not only the free energy difference between the ring conformations in the monomer but also how this difference is affected by the neighboring units in the polymer.

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Molecular Relaxation of Nearly Monodisperse Polystyrene Melts

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In a recent publication, Forsman and Grand[1] presented a statistical mechanical theory of entanglement for assemblies of monodisperse random-flight chains. They predicted that, because of the symmetry of the chains about their center segments, only the longest *odd-order relaxation* times as defined by Rouse[2] were affected by entanglement. These predictions were shown to be completely consistent with experimental results published by Wolkowicz and Forsman[3] on concentrated solutions of nearly monodisperse polystyrene. In this paper, we analyze dynamic data on polystyrene melts and observe that it is also consistent with the theory.

A number of workers[4-8] have reported dynamic data on polystyrene melts. Of these, only those of den Otter[4] and Onogi, et al.,[5] extend over a sufficiently broad range of frequency to allow interpretation according to molecular theory. We observed, however, that the value of the zero-shear-rate viscosity, η_0, obtained from the terminal zone of the G'' (dynamic loss modulus) data of Onogi, et al.,[5] was inconsistent with the values reported by over 13 groups of investigators[9-11] at corresponding temperatures. We elected, therefore, to study den Otter's[4] data on polystyrene of molecular weight 290,000 at 190°.

Analysis

According to Rouse,[2] the linear viscoelastic behavior of an assembly of monodisperse random-flight chains is described by a multiple Maxwell model in which there is a one-to-one correspondence between each spring and dashpot pair and a normal mode of backbone motion. Each normal mode is designated by an index p and corresponds to movement of the chain backbone in blocks of molecular weight equal to (M/p). In addition, the model predicts relaxation times, $\tau_{p\mathrm{R}}$, which can be obtained from the transition region by the relationship[2]

$$\tau_{p\mathrm{R}} = \frac{16M^2}{\pi^2 p^2 (\rho RT)^2}\left(\frac{G''^2}{\omega}\right)_{\text{transition}} \qquad (1)$$

where M is the molecular weight of the polymer, ρ is its density, RT is the gas constant times absolute temperature, and G'' is the value of the loss modulus at angular frequency ω. The subscript $p\mathrm{R}$ is used here to indicate that eq 1 gives the value of each relaxation time of index p as predicted by the Rouse theory for assemblies of unentangled chains. Each normal mode has associated with it a Maxwell-model spring constant, G_R, given by

$$G_\mathrm{R} = \rho RT/M \qquad (2)$$

According to Forsman and Grand,[1] there is a one-to-one correspondence between the relaxation mechanisms in entangled chains and their unentangled analogs treated by Rouse. The spring constant associated with each normal mode is $(\rho RT/M)$ as in unentangled systems, but some of the first few (longest) relaxation times having odd p are increased. As a measure of the increase in relaxation times, shift factors[3] Q_p were defined by the relationship

$$Q_p = \tau_p/\tau_{p\mathrm{R}} \qquad (3)$$

where the τ_p are the relaxation times for the entangled system, and $\tau_{p\mathrm{R}}$ are the corresponding values predicted by the Rouse theory for the unentangled analog. The analysis for entangled systems[1] thus predicted only the first several odd-order Q_p to be greater than unity but did not indicate how Q_p approached unity with increasing p. Because all τ_p approach corresponding values of $\tau_{p\mathrm{R}}$ with increasing p, the transition zone is predicted to be unaffected by entanglement.

Since the contribution of each normal mode to the dynamic storage and loss moduli G' and G'' are given by the simple expressions

$$G_p' = G_\mathrm{R}[\omega^2\tau_p^2/(1 + \omega^2\tau_p^2)] \qquad (4a)$$

$$G_p'' = G_\mathrm{R}[\omega\tau_p/(1 + \omega^2\tau_p^2)] \qquad (4b)$$

testing the predictions of the Forsman–Grand theory is straightforward. Because the transition zone is unaffected by entanglement, eq 1 and 2 are used to predict the G' and G'' for an unentangled analog. One then attempts to match experimental data with a theoretical curve obtained by summing contributions given by eq 4a and 4b but for which the longest several *odd-order* relaxation times have been shifted to longer times. It is important to emphasize that all even-order relaxation times remain fixed at their values predicted by the Rouse theory.

