within the limits of accuracy of the method.

The change in the phase separation temperature with pressure predicts a densification on mixing, which is also generally favorable for compatibility.

The phase separation at higher temperatures could be qualitatively explained by the variation of heat of mixing with temperature. The heat of mixing of the low molecular weight analogues does not change sign over the temperature range studied, which suggests that an unfavorable noncombinatorial entropy contribution is responsible for the phase separation in the high-polymer systems.

Registry No. EVA, 24937-78-8; 2-octyl acetate, 2051-50-5; octan-2-ol, 123-96-6.

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A Method for Studying the ^{13}C NMR Relaxation Time as a Function of Position along the Polymeric Chain

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ABSTRACT: A combination of selective deuteration and rapid pulse sequences in FT NMR allows one to determine ^{13}C T_1 in various portions of a polymeric molecule. This procedure has been applied to polystyrene. By preparing atactic polystyrene molecules selectively deuterated in the central portion of the chain, we have shown that carbons in the terminal portion have significantly greater T_1 than the average values determined in undeuterated and randomly deuterated molecules of comparable average molecular weights. These results indicate that the effective correlation times of the backbone carbons in long chains decrease from the center toward the terminals.

The use of NMR to investigate molecular dynamics in solution has been gaining in importance during the past decade. As can be seen from the recent review by Heatley,[1] the ^{13}C relaxation times (T_1 and T_2) in polymers are the most widely used NMR measurements for this purpose. In all such studies to date, the T_1's of various carbons in a polymer were measured as composite or effective relaxation times involving all carbons of any given type in the chain, without any attempt to separate the specific contribution of the relaxation times of terminal carbons or carbons in any particular portion of the chain. Such attempts were made only for some chain molecules of intermediate length, in which several distinct ^{13}C signals at the end of a chain can be resolved. Thus Levine et al.[2] and Lyerla et al.[3] measured the ^{13}C T_1 for resolved carbons in neat n-alkanes (n not exceeding 20). They found that the T_1's of the terminal carbons were considerably higher than those corresponding to the carbons in the central portion of the chain. Resonances of four terminal carbons could be resolved, and the indication was that there is a progressive increase in T_1 and corresponding decrease in τ_{eff} (effective correlation time) from the central to the terminal portion of the chain. Whether there is a corresponding monotonic increase in T_1 of macromolecules in general or whether this increase is largely limited to only a few terminal atoms in longer chains has never been experimentally answered. The purpose of this work was to devise an experimental procedure that will address the problem of variation of τ_{eff} of polymeric segments located in the different portions of the chain. It consists of a combination of selective deuteration and rapid pulse sequences in FT NMR. This procedure is described below.

Description of the Method

The ^{13}C relaxation times (T_1 and T_2) in polymers of protonated carbons are predominantly associated with a dipolar mechanism.[1] If any particular carbon is completely deuterated, its ^{13}C relaxation time (T_1) becomes considerably longer. In the case of isotropic rotational motion with a correlation time τ_C in the extreme narrowing limit ($\omega_0^2\tau_C^2 \ll 1$, ω_0 being the magnetic resonance frequency), the ratio of relaxation time of deuterated ^{13}C, $T_1^{\text{C-D}}$, to that of protonated ^{13}C, $T_1^{\text{C-H}}$, which we shall denote by Γ, is given by

$$\Gamma = \frac{T_1^{\text{C-D}}}{T_1^{\text{C-H}}} = \frac{\gamma_H^2}{\gamma_D^2}\,\frac{S(S+1)}{I(I+1)}$$

where γ_H and S are the magnetogyric ratio and spin

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Table I
Value of Γ for Some τ_C Calculated at the Magnetic Field Strength of 21.1 kG

τ_C, s	Γ	τ_C, s	Γ
1×10^{-11}	15.9	1×10^{-8}	6.8
5×10^{-10}	14.9	1×10^{-7}	4.6
2×10^{-9}	9.8	1×10^{-6}	4.5
6×10^{-9}	7.3		

