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Concentrated Solutions of Partly Deuterated Triblock Polybutadiene. Segmental Analysis of NMR Properties

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ABSTRACT: The comparison of proton transverse relaxation properties observed on polybutadiene (PB, $M = 1.07 \times 10^5$ or 2.08×10^5) with those observed on a triblock copolymer with deuterated end blocks (PB−DHD, $M = 0.98 \times 10^5$), was used to investigate two different segmental behaviors detected along any protonated chain. All relaxation curves recorded from PB or PB−DHD as a function of temperature or polymer concentration c in deuterated cyclohexane were found to exhibit two components: a fast decay and a long tail clearly governed by two distinct partial motional averages of proton−proton couplings called Δ_I and Δ_{II}, respectively. Δ_I, independent of molecular weight, obeyed the empirical dependence on polymer concentration: $\Delta_1 = 1740c(1 - 0.29c)$ rad·s^{-1} while $\Delta_{II} \approx \Delta_I/4.5$ ($0.51 \le c \le 1.0$ w/w). On one hand, the nonlinear $1/c$ dependence of the effective segmental length represented by $1/\Delta_1$ could not be directly correlated to the c^{-1} dependence usually assigned to the mean segmental spacing between entanglements. On the other hand, the long tail amplitude A_{II} observed from PB obeyed the empirical equation $MA_{II} = [5886 + 8800(1/c - 1)]$ corresponding to a number of monomeric units involved in the definition of A_{II} equal to 109 in the pure polymer and independent of molecular weight; a long tail was still observed on pure PB−DHD although the total number of deuterated units (185) in end blocks was higher than 109: the product MA_{II} varied as $[2816 + 5456(1/c - 1)]$ and showed that deuterated end blocks eliminated the relaxation of only $62/c$ units per chain. The relaxation tail observed from fully protonated PB was assigned both to monomeric units attached to so-called end segments formed from $2 \times 27/c$ units and to neighboring units in dynamic interaction with end segments.

1. Introduction

The objective of this work is to quantitatively characterize the behavior of end segments of polybutadiene chains in the melt or in concentrated solutions; the study is based on the comparison of proton transverse relaxation properties observed on fully protonated chains (PB) with those observed on an isotopic triblock copolymer DHD where D is a deuterated block and H is protonated polybutadiene. It is now well established that proton transverse relaxation curves recorded from high molecular weight polymers in melts or in concentrated solutions exhibit two distinct components: a decay over about 5 ms and a long tail which may spread over 20 ms or more.[1−6] Considering calibrated poly(ethylene oxide) (PEO, $37 \times 10^3 < M < 4.5 \times 10^5$) or polybutadiene (PB, $48 \times 10^3 < M < 4.3 \times 10^5$) chains, it has been recently shown that the amplitude of the long tail varied as the inverse of chain molecular weight; this result indicated that the number of units per chain involved in the long tail was a constant for a given polymer. Furthermore, forming well shaped pseudo-solid spin-echoes, it has been also shown that both components were governed by partial motional averages of proton−proton couplings independent of molecular weight.[7−9] Consequently, the two components were represented by suitable functions which accounted both for relaxation curves and for well-defined pseudo-solid spin-echoes; in no case could the two components be described as simple exponential time functions.[7−10]

Observing simple Hahn or pseudo-solid spin-echoes and considering long chains, our purpose for this study was not to attempt to detect long range chain fluctuations usually observed from well-known specific NMR approaches;[3,11;12] here, attention was focused on the characterization of NMR properties of the long time component and more precisely on the mean size of so-called end submolecules. The analysis of transverse relaxation curves was based on NMR studies recently reported about PEO and PB;[8,9] we have shown that the contribution to the proton relaxation due to fast and nonisotropic motions of monomeric units can be distinguished from the contribution due to residual spin−spin interactions of protons attached to the polymer; this anlysis applies to the two components of the proton magnetization called $M_x^T(t)$ hereafter. Namely, if one linear chain is considered, the normalized relaxation function is expressed as

$$M_x^T(t) = (1 - A_{II})M_x^I(t)\Phi_R^I(t) + A_{II}M_x^{II}(t)\Phi_R^{II}(t) \quad (1)$$

until now, normalized $M_x^{II}(t)$ and $\Phi_R^{II}(t)$ relaxation functions have been supposed to be assigned only to protons attached to end segments of chains; in polybutadiene, the relative amplitude A_{II} represents about 60 monomeric units. Normalized $M_x^I(t)$ and $\Phi_R^I(t)$ functions have been assigned to protons attached to the remaining part of the chain. $\Phi_R^{II}(t)$ and $\Phi_R^I(t)$ relaxation functions are independent of chain length and have been supposed to reflect fast rotations of monomeric units forming either end segments or the remaining part of one chain, respectively. $M_x^I(t)$ and $M_x^{II}(t)$ contributions are mainly governed by residual dipole−dipole interactions of protons represented by two parameters called Δ_I and Δ_{II}, respectively. $M_x^{II}(t)$ is independent of molec-

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ular weight while the relative amplitude A_{II} of the long component was proportional to M^{-1}; $M_x^{I}(t)$ hardly depends on chain length. These two functions can be determined independently of $\Phi_R^{I}(t)$ and $\Phi_R^{II}(t)$, as reported elsewhere.[13]

