

observed at low shear rates and at long times suggests that the relaxation mechanism for a slightly coiled molecule could be significantly different from that for a perfectly rodlike molecule.

Conclusions

We have demonstrated by TCFB measurements and TEM that the shortened bovine collagen prepared by the procedure described in this paper is indeed characterized by a shorter average contour length. The molecules are more rodlike since the contour length is now closer to the persistence length. The TCFB measurements under both steady-state and transient flow conditions were in excellent quantitative agreement with the DEMG model, thereby confirming the validity of the model. Comparisons with the results obtained on two slightly more flexible collagen samples reported previously suggested that the relaxation mechanism for a semiflexible molecule could be completely different from that for a rodlike molecule.

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Chain Dynamics and Molecular Weight Dependence of Carbon-13 and Hydrogen-1 Relaxation Times in Polystyrene and Polyethylene Melts

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ABSTRACT: It is shown that nuclear magnetic relaxation is a suitable tool for the investigation of global motions in polymer melts. The transverse relaxation time of the quaternary carbon of polystyrene shows the double-break molecular weight dependence predicted in a previous paper. The break at low molecular weights coincides with the rheological M_c value. The longitudinal relaxation times above 10 MHz show a molecular weight independent plateau indicating the existence of entirely local motions. The results are discussed in context with some statements concerning a recent Monte Carlo study by Kremer.

Introduction

The nuclear magnetic relaxation times T_1 and T_2 are sensitive to interactions in the close neighborhood of the observed nuclei. The technique nevertheless is not restricted to the investigation of local processes. Rather, T_1 at low frequencies ($\approx 10^4$ Hz) and T_2 show a molecular weight dependence¹ implying the features of that of the zero-shear viscosity. This finding was based on proton resonance data of polyethylene melts. Thus, it has been proved that global motions can be relevant for NMR relaxation.

Moreover, the NMR methods show additional effects hitherto unknown in rheology. Several "characteristic molecular weights" have been found. With polyethylene

melts it turned out, for instance, that the molecular weight dependence of T_2 or of T_1 at low frequencies ($\approx 10^4$ Hz) is characterized by a double-break behavior, where the lower break virtually coincides with the critical molecular weight^{1,2} M_c known from rheology. The upper break at a frequency-dependent molecular weight M_{BC} is due to a crossover to a region where coil-internal motions dominate. At high frequencies ($> 10^7$ Hz) finally a transition to a molecular weight independent region has been observed.

The molecular weight dependence of the NMR relaxation times is generally weaker than that of rheological quantities. In the temperature/frequency range permitting measurements below M_{BC} , for instance, the molecular weight dependence of T_1 and T_2 is roughly half as strong

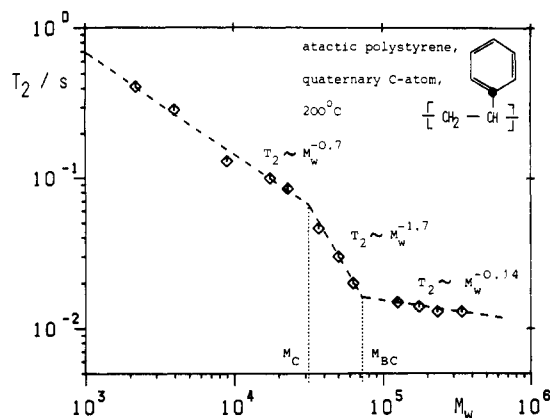


Figure 1. Molecular weight dependence of the transverse relaxation time of the quaternary carbon of atactic polystyrene.

as that of the zero-shear viscosity. As this finding is true both *above* and *below* M_c , a general scheme for the interpretation and comparison of these data is required. Previously we suggested¹ an extension of the three-component concept³ in order to account for this finding.

The molecular weight dependence of the proton T_2 of polystyrene melts shows only one break in contrast to polyethylene. A prediction^{1,4} on the basis of the above-mentioned concept was that the double-break behavior should be observable by monitoring other nuclei "seeing" local fields reduced compared with protons. The verification of this expectation will be shown in the following. Furthermore, we will discuss the crossover to the dominance of local processes which can be observed with the spin-lattice relaxation times at high frequencies. Finally, we will discuss to what extent the mobility of the matrix chains affects the dynamics of dissolved chains.

