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Dynamics of Entangled Polystyrene Solutions Studied by Pulsed Field Gradient Nuclear Magnetic Resonance

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ABSTRACT: The translational displacements of hydrogen nuclei have been measured in entangled solutions of polystyrene in CCl_4. Polymers with molecular weights of 390 000 and lower exhibit simple self-diffusion behavior, and the macroscopic self-diffusion coefficient vs. the concentration scaling law of de Gennes is verified for molecular weight 110 000. Polystyrene gel of molecular weight 2 000 000 has a renewal time of several milliseconds and for short time scale experiments the cooperative diffusion of the gel is observed. The cooperative diffusion coefficient obeys the relationship $D_c \sim c^{0.75}$. The theory of spin echo attenuations for gel systems is considered and it is shown that the distribution of wavelengths present in cooperative gel disturbances can be determined in the pulsed field gradient experiment. Viscosity measurements show a similar agreement with the concentration scaling law of de Gennes but both diffusion coefficients and viscosities scale with molecular weight less rapidly than predicted.

I. Introduction

Recent advances[1] in the pulsed field gradient nuclear magnetic resonance (PFG NMR) technique[2,3] have enabled the measurement of diffusion of polystyrene random-coil macromolecules in solution over a range of concentrations and experimental time scales.[4] In this work we show how PFG NMR may be used to investigate solutions sufficiently concentrated that gel behavior is observed. These gel states have been described extensively in theoretical papers by de Gennes, and some of the de Gennes scaling laws have been tested by authors using other techniques. We are able to verify much of the de Gennes model and, by extending our measurements to high molecular weight polymers, have observed diffusive behavior in two different time regimes specified by this author. We have also measured the viscosities of concentrated polystyrene solutions and compared these measurements with de Gennes' theory. PFG NMR is shown here to be an effective and direct probe of cooperative gel disturbances and to provide, in addition, a unique insight into the distribution of wavelengths inherent in such disturbances.

The de Gennes Model. In two papers[5,6] dealing with the dynamics of entangled polymer solutions de Gennes pointed out that a characteristic time in dealing with gels is the gel relaxation or renewal time, T_r. For experimental observation times long compared with T_r, the macroscopic self-diffusion of the chains is observed. This self-diffusion process can be described by a coefficient

$$D_s = R^2(c)/T_r \tag{1}$$

where $R(c)$ is the concentration-dependent random-coil radius. de Gennes has shown that D_s is expected to scale according to the relationship

$$D_s \sim N^{-2}c^{-1.75} \tag{2a}$$

where c is the polymer concentration and N is the number of polymer subunits. N is proportional to the molecular weight, for which we use the symbol M. Thus the scaling law of relation 2a can be written

$$D_s \sim M^{-2}c^{-1.75} \tag{2b}$$

The concept of a renewal time is central to the model and is estimated to be

$$T_r \simeq (6\pi\eta_0/k_BT)R_F^3(c/c^*)^{1.5} \tag{3}$$

R_F is the Flory radius of the random coil, η_0 is the solvent viscosity, and c^* is the polymer concentration at which the polymer random coils just overlap. c^* is difficult to quantify either experimentally or theoretically and where possible we arrange the scaling laws such that c^* does not explicitly appear when these laws are tested. The cubic dependence of T_r on the random-coil radius prescribes that the PFG NMR experiment operates only in the long-time regime except for very long chain polymers.

The de Gennes theory predicts that an experiment able to measure the polymer motion for times short compared with T_r observes cooperative, wavelike propagations in which the gel elasticity is determined by the number of cross-links per unit volume. The effect of friction is to provide a damping term such that the overall chain segment displacements obey a simple relaxation law suitably characterized by a constant which has the dimensions of a diffusion coefficient. de Gennes calls this constant the cooperative diffusion coefficient of the gel, D_c

$$D_c \simeq k_BT/6\pi\eta_0\xi \tag{4}$$

ξ is the mesh size or average distance between entanglement points. Since it can be shown that ξ scales as $c^{-0.75}$, the scaling law for D_c is deduced to be

$$D_c \sim c^{0.75} \tag{5}$$

This 0.75 scaling index is "the essential test of cooperative

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diffusion"[6] according to de Gennes.

Previous experimental tests of the de Gennes diffusion scaling laws have employed neutron scattering[7] and quasi-elastic light scattering from concentrated polystyrene–benzene solutions.[8] The light scattering study by Adam and Delsanti gave diffusion coefficients which were taken to be D_c. These authors expressed eq 5 in the form

$$D_c \simeq \frac{k_B T}{6\pi\eta_0 R_F}\left(\frac{c}{c^*}\right)^{0.75} \quad (6)$$

k_B is Boltzmann's constant, T is the absolute temperature, and η_0 is the solvent viscosity.

Their experimental value for the exponent of concentration was 0.67 ± 0.02. The neutron scattering work has verified some of the de Gennes scaling laws not directly examined here, in particular, the relationship between polymer concentration, the radius of gyration, and molecular weight, $R^2(c) \sim Mc^{-0.25}$.

The de Gennes theory of gels also predicts a scaling law for viscosity, η

$$\eta \sim c^{3.75}M^3 \quad (7)$$

Previous experimental studies[9] indicate that the M^3 relationship is not well obeyed, an index of 3.3 being closer to the observed behavior.