Since theory[1] does not predict the extent to which each relaxation time is affected by entanglement, additional assumptions must be considered in the interpretation of experimental results. The first approach (and that applied previously[3]) is to assume Q_p to be a smooth function of p.

Figure 1 shows a comparison of experiment and theory for such an assumption. We see that by shifting eight relaxation times (p = 1, 3, 5, 7, 9, 11, 13, and 15) experiment and theory are brought into excellent agreement. Figure 2 shows the extent to which entanglement affects these relaxation times as defined by the individual shift factors Q_p.

One might at first dismiss the agreement between the experimental and computed curves as being of little physical significance since there are "8 adjustable parameters." This is, however, an oversimplification. First, it is important to note that the spring constants were assigned their theoreti-

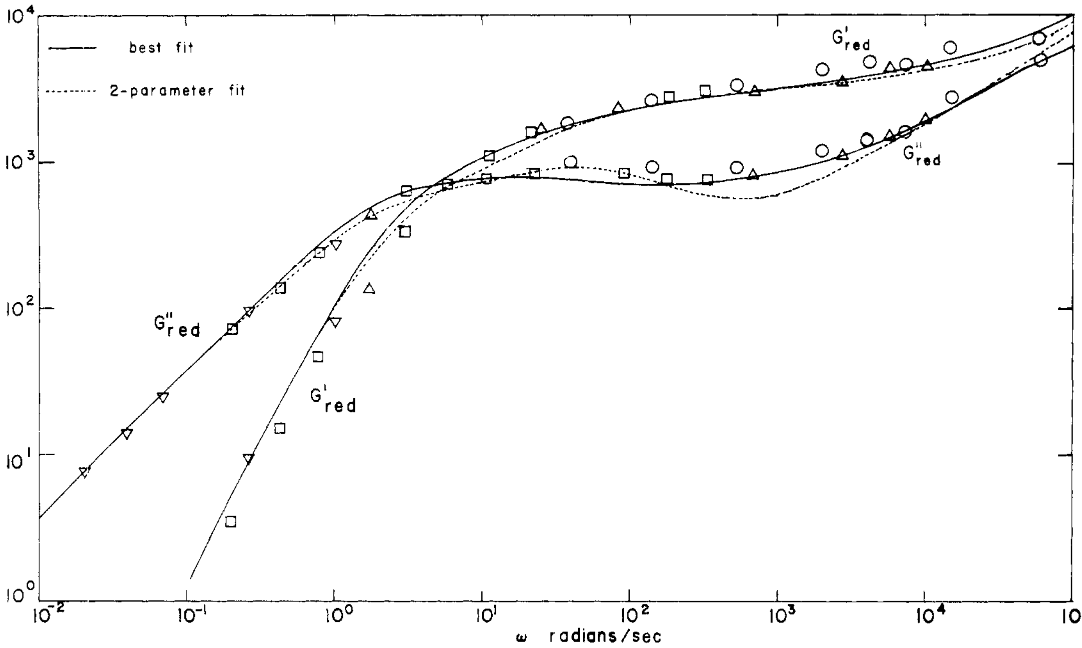

Figure 1. Den Otter's reduced dynamic moduli as functions of ω at 190°. Symbols represent data at various temperatures: ○, 140°; △, 159°; □, 190°; ▽, 224°. $G'_{red} = G'/\rho T$, $G''_{red} = G''/\rho T$. Solid lines represent theoretical curves obtained as described in the text.

