Carbon-13 Nuclear Magnetic Resonance Analysis of the Configuration of Stereoregular Poly(*tert*-butyl crotonate)

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ABSTRACT: The configuration of poly(*tert*-butyl crotonate) is analyzed by ^{13}C NMR spectroscopy on the basis of a propagation mechanism of a reversible double-Markovian process. A clear difference is observed between the configurations of the insoluble sample polymerized with phenylmagnesium bromide and of the soluble polymer obtained with an anionic initiator. From the analysis of the spectra for carbonyl, *tert*-butoxy, and β-methyl carbons, it is concluded that the soluble sample is a random mixture of six pentads, i.e., it is a kind of atactic polymer, whereas the insoluble sample consists of three kinds of stereospecific pentads.

Two kinds of poly(*tert*-butyl crotonate) (PTBC) having entirely different physical properties can be obtained by different polymerization techniques. One was obtained by Natta et al.[1] with a Grignard reagent, which usually causes a stereospecific polymerization. The sample is completely insoluble in any solvent once it is precipitated. The other kind of PTBC can be obtained with an anionic initiator.[2] The sample is soluble in most common solvents and has some interesting features in its physical properties. The sample has a semiflexible backbone due to the steric hindrance between β-methyl and *tert*-butyl carboxylate groups and also sharp molecular weight distributions if proper polymerization conditions are employed.

PTBC can have various configurations with respect to both β-methyl and *tert*-butyl carboxylate groups. It is reasonable, therefore, to predict that two kinds of samples may have different configurations. The purpose of this paper is to analyze the configuration of PTBC by ^{13}C NMR spectroscopy. One of the general methods for assigning observed NMR signals is by comparing the signals from samples with various tacticities. Because the tacticity of PTBC cannot be widely changed, however, the assignment of NMR peaks in PTBC is carried out on the basis of configurational statistics.[3]

Experimental Section

Materials. Four samples of PTBC (samples I-A through I-D) were obtained by polymerizing *trans-tert*-butyl crotonate with (2-methylbutyl)lithium in THF at −78 °C.[2] Their number-average molecular weights, determined by a vapor pressure osmometer (Hitachi Perkin-Elmer Model 115) or a high-speed membrane osmometer (Hewlett-Packard Type 502), were 3.2×10^3 (I-A), 1.58×10^4 (I-B), 1.64×10^4 (I-C), and 2.52×10^4 (I-D). Sample II was obtained by polymerizing the monomer with a Grignard reagent (phenylmagnesium bromide) in toluene-d_8 at room temperature.[4] Since sample II is insoluble in any solvent after precipitation, the polymerization was carried out in toluene-d_8 and concentrated to a suitable concentration (ca. 10 w/v %) in vacuo for NMR measurements. During this concentration procedure, a gellike polymer was formed. A part of the gellike polymer was removed when the resultant concentrated solution was injected into an NMR sample tube. However, the solution still contained a considerable amount of gellike polymer. It is unlikely that the gellike part removed has a microstructure different from the remaining part. The molecular weight of sample II could not be determined.

NMR Measurements. High-resolution nuclear magnetic resonance spectra of the polymers in a 10 w/v % solution in toluene-d_8 or chloroform-*d* were obtained with a Varian XL-100 spectrometer operated at 25.2 MHz and a Varian FT-80A spectrometer operated at 20.0 MHz. All spectra were obtained from the accumulated free induction decays (the number of iterated scannings was from 5000 to 10 000) by a Fourier transform and all possible C–H couplings were removed by noise decoupling. Since the signal-to-noise ratio was not significantly improved by raising the temperature, as shown in Figure 1, all experiments were carried out at room temperature.

