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Main-Chain Dynamics of Sodium Poly(acrylate) As Probed by NMR: A Comparison of Models

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ABSTRACT: Nuclear magnetic relaxation rates of sodium poly(acrylate) are analyzed and used to test two different models of polymer motion, i.e., the damped diffusion and the anisotropic rotation diffusion models. The spectral density function of ^{2}H methylene motion of sodium poly(acrylate) at various concentrations has recently been determined[1] in the range 0–80 MHz. A sharp increase of the low-frequency part of the spectral density function was observed in the semidilute regime, which could be ascribed to an enhanced electrostatic stiffness of the poly(acrylate) chains. Whereas in the more concentrated regime both models fit the data equally well, it is found that in the semidilute regime the rotation diffusion description seems more appropriate.

Introduction

A long-standing question in polymer physics is the relation between the rigidity of a polymer chain and its dynamic behavior.[1-4] The dynamic behavior of a polymer chain may be probed by techniques such as dielectric relaxation,[5] fluorescence depolarization,[6] and nuclear magnetic relaxation,[7-8] whereas the rigidity (cf. persistence length) may be determined by elastic light scattering experiments[9]—provided that the excluded volume parameter is known—or by small-angle neutron scattering experiments.[10]

Recently, Yamakawa[11] pointed out that for dielectric relaxation experiments[5] a clear correlation exists between the dynamic behavior and the rigidity of various flexible-chain polymers. For nuclear magnetic relaxation[12] experiments a less direct correlation was found. Generally, the relaxation rates do not depend solely on the rigidity of the polymer. They depend strongly on individual polymer characteristics. Instead of studying the effect of the rigidity on the dynamic behavior of a number of geometrically different polymers, it is preferable to study this effect on only one type of polyelectrolyte yet under different circumstances. The rigidity of a polyelectrolyte chain may be varied over a considerable range by changing the degree of neutralization and/or the ionic strength.

The total persistence length[13-15] of a polyelectrolyte chain is the sum of two contributions, the intrinsic persistence length and the electrostatic persistence length. The former is a measure of the rigidity of the uncharged chain while the latter is the additional contribution to the stiffness originating from the repulsive forces of the charges along the chain. The electrostatic persistence length is strongly influenced by the screening of the polyion charges by the small mobile counterions. In general the electrostatic persistence length will depend on many parameters like the solvent, the concentration, the degree of neutralization, the ionic strength, and the temperature.

In order to interpret the measurements correctly one must realize that in general the altered dynamic behavior as probed by nuclear magnetic relaxation will not originate solely from the altered electrostatic persistence length of the polyelectrolyte chain. When a polyelectrolyte chain is charged, an enhanced interaction of counterions and water molecules with the charged carboxylate groups will occur. This implies that effects due to the changed solvent and counterion mobility may influence the conformational transition rates.

Normally, the relaxation rates are not only determined by persistence-dependent segmental motions but also by limited reorientational movements (rotameric jumps) occurring on a subnanosecond time scale. The latter process contributes to both the longitudinal and the transverse nuclear magnetic relaxation rate. Fortunately, the effect of an altered persistence is observed by studying the movements of more extended backbone segments, and these occur on a much slower time scale (>10 ns). At moderate NMR frequencies (10–100 MHz) this means that the effect of an altered persistence will be mainly probed by the transverse relaxation rate via the spectral density value at frequency zero.

In studying the total spectral density function these two effects can be separated. In earlier work the different time scales of the polymer motion were characterized in relatively concentrated solutions of poly(methacrylic acid) (>0.2 monomol/L) as a function of the polymer charge.[16,17] Comparison of the rotation diffusion model and the damped diffusion model[18,19] for main-chain motion showed that only the former could describe the spectral density function. Surprisingly realistic persistence lengths were obtained with a primitive representation of the motional unit by a rotational ellipsoid.

In a previous paper[1] the dynamic behavior of poly(acrylic acid) was studied. As this is an intrinsically more flexible polymer with concomitant smaller relaxation rates, the experiments could be extended to lower concentrations (~0.01 monomol/L) where an important increase of the transverse rate occurs due to the increasing persistence length of the charged polyelectrolyte.