According to the fluctuation–dissipation theorem, fluctuations observed from NMR in the absence of any stress are connected to the linear viscoelastic response of a polymer melt to external stress. The relaxation modulus $G(t)$ as well as the frequency responses, $G'(\omega)$ and $G''(\omega)$, measured from long linear chains exhibit two well-separated dispersions; at high frequencies (short times), the transition dispersion associated with segmental fluctuations is insensitive to chain length variations. Large scale rearrangements of chain conformations are associated with the terminal dispersion of the dynamics spectrum of one chain described according to the reptation model.[14,15] The two dispersions are separated by a rubberlike plateau response at intermediate times (or frequencies); the plateau called G_N^o and attributed to chain entanglement interactions may be considered as a break in dynamic fluctuations that occur along one chain.[16,17] By analogy with properties of cross-linked chains, the temporary plateau value is conveniently converted into a mean segmental molecular weight called M_e and defined as $\rho RT/G_N^o$ (ρ is the polymer density). The plateau behavior is supposed to start from the terminal relaxation time τ_1^R defined from the Rouse model applied to one segment formed from N_e units corresponding to M_e and such that $\tau_1^R = N_e^2 \lambda b \zeta_0 / 3\pi^2 kT$ (b is the mean bond length per monomeric unit, λ is the Khun step length and ζ_0 is the monomeric friction coefficient); roughly, at the short-time end of the plateau, the Rouse relaxation modulus obeys the following equation: $G_R(t = \tau_1^R) \approx G_N^o$. This time (or the corresponding frequency) is independent of molecular weight while the plateau width is an increasing function of M.[18]

Regarding the NMR approach, the existence of residual spin–spin interactions has been interpreted as the result of the partial averaging process induced by segmental motions associated with the transition dispersion; like the spin–lattice relaxation of nuclei attached to polymer chains and submitted to collective motions of a few monomeric units, residual interactions are independent of molecular weight, and their order of magnitude is 10^3 rad·s^{-1}. The observation of residual interactions of protons gives evidence for a break in dynamic fluctuations resulting in a partial average of spin–spin couplings; it is considered that during the time interval corresponding to the width of the rubberlike plateau, any chain can be pictured as an ensemble of segments called NMR submolecules and undergoing nonisotropic and stochastically independent fluctuations. The expression of the residual proton–proton interaction resulting from the motional averaging process induced within any Gaussian segment with temporarily fixed ends is proportional to the inverse of the number of units forming this segment: the corresponding mean segmental size is defined from about 10^2 skeletal bonds. Inner submolecules should be distinguished from end submolecules which have only one fixed end. For long chains, the reptation process does not contribute to the motional averaging of proton–proton interactions because its relaxation time is much longer than the NMR time scale determined from residual interactions and about equal to 1 ms; in other words, the rate of isotropic fluctuations of one chain considered as a whole is not high enough to induce a full average of spin–spin interactions.

Our previously reported studies have been mainly focused on NMR properties of the short time component of PEO or PB relaxation curves; in this work, properties of the long time component probably associated with end submolecules were carefully analyzed in order to determine to what extent they might be distinguished from inner submolecules. Observing protonated ($M = 1.07 \times 10^5$ or 2.08×10^5) or partly deuterated polybutadiene and considering effects of solvent addition and temperature variations, it will be shown here that in addition to end submolecules other monomeric units are involved in the amplitude of the relaxation tail. and molecular; the observation of protons attached to end segments was eliminated by studying a partly deuterated triblock copolymer; the molecular weight of deuterated chain ends was about 2×5000 while the total chain molecular weight was 0.98×10^5. Samples are described in the next section while the basis of NMR analysis is shortly recalled in section 3; experimental results are interpreted and discussed in section 4.

2. Experimental Section

Protonated polybutadiene samples (polydispersity: $1.02 \leq I_p \leq 1.03$) were kindly supplied by Michelin (France); the chain microstructure was 47.9% *cis*-1,4, 45% *trans*-1,4 and 7.1% vinyl for one polymer (2.08×10^5) and 44.4% *cis*-1,4, 48.4% *trans*-1,4 and 7.2% vinyl for the other one (1.07×10^5). The partly deuterated triblock copolymer (polydispersity: $1.03 \leq I_p \leq 1.07$ and $M = 0.98 \times 10^5$) was bought from Polymer Source (Canada); the chain microstructure was around 68% *cis*-1,4, 27% *trans*-1,4, and 5% 1,2-vinyl. The molecular weights of deuterated end blocks were 4.5×10^3 and 5×10^3, respectively. The deuterated cyclohexane (99.7%) was bought from Spectrométrie Spin et Techniques, France; the polymer concentration c was varied over the range $0.5 \leq c \leq 1$. Proton relaxation curves were recorded using a Bruker MSL 300 spectrometer operating at 60 MHz. All samples were kept in tubes sealed under vacuum; the sample temperature was controlled within ±1 K. Relaxation curves were obtained by forming Hahn spin-echoes (pulse sequence, $90°/x-\tau-[180°/x-2\tau-180°/-x-2\tau-180°/-x-2\tau-180°/x-2\tau-]_n$); so-called pseudo-solid spin-echoes specific to the existence of a nonzero average of dipole–dipole interactions were formed by applying the following pulse sequence to the spin-system: $90°/x-\tau-180°/x-\tau-90°/y-\tau_1-[180°/x-2\tau_1-180°/-x-2\tau_1-180°/-x-2\tau_1-180°/x-2\tau_1-]_n$.[8] The difference between the volume fraction ϕ and the concentration c (w/w) used throughout this work was at most equal to 0.03.