Pulsed Field Gradient NMR. The PFG NMR technique is well established and has been used to determine self-diffusion coefficients in the range 10^{-13}–10^{-9} m^2 s^{-1}. The method consists of labeling nuclear spins by their Larmor precession frequencies in a spatially varying magnetic field. This perturbing magentic field gradient is applied as two pulses (magnitude G, duration δ, and separation Δ), one before and one after the 180° refocusing radio-frequency pulse in a spin echo sequence. Stejskal[3] has given a simple description for the case of narrow gradient pulses ($\delta \ll \Delta$). This description is based on the approach of McCall, Douglass, and Anderson.[10] The attenuation of the spin echo on applying the field gradient pulse $\mathbf{G}$ is given by

$$A(G)/A(0) = \int_{V_0} P(\mathbf{r}_0) \int_V P(\mathbf{r}_0|\mathbf{r}, \Delta) \exp[-i\gamma(\mathbf{r} - \mathbf{r}_0)\cdot\mathbf{G}]\, dV\, dV_0 \quad (8)$$

where $P(\mathbf{r}_0|\mathbf{r}, \Delta)$ gives the probability that a nuclear spin, initially at $\mathbf{r}_0$, will migrate to position $\mathbf{r}$ by the time the second gradient pulse arrives. $P(\mathbf{r}_0)$ is the probability distribution of the initial displacements for the nuclear spin ensemble. γ is the nuclear gyromagnetic ratio.

For nuclear spins undergoing a Brownian random walk characterized by a self-diffusion coefficient D, $P(\mathbf{r}_0|\mathbf{r}, \Delta)$ has a simple Gaussian form and eq 8 reduces to

$$A(G)/A(0) = \exp(-\tfrac{1}{2}\gamma^2G^2\delta^2\langle z^2\rangle) \quad (9)$$

where $\langle z^2\rangle$ is the mean-square nuclear displacement along the field gradient direction and may be written

$$\langle z^2\rangle = 2D\Delta \quad (10)$$

For the case of finite gradient pulses, eq 9 has the exact form[2]

$$A(G)/A(0) = \exp[-\gamma^2G^2\delta^2D(\Delta - \tfrac{1}{3}\delta)] \quad (11)$$

and the effective experimental observation time is taken to be $\Delta - \frac{1}{3}\delta$. Conventionally, D is determined by plotting the variation of ln $[A(G)/A(0)]$ against the gradient magnitude G.

When the nuclear spin displacements are not characterized by a simple, unique Gaussian probability distribution, a multiple-exponential behavior will be observed in the echo attenuation.

It should be noted that the time scale of the experiment is confined to the millisecond regime, in contrast to the neutron scattering experiment, where the experimental time is typically a few microseconds. The minimum time for which any echo attenuation can be observed is determined by the magnitude of magnetic field gradient available and the nuclear spin diffusion rate. This minimum time is typically 10 ms for $D \lesssim 10^{-12}$ m^2 s^{-1}. The spin–spin relaxation process, characterized by the relaxation time T_2, causes a relentless loss of phase coherence throughout the experiment and constrains the maximum observation time available to a few relaxation times. The benzene ring protons in concentrated polystyrene solutions have a T_2 of approximately 30 ms and in consequence the longest observation time used in this work was some 69 ms.

PFG NMR is sensitive to the net echo signal resulting from the individual nuclear displacements of the molecules under examination. For simple random walk behavior the PFG NMR experiment, as shown above, unambiguously yields the self-diffusion coefficient of the nuclei comprising the molecule and to this extent it differs from other techniques, notably quasi-elastic light scattering, which measures the mutual diffusion of solute and solvent[11] at finite concentrations.

In applying the NMR method to polymer solutions, one must choose a solvent whose nuclear spins are different from those of the solute. Since hydrogen nuclei were observed in this experiment, we have used carbon tetrachloride as the solvent, although it is possible to use deuterated analogues of other solvents.

II. Experimental Section

The PFG NMR apparatus used in this work has been described elsewhere.[1] It employs a home-built probe interfaced to an externally locked JEOL FX60 spectrometer operating at 60 MHz on hydrogen nuclei. Echoes are phase-sensitive detected, digitized, and accumulated following a $90|_x - \tau - 180|_y$ pulse sequence. The phase-alternating (PAPS) mode is used to avoid base-line distortion. Up to 1000 accumulations were used at each field gradient setting in the more dilute systems studied.

Echo sampling is started at the center of the echo at a time 2τ after the first radio-frequency pulse and the data are subsequently Fourier transformed once the desired number of echoes have been accumulated in the time domain. Frequency-domain analysis considerably improves the experimental signal-to-noise ratio by applying an effective band-pass filter. Echo amplitudes are then obtained by integrating peak areas after suitable (generally very small) base-line subtraction has been performed.

The PFG NMR system gives accurate values of the self-diffusion coefficients of benzene[12] and glycerol;[13] in particular, every set of pulse parameters used in this work has been applied to a glycerol sample and reproduced the literature value within the random errors of the experiment.

Temperature control was achieved by a thermocouple–hot air feedback system and the temperature was constant over the sample space to within 0.5 °C. The viscosity measurements were performed on a Ferranti-Shirley rotating cone-and-plate viscometer. All work reported here was carried out at 25.0 °C. Monodisperse random-coil polystyrenes were industrial standards obtained from Pressure Chemical Co. (see Table I). They were dissolved in spectroscopic-grade carbon tetrachloride, agitated, allowed to stand for ≥24 h, and stirred again before transfer to the 4-mm-diameter NMR tubes. The sample tubes were then sealed with Teflon plugs.

Concentrations are expressed in percent, where 1% represents a polymer concentration of 1 g of polymer/100 cm^3 of solution.

III. Pulsed Field Gradient NMR Results

"Short-Chain" Polystyrenes. In an earlier study[4] of 110 000 molecular weight polystyrene in CCl_4 single-exponential behavior was observed in the spin echo attenu-

Table I
Polystyrenes

batch no.	nominal mol wt	$\bar{M}_w/\bar{M}_n$
11b	4 000	<1.10
4b	110 000	<1.06
50124	233 000	<1.06
3b	390 000	<1.10
14b	2 000 000	<1.30

Table II

2% 4000 Molecular Weight Polystyrene in CCl_4

	time scale	
	$\Delta - 1/3\delta$ = 4.33 ms	$\Delta - 1/3\delta$ = 39.3 ms
D, m² s⁻¹	1.40 (3) × 10⁻¹⁰	1.50 (5) × 10⁻¹⁰

2% 390 000 Molecular Weight Polystyrene in CCl_4

	time scale	
	$\Delta - 1/3\delta$ = 8.67 ms	$\Delta - 1/3\delta$ = 38.0 ms
D, m² s⁻¹	4.9 (3) × 10⁻¹²	4.4 (2) × 10⁻¹²