In the present paper the applicability of the rotational diffusion and damped diffusion models will be investigated for poly(acrylate) solutions at relatively low concentrations where the spectral density function shows a pronounced frequency dependence.

Motional Models for Polymers

The description of the motion of a linear macromolecule

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in a viscous fluid is a delicate problem.[20] Macromolecules may exhibit many types of motion of widely different rates. Different motional models are used according to the structural properties of the polymer and the state of the system studied (e.g., dilute solutions and polymer melts).

Models that have been used to describe polymer motion in solution include the following:

Backbone rearrangements[21-24] or configurational transitions are models that are described as large orientational jumps of a small group of carbon bonds on a diamond lattice. An example is the gauche–antigauche rotameric jump. The damped diffusion of orientational defects[18,19,28] is, in a way, a generalization of the configurational jump models. The damped diffusion model also incorporates librations. In case steric hindrances are present the motion of a group of bonds is restricted to a limited angular domain.[25]

Internal rotation[16,17,26,27] is a model that describes reorientation of some group about a temporary internal axis that itself is subject to axial reorientation. The latter represents the reorientational motion of dynamically independent chain segments with an extension of the order of the persistence length. Refinements of the rotational diffusion model include limited internal reorientation in a cone.[7]

The microdynamic behavior of the polyelectrolyte solutions studied here does not allow very detailed modeling on a (sub)monomeric level. The comparison of motional models is therefore restricted to the shape of the spectral density functions of the two most general models, i.e., the damped diffusion and the rotation diffusion models. As was pointed out before,[17,30] the fact that the damped diffusion model predicts the same correlation time for tensors of different order suggests that this model may not be expected to describe solutions of polymers with an appreciable persistence length. It may however be adequate for flexible polymers such as PAA at low charge density and high ionic strength.

Damped Diffusion Model. In a paper[18] in 1982 Skolnick and Yaris proposed an equation[36] to describe the internal motions in polymer chains

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} - \beta\rho \tag{1}$$

Here D is the transition rate for three-bound motion and $\rho(\theta,x,t)$ is the probability for a bond orientation θ at position x of the chain and time t. The damping constant β limits the propagation of the slow reorientational modes. In a subsequent paper[19] they extended the model with chain-chain interactions

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} - \beta\rho + (-\beta_1 - i\gamma)\rho \tag{2}$$

where $\beta_1 + i\gamma$ represents the chain–chain interactions. With a different meaning of the constants, eq 1 and 2 encompass some earlier models.[22-24,28] Comparison with the rotational diffusion model will therefore be restricted to spectral density functions derived from eq 1 and 2. The spectral density function corresponding to the damped diffusion equation (1) reads

$$J_{\mathrm{SY}}(\omega) = \delta^{-1}\left[\frac{c(\omega)}{4k(\omega)}\ln\left(\frac{A(\omega)}{B(\omega)}\right) + \frac{s(\omega)}{2k(\omega)}\tan^{-1}\left\{\frac{2k(\omega)s(\omega)}{k^2(\omega)-1}\right\}\right] \tag{3}$$

where $A(\omega) = 1 - 2k(\omega)c(\omega) + k^2(\omega)$, $c(\omega) = [{}^1/{}_2(1 - \beta/(\omega^2 + \beta^2)^{1/2})]^{1/2}$, $B(\omega) = 1 + 2k(\omega)c(\omega) + k^2(\omega)$, $s(\omega) = [{}^1/{}_2(1 + \beta/(\omega^2 + \beta^2)^{1/2})]^{1/2}$, $k(\omega) = ((\omega^2 + \beta^2)/\delta^2)^{1/4}$, and $\delta = Dk_{\max}{}^2 - \beta$, δ is the high-frequency cutoff as determined through $k_{\max}$, the inverse short-wavelength cutoff, D, the transition rate, and β, the damping constant. The spectral density function corresponding to eq 2 is essentially the same as the one corresponding to eq 1 if one redefines β and ω

$$\begin{gathered}\beta \rightarrow \beta + \beta_1 \\ \omega \rightarrow \omega - \gamma\end{gathered} \tag{4}$$

So, the incorporation of segment–segment interactions will result in an enhanced damping constant β and a shift γ in the spectral density function given by eq 3.