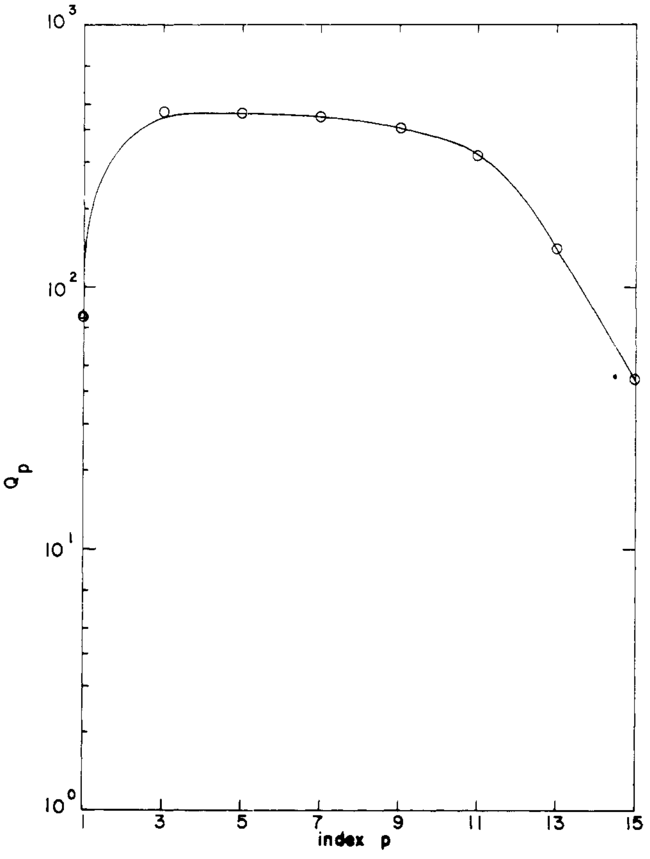

Figure 2. Q_p *vs.* p for den Otter's data.

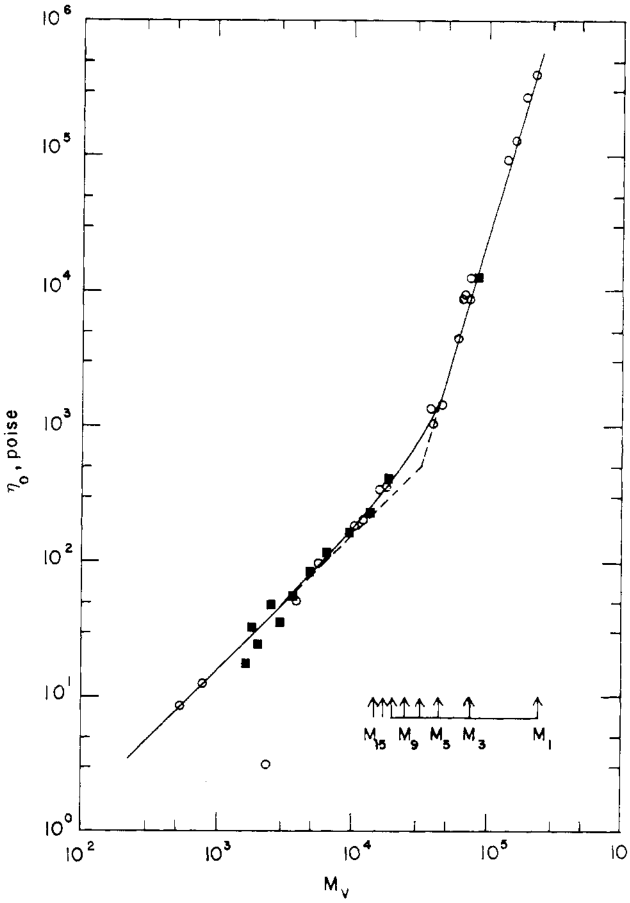

Figure 3. Log η_0 − log M_v for polystyrene melts at 190°. Arrows indicate various values of M_p.

cal value ($\rho RT/M$) and were not adjustable. Second, it is of foremost importance to consider the *number* of relaxation times shifted.

