solution. We note that Me_2SO does not solvate PSt anions.

In conclusion, the selective solvation effect, though small but definite, was observed in catalysis by polyelectrolytes.

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A Relationship between Steady State Shear Compliance and Molecular Weight Distribution

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The preponderant effect of polydispersity on the viscoelastic behavior of polymers is now well recognized.[1,2] Various empirical correlations of the experimental data of steady state recoverable compliance J_e and molecular weight distribution characterizing parameters have appeared in the literature. None of these correlations is widely accepted, which should not be surprising in view of the disagreement between the experimental data and the theoretical expectations in monodisperse systems.[2,3]

Ferry[4] was perhaps the first who proposed a functional relationship between J_e and molecular weight distribution in a polydisperse system. Extending the Rouse theory he showed

$$J_e = \tfrac{2}{5} M_{z+1} M_z / M_w \rho R T \qquad (1)$$

where ρ is the density of the polymer, R is the gas constant, T is the absolute temperature and M_w, M_z, and M_{z+1} are the usual molecular weight averages. The following was obtained by Ninomiya[5] on the basis of his experimental success with Rouse's blending law for viscosity,

$$J_{e_b} = w_1 J_{e_1} (M_1/M_w)^2 + w_2 J_{e_2} (M_2/M_w)^2 \qquad (2)$$

where J_{e_b} is the steady state compliance for the blend and w_1 and w_2 are the weight fraction of monodisperse polymers having molecular weights M_1 and M_2 and steady state compliance J_{e_1} and J_{e_2}, respectively. M_w is the weight average molecular weight of the blend.

Several other linear and higher order blending laws have been proposed on the basis of the Rouse model. One due to Ninomiya and Ferry[6] is:

$$H_b(\tau) = v_1 H_1(\tau/\lambda_1) + v_2 H_2(\tau/\lambda_2) \qquad (3)$$

where the H's are the relaxation spectra and the λ's are dimensionless shift factors, which represent the amount of shift of relaxation times of the monodisperse polymers in the blend. To deal with the problem more generally and to get rid of shift factors, Masuda[7] et al. proposed a quadratic mixing law

$$H_b(\tau) = w_1^2 H_{11} + 2 w_1 w_2 H_{12} + w_2^2 H_{22} \qquad (4)$$

where $H_{12}(\tau)$ is the cross-relaxation spectrum. On the basis of results on the blends of polystyrene for which J_e becomes proportional to the inverse of the square of high molecular weight fraction w_2, when $w_2 \rightarrow 1$, Bogue[8] et al. presented a quadratic blending law.

$$H_b(\tau) = v_1^2 H_{11}(\tau/\lambda_{11}) + 2 v_1 v_2 H_2(\tau/\lambda_{12}) + v_2^2 H_{22}(\tau/\lambda_{22}) \qquad (5)$$

Mills,[9] based on his experimental results on poly(dimethylsiloxane), polystyrene, and polyethylene, proposed the following empirical relationship.

$$J_e \propto (M_z/M_w)^{3.7} \qquad (6)$$

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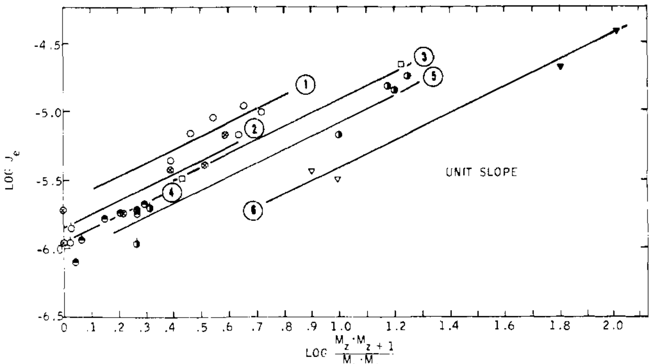

Figure 1. Logarithmic plot of the steady state compliance J_e, cm^2/dyn, vs. (M_zM_{z+1}/M_nM_w): (○) Prest and Porter,[12] (⊗) Onogi et al.,[13] (□) Prest,[14] (◒) Akovali,[15] (◑) Mills and Nevin,[16] and (▽) Orbon and Plazek.[17]

A binary blending law similar to eq 1 has been developed by Graesley[10] by introducing an uncorrelated drag interaction term into the Rouse model by considering elastic contribution of entanglements. His blending equation is

$$J_{e_b} = J_{e_1}\frac{w_1^2 + d_2w_1w_2 + R^2w_2^2}{(w_1^2 + d_1w_1w_2 + Rw_2^2)^2} \tag{7}$$

where R is $(E_2/E_1)^{7/2}$, E_2/E_1 is the ratio of entanglement points per molecule and is simply equal to the ratio of M_2/M_1, and d_1 and d_2 are constants depending upon the value of R. Recently, along the lines of Bogue et al., Kurata[11] and his co-workers have presented a cubic blending law according to which

$$J_e \propto (M_z/M_w)^3 \tag{8}$$

a relation similar to one observed by Mills earlier.