Results and Discussion

Figure 2 shows the ^{13}C NMR spectrum of sample I-B in toluene-d_8 as an example. The rather poor resolution of this spectrum is a general feature of this polymer and may be due to the fairly stiff backbone of PTBC. The multiplets centered at ca. 12.0, 28.5, 32.3, 51.8, 80.7, and 172.5 ppm from the tetramethylsilane resonance as an internal reference are assigned to β-methyl, *tert*-butyl methyl, β-methine, α-methine, *tert*-butoxy, and carbonyl carbons, respectively. Two groups of multiplets and one peak centered at ca. 20, 129, and 137 ppm are assigned to carbons of toluene-d_8 used as solvent (the latter two signals are not shown in Figure 2). Owing to negligible couplings between adjacent carbons and the absence of all possible C–H couplings, it is clear that the multiplet splitting of the signal assigned to each carbon in the polymer chain reflects the existence of a variety of configurations in sample I-B. Similar splittings are observed in the spectra of the other samples, I-A, I-C, I-D, and II. The spectra of samples I-C and I-D are close to those of sample I-B.

In the spectra of all five samples, resolution of the signals of the α- and β-methine carbons is generally poor compared with the other carbon signals, and the multiplet peaks of the *tert*-butyl methyl carbons appear as signals with very high intensities and very small relative chemical shifts. These three signals, therefore, are excluded from the present analysis. The expanded ^{13}C NMR spectra of the β-methyl, *tert*-butoxy, and carbonyl carbons of the three samples I-A, I-B, and II are shown in Figures 3–5. All spectra were taken in toluene-d_8 solution.

Before carrying out the analysis, it seems necessary to define the terms used in this paper. The configurations of α,β-disubstituted polymers, i.e., the stereochemical structures with respect to two substituents bonded with α and β carbons, R_2 and R_1, respectively, are defined in the same manner as in the paper of Chûjô et al.[3] In the case of poly(*tert*-butyl crotonate), the β-methyl group and *tert*-butyl carboxylate group are indicated as R_1 and R_2, respectively. The small letters m and r denote the meso and racemic dyads of the $[R_2, R_1]$ type, respectively, while the capital letters M and R denote those of the $[R_1, R_2]$ type, respectively. With these definitions, the β-methyl-group triads are represented by mM, mR, and rR and those for *tert*-butyl carboxylate group by Mm, Mr, and Rr. Possible sequences in *n*-ads of higher orders are easily produced by connecting suitable units successively.

From Figures 3 and 4, it can safely be assumed that the multiplets of the β-methyl and *tert*-butoxy carbons of samples I-A and I-B appear as a doublet and a triplet, respectively, and, therefore, their splittings are due to triad stereochemical configurations. The relative sizes of the

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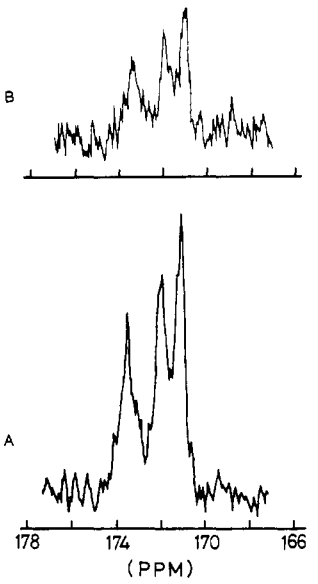


Figure 1. ^{13}C NMR spectra of the carbonyl carbons of sample I-B: (A) room temperature; (B) 70 °C. The spectra were obtained at 25.2 (A) and 20.0 MHz (B), using about 10 w/v % solutions in chloroform-*d*.