3. Basic Description of NMR

The quantitative description of the two relaxation parts of the observed magnetization accounts both for two different decays and for two different spin-echoes specific to distinct residual spin–spin couplings.

a. Relaxation Functions. The hierarchy of segmental fluctuations is one of the characteristics that has been attributed to linear macromolecules; the expression of the relaxation function which has proved to be a suitable tool for describing quantitatively the effect of chain dynamics on NMR (including the analysis of spin-echoes) is built from a series of relaxation modes and has been already reported elsewhere.[13] Parts I and II were described from the same basic mathematical function $M_x(t)$ using only different parameters to distinguish $M_x^{I}(t)$ and $M_x^{II}(t)$ magnetizations from each other; $M_x(t)$ was written as an exponential function of the second-order term of a cumulant expansion:

$$M_x(t) = \exp[-C(t)] \tag{2}$$

with

$$C(t) = \Delta^2 \left(\frac{1}{n_s}\right)^2 \sum_{p-1}^{n_s-1} \sum_{p-1}^{n_s-1} [\exp(-t/\tau_{p,q}) + t/\tau_{p,q} - 1] \tag{3}$$

and

$$\tau_{p,q}{}^{-1} = \tau_s{}^{-1} (\sin^2(\pi p/n_s) + \sin^2(\pi q/n_s)) \tag{4}$$

τ_s plays the role of a correlation time. Alternatively, τ_s might be considered more as a parameter used to adjust the probably complex distribution function of residual couplings to relaxation curves than as a real correlation time. Applying eqs 2–4, the analysis of parts I and II of relaxation curves provides numerical values of residual dipole–dipole interactions $\Delta = \Delta_I$ and $\tau_s = \tau_I$ for part I or $\Delta = \Delta_{II}$ and $\tau_s = \tau_{II}$ for part II; these quantities are independent of chain molecular weight except for τ_I which was found to vary as $M^{0.35}$.

b. Pseudo-Solid Spin Echoes. The residual dipole–dipole coupling confers a pseudo-solid behavior on the proton magnetization which is well detected from the formation of spin-echoes specific to pure solid-state NMR too. For example, in accordance with the description of $M_x(t)$ already reported for noninteracting proton pairs, the pseudo-solid spin-echo $E_x^{II}(t;\tau)$ formed at $t = \tau$ from the part II relaxation is expressed according to the function:

$$E_x^{II}(t;\tau) = \exp[-(2C_{II}(\tau) + 2C_{II}(t-\tau) - C_{II}(t))]\Phi_R^{II}(t) \tag{5}$$

$C_{II}(t)$ was calculated according to eqs 3 and 4, using parameters determined for the part II relaxation. The observation of long tails from polymer relaxation curves has been already reported; however, no residual interaction was mentioned about their properties.[9,10]

4. Experimental Results and Discussion

The procedure of numerical analysis of proton transverse relaxation curves starts from the characterization of the part II magnetization observed at long times (t > 10 ms). The simultaneous analysis of relaxation curves and spin-echoes ensured an accurate determination of numerical values of parameters. Then, convenient $\ln(M_x(t))/t$ plots were used for characterizing the part I magnetization and for determining exponential relaxation rates $1/T_2^I$ and $1/T_2^{II}$ of $\Phi_R^I(t)$ and $\Phi_R^{II}(t)$ functions (Figure 1A). Also, this plot illustrates the translation along the y axis induced by the logarithm of the $\Phi_R^I(t)$ exponential contribution at short times ($t \leq 5$ ms) while the translation induced by the logarithm of the exponential time function $\Phi_R^{II}(t)$ is observed at long times ($t \geq 15$ ms). A pseudo-solid spin-echo formed from the part II of the relaxation function is illustrated in Figure 1B. Numerical values of Δ_I, τ_I, Δ_{II}, τ_{II}, $1/T_2^I$, $1/T_2^{II}$, and $A_{II}(c)$ are reported in Tables 1 and 2 as a concentration function.

a. Correlations between Residual Spin–Spin Interactions. The dependence of the residual dipole–dipole coupling of protons Δ_1 governing the time variation of $M_x^I(t, c)$ on polymer concentration (w/w) is shown in Figure 2A for the two protonated polymers and the partly deuterated triblock; this dependence is represented by the empirical equation:

$$\Delta_1 = 1.74c(1 - 0.29c) \tag{6}$$

the nonnegligible deviation from linearity is described by the product 0.29c; the residual interaction $\Delta_{II}(c)$ governing the time evolution of $M_x^{II}(t, c)$ is closely correlated to $\Delta_1(c)$. The correlation applies to the three polymers correlation; it is illustrated in Figure 2B and represented by the empirical equation $\Delta_1(c) = 4.5\Delta_{II}(c)$. The existence of such a correlation is reinforced by considering the temperature dependence of Δ_I and Δ_{II} reported in Table 1 for the pure polymer (2.08×10^5): the ratio Δ_I/Δ_{II} is equal to 4.5 and 4.6 at 340 and 370 K, respectively. The correlation shows that Δ_I and Δ_{II} result from similar motional averaging processes; how-