During a literature survey of the binary blend data of polystyrene systems we noted the following empirical observation relating J_e and molecular weight averages.

$$J_e \propto \frac{M_zM_{z+1}}{M_nM_w} \tag{9}$$

Figure 1 is a logarithmic plot of J_e vs. M_zM_{z+1}/M_nM_w based on the results of Prest and Porter,[12] Onogi et al.,[13] Prest,[14] Akovali,[15] Mills and Nevin,[16] and Orbon and Plazek.[17] Various molecular weight averages of the blends used in calculating the right hand function of eq 9 were either those reported by the authors or were calculated by the usual techniques,[18] assuming that individual components used in the blend are monodisperse. Table I lists all the data. It was found that within experimental error for each set of data a straight line with unit slope could be drawn. Close examination of the figure reveals that almost all the blend data points are within 20% of the drawn line. Maximum deviation of the points (marked with a pip) is found with those corresponding to the original blend components.

Further it can be noted that lines 1 to 5, when extrapolated to zero abscissa, yield log J_e in the neighborhood of −5.9, which is in accord with the observed experimental value of monodisperse systems whose molecular weight is >90 000. The systems represented by these lines are based on blends whose individual components are in this molecular weight range.

The reason for the deviation of the data from a single line is not obvious. The J_e data spread over a factor of about 2.5. Some possible factors can be cited, however. Besides errors associated with the characterization of samples, accurate measurement of the steady state compliance is difficult. Differences greater than a factor of 2 in the J_e value on the same sample from two laboratories have been reported in the literature.[16,19]

Table I
Steady State Recoverable Compliance and Molecular Weight Distribution of the Blends

log w_2	log M_w	log $\frac{M_zM_z + 1}{M_nM_w}$	log J_e
1. Data of Prest and Porter (1973),[a] ref 12			
	4.99	0.02	−5.96
−1.64	5.02	0.38	−5.35
−1.48	5.03	0.46	−5.16
−1.31	5.05	0.54	−5.05
−1.05	5.10	0.65	−4.98
−0.68	5.21	0.71	−4.98
−0.40	5.35	0.63	−5.17
0.00	5.61	0.02	−5.85
2. Data of Onogi et al. (1970),[b] ref 13			
	4.67	0.00	−5.73
−0.70	4.85	0.58	−5.16
−0.40	4.98	0.51	−5.38
−0.22	5.08	0.39	−5.42
−0.10	5.16	0.22	−5.75
0.00	5.22	0.00	−5.96
3. Data of Prest (1970),[c] ref 14			
−0.37	4.99	0.43	−5.48
−0.89	4.99	1.22	−4.64
4. Data of Akovali (1967),[d] ref 15			
	5.10	0.04	−6.10
−0.77	5.17	0.27	−5.73
−0.48	5.24	0.29	−5.67
−0.30	5.29	0.27	−5.70
−0.18	5.34	0.21	−5.74
−0.08	5.39	0.15	−5.79
0.00	5.43	0.00	−5.94
5. Data of Mills and Nevin (1971),[e] ref 16			
	4.94	0.26	5.96
−1.20	5.05	1.16	4.80
−0.93	5.14	1.24	4.72
−0.60	5.28	1.20	4.82
−0.30	5.47	0.99	5.16
0.00	5.70	0.00	5.70
6. Data of Orbon and Plazek (to be published),[f] ref 17			
	5.13	1.97	−4.40
	5.68	0.90	−5.42
	5.66	0.99	−5.48
	5.27	1.79	−4.65
	4.90	2.57	−3.81

[a] Sample: Pressure Chemical's polystyrene M_1 = 97 200, M_2 = 411 000. Experiments: Dynamic measurements on Weissenberg rheogoniometer, Model R-17. [b] Sample: anionic polystyrenes M_1 = 46 900, M_2 = 167 000. Experiments: dynamic measurements on Concentric cylinder rheometer. [c] Sample: Pressure Chemical's polystyrenes. Experiments: dynamic measurements on Weissenberg rheogoniometer. [d] Sample: anionic polystyrenes M_1 = 125 000, M_2 = 267 000. Experiments: stress relaxation. [e] Sample: Pressure Chemical's polystyrenes M_1 = 86 000, M_2 = 500 000. Experiments: Dynamic measurements on modified Weissenberg rheogoniometer, Model R-16. [f] Sample: anionic polystyrenes. Experiments: creep recovery.

Line 6 represents the data of Orbon and Plazek when extrapolated in the limit of $M_zM_{z+1}/M_nM_w \rightarrow 1$ and yields log $J_e \sim -6.5$. The low molecular weight component in two of their blends (points with filled triangles) has a molecular weight of ~22 000 which, according to the Rouse theory and experimentally verified, have log $J_e \sim -6.5$.