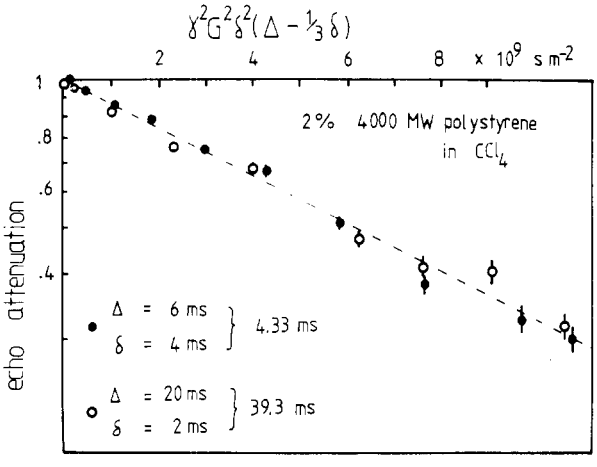

Figure 1. Echo attenuation plot for a 2% solution of 4000 molecular weight polystyrene in CCl_4 at 25.0 °C for experimental observation times ($\Delta - 1/3\delta$) of 4.33 and 39.3 ms. The attenuation is plotted on a logarithmic scale and the data obey the Stejskal–Tanner relationship for a unique diffusion coefficient (Table II).

ation under the influence of a pulsed magnetic field gradient. Simple diffusion was therefore indicated and the diffusion coefficients thus obtained were independent of the experimental time scale used. In the present work we have extended our investigation to 4000, 233 000, 390 000, and 2 000 000 molecular weight polystyrenes in CCl_4. While the 4000, 233 000, and 390 000 molecular weight polystyrenes exhibit the same simple diffusive behavior as found for 110 000 molecular weight polystyrene, the behavior of the 2 000 000 molecular weight solution is dramatically different. For the purpose of the NMR experiment, the polymers of 390 000 molecular weight and lower may be considered short since their Flory radii are insufficient to give a gel renewal time greater than or equal to the NMR observation period ($\Delta - 1/3\delta$).

Using eq 3, we find that for a 2% solution of 390 000 molecular weight polystyrene in CCl_4, $T_r \simeq 0.7$ ms, with very much smaller values for the lower molecular weights. Because this gel lifetime is much too short for cooperative effects to be observed, the simple macroscopic self-diffusion description of eq 1 prevails.

Figure 1 shows the spin echo attenuation plots for 2% solutions of 4000 molecular weight polystyrene in CCl_4 at observation times of 4.33 and 39.3 ms, while Figure 2 shows a similar pair of experiments for a 2% 390 000 molecular

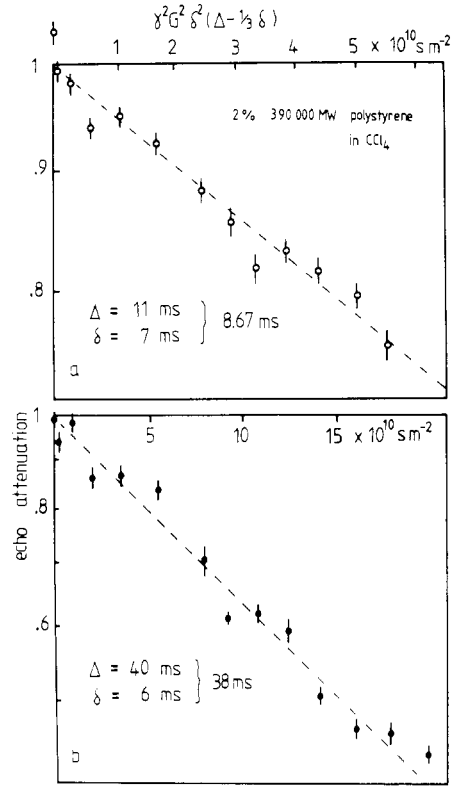

Figure 2. Echo attenuation plots for a 2% solution of 390 000 molecular weight polystyrene in CCl_4 for experimental observation times of (a) 8.67 and (b) 38.0 ms. The diffusion coefficients obtained agree within experimental error.

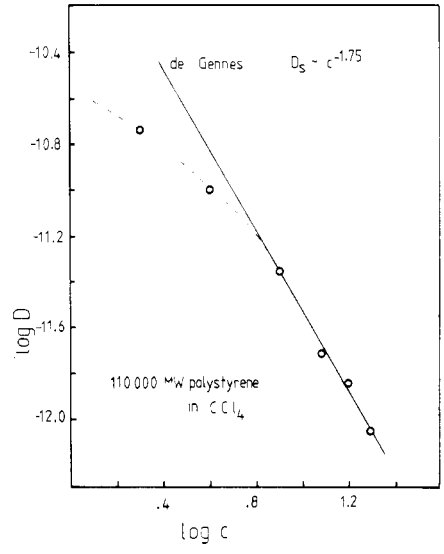

Figure 3. Scaling of diffusion coefficient with concentration. log D has been plotted vs. log c for solutions of 110 000 molecular weight polystyrene in CCl_4 at 25.0 °C. In each case the echo attenuation data obeyed the Stejskal–Tanner relationship[2] and yielded a unique diffusion coefficient. The solid line represents the scaling law of de Gennes for macroscopic self-diffusion over a time long compared with the gel renewal time, T_r. Gellike behavior is observed for $c/c^* > 5$.

weight solution. The data can be adequately described by single-exponential functions and the diffusion coefficients obtained are time independent, as is evident in Table II. Similar behavior is found for 110 000 molecular weight polystyrene.