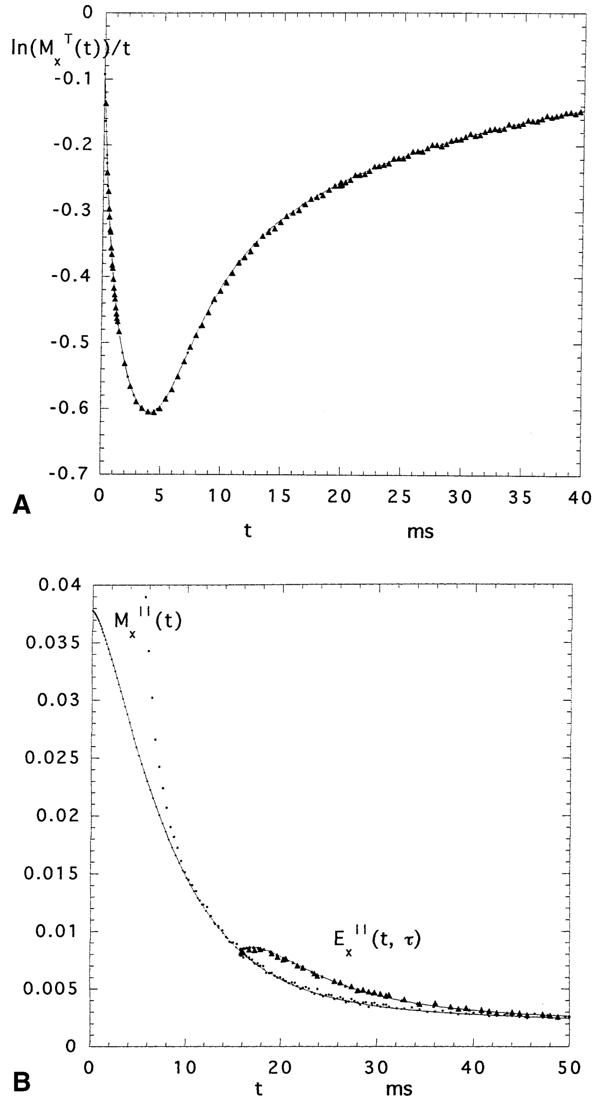

Figure 1. A. $\ln[M_x^T(t,M)]/t$ plot of the proton transverse relaxation curve recorded from molten polybutadiene (▲) at 300 K ($c = 0.81$ w/w, 2.08×10^5). Illustration of the numerical fit (continuous curve) calculated according to eqs 2–4, using the following numerical values independent of chain molecular weight: $\Delta_I = 1120$ rad·s^{-1}, $1/T_2^I = 80$ s^{-1}; $\Delta_{II} = 240$ rad·s^{-1}, $1/T_2^{II} = 24$ s^{-1}, and $\tau_s^{II} = 1.6$ ms; $\tau_s^I = 0.43$ ms and $A_{II} = 0.036$. B. Pseudo-solid spin-echo formed at $\tau = 15.9$ ms from the part II relaxation recorded from the polymer solution described in Figure 1A and calculated according to eq 5.

Table 1. Numerical Values Determined from Relaxation Curves Recorded from Fully Protonated Polybutadiene Solutions

A. $M = 2.082 \times 10^5$

	$T = 300$ K					$T =$ 340 K	$T =$ 370 K
c (w/w)	1	0.91	0.81	0.72	0.43	1	1
$\Delta_{\rm I}$, ms^{-1}	1.19	1.16	1.12	0.96	0.73	1	0.88
$\tau_{\rm I}$, ms	0.5	0.44	0.43	0.4	0.32	0.45	0.42
$1/T_1^{\rm I}$, ms^{-1}	0.14	0.09	0.08	0.05	0	0.05	0.035
$\Delta_{\rm II}$, ms^{-1}	0.26	0.25	0.24	0.21	0.155	0.22	0.19
$\tau_{\rm II}$, ms	1.6	1.6	1.6	1.6	1.6	1.6	1.6
$1/T_2^{\rm II}$, ms^{-1}	0.04	0.026	0.024	0.015	0	0.015	0.012
$A_{\rm II}$	0.027	0.03	0.036	0.046	0.0825	0.057	0.081

B. $M = 1.072 \times 10^5$

	T = 300 K				
c (w/w)	1	0.90	0.80	0.72	0.62
$\Delta_{\rm I}$, ms^{-1}	1.19	1.16	1.12	0.96	0.9
τ_1, ms	0.4	0.35	0.33	0.315	0.29
$1/T_2^{\rm I}$, ms^{-1}	0.14	0.09	0.08	0.05	0.03
$\Delta_{\rm II}$, ms^{-1}	0.26	0.25	0.24	0.21	0.18
$\tau_{\rm II}$, ms	1.6	1.6	1.6	1.6	1.8
$1/T_2^{\rm II}$, ms^{-1}	0.04	0.024	0.023	0.013	0.01
$A_{\rm II}$	0.057	0.066	0.077	0.083	0.095

