cal-point phenomena generally (see Fisher and Scesney[17]), the true effect is allowed for[14] by the appropriate rescaling, *i.e.*, replacing γ by γ/γ_c in comparing experiments with plots like b, Figure 1, to an excellent approximation. The recent Faraday discussion on gels did reveal a more general lack of awareness, especially of the Scanlan-Case EANC concept. I propose to review the subject at the forthcoming IUPAC microsymposium on cross-linking and networks in Prague.[18]

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Manfred Gordon
Institute of Polymer Science, University of Essex
Wivenhoe Park, Colchester, C04, 3SQ, Essex, England

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Comments on "Rubber Elasticity. Flaws in the Theory of Networks"

In the accompanying communication[1] Gordon levels two criticisms at our recent work "Elastically Ineffective Cross-links in Rubbers." [2] His first comment is that we have treated chain ends with concepts first employed by Flory,[3] but no longer considered to be the most applicable approach. Scanlan[4] and Case[5] have presented a superior point of view on the elastic activity of cross-links, which Gordon suggests we use. Actually, at the time we first received this comment from Gordon we were about to submit a paper in which, among other things, just such a change had been made, and this work is now published.[6] Chain ends are not central to the counting of elastically ineffective cross-links, except near the gel point. Hence, the modifications of the numerical results we published earlier[2] are slight. We agree, however, that if the free-end correction is to be made at all, it should be made with the theory of Scanlan and Case.

In section b of his communication Gordon claims that in Gordon, Ward, and Whitney (GWW)[7] the correct theory of loop formation in rubbers has been presented. We do not agree that this is the case. (Most of Gordon's work is specific to network formation by condensation reactions of polyfunctional groups, but we are willing to assume that somehow this can be related to rubber vulcanization.)

Our major reservation about GWW is the complete disregard, by fiat, of any correlation between pairs of units which are part of the gel. This includes the case where units are separated by only a few links, a case that we know dominates the loop formation problem. It is not hard to see that this omission of correlation results in no loop formation. However, we do not accept the hypothesis; nor do we regard GWW's four-parameter fit to condensation rates as proof of the approximation as it applies to loop formation. Furthermore, we do not believe that James and Guth[8] felt that such a hypothesis was to be made. While it is true that they pursue its consequence in one section (from which GWW quote), they also consider other, indeed strong, correlation schemes. The major thrust of James and Guth's argument is that the elasticity formula obtained is not overly sensitive to the correlation assumed.

GWW do consider certain loops, *viz.*, those formed in the sol. These are not directly equivalent to any of our elastically ineffective loops. As the functionalities along sol loops join the gel such loops may, in fact probably will, become elastically effective in the sense of the topological theories of rubbers.[9] (By the topological theories we mean those approaches which are based on the number of effective chains in the network, and are independent of the way the cross-links were formed.) Of course, if one adheres strictly to the 1947 James and Guth[8] ideas, it is the condition of a bond at the moment of formation that counts (but in James and Guth[8] all network cross-links, including loops, contribute to the elastic modulus). We do not wish to comment on this disagreement here, but feel free to carry out calculations which are of interest to adherents to the topological school.

We think that some of the kinetic equations of GWW could be adapted to the calculation of elastically ineffective looping (as we define it) by allowing for gel loop formation and by statistically monitoring the subsequent connectivity of those loops to the network. This is not a program we intend to implement at this time.

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Eugene Helfand* and Alan E. Tonelli
Bell Laboratories, Murray Hill, New Jersey 07974

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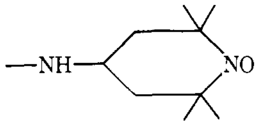
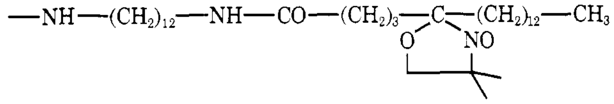
Motion of Nitroxide Spin Labels Covalently Attached to Synthetic Polymers

The use of nitroxide spin labels to study motion, environment, conformation, etc., in biological systems is extensive.[1,2] The type of problems involving synthetic polymer systems which can be usefully explored by this technique is not so well established. A few studies on motion in dilute polymer solutions have appeared,[3-10] as well as studies on motion in more concentrated solutions[9,11,12] and also in the pure polymer.[6,9,12-16] In dilute solution spin labels attached to random coil polymers typically undergo rapid motion ($\tau_R \approx 10^{-10}$ sec) which can be analyzed using theory for motionally narrowed spectra.[17] In solid polymers the motion of the spin label may be several orders of magnitude slower. Recent advances in line-shape theory make possible the analysis of the motionally slowed spectra.[18-21] A complete line-shape analysis can yield details concerning the nature of the motion in addition to an apparent rotational correlation time.