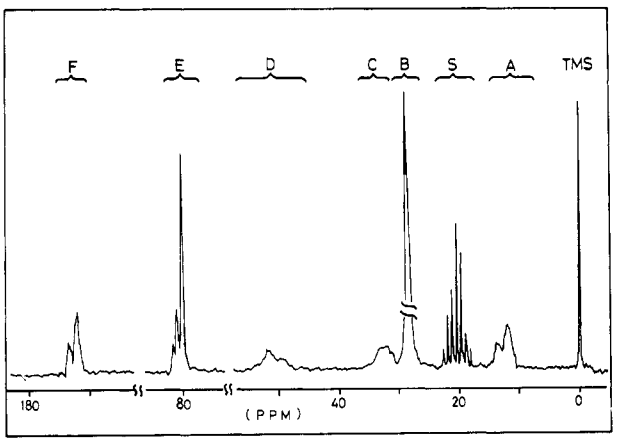


Figure 2. 25.2-MHz ^{13}C NMR spectrum of poly(*tert*-butyl crotonate) (sample I-B) obtained using about 10 w/v % solutions in toluene-d_8 at room temperature. Letters represent all carbons in this polymer and the solvent: A, CH_3 (β); B, CH_3 (in *tert*-butyl group); C, CH (β); D, CH (α); E, *tert*-butoxy carbon; F, C=O; S, solvent.

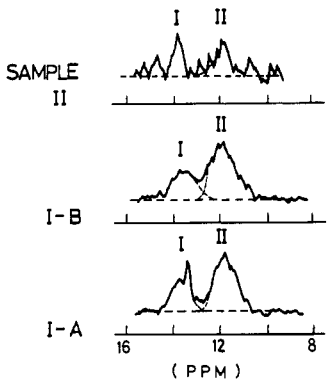


Figure 3. Expanded ^{13}C NMR spectra of the β-methyl carbons for three samples obtained under the same conditions as in Figure 2.

resonances for samples I-A through I-D, which were calculated through their area ratios, are given in Table I. The resonances are designated I, II, and III from downfield to upfield, respectively. It should be noted that in Figure 3

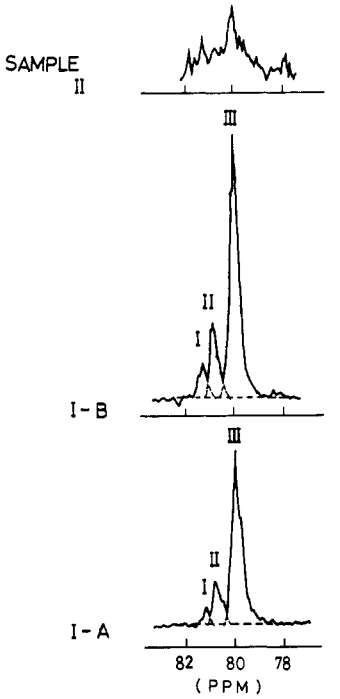


Figure 4. Expanded ^{13}C NMR spectra of the *tert*-butoxy carbons for three samples obtained under the same conditions as in Figure 2.

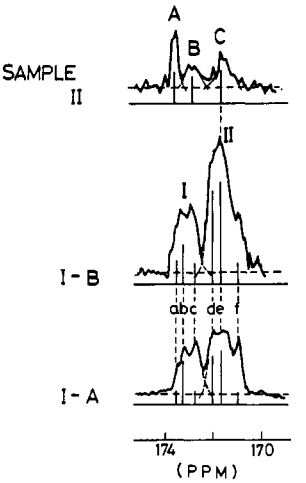


Figure 5. Expanded ^{13}C NMR spectra of the carbonyl carbons for three samples obtained under the same conditions as in Figure 2. Stick spectra were calculated by the procedure described in the text. Letters represent the eight types of pentads. a, (mRrM); b, (mRmR); c, (mMrM); d, (mMmR); e, (mMmM); f, (rMmR). A, (rRrR); B, (mMrR); C, (mMmM).

the spectrum of the β-methyl carbon from sample I-A has a distinct spike on the low-field resonance. Therefore, it can be predicted that resonance I of the β-methyl carbon spectrum is composed of any two of the three triad configurations, whereas resonance II is composed of the third.