Table 2. Numerical Values Determined from Relaxation Curves Recorded from Partly Deuterated Triblock Copolymer (Molecular Weight 98 000) Solutions

c (w/w)	1	0.76	0.60	0.51
$\Delta_{\rm I}$, ms^{-1}	1.23	1.07	0.91	0.75
$\tau_{\rm I}$, ms	0.35	0.275	0.24	0.22
$1/T_2^{\rm I}$, ms^{-1}	0.14	0.06	0.035	0.0
$\Delta_{\rm II}$, ms^{-1}	0.26	0.22	0.18	0.16
$\tau_{\rm II}$, ms	1.6	1.6	1.7	1.6
$1/T_2^{\rm II}$, ms^{-1}	0.040	0.016	0.010	0.0
$A_{\rm II}$	0.033	0.049	0.075	0.091

ever, random motions which occur along chain segments represented by protons associated with $M_x^{\rm II}(t, c)$ are less anisotropic than segmental fluctuations reflected by $M_x^{\rm I}(t, c)$. The decrease of $\Delta_{\rm I}$ ($\Delta_{\rm II}$) upon dilution indicates that the length of segments involved in the partial averages of dipole–dipole interactions is increased upon addition of solvent. It is noted that the plateau modulus of elasticity is usually lowered upon addition of solvent to a polymer: $G_{\rm N}^{\rm o}(c) \approx G_{\rm N}^{\rm o}/c^{\alpha}$ (with $\alpha = 2$ or 2.3); correspondingly, the mean size of the characteristic segment associated with the plateau modulus is lengthened according to the factor $c^{1-\alpha}$. Furthermore, the short-time end of the plateau is shifted toward short times upon addition of solvent because of the increase of free volume in the polymeric system. However, the deviation from linearity (or from $c^{1.3}$ dependence) observed both for $\Delta_{\rm I}(c)$ and $\Delta_{\rm II}(c)$ shows that these two quantities are not directly related to $G_{\rm N}^{\rm o}(c)$.

b. Correlations between Fast Monomeric Motions. Nonisotropic motions of monomeric units giving rise to residual dipole–dipole couplings are reflected by exponential relaxation contributions $\Phi_{\rm R}^{\rm I}(t)$ and $\Phi_{\rm R}^{\rm II}(t)$, characterized by $1/T_2^{\rm I}(c)$ and $1/T_2^{\rm II}(c)$ rates, respectively; there exists also a correlation between $1/T_2^{\rm I}(c)$ and $1/T_2^{\rm II}(c)$ rates. The dependence of $1/T_2^{\rm I}(c)$ on concentration is shown in Figure 3A while its correlation with $1/T_2^{\rm II}(c)$ is illustrated in Figure 3B. The correlation shows that the two relaxation rates result from the same types of monomeric unit motions; however, it may be assumed that the rates are defined from the same correlation time while the local motional averaging of interactions reveals more isotropy for units represented by $M_x^{\rm II}(t, c)$. The large differences between $\Delta_{\rm I}(c)$ and $\Delta_{\rm II}(c)$, on one hand and $1/T_2^{\rm I}(c)$ and $1/T_2^{\rm II}(c)$ on the other hand show that the slow relaxation of $M_x^{\rm I}(t, c)$ is well distinguished from that of $M_x^{\rm II}(t, c)$.