In order to test de Gennes' macroscopic self-diffusion scaling law (eq 2), we have plotted the concentration-dependent diffusion coefficients for 110 000 molecular weight

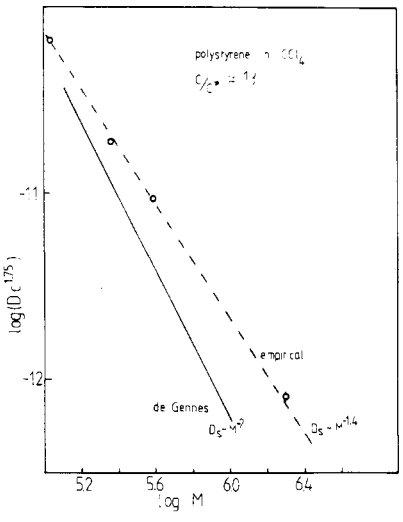

Figure 4. Scaling of diffusion coefficient with molecular weight at approximately constant polymer overlap achieved by setting $c/c^* \simeq 13$. Concentration effects have been normalized by plotting log $Dc^{1.75}$ vs. log M. The de Gennes scaling index is −2 whereas the empirical value here is −1.4. Note that the 2 000 000 molecular weight data point is from the long time scale experiment of Table III.

Table III

concn, % (2 000 000 MW)	$\Delta - {}^1/_3\delta$ = 16.0 ms D_{fast}	D_{slow}[a]	$\Delta - {}^1/_3\delta$ = 69.3 ms
2	6.3 (4)	0.24 (7)	0.65 (7)
4	13 (1)	0.19 (4)	0.30 (2)
8	19 (2)	0.15 (3)	0.23 (2)

[a] The slow components are multiexponential and the values of D_{slow} quoted here are averages obtained from the data of Figures 5a, 6a, and 7a for large values of $\gamma^2G^2\delta^2(\Delta - {}^1/_3\delta)$. Values of D are quoted in units of 10^{-12} m^2 s^{-1}.

from 2 to 19% on a log–log scale (Figure 3). It is apparent that they are consistent with a simple power law except for the low-concentration region, where the solution probably no longer constitutes a gel. The scaling index is clearly very close to the predicted value of 1.75 for $c/c^* > 5$. The order of magnitude of the diffusion coefficients for the concentrated 110 000 molecular weight solutions agrees well with the theoretical values obtained with eq 1.

The de Gennes scaling law for self-diffusion also predicts that the self-diffusion coefficient should scale as N^{-2}, i.e., to the inverse square of the polymer molecular weight, M. However, this aspect of the scaling law should be approached with some caution, for care must be taken to ensure that all the solutions are sufficiently concentrated to be in the gel state. We prepared solutions of the 110 000, 233 000, 390 000, and 2 000 000 molecular weight polystyrene fractions such that c/c^* was approximately 13 in each case. We then plotted log $(Dc^{1.75})$ against log M. The de Gennes theoretical value for the slope is 2. Figure 4 indicates that our experimental value is 1.4.

"Long-Chain" Polystyrenes. The highest molecular weight polystyrene used in this work exhibited a quite different diffusion behavior in the PFG NMR experiment. Figures 5a, 6a, and 7a show the spin echo attenuation obtained for an experimental observation time of 16.0 ms with 2, 4, and 8% 2 000 000 molecular weight polystyrene in CCl_4. Each can be represented to a first approximation by a two-exponential fit with fast and slow diffusion coefficients as given in Table III. At much longer observation times these rapid components are not present

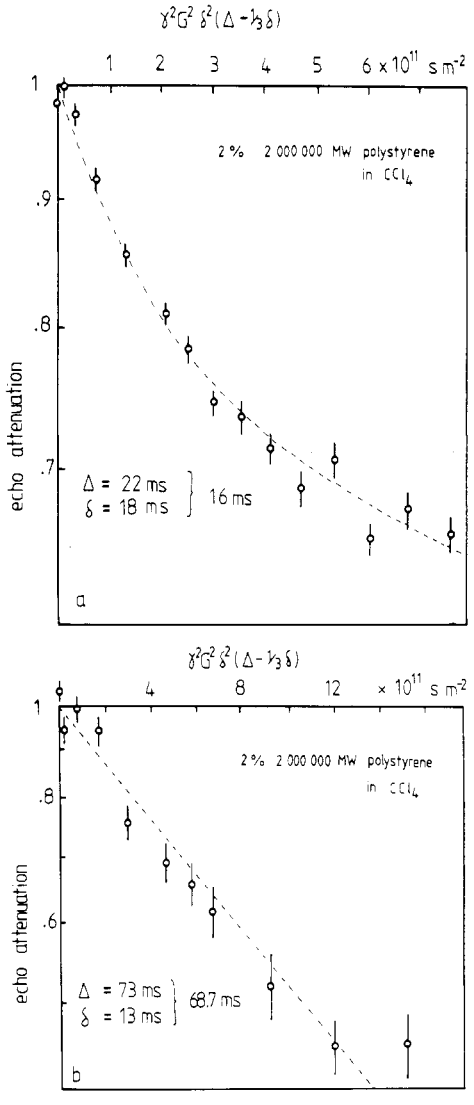

Figure 5. Echo attenuation plots for a 2% solution of 2 000 000 molecular weight polystyrene in CCl_4 for experimental observation times of (a) 16.0 and (b) 68.7 ms. The effect of an experimental observation time less than the gel renewal time can be seen in a. The dashed line is a two-exponential fit and the two resulting diffusion coefficients are given in Table III, where at least two diffusion processes are observed. We identify the fast component as D_c, the cooperative diffusion coefficient. In b, with a longer experimental time, a unique diffusion rate is found. This yields the macroscopic self-diffusion coefficient used for the 2 000 000 molecular weight point in Figure 4.

and the attenuations tend to display single-exponential behavior. Figures 5b, 6b, and 7b show the results obtained with $(\Delta - {}^1/_3\delta)$ = 68.7 ms and the corresponding diffusion coefficients are again given in Table III. In order to check that our results were not due to sample irregularities, we repeated each of the experiments at a later date with fresh samples prepared with more vigorous mixing. The results were identical for all experiments, as is evident, for example, in Figure 6a for the 4% sample. Besides, uniform mixing was not a problem in the 110 000 molecular weight experiments, where single-exponential behavior was observed over a wide concentration range, including solutions no less viscous than those used in the 2 000 000 molecular weight work.