In order to assign the multiplets of the β-methyl and *tert*-butoxy carbons of samples I by triad representations, we can use relationships 1 and 2 among the observable

$$2(\mathrm{Mm}) + (\mathrm{Mr}) = 2(\mathrm{mM}) + (\mathrm{rM}) \quad (1)$$

$$(\mathrm{Mm}) - (\mathrm{Rr}) = (\mathrm{mM}) - (\mathrm{rR}) \quad (2)$$

sequence frequencies, indicated in (1) and (2) by parentheses. Equations 1 and 2 are derived from the requirement of the continuity of the chain.[3] Six ways of assignment are possible for the three resonances I, II, and III of the *tert*-butoxy carbons and three ways for resonances I and II of the β-methyl carbons. In total, therefore,

Table I
Relative Abundances of Resonances of β-Methyl, *tert*-Butoxy, and Carbonyl Carbons for Samples I and Their Assignments by Triad Representation

carbon	peak	I-A	I-B	I-C	I-D	triad
β-methyl	I	0.34{0.11, 0.23}	0.34{0.02, 0.32}	0.30{0.10, 0.20}	0.30{0.00, 0.30}	(rR), (mR)
	II	0.66	0.66	0.70	0.70	(mM)
tert-butoxy	I	0.07	0.08	0.12	0.05	(Rr)
	II	0.31	0.20	0.16	0.20	(Mr)
	III	0.62	0.72	0.72	0.75	(Mm)
carbonyl	I	0.38	0.27	0.31	0.31	(Rr) + (Mr)
	II	0.62	0.73	0.69	0.69	(Mm)

Table II
Two Possible Assignments for the Resonances of the β-Methyl and the *tert*-Butoxy Carbons in Samples I-A and I-B

	β-methyl peaks		*tert*-butoxy peaks		
	I	II	I	II	III
	Assignment A				
assignment	(rR) + (mR)	(mM)	(Rr)	(Mr)	(Mm)
rel abund					
I-A	0.34	0.66	0.07	0.31	0.62
I-B	0.34	0.66	0.08	0.20	0.72
	Assignment B				
assignment	(mM) + (mR)	(rR)	(Mm)	(Mr)	(Rr)
rel abund					
I-A	0.34	0.66	0.07	0.31	0.62
I-B	0.34	0.66	0.08	0.20	0.72

there are 18 possible ways of assignment. Among these possiblities, two ways, as shown in Table II, can fulfill requirements 1 and 2. However, assignment A may be more likely than assignment B, since if the sample has a high content of both Rr and rR, it would not be soluble. The assignments thus determined are shown in Table I, where resonance I of the β-methyl carbons was divided into two portions, (rR) and (mR), by using relations 1 and 2.

Since the triad represenation of *tert*-butoxy and carbonyl carbons must be the same, we can divide the multiplet of the carbonyl carbons (Figure 5) into two resonances I and II by a boundary at 172.5 ppm and assign them as shown in Table I. In chloroform-*d* solution, moreover, the carbonyl spectrum of sample I-B has quite a different appearance from that observed in toluene-d_8, as shown in Figure 6. The resonances are labeled I, II, and III, as in Figure 6. By comparing their area ratios with the data for the carbonyl groups in Table I, resonance I is assigned to the sum of Rr and Mr, and the sum of resonances II and III to Mm.

In a similar way, the spectra of the β-methyl and carbonyl carbons for sample II can be analyzed, though that of the *tert*-butoxy carbon is too broad to be analyzed exactly. Only when the two resonances I and II in the β-methyl carbon spectrum (Figure 3) and the three resonances A, B, and C in the carbonyl carbon spectrum (Figure 5) are assigned as given in Table III can the above requirements (1) and (2) be satisfied. It appears that the proportion of (mR) in sample II is nearly zero.

The microstructure of the sample can be further studied by decomposing each resonance into pentad fine structure and by determining their relative abundances. The spectra of carbonyl carbons in Figures 5 and 6 appear to be useful for this purpose. However, since the resolution of the spectra and the variety in tacticity of samples available for analysis are limited, further analysis of the fine structure of the carbonyl carbon resonances can be carried out by consideration of the propagation statistics of this polymer. It is generally assumed[3] that the propagation mechanism of α,β-disubstituted olefins can be described

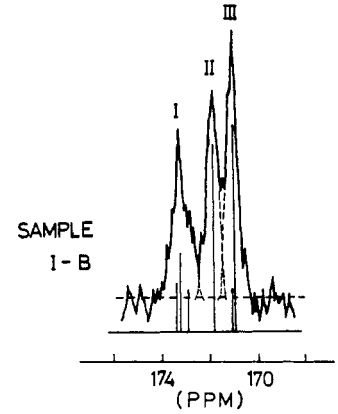


Figure 6. Expanded ^{13}C NMR spectrum of the carbonyl carbons of sample I-B obtained at 25.2 MHz using an approximate 10 w/v % solution in chloroform-*d* at room temperature. Stick spectrum was obtained by using the same relative intensities as in sample I-B of Figure 5.