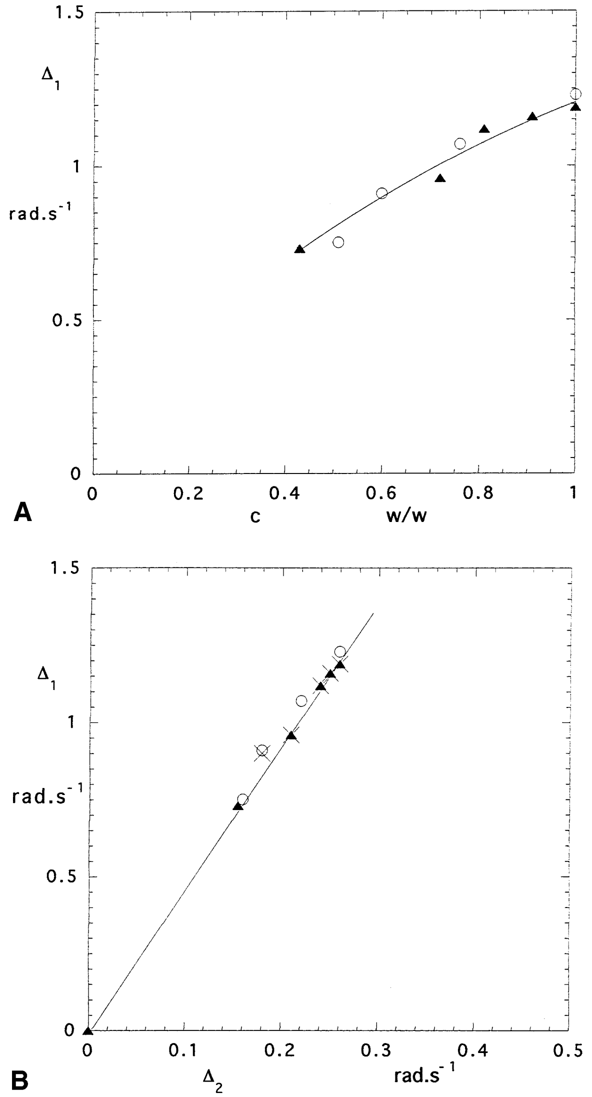

Figure 2. A. Concentration dependence of the residual dipole–dipole coupling $\Delta_{\rm I}(c)$ determined from the protonated polymer, 2.08×10^5 (▲) or from the triblock copolymer (○) (continuous curve as a guide for eyes). B. Correlation between residual couplings $\Delta_{\rm I}(c)$ and $\Delta_2(c)$; protonated polymers: (▲) $M = 2.08 \times 10^5$; (×) $M = 1.07 \times 10^5$. Triblock copolymer (○).

c. Correlation between $\tau_{\rm I}$ and Fast Monomeric Motions. It has been already shown that the molecular weight dependence of $\tau_{\rm I}$ defined in section 3a varies according to the power law $M^{0.35}$; in this work, it is shown that $\tau_{\rm I}$ is a function of polymer concentration, too. The plot of $\tau_{\rm I}(c)/M^{0.35}$ as a function of $1/T_2^{\rm I}(c)$ illustrates the linear correlation between $\tau_{\rm I}$ and $1/T_2^{\rm I}$ characterizing fast motions of monomeric units (Figure 4). This correlation reinforces the interpretation of $\tau_{\rm I}$ as a correlation time associated with segmental fluctuations ($\tau_{\rm I} \approx 0.5$ ms at room temperature in the pure polymer); however, it is much longer than the terminal relaxation time involving estimated from the Rouse model applied to segments associated with the plateau modulus in polybutadiene: $\tau_1^{\rm R} = (37)^2\, \lambda b \zeta_0 / 3\pi^2 kT$. $\tau_1^{\rm R} =$

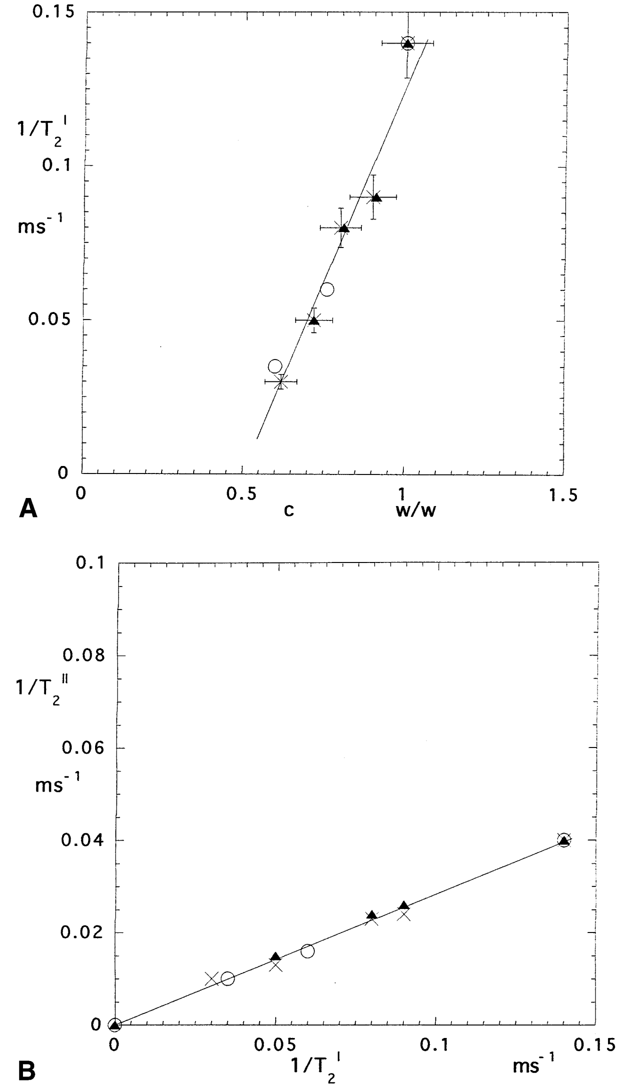

Figure 3. A. Concentration dependence of the relaxation rate $1/T_2^I(c)$ associated with fast and nonisotropic motions of monomeric units. respectively. B. Correlation between $1/T_2^I(c)$ and $1/T_2^{II}(c)$ relaxation rates; key to points as for Figure 2B.