Experimental Section

We have investigated atactic polystyrene (PS; $M_w/M_n < 1.1$) and linear polyethylene (PE; $M_w/M_n < 1.5$) from diverse sources (see ref 1). All samples were sealed after prolonged evacuation. The ^{13}C data have been recorded with a Bruker HX 90 high-resolution FT NMR spectrometer applying Hahn's spin-echo technique for T_2 and progressive saturation for T_1 . Proton broad-band decoupling was applied, but no sample spinning in order to avoid interference with the spin-echo formation. Sample spinning increased the echo decay rate at low molecular weights by a factor of 10, while proton decoupling showed no influence. The ^2H lock-signal originated from perdeuterated palmitic acid filled in a capillary concentric to the sample tube. The ^{13}C relaxation times have been measured at least twice. The data could be reproduced within $\pm 15\%$. The sample temperature was constant within $\pm 1^\circ\text{C}$. The proton data have been recorded with a Bruker SXPC 4-100 spectrometer and standard pulse techniques. The longitudinal relaxation curves were exponential at least over one decade. In the case of transverse relaxation slight deviations from exponential decays have been found. The T_2 data therefore refer to the decay to $1/e$ of the initial value extrapolated to time 0.

Results

Figure 1 shows the T_2 data of the quaternary carbon of polystyrene. A clear double-break behavior is visible. The intersections of the straight lines are at $M_c = 31000$ and $M_{BC} = 71000$. M_c favorably compares with the rheological value.⁵ M_{BC} and the slopes of the straight lines are rather close to those found for polyethylene melts,¹ so that an equivalent behavior of the two polymer examples can be stated.

The fact that the double-break behavior could be observed with ^{13}C but not with ^1H resonance must be attributed to the lower local fields sensed by the quaternary

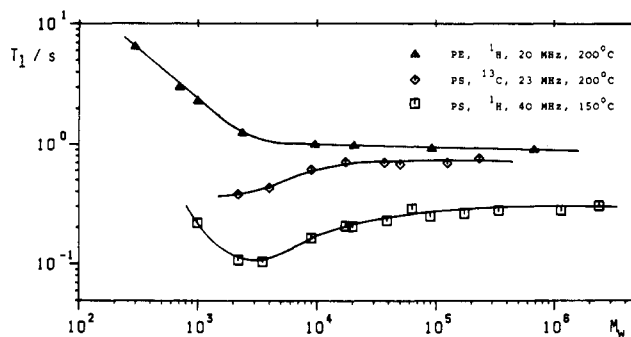


Figure 2. Molecular weight dependence of the high-frequency spin-lattice relaxation times of polyethylene and polystyrene. The ^{13}C data again refer to the quaternary carbon of polystyrene.

carbon. Lower local fields mean that T_2 is determined to a minor degree by fast fluctuations. From the low-frequency proton T_1 data of our previous study it follows that the local fields sensed by the quaternary ^{13}C nuclei correspond to frequencies much less than 10^4 Hz.

A crucial finding of this study is that the slopes in Figure 1 are rather flat compared with those found with other techniques also sensitive to chain dynamics.^{4,5} The range $M_w > M_{BC}$ indicates a behavior particularly intrinsic to nuclear magnetic relaxation. No other technique is known indicating the M_{BC} crossover. Below M_{BC} the M dependence qualitatively corresponds to that of the zero-shear viscosity. The slopes of the T_2^{-1} curves are, however, at most half as steep. This fact is again specific for the NMR mechanisms and can be interpreted by the aid of the three-component concept.¹

The other ring carbons showed a less pronounced M dependence of T_2 . This is due to the fact that the quaternary carbon is the only ring carbon which has a neighboring main-chain hydrogen atom. The main-chain carbons, on the other hand, relax very fast ($T_2 < 10^{-2}$ s) so that it was difficult to measure T_2 with our instrument.

Figure 2 shows the spin-lattice relaxation times at high frequencies ($\approx 10^7$ Hz). For comparison, the proton T_1 data of polyethylene are also plotted. The behavior of the quaternary carbon of polystyrene is equivalent to the unresolved proton resonance data. The polystyrene curves are characterized by a minimum at low molecular weights and a plateau at high molecular weights. The latter, of course, is due to entirely local mechanisms of the chain segments.