According to theory,[1,2] the pth normal mode corresponds to motion of the chain backbone in blocks of molecular weight $M_p = (M/p)$. In Figure 3 these molecular weight values for the shifted normal modes are superimposed upon a log–log plot of η_0 *vs.* M taken from the work of Allen and Fox.[10,11] We note the longest four relaxation times (p = 1, 3, 5, and 7) correspond to motion of the chain backbone in blocks of molecular weight greater than M_c (the critical molecular weight for chain entanglement defined by the intersection of two straight-line segments). The next four shifted relaxation times correspond to molecular weights in the partial entanglement region as described

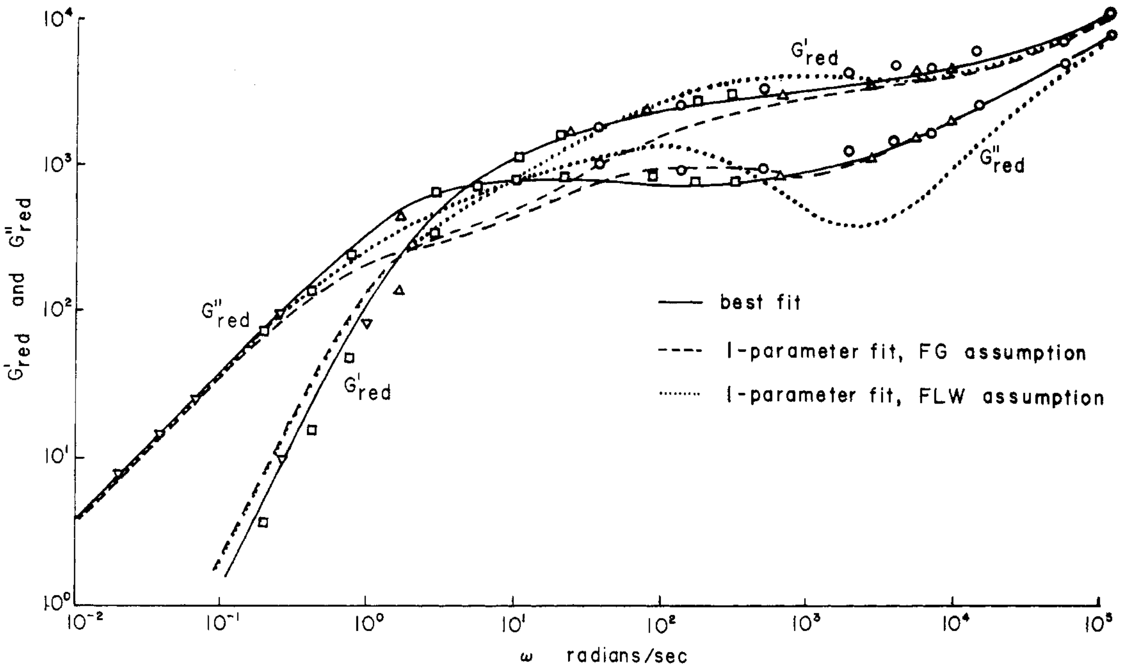

Figure 4. One-parameter fit to den Otter's reduced dynamic moduli as functions of ω at 190° according to Forsman and Grand and Ferry, Landel, and Williams.

previously.[2] All higher order relaxation times correspond to molecular weights in the unentangled region of the η–M curve and are unaffected by entanglement.

Although the extent of the shifts was empirical, we note that just the correct number of relaxation times were shifted, namely those that correspond to chain lengths which are entangled (or partially so) according to the log–log plot of η *vs.* M. This is as would be expected. For example, a polystyrene sample of twice the molecular weight would be expected to have twice as many relaxation times affected by entanglement.

Since the relaxation times were shifted to optimize the agreement between the computed and experimental curves, it is clear that the Q_p values are, to a degree, arbitrary (even though the process is not at all equivalent to curve fitting with eight adjustable parameters). It would thus be useful to explore the possibility of establishing some simple rule for determining Q_p that might prove useful in predicting linear viscoelastic behavior of entangled, nearly monodisperse systems. We will thus consider one- and two-parameter shifts.