We believe that our results constitute a manifest display of the cooperative gel displacements suggested by de Gennes. The gel renewal time for 2 000 000 molecular weight polystyrene is sufficiently long that the PFG NMR experiment has been given access to the $t \lesssim T_r$ regime.

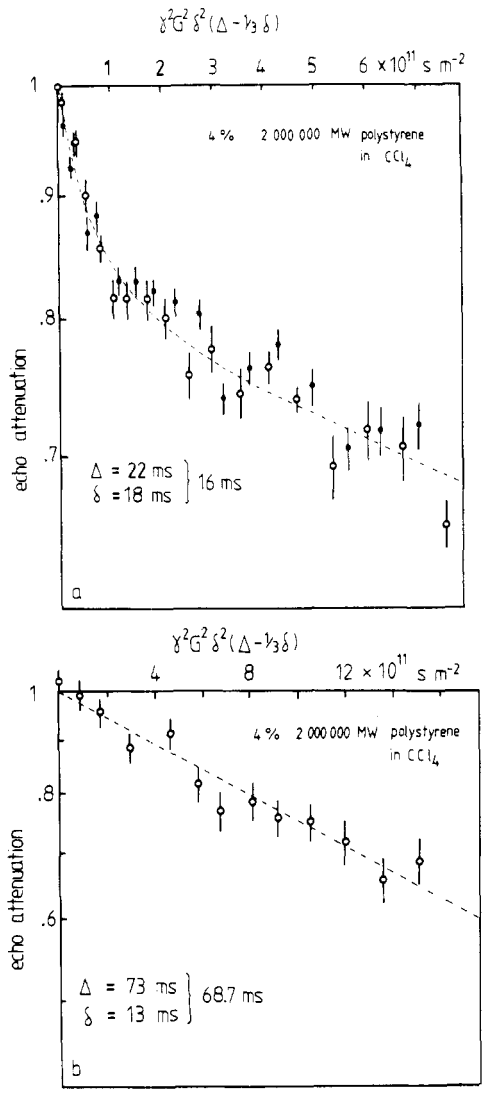

Figure 6. As for Figure 5 but for a 4% solution. Figure 5a shows data for two independently prepared 4% samples of 2 000 000 molecular weight polystyrene in CCl_4. Similar agreement is found for independent experiments performed on the 2 and 8% systems.

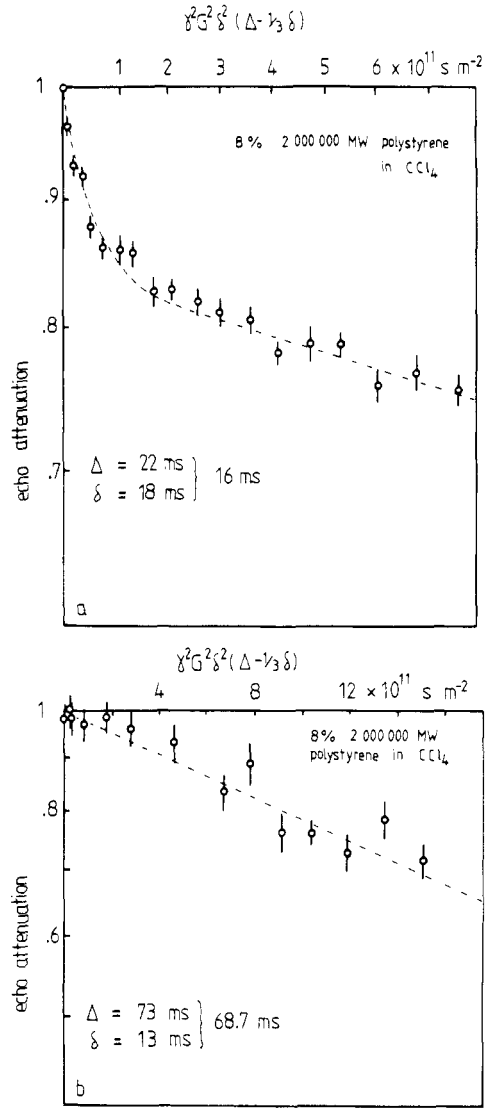

Figure 7. As for Figure 5 but for an 8% solution of 2 000 000 molecular weight polystyrene in CCl_4.

Equation 3 gives $T_r \simeq 100$ ms for 2% 2 000 000 molecular weight polystyrene in CCl_4, using 800 Å[14] for the Flory radius. We assign the rapid component apparent in the 16-ms experiments to the molecular segments undergoing cooperative displacements. It is shown in the next section that this fast component corresponds to long-wavelength disturbances, while the slow term is caused by short-range fluctuations.

As collaborative evidence for this interpretation of the short time scale results we offer the following observations. First, there is the change in the echo attenuation behavior as the experimental time scale is increased to the order of the predicted gel renewal time. In this regime simple macroscopic diffusion is observed, as evidenced by the slow single-exponential behavior which scales inversely with concentration, albeit more slowly than the full de Gennes rate of 1.75.

Second, in the short-time experiment, we observe a clearly defined fast-diffusion process, where the order of magnitude of this component agrees well with that predicted. For example, the 8% solution of Figure 6a shows an extremely rapid fast component whose associated diffusion coefficient is of order 10^{-11} m^2 s^{-1}, in agreement with that given by eq 6. In the next section we demonstrate that the fast-component slope yields the cooperative diffusion coefficient, D_c, in accordance with eq 11.