Discussion

The ^{13}C data confirm the essence of the three-component concept¹ of nuclear magnetic relaxation in polymer melts. On this basis one expects at low frequencies, i.e., especially for T_2 , a behavior in the range $M_w < M_{BC}$ governed by an effective correlation time

$$\tau_c = (\tau_r \tau_1)^{1/2} \quad (1)$$

where τ_r is the longest chain relaxation time which—above M_c —often is denoted as "tube renewal" time ("component C"). τ_1 is the time constant for reorientations caused in the first instance by longitudinal intracoil displacements ("component B"). It is obvious that τ_r depends much more on M than τ_1 , which reveals its weak M dependence in the limit $M_w > M_{BC}$. Hence, it can be understood that the low-frequency NMR relaxation times show a weaker M dependence than quantities governed by τ_r alone as it is the case with the zero-shear viscosity.⁵

Equation 1 can be traced back to elements of de Gennes' reptation model. Thus, one expects, e.g., the molecular weight dependence

$$\tau_r \sim M^3 \quad (2)$$

in the regime usually attributed to "entangled behavior". On the other hand, prerequisites had to be made which are not compatible with the reptation model in the original sense.⁶ de Gennes had assumed that a time scale $t < T_d$ could be relevant under experimental conditions. T_d is the equilibration time of the defect "gas" responsible for the reptation mechanism. For this limit he predicted for the mean square displacement on a curvilinear path

$$\langle s^2 \rangle \sim t^{1/2} \quad (3a)$$

In three dimensions this means

$$\langle r^2 \rangle \sim t^{1/4} \quad (3b)$$

A consequence thereof would be a frequency dependence

$$T_1 \sim \nu^{3/4} \quad (4)$$

which contradicts the experimental finding (Figure 4 of ref 1)

$$T_1 \sim \nu^{1/2} \quad (5)$$

It also contradicts recent Monte Carlo studies⁷⁻⁹ and the behavior of the structure factor of coherent neutron scattering,⁸ which clearly favor Rouse-like displacements. The conclusion is that under the experimental conditions the limit $t \ll T_d$ cannot be realized. Rather one finds the behavior predicted by de Gennes for $T_d < t < \tau_r$

$$\langle s^2 \rangle \sim t \quad (6a)$$

$$\langle r^2 \rangle \sim t^{1/2} \quad (6b)$$

The proportionality eq 6a has been assumed in the derivation of eq 1 and 5, which simultaneously represent experimental findings.¹

The fact that the limit $t < T_d$ could not be realized under experimental conditions can be made plausible by assuming a less static tube than originally suggested.⁶ A limited degree of freedom for lateral chain fluctuations can accelerate defect equilibration so to say by partial decoupling of different chain parts. The limit $t < T_d$ thus could be shifted to a range not accessible by experiments. The Monte Carlo simulations of mobile matrix systems possibly also imply such a local equilibration of the defect gas.

On the other hand, Kremer⁷ predicted that short chains dissolved in a long-chain matrix should show a crossover to the displacement behavior of eq 3b. This is at variance with a finding of our NMR experiments (ref 1, Figure 12c). The transverse proton relaxation curve of PE ($M_w = 7200$) diluted in a deuterated matrix PE_D ($M_w = 430000$) is identical with that of the undiluted material, albeit τ_r (eq 2) of the matrix chains is expected to be 5 orders of magnitude greater than that of the short chains. (Note

that the M_{BC} values for T_2 of polyethylene is greater than 50 000.¹) The long-chain matrix obviously does not influence the dynamics of the dissolved chains apart from a minor reduction of the free volume, the effect of which almost completely is compensated by the reduced inter-chain dipolar coupling. Thus, a crossover to a different type of dynamics cannot be stated.

Summarizing the findings of the low-frequency NMR experiments we can conclude that the reptation model is suitable to describe the data only under the condition $t > T_d$. This limit must be valid irrespective of the matrix chain length, so that certain lateral tube fluctuation degrees of freedom in general must be assumed.

The transverse relaxation behavior is contrasted with high-frequency T_1 data. The first are clearly influenced by global processes, the latter equally clear by local mechanisms summarized as "component A". The experimental evidence of the latter is the molecular weight independent plateau in the limit of long chains (Figure 2). Note that the T_1 minimum of polystyrene data of Figure 2 corresponds to that of the temperature dependence discussed by Sillescu et al.¹⁰ The condition $\omega\tau_s < 1$ (τ_s effective correlation time of component A) is well fulfilled for polyethylene as indicated by the T_1 dispersion behavior. Under this condition a further characteristic molecular weight, M_{AB} , can be defined. It separates the plateau from a region where the M -dependent components B and potentially also C play a role.

The purely local processes can be interpreted as the anisotropic reorientation of segments in consequence of the "defect" migration proposed by de Gennes.⁶ Thus, a further element of the reptation model in a more general sense fits the experimental findings. Nevertheless, there is a certain need to expand the present discussion of melt theories to take account of all the above effects in detail.

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