The one-parameter shift is analogous to the notion introduced by Ferry, Landel, and Williams[12] that all entangled relaxation times should be shifted by the same amount. In this case, we first assume all odd-order entangled relaxation times are shifted by the same amount to give agreement with the experimentally determined terminal zone. Figure 4 shows the comparison between the data and computed behavior with

$$Q_p = 178 \qquad 1 \leq p \leq 15 \qquad (p \text{ odd})$$
$$Q_p = 1 \qquad \text{otherwise}$$

In addition, Figure 4 shows the result obtained by shifting all relaxation times, as previously suggested,[12] by a factor $Q_p = 143$ for $p < 15$. The one-parameter shifts give computed values of G' and G'' that are semiquantitatively in agreement with experiment, with the result obtained by shifting only the odd-order relaxation times yielding a curve more nearly the shape of that determined experimentally.

A far better fit is obtained, however, by introducing an additional element of flexibility and using a two-parameter shift for the odd-order relaxation times. Figure 1 also shows the comparison between computed behavior and experimental results when

$$Q_1 = 80$$
$$Q_p = 435 \qquad 3 \leq p \leq 15 \qquad (p \text{ odd})$$
$$Q_p = 1 \qquad \text{otherwise}$$

Considering the experimental difficulty in determining linear viscoelastic functions of polymer melts, with attendant experimental error, the two-parameter fit is probably as physically significant as the best fit. With further investigation, it might prove to be a general description of the linear viscoelastic behavior of entangled, nearly monodisperse polymer solutions and melts.

It is worth noting that the interpretation presented here is frustrated by the fact that we are considering the behavior of a (slightly) polydisperse sample in terms of a theory for monodisperse systems, a difficulty confounding various aspects of polymer science. This problem blurs interpretation, especially in polymer rheology.[13] Possibly, this could account for the necessity of introducting two shifting parameters to bring theory and experiment into agreement.

We conclude by commenting that no corresponding two-parameter shift would improve agreement between theory and experiment when both even- and odd-order relaxation times were affected. Bringing better agreement between theory and experiment for $10^2 \lesssim \omega \lesssim 10^4$ worsened agreement for $10^0 \lesssim \omega \lesssim 10^4$, and *visa versa*. This analysis shows, therefore, that the predictions of the Forsman–Grand theory are consistent with the observed behavior of melts of nearly monodisperse polystyrene as well as for their concentrated solutions. Furthermore, the molecular weights associated with the normal modes affected by entanglement are consistent with the commonly accepted notion that entanglement effects become important for molecular weights approximately equal to and greater than M_c and are essentially absent below M_c. This observation is strong evidence for the applicability of a normal mode interpretation of the viscoelastic behavior of entangled polymer systems.

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Poly(2-vinylfluorenone). II. Synthesis and Photochemistry of a Diazofluorene-Containing Polymer

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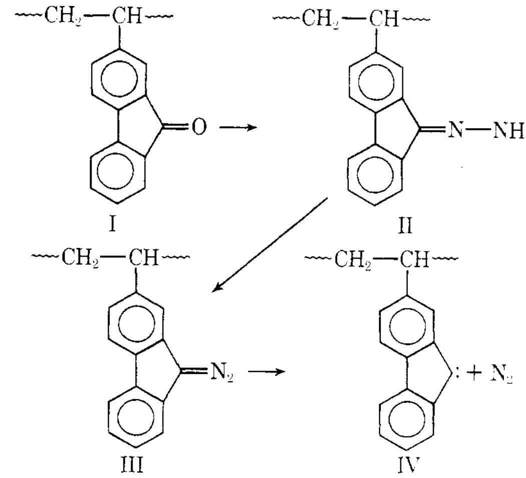
Photosensitive polymers are widely used in a number of important industrial technologies. Most of these utilize the difference in solubility, resulting from crosslinking reactions induced by light of the appropriate wavelength, in light and dark areas to create relief images which are further processed, *e.g.*, by photoresist techniques. The recent literature describes a number of interesting polymeric materials containing cinnamate,[1] acetylenic,[2] cyclopropene,[3] azido, and sulfonylazido[4] functions, and several comprehensive reviews[5,6] have appeared.