We wish to report studies on the motion of the spin labels (I–III) attached to three types of polymer systems

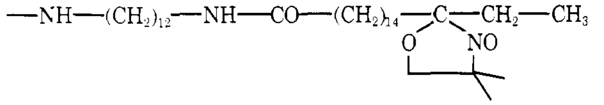


I



$-\mathrm{NH}-(\mathrm{CH_2})_{12}-\mathrm{NH}-\mathrm{CO}-(\mathrm{CH_2})_3-\underset{\mathrm{O}\quad\mathrm{NO}}{\mathrm{C}}-(\mathrm{CH_2})_{12}-\mathrm{CH_3}$

II



$-\mathrm{NH}-(\mathrm{CH_2})_{12}-\mathrm{NH}-\mathrm{CO}-(\mathrm{CH_2})_{14}-\underset{\mathrm{O}\quad\mathrm{NO}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH_3}$

III

(A–C) [(A) randomly labeled, linear polymer; (B) surface labeled, cross-linked (2%) latex spheres; (C) homogeneously labeled, cross-linked (2%) latex spheres] and in the presence or absence of various solvents and nonsolvents. Esters of methacrylate or acrylate polymers have been labeled by use of the amide–ester interchange reaction thereby attaching the label to an occasional side chain carboxyl in the form of an amide bond. Through use of an ester cross-linking agent during polymerization, such as ethylene glycol dimethacrylate, or by a copolymerization using a monofunctional ester as a trace component, vinyl polymers such as polystryene also may be easily labeled by the amide–ester interchange reaction. The label, however, is attached to the nonstyrene component. The latex spheres, prepared by emulsion polymerization with a typical diameter of about 1000 Å, were cross-linked so that they could be redispersed, after emulsifier stripping, in either solvents or nonsolvents with retention of their particulate nature. Systems of type B and C were prepared in the hope of differentiating surface motion from motions in the bulk polymer. In type C the amount of label at the surface is too small to measure. In all cases the level of labeling was low enough to avoid spin–spin interaction.

Nitroxide labels of type I attached to form system A, B, or C have been studied as a function of solvent composition and temperature. Typical spectra are illustrated with type B shown in Figure 1. Occasionally when using nonsolvents with system B a spectrum was obtained which appeared to have a motionally slowed component superimposed on a motionally narrowed spectrum. This is likely a result of incomplete dispersal of the latex in the nonsolvent, even after sonicating. Of particular importance is the absence of a doublet in the low field component of most of the motionally slowed spectra. Recent interpretation[21] of experimental data[9] shows clearly that rapid motion about a single bond, in particular the N–C bond in the nitroxide I, gives rise to a doublet in the low-field component. Consequently the absence of such a doublet in going from the rigid glass to a motionally narrowed, three-line spectrum, effected by an increase in temperature or by addition of a solvent, indicates that there is a significant contribution from motion about more than one bond. In addition, polymer systems of type B, labeled with either II or III and dispersed in a series of nonsolvents, yield spectra which depend on the nature of the nonsolvent and not on which of the labels is at-

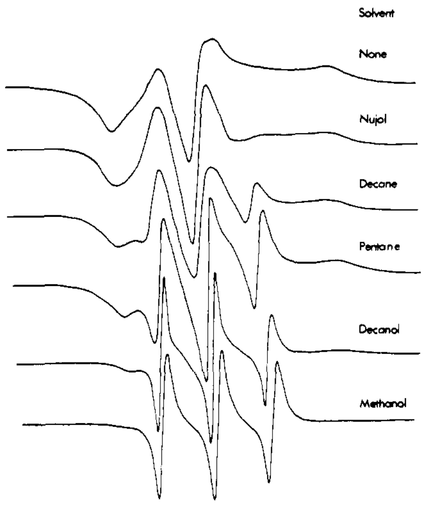


Figure 1. Effect of several nonsolvents on the motion of spin label I attached to polystyrene (PS) spheres of type B. The latex spheres were dispersed in an excess of nonsolvent; *i.e.*, the system was visually a two-phase system. All measurements were at room temperature.

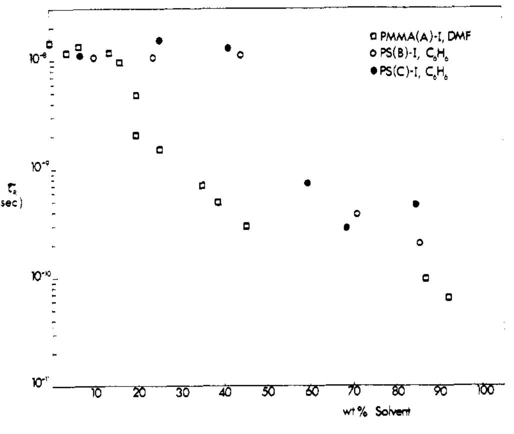


Figure 2. Rotational correlation time[17,20] as a function of solvent composition: □, PMMA(A)–I, DMF; ○, PS(B)–I, C_6H_6; ●, PS(C)–I, C_6H_6. All measurements were at room temperature.