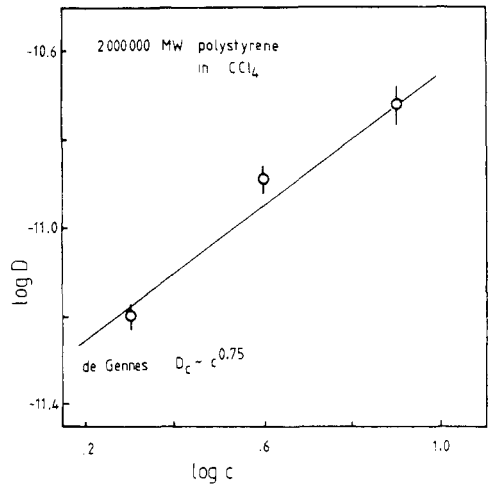

Figure 8. Scaling with concentration of the fast-diffusion term evident in Figures 5a, 6a, and 7a. The data are consistent with the de Gennes scaling law for cooperative diffusion.

Third, we have the evidence of the fast-diffusion rate scaling with concentration. Figure 8 shows log D vs. log c in comparison with a straight line of slope 0.75. The agreement is good and provides the most convincing

demonstration that what we are seeing are the wavelike disturbances predicted by de Gennes.

For a more detailed interpretation of the attenuations evident in the short time scale experiments one must understand how the nuclear spin displacements under cooperative gel disturbances will influence the spin echo in the pulsed field gradient experiment.

IV. Detection of Cooperative Diffusion Using Pulsed Field Gradient NMR

While there exists a simple relationship between the cooperative diffusion coefficient of de Gennes and the correlation time in quasi-elastic light scattering, the influence of cooperative effects on the echo attenuation in the pulsed field gradient experiment is not immediately obvious. de Gennes has shown[5] that for a longitudinal gel fluctuation of wave vector $\mathbf{k}$, the elastic restoring force per unit volume is given by

$$\mathbf{F}_{el} = -Ek^2\mathbf{r} \tag{12}$$

where E is the gel bulk modulus. In the de Gennes picture the disturbances are heavily damped by the friction force $-\Phi\dot{\mathbf{r}}$ so that under conditions of equilibrium one may write

$$\dot{\mathbf{r}} = -D_c k^2\mathbf{r} \tag{13}$$

where

$$D_c = E/\Phi \tag{14}$$

Thermal energy is responsible for the production of the gel disturbances which relax according to eq 13. This thermal agitation of the gel segments may be treated as a diffusion process in its own right. We assign this gel diffusion a coefficient D_g. This process should not be confused with the individual chain reptation.

Stejskal[2] has considered the case of a particle undergoing diffusion in a harmonic well under friction damping, and we follow his argument here for the case of the gel disturbances of wave vector $\mathbf{k}$. We will consider the behavior of one segment of the gel structure.

Suppose that a segment of gel has an initial displacement $\mathbf{r}_0$ and a displacement $\mathbf{r}$ at a later time t. The probability distribution $P(\mathbf{r}_0|\mathbf{r}, t)$ will satisfy a continuity equation[15] of the form

$$\begin{aligned}\partial P/\partial t &= -\nabla(\dot{\mathbf{r}}P) + D_g\nabla^2 P \\ &= D_c k^2\nabla(\mathbf{r}P) + D_g\nabla^2 P\end{aligned} \tag{15}$$

The solution to eq 15 has the form

$$P(\mathbf{r}_0|\mathbf{r}, t) = [2\pi D_g(1 - e^{-2D_c k^2 t})/D_c k^2]^{-3/2} \times \exp[-D_c k^2(\mathbf{r} - \mathbf{r}_0 e^{-D_c k^2 t})^2/2D_g(1 - e^{-2D_c k^2 t})]$$

and

$$P(r_0) = \lim_{t\to\infty} P(0|\mathbf{r}_0, t) = (2\pi D_g/D_c k^2)^{3/2} \exp(-D_c k^2 r_0^2/2D_g) \tag{16}$$

The echo attenuation for each gel segment in the pulsed gradient experiment is thus

$$A(G)/A(0) = \exp[-\gamma^2\delta^2 G^2 D_g(1 - e^{-D_c k^2\Delta})/D_c k^2] \tag{17}$$

For the sample as a whole the signal will be a superposition of echoes with attenuations depending on the wave vector of the local disturbance. Thus we may identify two regimes. For nuclei residing in gel segments undergoing long-wavelength disturbances, $k \ll (1/D_c\Delta)^{1/2}$, the echo attenuation is given by

$$A(G)/A(0) = \exp(-\gamma^2\delta^2 G^2 D_g\Delta) \tag{18}$$

In this case the result is independent of the magnitude of the wave vector and yields a unique diffusion coefficient D_g. (To a first approximation we may replace Δ with $(\Delta - {}^1/_3\delta)$ for the case of finite-width gradient pulses and eq 11 may be used to obtain D_g from the echo attenuation.)

For segments undergoing short-wavelength disturbances, $k \gg (1/D_c\Delta)^{1/2}$, we have

$$A(G)/A(0) = \exp[-\gamma^2\delta^2 G^2(D_g/D_c k^2\Delta)\Delta] \tag{19}$$

and for this case a variety of slower exponentials are observed with effective diffusion coefficients $D_g/D_c k^2\Delta$. Thus only the fast component in the overall sample echo decay is well defined and the relative amplitude of this component indicates the proportion of disturbances with a wave vector sufficiently small that $D_c k^2\Delta \ll 1$. One would therefore expect this amplitude to decrease with increasing Δ.

In our experiments on 2 000 000 molecular weight polystyrene in CCl_4 on a time scale less than the gel renewal time we observe clearly indentifiable fast components. In the light of the present analysis it is difficult to attach significance to the apparent slope of the slower component. Indeed it is clear that a unique "slow" slope is unlikely. We have shown that the fast component, described as D_g in the above analysis, scales empirically as if it were the de Gennes cooperative diffusion coefficient D_c. The identity of D_g and D_c can be demonstrated.

