Table III
Analytical Data of Polymers

no.	formula	calcd % C	calcd % H	calcd % P	found % C	found % H	found % P
1	$(C_{11}H_{13}O_6P)_n$	48.54	4.81	11.38	48.58	4.90	11.04
3	$(C_{17}H_{17}O_6P)_n$	58.62	4.92	8.89	58.47	5.02	8.62
4	$(C_{10}H_{11}O_7P)_n$	43.80	4.04	11.30	43.97	3.91	10.94
5	$(C_8H_{13}O_7P)_n$	38.10	5.20	12.28	38.48	5.39	11.97

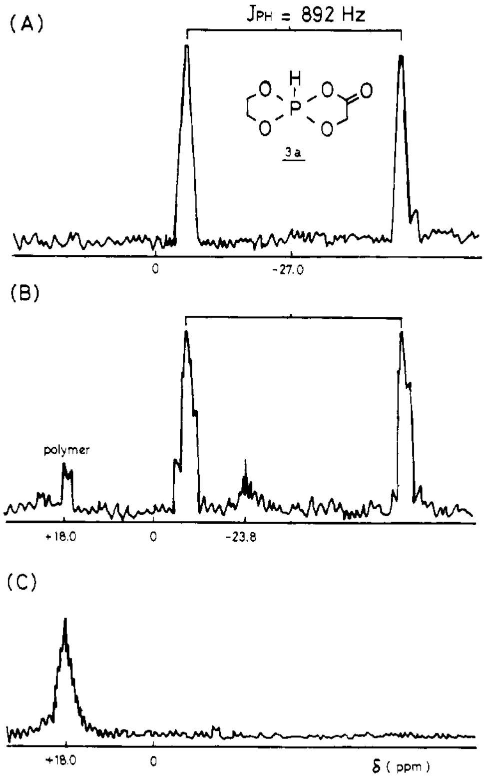


Figure 1. ^{31}P NMR spectra: (A) **5** + glycolic acid; (B) benzaldehyde added to system (A); (C) after polymerization was complete.

to a new spiro(acyloxy)phosphorane, **13**. After further reaction at 90 °C for 18 h only one peak, due to polymer **8a**, was observed (Figure 1C).

From these results a possible reaction course is given in Scheme I. An electrophile X reacts with **7** to give a transient zwitterion **11**. Since **11** has an acidic hydrogen on the carboxyl group, proton transfer takes place to give a more stable phosphonium-carboxylate zwitterion **12**. This species is in equilibrium with spiro(acyloxy)phosphorane **13**, which was actually observed directly by ^{31}P NMR during the reaction as a stable intermediate (Figure 1B). It is also conceivable that the direct reaction between **3** and X gives rise to **13**. Intermediate **12** is the key intermediate of the polymerization responsible for the production of polymers **8**–**10**.

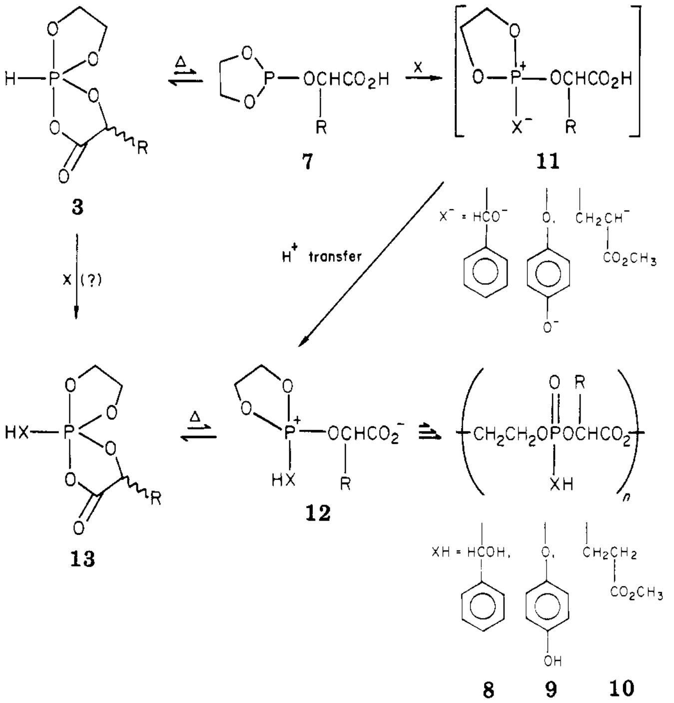
In order to express the above functions of the electrophile X, we wish to call X a "proton-trapping agent". The reactivity of **3** is modified by X and **3** becomes polymerizable.

Experimental Section

Materials. Glycolic acid and mandelic acid were commercial reagents, which were purified by recrystallization. 2-Phenoxy-1,3,2-dioxaphospholane (**5**) was prepared according to the reported method; bp 65 °C (0.2 mmHg).[4] Solvents were dried over P_2O_5 and fractionally distilled before use under nitrogen.