0.005 ms at 300 K for a number of monomeric units equal to 37, with $\lambda b = 47.3$ Å^2 per monomeric unit and $\zeta_0 = 10^{-9}$ kg·s^{-1}. Its weak molecular weight dependence may be connected to the width of the plateau modulus.

d. Relative Amplitude of Part II Relaxation. The relative number of monomeric units associated with $M_x^{II}(t, c)$ is represented by A_{II}; the plot of $A_{II}M \times 10^{-5}$ drawn in Figure 5 as a function of the inverse of the concentration, shows that A_{II} is both proportional to the inverse of molecular weight and a linear fonction of the inverse of polymer concentration; the product $A_{II}M$ obeys the following empirical equation:

$$A_{II}M = 5886 + 8800(1/c - 1) \tag{7}$$

For $c = 1$, the invariance of the product MA_{II} with respect to molecular weight has been already shown over the molecular weight range 0.6×10^5 to 3.75×10^5 for polybutadiene and over the range 0.8×10^5 to 7.6×10^5 for PEO.[1,2] The slope of the straight line, independent of molecular weight, reveals that 163 ± 5 monomeric units per chain are sensitive to the addition of solvent; for the pure polymer ($c = 1$), the product $A_{II}M$ corresponds to 109 ± 3 units specific to the $M_x^{II}(t)$ relaxation tail. It may be noted from Table 1 that the value of A_{II}, determined from the pure polymer at $T = 370$ K is equal to A_{II} determined in solution at $T = 300$ K and $c = 0.43$ w/w.

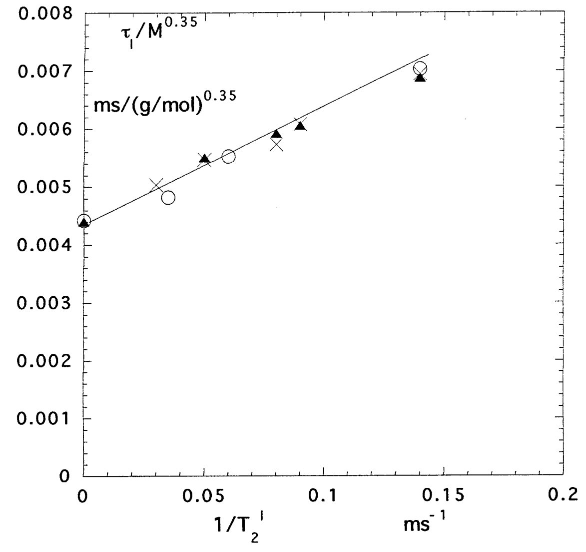

Figure 4. Correlation between $\tau_1/M^{0.35}$ with τ_1 associated with $M_x^I(t, c)$ and $1/T_1^I(c)$ associated with nonisotropic motions of monomeric units.

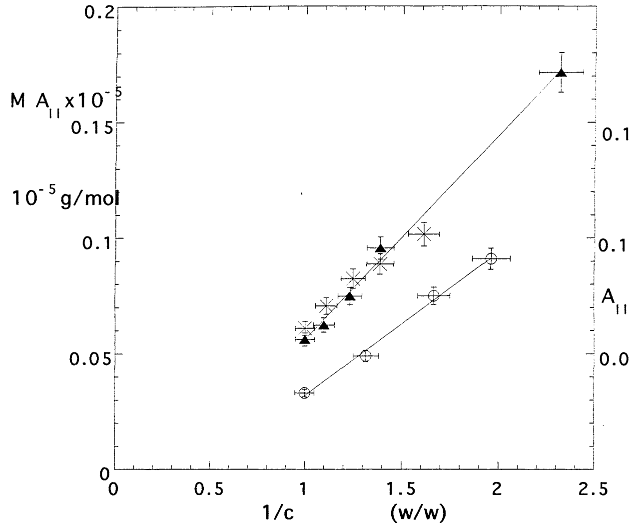

Figure 5. Linear dependence of the product $A_{II}M \times 10^5$ on the inverse of polymer concentration: (▲) $M = 2.08 \times 10^5$; (×) $M = 1.07 \times 10^5$. (○) representation of A_{II}* for the triblock copolymer.

e. Partly Deuterated Triblock Copolymer. It has been assumed until now that $M_x^{II}(t, c)$ was a relaxation function only assigned to protons attached to end segments; to check this hypothesis, the proton relaxation of partly deuterated triblock copolymers was observed as a concentration function. Molecular weights of deuterated end blocks were 4500 and 5500 (83 and 102 monomeric units, respectively); deuterated blocks were chosen for possibly eliminating the observation of 185 units. Considering the partly deuterated triblock copolymer, the analysis of the pattern of relaxation curves recorded as a concentation function lead to numerical values of parameters close to those determined from fully protonated polymers except for the amplitude of the long tail A_{II}. Surprisingly enough, the part II contribution was not completely eliminated from recorded relaxation curves. In other words, the relaxation function $M_x^{II}(t, c)$ could not be assigned only to protons attached to end segments. It must be assumed that random motions of end segments affect a few nearest neighboring segments too; the relative amplitude of part II, called A_{II}*, was determined with respect to the molecular weight (88 000) of the protonated block; it obeyed the following empirical equation:

$$A_{II}^* = a_D + b_D(1/c - 1) \tag{8}$$

with $a_D = 0.032 \pm 0.001$ and $b_D = 0.062 \pm 0.002$ (Figure 5). Now, the slope reveals that 101 ± 3 monomeric units per triblock copolymer are sensitive to the progressive additon of solvent while for $c = 1$, A_{II}* corresponds to 52 ± 2 units. Considering eqs 7 and 8, it is seen that in the pure polymer ($c = 1$), deuterated end blocks eliminate only 57 ± 5 monomeric units instead of 109 ± 3 from the observation of relaxation curves and 52 ± 2 units are still observed; similarly, for $c = 0.5$ g/g, the amplitude A_{II} corresponds to 272 ± 7 units while deuterated end blocks eliminate only 119 ± 10 units instead of 185 and 153 ± 3 units are still observed. The analysis of eq 8 amounts to considering that a number of deuterated units equal to ν/c must be subtracted from the right-hand member of eq 7; this number, independent of molecular weight, is also written as $\nu(1/c - 1) + \nu$. In other words, $a_D + \nu$ must be equal to 109 ± 3 with $\nu = 57 \pm 5$ while the slope $b_D + \nu$ must be equal to 163 ± 5 with $\nu = 62 \pm 8$; the two values of ν are in reasonable agreement with each other.

Furthermore, it can be shown that the distribution of 109 units associated with $M_x^{II}(t)$ in the pure polymer is not uniform along one chain; for an uniform distribution, the number of monomeric units eliminated from the part II relaxation by observing the partly deuterated triblock should be equal to 11 instead of 57 ± 5. Consequently, it is supposed that there exist NMR end submolecules comprised of $2N_{End}$ units while the remaining $(109 - 2N_{End})$ units are now distributed along one chain between end submolecules. For the triblock copolymer formed from 1815 units, the fraction of units located between end submolecules is simply written as $(109 - 2N_{End})/(1815 - 2N_{End})$; it must be applied to the protonated block (1630 units) to obtain 52 ± 2 units associated with the observed part II: this fraction gives $N_{End} = 27$ monomeric units. Similarly, the description of the effect of progressive solvent addition is analyzed by assuming that the number of units forming end submolecules varies as N_{End}/c; the fraction of units located between end submolecules is now expressed as $[109 + 163(1/c - 1) - 2N_{end}/c]/(1815 - 2N_{end}/c)$. This fraction applied to the protonated block (1630 units) must be in accordance with eq 8 expressed in numbers of monomeric units: $52 + 101(1/c - 1)$. N_{End} is again equal to 27 and the end submolecule size varies as N_{End}/c; in the pure polymer, about 55 units located between end submolecules along one chain are in dynamic interaction with end submolecules possibly attached to other chains.

5. Conclusion

One of the main features about the description of polymer properties in solution is the partition of chains into submolecules which behave statistically like subsystems; the scaling property of the segmental size is specific to the observed domain of concentration c (w/w). For example, the description of static properties of concentrated solutions is known to rely on the existence of Gaussian segments characterized by a size varying as c^{-2} while in semidilute solutions, submolecules obey an excluded volume statistics with a mean segmental size varying as $c^{-5/4}$. Considering viscoelastic properties, a mean submolecule comprised of about 40 monomeric units for polybutadiene is usually introduced; its size varies as $40/c^{\alpha}$ ($\alpha \approx 1$ or 1.25). In this work, it is shown that there exist NMR end submolecules shorter than viscoelastic ones and their segmental size, independent of molecular weight, was found to scale as $27/c$ rather than $27/c^2$. Random motions of end submolecules, restricted by one end only, are more isotropic than those of inner submolecules located between end submolecules along one chain and also detected from NMR; consequently, residual proton−proton couplings associated with end submolecules are weaker than those associated with inner submolecules. Furthermore, observing a triblock copolymer with deuterated end blocks, it is also shown here that end submolecules are in dynamic interaction with other monomeric units possibly located on other chains between end submolecules; the number of such units is about 55 per chain for pure polybutadiene. Regarding NMR properties of inner submolecules, they are usually supposed to reflect the break in chain fluctuations associated with the plateau modulus of elasticity; random motions which occur within these submolecules comprised of about 100 skeletal bonds are characterized by fluctuation rates higher than about 10^5 rad·s^{-1}. Partial averages resulting from these motions give rise to residual dipole−dipole couplings about equal to 10^3 rad·s^{-1} and independent of molecular weight; it is worth noting that the reptational motion of long chains ($M \geq 10^5$) is not fast enough to induce a motional averaging of residual interactions. The expected Gaussian average of spin−spin couplings should scale as c; the deviation from this scaling property observed in this work may be induced by concentration dependent spin−spin interactions between different segments. Results reported in this paper call for two remarks; On one hand, monomeric units in dynamic interaction with end submolecules may play the role of a solvent; their number is independent of molecular weight M. Consequently, their concentration varies as $3 \times 10^3/M$ (g/g) and becomes negligible for $M \geq 4 \times 10^5$. These units may be responsible for the molecular weight dependence of the correlation time τ_I(M) (≈0.5 ms) varying according to the apparent power law $M^{0.35}$ and associated with inner submolecules observed in this work. On the other hand, the theory of reptation is known to be based on the existence of end submolecules which determine randomly the back and forth motion of one chain in its tube;[14,15] these end submolecules may be those detected from NMR. It is considered that the interpretation of NMR properties of polymers in solution can rely on the existence of two types of submolecules; both their segmental size and its concentration dependence show that the analysis is probably close to the picture of the ensemble of submolecules used for the description of viscoelastic properties.

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