Rotation Diffusion Model. The rotation diffusion model has been discussed amply in previous publications.[1,16,29] Here, only the main features and the resulting spectral density will be presented. It was shown[1] that for the methylene ^{2}H relaxation in poly(acrylic acid) (CD_2PAA) the axially symmetric diffusion model is adequate. Two limiting interpretations of the three correlation times involved were found to be useful in the case of CD_2PAA. At high concentrations of the polymer, the correlation times are determined by a diffusion constant D_0 for spherical overall rotation of part of the chain, and D_{I}, representing internal rotation about a reorienting axis. The persistence length is estimated from the radius of the equivalent sphere. At low concentrations where more stretched conformations are probable, an interpretation in terms of an axially symmetric overall rotation[30] diffusion is more satisfactory. Here the persistence length is estimated as the half-length of the major axis of the reorienting equivalent prolate ellipsoid.

The reduced spectral density function for the rotation diffusion model[1] is

$$J(\omega) = \sum_{n=0}^{2} |D^{(2)}_{0n}(0,\beta\pm\Delta\beta,0)|^2 2\tau_n/(1 + \omega^2\tau_n{}^2)(2 - \delta_{0n}) \tag{5}$$

where $\tau_n = (6D_0 + n^2D_{\mathrm{I}})^{-1}$ for the sperical model with internal rotation or $\tau_n = ((6 - n^2)D_\perp + n^2D_\parallel)^{-1}$ for the axially symmetric model. The width of the distribution of the CD orientation with respect to the D_0 (or $D_\parallel$) axis is represented by the introduction of the two angles $\beta \pm \Delta\beta$. In this way the nonexponential ^{2}H relaxation is satisfactorily reproduced with a biexponential decay. In the tentative transformations of D_0, $D_\perp$, and $D_\parallel$ into persistence lengths the radius of a reorienting sphere and the half-lengths of a Perrin ellipsoid[31] have been used.[19]

Results

The nuclear magnetic relaxation data for methylene-deuteriated poly(acrylic acid) have been published[1] before. The relaxation rates were measured in the concentration range 0.01–0.2 monomol/L. The degree of sodium neutralization α was kept constant; $\alpha = 0.78$ (see Table I). The transverse relaxation rates were found to be nonexponential but could well be described with two exponents,[32] a slow one, R_{2s}, and a fast one, R_{2f}. The corresponding spectral density values for each sample were obtained by linearly transforming the six relaxation rate equations[33] with an equal number of unknowns twice for each sample (i.e., using a set (R_1,R_{2s}) and a set (R_1,R_{2f}) of sample x with corresponding spectral densities set S_{xs} and S_{xf}, respectively). The quadrupole coupling constant of the CD bond was chosen to be 170 ± 5 kHz.[34]

A weighted least-squares algorithm[35] was used in fitting the theoretical spectral density functions (eq 3 and 5) to the experimental spectral density values.

Damped Diffusion Model. The damped diffusion model is either a two- or a three-parameter model. The

Table I
Relaxation Rates[a] CD_2PAA (DP = 850, T = 298 K) at Three Larmor Frequencies

sample	c_p, monomol/L	α	ω_L = 4.6 MHz				ω_L = 9.2 MHz				ω_L = 41.4 MHz			
			R_1, s^{-1}	R_2, s^{-1}	R_{2s}, s^{-1}	R_{2f}, s^{-1}	R_1, s^{-1}	R_2, s^{-1}	R_{2s}, s^{-1}	R_{2f}, s^{-1}	R_1, s^{-1}	R_2, s^{-1}	R_{2s}, s^{-1}	R_{2f}, s^{-1}
1	0.23	0.78	415	476	434	524	373	459	408	507	211	352	320	400
2	0.082	0.78	416	615	435	865	316	545	410	795	218	450	315	695
3	0.026	0.78	421	745	435	1655	333	696	401	1606	209	590	290	1510
4	0.012	0.78	422	950	520	2200	300	860	475	2110	191	750	365	2020

[a] Estimated errors are 5% for R_1 and R_2. Nonexponential decays were resolved in two exponents R_{2s} and R_{2f}. The errors in R_{2s} are the same as for R_2 and nearly double for R_{2f}.