Polymerization Procedure. A typical run was as follows. At room temperature glycolic acid and **5** (3.0 mmol each) were placed in benzonitrile (1.5 mL) in an ampule under nitrogen and allowed to stand for 0.5 h to give **3** quantitatively. Into this mixture 3.0 mmol of benzaldehyde was added and the ampule was sealed and kept at 130 °C for 45 h. Then, the ampule was opened and the benzonitrile was distilled out in vacuo from the mixture. Chloroform was added to dissolve the polymer and the solution was poured into a large amount of diethyl ether to precipitate the polymer. This reprecipitation procedure was repeated 3 times to separate the polymer, which was then dried in vacuo to give 0.44 g (54% yield) of a white powdery polymeric material (**8a**).

Scheme I



References and Notes

(1) Saegusa, T.; Kobayashi, S. *J. Macromol. Sci., Chem.* **1979**, *A13*, 295.
(2) Kobayshi, S.; Saegusa, T. *Pure Appl. Chem.* **1981**, *53*, 1663.
(3) Munoz, A.; Sunchez, M.; Koenig, M.; Wolf, R. *Bull. Soc. Chim. Fr.* **1974**, 2193.
(4) Ayres, D. C.; Rydon, H. N. *J. Chem. Soc.* **1957**, 1109.

On the Applicability of Raman Scattering to the Study of Reorientational Motions in Polymers

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A paper appeared in *Macromolecules*[1] which claimed to obtain reorientation times for phenyl groups in polystyrene

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chains in solution using Raman line shape analysis. This paper was presented as the second in a series of papers on this subject. The first paper was published in *Polymer Journal* (*Japan*).[2] The purpose of this note is to point out that Raman line shape analysis is entirely inapplicable to the study of slow reorientational motions in polymers.

The problem of obtaining reorientational information from Raman line shape analysis can be divided into purely theoretical questions and largely practical issues. Light scattering is due to fluctuations in the dielectric tensor of the medium being studied. These fluctutions are intrinsically collective in nature in liquids, but it is usually assumed that vibrations on different molecules are independent and hence that Raman scattering can be expressed purely in terms of single-molecule vibrational modes. Corresponding to each vibrational mode q, there is a Raman polarizability tensor α_q. This quantity can be expressed in terms of a rapidly oscillating part, which determines the Raman shift, and a more slowly changing part, which depends on the vibrational state dynamics and the orientation of the oscillator in the laboratory frame. For small symmetric or spherical-top molecules in dilute solution it is valid to assume that each oscillator is independent, but for vinyl polymers such as polystyrene the oscillators are definitely coupled by the polymer chain. For small highly symmetric molecules the frequency associated with each vibrational mode in the liquid state is nearly the same for every molecule (inhomogeneous broadening in dilute solution may be a small effect), but for polymer molecules the frequency associated with each local vibrational mode along the chain is usually sensitive to the conformation of the chain, and inhomogeneity in the Raman shift can be the dominant source of line broadening. The conformational sensitivity of the Raman shift can be used to measure trans–gauche ratios of polymers in solution,[3] but, in general, it will only lead to strangely shaped Raman lines.

In order to obtain quantitative reorientational information from the Raman line shape, it is usually assumed that the time dependence of the vibrational part of α_q is independent of the reorientational part. This assumption is only weakly valid for highly symmetric molecules and is almost certainly not true for polymers. Even if the above assumption were true, it is still necessary to deconvolute out the vibrational contribution to the observed Raman line shape. The Raman polarizability tensor can be expressed in terms of a scalar isotropic part ($\bar{\alpha}_q = {}^1/_3 Tr\alpha_q$) which reflects only the vibrational motions and an anisotropic part ($\hat{\alpha}_q = \alpha_q - \bar{\alpha}_q E_3$) which reflects both vibrational and reorientational motions. Depolarized Raman scattering depends only on $\hat{\alpha}_q$, while polarized scattering depends on both $\bar{\alpha}_q$ and $\hat{\alpha}_q$. In principle, the pure isotropic Raman spectrum associated with mode q can be obtained by subtracting the anisotropic spectrum obtained from the depolarized Raman scattering from the observed polarized spectrum according to

$$S_{\mathrm{iso}}(\omega) = S_{\mathrm{VV}}(\omega) - {}^4/_3 S_{\mathrm{HV}}(\omega) \tag{1}$$

where VV denotes vertically polarized incident and scattered light and HV denotes the geometry with vertically polarized incident light and scattered light observed with polarization parallel to the scattering plane. The pure reorientational spectrum can then be obtained by assuming that the observed depolarized spectrum is a convolution of $S_{\mathrm{iso}}(\omega)$ and $S_{\mathrm{or}}(\omega)$.

In spite of the objections raised above it might still be argued that, in practice, Raman scattering would be useful as a qualitative tool in the study of reorientational motions in polymers. However, as we show below, the practical objections are far more telling than any of the fundamental theoretical reservations already expressed.