According to eq 16, the equilibrium gel segment displacement $(\Delta - {}^1/_3\delta)$ positions are described by a Gaussian distribution with a mean-square displacement

$$\langle r_0^2\rangle = D_g/D_c k^2 \tag{20}$$

Since the average elastic energy is half the thermal energy per statistical element, we may write the average elastic energy per unit volume as

$$\tfrac{1}{2}Ek^2\langle r_0^2\rangle = \tfrac{1}{2}k_B T/\xi^3 \tag{21}$$

where each segment of length ξ between entanglement points is treated as a statistical element. Equations 20 and 21 then give

$$D_g = k_B T/\Phi\xi^3 \tag{22}$$

which is exactly the cooperative diffusion coefficient, D_c, defined by de Gennes.[5]

For the 4% 2 000 000 molecular weight polystyrene experiment with $(\Delta - {}^1/_3\delta) = 16$ ms we might interpret the result as follows. Since $D_c \sim 1 \times 10^{-11}$ m^2 s^{-1} and the fast component is approximately 15% of the total signal, the same proportion of nuclei experience gel disturbances with wave vectors such that $D_c k^2\Delta \ll 1$. In other words, 15% of the macromolecules experience disturbances with wavelengths in excess of 2 μm.

V. Viscosity Measurements

To test the dependence of viscosity on concentration at fixed molecular weight (eq 7), we have measured the viscosity of 110 000 molecular weight random-coil polystyrene in carbon tetrachloride over a series of concentrations between 2 and 30%. In each case we extrapolated viscosities to zero shear rate. The results are presented in Figure 9 as a graph of log η against log c. The de Gennes scaling law is also shown on the same figure. It is clear that as the concentration increases, the experimental results more closely approach the theoretical slope. However, an interesting feature of these results is that the de Gennes scaling law is only approached at concentrations in excess of 20%, corresponding to $c/c^* \gtrsim 14$. In order to test the dependence of η upon M, we have measured the solution viscosities of other polystyrene fractions (233 000, 390 000, and 2 000 000 molecular weight). In each case the solution

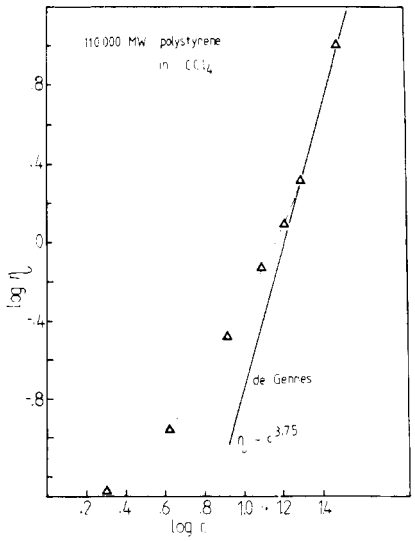

Figure 9. Scaling of viscosity with concentration for 110 000 molecular weight polystyrene in CCl_4 at 25.0 °C. The diagram is analogous to Figure 3 and shows agreement with the de Gennes scaling law for $c/c^* > 14$.

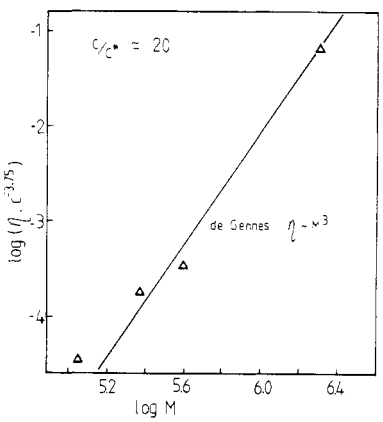

Figure 10. Scaling of viscosity with molecular weight at approximately constant polymer overlap achieved by setting $c/c^* \simeq 20$. Concentration effects have been normalized by plotting log $\eta c^{3.75}$ vs. log M. The 2 000 000 molecular weight data point is unreliable, as is evident in Figure 11. The remaining data points suggest a scaling index of approximately 2 compared with the de Gennes index of 3.

concentration was chosen such that c/c^* was approximately 20, so that we might expect the solutions to be sufficiently gellike for the viscosity–concentration scaling law to apply. Our results are presented in Figure 10 as a graph of log $(\eta c^{-3.75})$ vs. log M. The data do not obey a simple scaling law, although the de Gennes scaling rate of M^3 broadly characterizes their average rate of change. In fact the 2 000 000 molecular weight viscosity is unreliable and, on omitting this data point, we find that η scales approximately as M^2, in contrast with the predicted index of 3. For practical reasons we could not repeat these measurements for larger c/c^* values but the scaling behavior found with a lower value $c/c^* \simeq 13$ was essentially identical with that found for $c/c^* \simeq 20$.

As with the NMR experiments, the viscosity measurements on 2 000 000 molecular weight polystyrene solutions showed a distinctive characteristic which we believe reflects the comparative magnitude of the experimental time scale and the gel renewal time. It is apparent in Figure 11 that the 390 000 and lower polystyrene molecular weight solutions behave as Newtonian fluids with viscosities independent of shear rate. In contrast, the 2 000 000 molecular weight solution viscosity is rapidly changing in the region

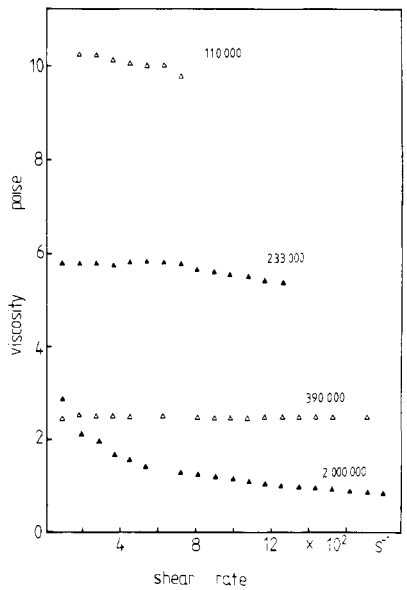

Figure 11. Viscosity vs. shear rate for the various molecular weight polystyrene solutions used in the data for Figure 10 ($c/c^* \simeq 20$). The 2 000 000 molecular weight solution is non-Newtonian and shows the effect of shear rates comparable with or greater than the gel renewal rate, $1/T_r$. Evaporation effects have limited the number of viscosity measurements obtainable for the highly concentrated 110 000 molecular weight solution.

of the lowest shear rate used, approximately 80 s^{-1}. It is noteworthy that this is the order of the gel renewal frequency, $1/T_r$, for this system. In the lower molecular weight solutions the gel renewal frequency is significantly higher than the shear rate throughout the experimental range.