Table II
Reduced Spectral Density Values[a] of CD_2PAA Corresponding to the Relaxation Rates of Table I

set	reduced spectral density, 10^{-11} s, at freq (MHz)					
	0	4.6	9.2	18.4	41.4	82.8
S_{1s}	204 ± 16	207 ± 14	190 ± 7	170 ± 7	141 ± 16	88 ± 8
S_{2s}	224 ± 16	194 ± 13	194 ± 6	136 ± 7	121 ± 16	97 ± 8
S_{3s}	204 ± 16	206 ± 13	194 ± 6	146 ± 7	111 ± 16	94 ± 8
S_{4s}	332 ± 20	209 ± 13	194 ± 6	126 ± 7	108 ± 16	84 ± 8
S_{1f}	355 ± 20	199 ± 13	192 ± 6	170 ± 7	123 ± 15	92 ± 8
S_{2f}	840 ± 50	232 ± 13	185 ± 6	138 ± 7	112 ± 16	99 ± 8
S_{3f}	2080 ± 150	219 ± 14	191 ± 6	147 ± 6	113 ± 15	94 ± 8
S_{4f}	2900 ± 200	246 ± 15	185 ± 6	129 ± 7	99 ± 15	87 ± 8

[a] Obtained by linear transformation of the relaxation rates to spectral density values.

Table III
Damped Diffusion Model[a]

set	$\beta \pm \Delta\beta$, 10^6 Hz	γ, 10^6 Hz	$\delta \pm \Delta\delta$, 10^8 Hz	ΔJ_{av}
S_{1s}	280 ± 35	0	11 ± 2	0.6
S_{2s}	250 ± 30	0–1	14 ± 3	2.0
S_{3s}	190 ± 20	0–2	20 ± 3	1.5
S_{4s}	36 ± 3	0–4	64 ± 3	2.0
S_{1f}	280 ± 30	0	7 ± 2	3.6
S_{2f}	5.2 ± 0.3	0–2	61 ± 3	2.8
S_{3f}	1.0 ± 0.05	0–4	53 ± 3	2.9
S_{4f}	0.5 ± 0.03	0–5	53 ± 3	1.7

[a] The spectral density function eq 3 was fitted to the spectral density values of Table II. The high-frequency parameter δ is related to the fast motions. The damping constant β determines the presence of low-frequency modes. Its value decreases upon diluting the neutralized CD_2PAA solutions.

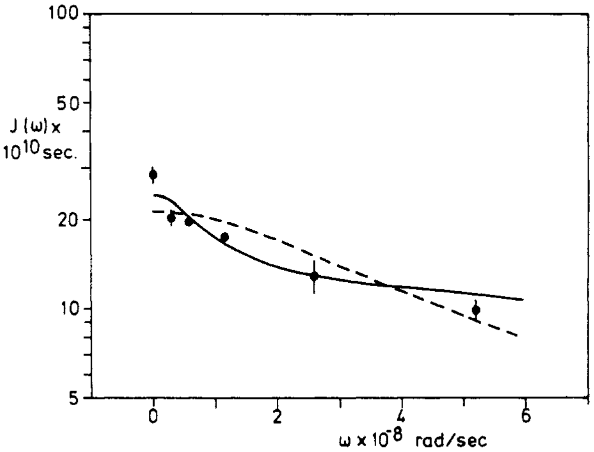

Figure 1. Reduced spectral density $J(\omega)$ of CD_2PAA (DP = 850) quadrupolar ^2H relaxation at 0.23 monomol/L; α = 0.78 and T = 298 K. The frequency ω is linearly represented. The rotation diffusion model (solid line) and the damped diffusion model (dashed line) were fitted to the mean spectral density values of Table II.