In summary, it appears that for these blend data a simple linear relationship between J_e and the function M_zM_{z+1}/M_nM_w holds. We have no theoretical justification for this functional form at present. However, its simplicity

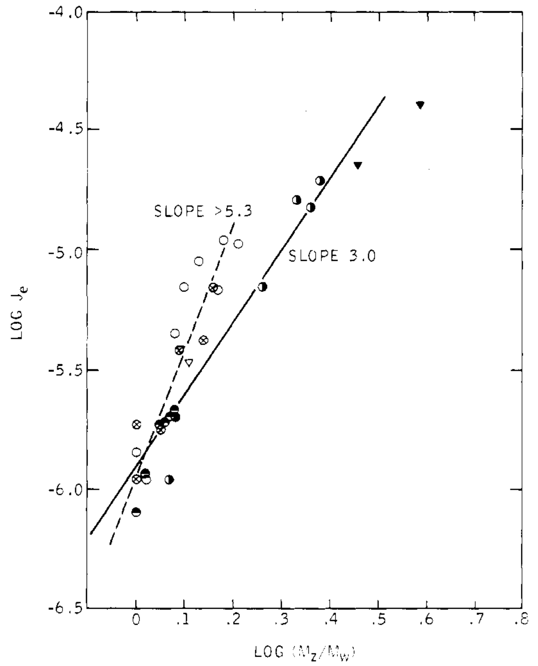

Figure 2. Logarithmic plot of the steady state compliance J_e, cm^2/dyn, vs. (M_z/M_w). See Figure 1 for data point details.

makes it a useful empirical contribution.

One of the referees is of the viewpoint that the relationship presented in this note is no better than the Kurata et al. relation (eq 8) and insisted that the bottom half of their Figure 12 (ref 11) be reproduced in the manuscript so that the reader can draw his own conclusion. In Figure 2 the (M_z/M_w) relationship is presented with additional data shown in Figure 1. The solid line has a slope of 3.0. The dashed line which best fits Prest and Porter and Onogi et al.'s data has a slope of more than 5.3. It can be noted that only the data of Mills and Nevin and Akovali's fall on the line of slope 3.0. As mentioned earlier in the text, Mills and Nevin had observed a slope of 3.7. The range of Akovali's (M_z/M_w) data is only within 20% and cannot be heavily relied upon for the critical test of such relations.

Acknowledgment. The author is thankful to Dr. Gary Ver Strate for helpful discussions.

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Remarks on Organodilithium Initiators

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The synthesis of difunctional organolithium initiators is of interest since these species offer a route for the preparation of near-monodisperse elastomeric polydienes possessing reactive groups at each chain end as a result of a controlled termination reaction,[1] e.g., the addition of ethylene oxide. These α,ω-polydienes (telechelic polymers) are then candidates for the preparation of model networks via the appropriate postpolymerization cross-linking reactions.

The synthesis of these organodilithium initiators has generally followed two methods, viz., (a) the generation of ion–radical species which then couple to yield the dicarbanionic initiator[2–7] and (b) the reaction of a monofunctional organolithium with an appropriate diolefinic species in the ratio of 2:1 (RLi–diolefin).[8–17] These procedures are carried out with nonpolymerizable substrates or under conditions where polymerization is suppressed.

Discussion

A common feature of organodilithium preparations is that they have been carried out in a polar solvent or polar solvent–hydrocarbon mixture. This was done in order to enhance both the rate of initiator formation and the solubility of the resultant difunctional initiator. It has been found[3,5–7,11–16] that aromatic ethers or tertiary amines can be used as cosolvents and unlike the aliphatic ethers, for example, their presence exerts minimal influence on polydiene 1,4 microstructure.

Summarizing previous attempts to synthesize organodilithium compounds suitable as initiators of polymerization Lutz et al.[18] and Beinert et al.[19] report that a number of papers and patents describe organodilithium initiators. They assert that the molecular weight distributions of the polymers derived from some of these initiators are broad as (apparently) a consequence of slow initiation and, in the case of the polydienes, the 1,4 content is reduced by the presence of triethylamine. However, these conclusions are at variance with results presented by the original authors. For example, it is stated in ref 11 to 14 that an efficient difunctional initiator, 1,3-bis(1-lithio-3-methylpentyl)benzene, can be prepared from *sec*-butyllithium and *m*-divinylbenzene in the presence of small quantities of triethylamine. The culmination of some of the work described therein was the synthesis[11] of a poly(styrene–isoprene–styrene) triblock copolymer of high tensile strength, predictable molecular weight, and possessing diene stereochemistry little different from that obtainable on polymerization in a pure hydrocarbon solvent.

The claim that, for example, small amounts of triethylamine exert a minimal influence on polydiene microstructure is fortified by results for polybutadiene prepared by the difunctional lithium initiator prepared from, in this case, the mixed isomers of 2,4-hexadiene.[6,7] The amine–chain end ratio was about 1.2:1. These microstructure data are shown in Table I along with that for a polybutadiene prepared by *sec*-butyllithium initiation

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