With few exceptions, the chemistry in these systems involves coupling processes leading to crosslinked, insoluble materials, *e.g.*, the photocyclodimerization of cinnamate groups and the formation and reactions of highly reactive radical fragments (nitrenes) produced in the photodissociation of azides. More recent efforts have been directed toward increased speeds and higher sensitivity through synthetic modification and improved sensitizers.

This note describes the synthesis of a novel photosensitive polymer containing diazofluorene groups. Photolysis of aryl and diaryldiazo compounds in solution has been reported[7] to give the corresponding carbene and nitrogen with high quantum efficiency ($\phi \sim 0.7$ to 0.9). Carbenes, or divalent carbon intermediates, are highly reactive species which undergo a wide range of addition, abstraction, and insertion reactions as well as coupling reactions.[8] The products from many of these highly nonselective processes are free radical in nature and these can react further by conventional radical reactions. A wide variety of crosslinking possibilities can be readily recognized if such entities could be introduced into a polymer material. Polymers possessing diazo groups have not been reported, probably due to the pronounced thermal instability of such compounds. Diazo compounds are, however, claimed[9] to be extremely efficient photocrosslinking agents for certain polymers.

The synthesis of 2-vinylfluorenone has made polymers and copolymers containing fluorenone groups (I) a reality.[10] 9-Fluorenone can be readily converted into 9-diazofluorenone and this diazo compound has a melting point of 94–95° and good thermal stability. Polymers containing diazofluorene groups have been prepared from 2-vinylfluorenone polymers by conversion to the hydrazone and subsequent oxidation. Treatment of the homopolymer of 2-vinylfluorenone or copolymers of 2-vinylfluorenone, *e.g.*, with styrene, in pyridine at 50° with hydrazine gave the corresponding hydrazone (II)-containing polymer which was isolated and purified. The conversion was best controlled by varying the concentration of hydrazine and the reaction time. At temperatures above 50° polymer insolubility became a severe problem. The use of excess hydrazine resulted both in conversion of fluorenone to fluorene groups (the result of an unusually facile Wolff–Kishner rearrangement) and insoluble products. The hydrazone-containing polymers were characterized by ir analysis. Oxidation of the hydrazone groups in the polymers to diazofluorene (III) groups was most effectively carried out at ambient temperatures using silver oxide. The hydrazone polymer was dissolved in a 90:10 THF/Et_2O mixture and freshly prepared silver oxide, and a few drops of alcoholic KOH were introduced and the reaction mixture stirred for 15–30 min. The polymer was isolated by precipitation into a nonsolvent. Longer reaction times and higher temperatures gave insoluble products. On the basis of small molecule control experiments the conversion of hydrazone to diazofluorene was assumed to be nearly quantitative under the experimental conditions employed. The polymers were yellow/orange/red in color, depending on the concentration of diazo groups. The ir spectra of poly(2-vinylfluorenone) and a polymer containing 5–10 mol % of diazofluorene groups are shown in Figure 1, top and bottom, respectively. The characteristic diazo band at 2060 cm^{-1} is evident. The reaction sequences shown were carried out on poly(2-vinylfluorenones) and on a styrene/2-vinylfluorenone (90:10) copolymer. The conversion of fluorenone to hydrazone and hydrazone to diazofluorene could be controlled by varying the reaction times using the prescribed experimental conditions. In general, polymers containing only a few mole per cent of diazofluorene groups were prepared and investigated, although a 50/50 copolymer of 2-vinylfluorenone/2-vinyl-9-diazofluorene was successfully isolated.



Although diazofluorene is apparently stable at ambient temperatures in the dark, polymers containing this functional group rapidly (within several days) became insoluble on storage in bulk or in solution. Storage at temperatures below 0° increased the functional lifetime of the material but such a limitation clearly precludes their practical utility. Apparently the thermal decomposition of diazofluorene