additional parameter γ that includes some aspects of chain–chain interactions may be introduced. For each sample a double set of spectral density values was obtained. This presents a serious complication in fitting the damped diffusion model to these double set of spectral density values. At least one of the model parameters should vary in order to account for the double set of spectral density values. At the present it is unclear which parameter should be chosen. Therefore the fits have been made separate, i.e., one fit for each set of spectral density values, see Table III. From this table it is seen that at least two parameters, β and δ, vary. In the figures only mean spectral density values are used for fitting in order to keep the number of parameters as small as possible. The parameters δ, β, and γ were fitted to the spectral density values (Table III). The high-frequency cutoff parameters δ fluctuates between 7 × 10^8 and 65 × 10^8 Hz for the different samples. The damping constant β strongly diminishes upon dilution, from 280 × 10^6 to 0.5 × 10^6 Hz. For the lower values of the damping constant there are more extended correlated chain movements possible. An intriguing appearance is the presence of the frequency shift γ in the spectral density functions at lower concentrations. This means that the spectral density has a maximum value at a frequency ω shifted from zero. However, the fit error parameter $\Delta J_{av} \equiv \langle |J_{fit} - J_{obsd}| / \sigma(J) \rangle$ is quite large, and from the fits it is at the present not possible to extract an explicit value for γ. Therefore upper and lower limits for γ are given in Table III. At moderately high concentrations (>0.1 monomol/L) the damped diffusion model covers the measured spectral density values quite well. At lower concentrations it seems that the spectral density values at higher frequencies are underestimated (compare Figures 1 and 2). When the behavior of the spectral density function of some earlier versions of the model[22,28] was examined, the same effect was observed: a noticeable underestimation of the reduced spectral density at higher frequencies.

Rotation Diffusion Model. The expression of the spectral density, eq 5, was used in fitting the spectral

Table IV
Results of Fits to Rotation Diffusion Model[a]

set	$D_0^{-1} \pm \Delta D_0^{-1}$, ns	$D_1^{-1} \pm \Delta D_1^{-1}$, ns	β, rad	$\Delta\beta$, rad	radius sphere, Å	long semiaxis, Å	ΔJ_{av}
S_1	71 ± 10	0.74 ± 0.04	0.8	0.007	25	52	1.0
S_2	232 ± 16	0.73 ± 0.03	0.8	0.042	37	82	1.4
S_3	447 ± 26	0.89 ± 0.04	0.8	0.09	46	104	1.5
S_4	651 ± 34	0.84 ± 0.03	0.8	0.085	51	120	1.2

[a] Simultaneous fit to the double-valued spectral density of the rotation diffusion model eq 5. A variation of the angle β was used in describing the double-valued spectral density. The variation $\Delta\beta$ is rather small (1–10% of β).

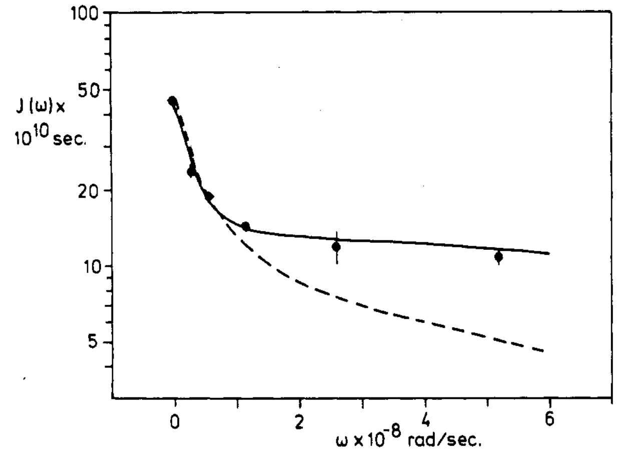

Figure 2. Reduced spectral density $J(\omega)$ of CD_2PAA (DP = 850) quadrupolar ^2H relaxation at 0.082 monomol/L; $\alpha = 0.78$ and $T = 298$ K. The damped diffusion model (dashed line) underestimates the mean spectral density values at high frequencies. The rotation diffusion model describes the experimental values reasonably well.