Raman scattering is a weak effect. It is often difficult to carry out an accurate analysis on the pure liquid of a small molecule. Although analyses of Raman scattering from solutions have been carried out by Wang and coworkers,[4] applications to dilute polymer solutions seem unwarranted.

In order to obtain the isotropic Raman spectrum it is necessary to study a partially polarized band. In practice, a strongly polarized band is often chosen. However, the depolarization ratio of 0.01% reported by Koda, Nomura, and Miyahara[1] must be an error. A more typical value for ρ for the 1002-cm^{-1} band of polystyrene is 0.07.[5] Because of the low intensity of the depolarized Raman spectrum, it is difficult to study the spectrum with narrow slit widths. One solution to the problem is to record the spectrum under conditions where the signal-to-noise ratio is good and to actually deconvolute the instrumental spectrum from the observed spectrum to obtain the true Raman spectrum. This procedure is seldom followed in practice. Instead, the spectrum is recorded as a function of slit width until it becomes independent of slit width. In a paper[6] apparently held in high esteem by the Japanese authors (but missing from their list of references) Gillen and Griffiths found that slit widths less than 20 μm were required to obtain the instrument-limited spectrum. This is still not the true spectrum, but at least it allows the polarized and depolarized spectrum to be compared under conditions where the instrumental function is the same and hopefully narrow in comparison with the true spectrum. However, as the slits are narrowed, it becomes increasingly difficult to see any depolarized scattering above the noise. This places severe limitations on the precision with which the spectrum can be analyzed.

Up to this point nothing has been said about the actual line shape. The effective instrumental line shape depends on the spectrum of the incident light as well as the transmission function of the double monochromator. A typical multimode laser has an emission profile that may be approximated by a Gaussian function with a half-width at half-height of 0.1 cm^{-1}. Thus, the effect of the laser is normally ignored in Raman scattering measurements, where the line widths are typically a few cm^{-1}. Under ideal conditions the transmission function of double monochromator can also be represented by a Guassian profile with a width near 0.2 cm^{-1}. However, when the slits are open wide enough to record the depolarized Raman spectrum, the slit function is approximately triangular and probably wide enough to affect the shape of the observed spectrum.

It is usually assumed that the vibrational and reorientational relaxation functions are exponentials and hence that the corresponding spectra are Lorentzians. This means that the line width of the pure reorientational spectrum can be obtained according to

$$\Gamma_{\mathrm{or}} = \Gamma_{\mathrm{HV}} - \Gamma_{\mathrm{iso}} \tag{2}$$

where the Γ's are the half-widths at half-height of the Lorentzian peaks. The Japanese authors made the usual mistake of confusing half-widths with full-widths. In practice, Raman peaks in polymers are almost never actually Lorentzian. With the large numbers of modes available there are almost always overtone and combination bands near any peak of interest. Hot bands are usually present. Isotope bands due to the presence of carbon-13 cannot be avoided, especially when the mode 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 $\pm 0.8\ \mathrm{cm}^{-1}$ since each observed line had a precision of $\pm 0.4\ \mathrm{cm}^{-1}$ due to the 10% uncertainty in the absolute line width. The Japanese authors in their first paper reported line widths with a precision of $\pm 0.01\ \mathrm{cm}^{-1}$. This claimed precision is not valid. A corresponding relaxation time can be obtained from the half-width at half-height according to

$$\tau_{\mathrm{or}} = 1/2\pi\Gamma_{\mathrm{or}} \tag{3}$$

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.

References and Notes

(1) Koda, S.; Nomura, H.; Miyahara, Y. *Macromolecules* **1978**, *11*, 604–606.

(2) Nomura, H.; Miyahara, Y. *Polym. J.* **1976**, *8*, 30–34.

(3) Wunder, S.; Merajver, S. D. *J. Chem. Phys.* **1981**, *74*, 5341–5346.

(4) Whittenburg, S. L.; Wang, C. H. *J. Chem. Phys.* **1977**, *66*, 4255–4262.

(5) Sears, W. M.; Hunt, J. L.; Stevens, J. R. *J. Chem. Phys.* **1981**, *75*, 1589–1598.

(6) Gillen, K. T.; Griffiths, J. E. *Chem. Phys. Lett.* **1972**, *17*, 359–364.

(7) Patterson, G. D.; Griffiths, J. E. *J. Chem. Phys.* **1975**, *63*, 2406–2413.

(8) Patterson, G. D.; Lindsey, C. P.; Alms, G. R. *J. Chem. Phys.* **1978**, *69*, 3250–3253.

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

$$\eta = K\bar{M}_{\mathrm{w}}^{3.4} \tag{1}$$

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

$$v_2\bar{M}_{\mathrm{w}} > 2M_{\mathrm{e}} \tag{2}$$

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

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

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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