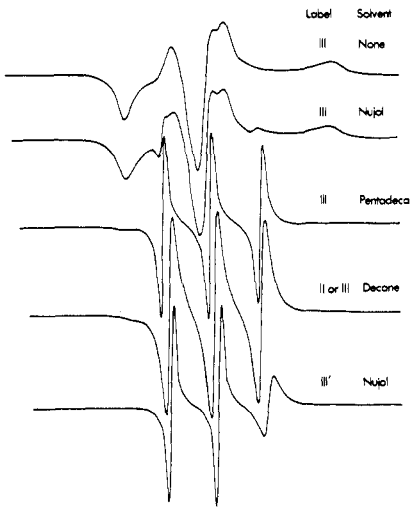
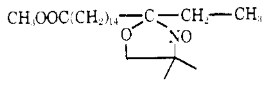


Figure 3. Analogous to Figure 1 except the label was either II or III. Free spin label III′ is



$\mathrm{CH_3OOC(CH_2)_{14}}-\underset{\mathrm{O}\quad\mathrm{NO}}{\mathrm{C}}-\mathrm{CH_2}-\mathrm{CH_3}$

tached, indicating also a contribution from motion about several bonds.

We turn next to the effect of a thermodynamically good solvent for the polymer on the motion of the nitroxide. We consider a good solvent to be one which will mix with the polymer in all proportions to form a single phase system, or as an alternate definition one with a solubility parameter within 0.5 units of that of the polymer. Upon addition of a good solvent all three types of systems show similar behavior, which depends little on the nature of the label. Typical results are shown in Figure 2, where correlation times longer than 2×10^{-9} sec were calculated from the outer hyperfine extreme by the method of Goldman, Bruno, and Freed,[20] and not by a complete line-shape analysis. The absolute values depend somewhat on the choice of the diffusion model and the intrinsic line width, but the qualitative features exhibited in Figure 2 are unchanged. Addition of small amounts of good solvent to either poly(methyl methylacrylate) (PMMA) or polystyrene (PS) results in little change in motion until a critical solvent concentration is reached. Further addition results in a rapid increase in nitroxide motion. Both polymers have a glass transition temperature (T_g) of about 100°.[22] Addition of a good solvent lowers T_g in a well-defined manner.[23] Differential scanning calorimeter measurements on the PMMA(A)–I, dimethylformamide (DMF) system indicate that rapid increase in nitroxide motion does not begin until T_g drops below the temperature of the esr measurements. This result, if general, suggests that either main chain motion is necessary in order to get greatly increased nitroxide motion, or that nitroxide motion is much enhanced by increased motion in nearby side chains, which may come just before significant main chain motion. The fact that the type of polymeric system (A–C) is unimportant suggests that surface motion is little different from interior motion in these systems. Our results indicate that the τ_R-solvent uptake curve depends significantly on the nature of the polymer–solvent pair, in contrast to the conclusion of Regen.[12] The reasons for the discrepancy are complex and will be discussed elsewhere.

The application of a homologous series of linear, saturated hydrocarbons to polystyrene latexes of types B and C gave particularly interesting results, shown for type B in Figures 1 and 3. The solubility parameter of the hydrocarbon is about 2 units less than that of the polymer. The solubility of the polymer in these solvents is very low, *i.e.*, the solvents can be classified as nonsolvents for the polymer. The motion of the nitroxide is not affected by dispersal of the inside or homogeneously labeled spheres in linear hydrocarbons. The outside or surface labels do respond, but in a manner which depends both on the length of the side-chain attached label and the length of the hydrocarbon. As the length of the hydrocarbon is increased the nitroxide motion slows down. In Nujol it is similar to that in the pure, dry polystyrene spheres. Increasing the length of the side chain to which the spin label is attached requires a longer hydrocarbon solvent to slow the nitroxide motion. The free spin labels are reasonably soluble in the hydrocarbon and show rapid motion. Whether these results depend on the chemical nature of the latex surface or are general is not known.

The dispersal of a latex in solvents having solubility parameters greater than that of the polymer latex produces motion quite different than that of the linear hydrocarbon solvents. Dispersal in a homologous series of linear alcohols (C_6 to C_{10}) results in rapid nitroxide motion ($\tau_R \approx 10^{-10}$ sec). Of the high solubility parameter nonsolvents only water had no effect on the nitroxide motion. These results suggest specific solvation of the nitroxide may occur and give motional freedom to the nitroxide. But the finding that water imparts no additional motion suggests that the presence of the surface has an effect also.

On the basis of these studies we believe that nitroxide labels may provide a unique tool to study molecular motion at polymer surfaces. However, the possibility of specific solvation and the effects of solvents on motion of the entire polymer chain make extreme caution necessary in interpreting results.

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(24) On leave from Institute, Rudjer Bošković, Zagreb, Yugoslavia.

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Zorica Veksli[24,25] and Wilmer G. Miller*[25]
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota 55455

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