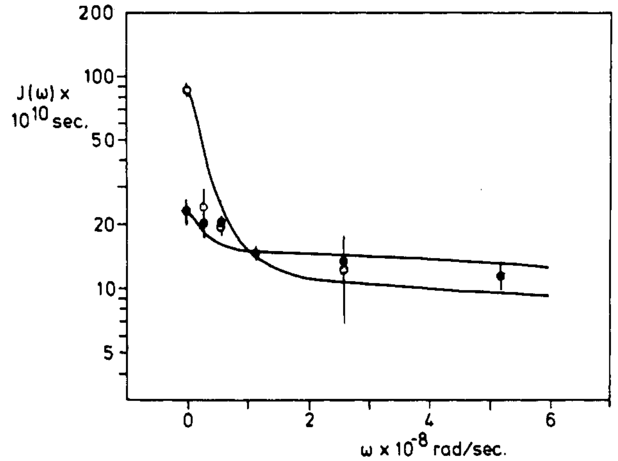

Figure 3. Reduced spectral density $J(\omega)$ of CD_2PAA (DP = 850) quadrupolar ^2H relaxation at 0.082 monomol/L. Two sets of spectral density values are shown: (○) S_{2s}, (●) S_{2f}. Lines drawn are the result of a simultaneous fit of the four-parameter rotation diffusion model eq 5 to the 12 points.

density values (Table II). Four parameters were found, i.e., D_0, D_I, and $\beta \pm \Delta\beta$, on fitting simultaneously two sets of spectral density values. The isotropic diffusion constant D_0 strongly decreased upon dilution. This parameter is related to the movements of large backbone segments. On using the relation[19] for the radius of a reorienting sphere, one finds an increase from 25 to 51 Å. For η the value of pure water was taken at 25 °C. The other diffusion constant, D_I, is associated with the fast internal motions and remains essentially constant ($1/D_I \sim 0.7$–0.9 ns), in agreement with the concentration-independent longitudinal relaxation rates.

Alternatively, the found correlation times may be interpreted with the axially symmetric model.[1] In this case the long semiaxis varies between 52 and 120 Å. The simultaneous fits describe the experimental data rather well (see Figure 3). Only one parameter, $\beta \rightarrow \beta \pm \Delta\beta$ should be varied in describing the spectral density points.

Conclusions

In making general remarks about the models discussed here, one must be very careful. If one limits the comparison of the models to the observed values of the fit error parameter ΔJ_{ac}, one may state that the rotation diffusion description yields lower values $\Delta J_{av} \simeq 1$–1.5 than the damped diffusion description $\Delta J_{av} \simeq 1.5$–3.5. Although the number of independent fit parameters of the damped diffusion description is smaller than in case of the rotation diffusion description (2 or 3 against 4, respectively), one must realize that the rotation diffusion description fits simultaneously two sets of spectral density points (4 parameters are fitted to 2 × 6 spectral densities). Moreover, only a small variation of the orientation of the interaction tensor with respect to the diffusion tensor is sufficient to describe the nonexponential transverse relaxation. The adaptation of the damped diffusion model to yield a nonexponential decay seems to be less straightforward.

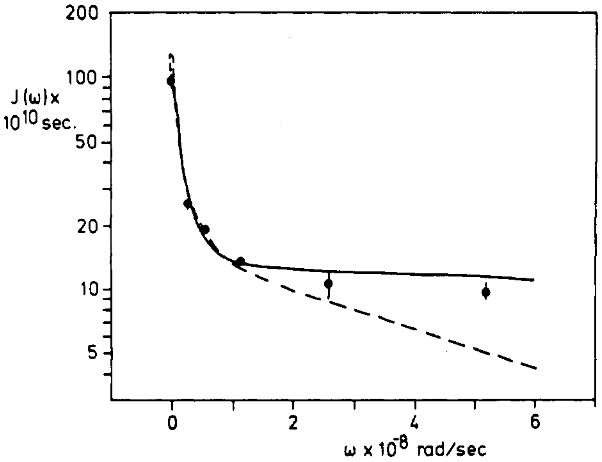

Figure 4. The rotation diffusion model (solid line) is depicted together with the damped diffusion model (dashed line) CD_2PAA at 0.026 monomol/L. The rotation diffusion model describes the mean values rather well. Two independent diffusion constants D_0 and D_I are sufficient to describe the total spectral density.

Apart from the complicating factor of double-valued spectral density points for each sample, it may be concluded from the figures and the fit error parameter that (a) in the concentrated regime both models fit the data reasonably well and (b) in the semidilute regime the rotation diffusion description seems more appropriate.