VI. Conclusions

The pulsed field gradient NMR measurements on "short-chain" polystyrenes clearly verify one of the de Gennes self-diffusion scaling laws for macroscopic diffusion on a time scale long compared with T_r. We find that for c/c^* greater than about 5 the self-diffusion coefficients scale with concentration in the predicted manner. However, our results do not validate the de Gennes scaling law relating the macroscopic self-diffusion coefficient and molecular weight. Indeed our results indicate that D_s scales as $M^{1.4}$ rather than M^2.

The PFG NMR measurements on long-chain polystyrenes have detected the cooperative wavelike displacements predicted by de Gennes and the cooperative diffusion coefficients obtained very closely follow his $c^{0.75}$ scaling law. The magnitude of the experimental time scale dividing the region of macroscopic and cooperative diffusion observations agrees well with that predicted by de Gennes.

In testing de Gennes' viscosity scaling laws, we find that for c/c^* greater than 14, η scales with concentration in the predicted manner. It is an interesting feature of these results that to observe gellike viscosity behavior the polymer concentrations must be 3 times larger than those necessary for the observation of gellike diffusive behavior. It is possible that the rotating-plate method of viscosity measurement introduces an additional perturbing gel relaxation mechanism.

In both the diffusion and viscosity measurements reported here it is the dependence on polymer molecular weight which conflicts with the de Gennes theory. In the diffusion experiments and, by interpretation, in the viscosity experiments, we find a scaling index approximately $^2/_3$ that predicted.

The importance of clearly defining the experimental time scale has been demonstrated. By working with large molecular weight polystyrene, we have been given access to regimes both short and long compared with the gel renewal time. The analysis presented here shows that the spin echo attenuation in the short time scale experiment can yield not only the cooperative diffusion coefficient of the gel but also the distribution of wavelengths present in these cooperative gel disturbances. Pulsed field gradient NMR thus offers an experimental probe not envisaged in previous theoretical studies.

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Cationic Copolymers of Isobutylene. 2. Nuclear Magnetic Resonance Investigation of the Structure of Isobutylene–Isoprene Copolymers

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ABSTRACT: The structure of isobutylene (I_B)–isoprene (I_P) copolymers, obtained in a homogeneous medium with a cationic catalyst, has been investigated by ^1H and ^{13}C NMR spectroscopy. The spectra of these copolymers and their hydrogenated derivatives were interpreted. From the assignments made, which allow the calculation of monomer triad, tetrad, and pentad fractions, the I_B–I_P copolymer was found to have an almost completely head-to-tail structure. The incorporation of the monomers arises by 1,2 addition of I_B and trans-1,4 addition of I_P to the growing carbenium ion.

We have previously undertaken the study[1a] of isobutylene–butadiene copolymers by means of ^1H and ^{13}C NMR spectroscopy since little detailed information was available on their copolymerization mechanism and copolymer structure. The calculation of the triad fractions of the original and hydrogenated copolymers revealed that both *trans*-1,4- and -1,2-butadiene units are present and that they have an essentially block distribution. These conclusions are clear evidence of the complicated structure of isobutylene–butadiene copolymers which cannot be described by the two-component copolymerization equation, even in a revised form.[2]

In order to investigate the crucial role of the diene in the cationic copolymerization of isobutylene, we have extended our investigations to isobutylene (I_B)–isoprene (I_P) copolymers. Because of the great and long-standing industrial significance of these elastomers,[3] several papers have been published on their structural characterization by both chemical and physicochemical methods,[4-7] in particular ^1H NMR spectroscopy. ^{13}C NMR spectroscopy provides substantial information on the distribution of the monomers and on the nature of their linkages which is not available from ^1H NMR. This paper describes mainly the interpretation of the ^{13}C NMR spectra of the I_B–I_P copolymers and their hydrogenated derivatives. The quantitative aspects and the correlation of the structural features with the mechanism of the cationic copolymerization of I_B and I_P will be the subject of a subsequent paper.[8]

Experimental Section

Materials. Both isobutylene and isoprene were commercial pure-grade products and were treated before use as reported previously.[9] Solvents (*n*-pentane and CH_2Cl_2) and catalyst ($C_2H_5AlCl_2$) were purified and used as reported elsewhere.[9]

Procedure. Catalyst, monomer, and solvent handling was performed under a dry N_2 atmosphere. The copolymerization equipment and procedure were essentially the same as described previously.[9] In practice, I_B and I_P were added to a mixture of *n*-pentane and CH_2Cl_2 (1:1 by volume) in varying mole ratios, depending on the desired content of the diene in the copolymers. Their total concentration was kept constant at 3.3 mol/L. $EtAlCl_2$ (0.005–0.020 mol/L) was added to the polymerization system, maintained at −70 °C, and the reaction was allowed to continue for 15 min. The copolymers formed under these conditions were completely soluble and the resulting reaction mixture was homogeneous. The monomer conversion was controlled by using an appropriate concentration of catalyst. The conditions adopted for preparing a typical sample and the main characteristics of the copolymer obtained were as follows: $[I_B]/[I_P] = 1.20$, $[I_P] = 1.5$ mol/L, $[EtAlCl_2] = 0.015$ mol/L, yield = 42%; I_P content of the copolymer = 35 mol %; $[\eta] = 0.36$ dL/g (in cyclohexane at 30 °C). The copolymer was hydrogenated in cyclohexane at 180 °C, in the presence of Pd on charcoal, as described previously.[1a]

Analyses. ^1H NMR spectra were obtained in the CW mode at 100 MHz, using a Varian XL-100 spectrometer and $CDCl_3$ solutions at 25 °C. ^{13}C NMR spectra were recorded at 25.14 MHz at 25 °C on a Varian XL-100 NMR spectrometer equipped with

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