Table III
Relative Abundances of Resonances of β-Methyl and Carbonyl Carbons in Sample II and Their Assignments by Triad Representation

carbon	peak	rel abund	triad
β-methyl	I	0.49{0.48, 0.01}	(rR), (mR)
	II	0.51	(mM)
carbonyl	A	0.34	(Rr)
	B	0.30	(Mr)
	C	0.36	(Mm)

and analyzed on the basis of a reversible stochastic process with simple-Markovian or double-Markovian statistics. The theoretical relative intensities of *n*-ads for this process have been calculated by Chûjô et al.[3]

Both statistics, simple Markovian and double Markovian, were applied to the analysis of the carbonyl carbon signal of sample I-B, in which (rR) is nearly zero. In either statistics, the resonances I and II in Figure 5 must be composed of three pentads mRrM, mRmR, and mMrM and mMmR, mMmM, and rMmR, respectively, if (rR) = 0. The resonances I and II + III in Figure 6 are also composed of the same pentads as the resonances I and II in Figure 5, respectively. If we take into account the fact that a small shoulder is observed on resonance III in Figure 6, moreover, it may be resonable to assume that the resonances II and III in Figure 6 are composed of one and two pentads, respectively. Even though we make use of the above facts, the correct manner of decomposing resonance II in Figure 5 and resonances II and III in Figure 6 into pentad components cannot absolutely be determined. There still remain four possible ways of decomposing resonance II of sample I-B (Figure 5) into its components. At least, however, it can be noted that the area ratio of resonance II to resonance III in Figure 6 can be explained only by double-Markovian statistics.

Table IV
Values of Conditional Probabilities for Samples I-B and II

symbols for probability[a]	sample I-B	sample II
P_{MmM}	0.68	1.00
P_{MmR}	0.32	0.00
P_{MrM}	1.00	0.00
P_{MrR}	0.00	1.00
P_{RmM}	0.33	1.00
P_{RmR}	0.67	0.00
P_{RrM}	1.00	0.00
P_{RrR}	0.00	1.00
P_{mMm}	0.77	0.70
P_{mMr}	0.23	0.30
P_{mRm}	0.56	*b*
P_{mRr}	0.44	*b*
P_{rMm}	0.79	*b*
P_{rMr}	0.21	*b*
P_{rRm}	*b*	0.31
P_{rRr}	*b*	0.69

[a] The symbol P_{mMm}, for example, designates the probability of the sequence mMm. [b] Indefinite value.

If we take into account the negligible abundance of (mR) in sample II (Table III), it must be admitted that the microstructure of sample II may be analyzed on the basis of a specialized double-Markovian statistics, where (mR) is zero. In this case, there would appear only three kinds of pentads, mMmM, mMrR, and rRrR, in the spectrum of the carbonyl carbon. From this fact and the assignment of the carbonyl carbon by a triad represenation (Table III), the three resonances A, B, and C in the carbonyl carbon spectrum are assigned to rRrR, mMrR, and mMmM, respectively.

Taking into account the assignment for the carbonyl carbon spectrum of sample II, the three peaks d, e, and f in the carbonyl carbon spectrum of sample I-B (Figure 5) are assigned to the pentads mMmR, mMmM, and rMmR, respectively. Once the relative abundances of these three pentads are determined, conditional probabilities used in double-Markovian statistics can be calculated, except for some indeterminate ones, as shown in Table IV. By using these conditional probabilities, we can estimate the relative abundances of the other three pentads, mRrM, mRmR, and mMrM. By comparing the observed appearance of resonance I of the carbonyl carbons (Figure 5) with a theoretical spectrum composed of three pentads, mRrM, mRmR, and mMrM, of corresponding estimated relative intensities, the three peaks a, b, and c are assigned to mRrM, mRmR, and mMrM, respectively.