The rotation diffusion description uses a weighted sum of Lorentzians in characterizing the spectral density function. Descriptions related to the semiempirical model free approach[7,8] use also a sum of Lorentzians for the spectral density function. This means that these models are also more applicable than the models that are based on a diamond lattice description.

Further work on the rotation diffusion description is necessary. More internal rotations may be incorporated in the model and possibly a more precise relation can be obtained between the rotation diffusion parameters, the concept of dynamic stiffness, and the persistence of a polymer chain. This work extends the results of Mulder et al.[30] obtained for poly(methacrylic acid) at high concentration, where similar conclusions with respect to the rotation diffusion and the damped diffusion model were reached.

Registry No. Sodium poly(acrylate), 9003-04-7.

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(36) Apart from the meaning of the symbols, this equation is similar to an earlier equation as proposed by Valeur et al.[22] They derived an approximate differential equation for the correlation function $Q_{\mathrm{nn}^0}(t)$ between bond n and n^0

$$\frac{\partial Q_{\mathrm{nn}^0}(t)}{\partial t} = A\frac{\partial Q_{\mathrm{nn}^0}(t)}{\partial n^2} - BQ_{\mathrm{nn}^0}(t)$$

where $A = 3.16W_3 - 9.61W_4$, $B = 4.74W_4$, and W_3 and W_4 are respectively the jump rates of three and four bond rearrangements.

New Method for the Microstructure Determination of Polybutadiene with Cis-1,4, Trans-1,4, and Vinyl-1,2 Units by ^{13}C NMR

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ABSTRACT: The assignment of the olefinic resonances in the ^{13}C NMR spectra of various polybutadienes has been tested by comparing experimentally determined and theoretically calculated peak areas. On the basis of a good agreement between the two results, an elegant numerical and graphical method has been outlined for the rapid determination of the cis-1,4, trans-1,4, and vinyl-1,2 ratio of these polymers.

Introduction

Infrared and Raman spectra of polybutadienes have been used for the determination of the microstructure of polybutadienes consisting of sequences of cis-1,4 (c), trans-1,4 (t), and vinyl-1,2 (v) units.[1,2] Both methods rely more or less on isomerically pure polymers, each containing relatively high concentrations of one of the three kind of base units.

Another method not requiring pure polymers is ^{1}H NMR. Direct information about the ratio v/(c + t) can be obtained from the ^{1}H NMR spectrum.[3] However, except for polymers that contain only two base units, i.e., v and c or t, it is not possible to extract information about the amounts of the three base units that are present in polybutadienes containing significant fractions of all three parts.[3-5] Even at 400 MHz, the resolution of the olefinic resonances is insufficient to resolve c and t signals.[6]

^{13}C NMR spectroscopy, on the other hand, offers more information because detailed assignments have been described for the aliphatic[7-10] and olefinic carbons.[8,11] Therefore, a quantitative analysis, excluding the necessity of using model polymers, has been attempted by measuring the v/(c + t) ratio by ^{1}H NMR[6] and the ratio c/t via ^{13}C NMR[6] (aliphatic carbon resonances). The combination of these two techniques results in a c, t, and v ratio for polybutadienes. Alternatively the aliphatic ^{13}C resonances[7,9] have been used (assuming Bernoullian statistics) to give indirect information on the relative abundance of the three base units.

The first method necessitates two independent measurements (^{1}H/^{13}C NMR); the second (^{13}C NMR) is severely hampered by questionable assignments[6,10] and different compositionally induced diads for the methylene carbons and triads for the methine carbons.[9] Furthermore T_1 and NOE effects are not necessarily equal for these different signals.

A similar ^{13}C NMR analysis has not been employed for the olefinic resonances, although general agreement exists about the assignments.[8,11] This might be due to the decreasing chemical shift dispersion going from the aliphatic carbon resonances to the olefinic resonances, leading to complex, partially overlapping signals. With the above mentioned assignments of Elgert et al.[11] a simple method is outlined for measuring the isomeric distribution along the polybutadiene (PB) chains. Sequence analysis therefore is used to quantify the microstructure of PB.

Experimental Section

A series of five PB rubbers (unfilled, uncured) is examined here. The commercially available polymers, arranged in succession of increasing v content are from Hüls (all cis) (A), Goodyear (liquid

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