In Figure 5 the observed spectrum of the carbonyl carbons of sample I-B is compared with the corresponding theoretical stick spectrum. The agreement between them is satisfactory. This conclusion is also supported by the fact that the same assignment and the same relative intensity of each peak as in Figure 5 reproduces well the observed carbonyl carbon signals of sample I-B in chloroform-*d* solution (Figure 6), although the relative chemical shift of each peak is different from that in toluene-d_8 solution (Figure 5). In Figure 5 is also shown a stick spectrum of the carbonyl carbons for sample II, which was obtained from area ratios of the three resonances, A, B, and C.

Stereochemical structures and their relative abundances thus obtained for two samples, I-B and II, are shown in Table V. Table V reveals that sample I-B consists of random mixtures of six pentads. In the case of samples of I-A and I-C, each one of six types of triads has a finite relative abundance (Table I). In such a case, it is impossibly difficult to analyze the spectra because of too many adjustable parameters. However, these samples should consist of random mixtures of various pentads because they are soluble in ordinary organic solvents. In Figure 5 the observed spectrum of the carbonyl carbons in sample I-A is compared with a theoretical spectrum obtained under the assumption of (rR) = 0. The agreement appears to be reasonable.

Table V

A. Relative Abundances of Six Types of Pentads for Sample I-B

type of pentad	peak symbol	rel abund
(mRrM)	a	0.08
(mRmR)	b	0.03
(mMrM)	c	0.17
(mMmR)	d	0.31
(mMmM)	e	0.34
(rMmR)	f	0.07

B. Relative Abundances of Three Types of Pentads for Sample II

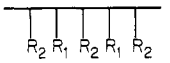
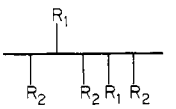
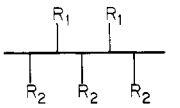
type of pentad	peak	rel abund	structure
(rRrR)	A	0.34	
(mMrR)	B	0.30	
(mMmM)	C	0.36	

Table V also reveals that sample II consists of three pentads, mMmM, rRrR, and mMrR. The presence of mMrR is clear from the appearance of the middle resonance (B) in Figure 5. That is, sample II is isotactic with respect to R_2 (*tert*-butyl carboxylate), in agreement with the conclusion obtained from the polymerization studies of vinyl monomers.[5]

The microstructure of poly(α,β-disubstituted monomer) is determined by the direction of the steric attack of the growing chain end on the plane of the monomer, having two faces conventionally designated as the D and L faces,[6] and the scheme of double-bond opening (cis (c) or trans (t)). Table IV shows that in the anionic polymerization of *trans-tert*-butyl crotonate with a Grignard reagent, the steric attack occurs from both faces (L and D) with equal probabilities since $P_{MmM} = P_{MrR}$, $P_{RmM} = P_{RrR}$, and $P_{mMm} + P_{rRm} = P_{mMr} + P_{rRr}$. Combining this fact with the fact that the polymer is isotactic with respect to the carboxylate group, one concludes that the monomer addition should occur as a D attack–cis opening (abbreviated as Dc) and an L attack–trans opening (Lt) with equal probabilities (or Lc and Dt, depending on the definition of direction). The relative abundances of pentads for sample II in Table V, moreover, shows that these two types of monomer addition, Dc and Lt, occur somewhat regularly. If they occurred randomly, the relative abundances of (rRrR), (mMrR), and (mMmM) would be 1:2:1. It cannot be determined in the present work whether three pentads exist intermolecularly or intramolecularly.

According to Yoshino et al.[7], when isopropyl acrylate-β-*d* is polymerized in toluene at −78 °C with phenylmagnesium bromide as initiator, the configuration of the polymer obtained is a mixture of mMmM and rRrR sequences but with no mMrR sequence.

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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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