quantum number for proton, respectively, and the γ_D and I are their counterparts for deuteron. When the condition of extreme narrowing is not obtained, the formulation for this ratio is more complicated, depending on the angular resonance frequencies, ω_0^C, ω_0^H, and ω_0^D, of all three nuclei in question.[4] Some representative values of this ratio (at 21.1-kG magnetic field strength) are listed in Table I. The considerably longer relaxation time associated with a deuterated carbon can be exploited in the following way. If there are two overlapping protonated ^{13}C signals of comparable relaxation times, by completely deuterating one of the carbons one can effectively saturate the deuterated carbon signal (signal A) without affecting the intensity of the protonated carbon signal (signal B) using an appropriate pulse repetition time. This technique may be used for determining the ^{13}C T_1 corresponding to signal B in the presence of overlapping signal A, within experimental error, by ignoring the contribution of the latter to the intensity of the former. We have demonstrated the efficacy of this procedure by measuring T_1 on the methine carbon of polystyrene at a certain fixed concentration and temperature in $CDCl_3$ and by measuring it in the presence of 50% admixture of polystyrene deuterated in the methine position synthesized in our laboratory at the same overall polymer concentration, same solvent, and same temperature. The T_1 results were the same within experimental error. The undecoupled spectrum resulted in the splitting of the methine carbon signal, thereby revealing the greatly reduced signal corresponding to the deuterated methine carbon.

By employing anionic polymerization procedures, one may react an ionic initiator with a monomer that is either deuterium labeled or not, yielding a "living" polymer whose length will depend on the concentration of reagents; then a monomer may be introduced with the opposite labeling (deuterated if the original was not and vice versa), thus yielding an isotopomeric triblock copolymer that is deuterated according to selective portions (e.g., terminal or central) of various lengths. This procedure coupled with the technique described above allows one to study ^{13}C relaxation as a function of position along the polymer chain. We have applied this procedure to polystyrene (PS) as described below.

Experimental Section

Anionic polymerization techniques[5,6] were employed to prepare the isotopomeric triblock copolymers selectively deuterated in the methine position, with sodium biphenyl in tetrahydrofuran as the initiator and solvent. High molecular weight PS and high molecular weight randomly deuterated PS were prepared under identical conditions using radical polymerization with benzoyl peroxide in toluene. These polymers and a set of PS molecular weight standards, purchased from Polysciences, Inc., were made into 10% (w/v) solutions in $CDCl_3$. The relaxation time measurements were performed on a Jeol FX 90 Q NMR spectrometer operating at 22.5 MHz in the FT mode. The 180°–τ–90° inversion–recovery pulse sequence was employed, using at least 10 different τ values with ca. 1000 scans each. At least three different determinations were made on each sample and at least five determinations on each PS standard. The estimated error is ±3%. All the reported results were obtained at 30 ± 1 °C. The T_1 values of the quaternary and the methylene carbons in these atactic polymers could not be measured with sufficient accuracy to contribute to the study and are not reported.

Table II
^{13}C T_1 of Aromatic and Methine Carbons in PS Standards at 30 °C in ms

mol wt	ortho, meta	para	methine	ρ
4 000	181	165	136	0.82
17 500	145	130	110	0.85
35 000	139	125	109	0.87
100 000	137	119	106	0.89

Table III
^{13}C T_1 of Aromatic and Methine Carbons in High Molecular Weight PS Polymers I and II at 30 °C in ms

type (PS)	ortho, meta	para	methine	ρ
I	134	112	104	0.93
II	132	114	136	1.19

Results and Discussion

Table II summarizes the results of T_1 measurements carried out on the PS standards of various molecular weights. Listed in the first column of this table are the average molecular weights of PS standards with $M_w/M_n \leq 1.06$. The second column lists the T_1 corresponding to unresolved resonances of ortho- and meta-aromatic carbons. The third column lists the T_1 of the para-aromatic carbon and the fourth column that of the methine carbon. Finally, the last column lists the ratio, ρ, of the T_1 of the methine carbon to the T_1 of the para carbon. These results have the following features. All T_1 values in question show a significant decrease with increasing molecular weight up to molecular weights of 20 000, after which they become relatively constant. The T_1's of the methine carbons do not decrease exactly by the same absolute magnitudes as those of the aromatic carbons. However, the ratios ρ increase with molecular weight only over a rather small range of about 0.8–0.9.

Listed in Table III are the relaxation data obtained on two high molecular weight PS polymers, I and II (T_g = 383 K) synthesized in this laboratory. Polymer I is a PS synthesized with about 30% random deuteration in the methine position. Polymer II is an isotopomeric triblock copolymer synthesized by anionic polymerization with deuteration in the methine position of about 30% of the central portion of the chain, so that the T_1 of the methine carbons corresponds to 70% of all carbons and is confined to the terminal portions of the chain. Whereas the ρ value for polymer I is within experimental error of that observed for an undeuterated high molecular weight polymer, the ρ value of 1.19 for polymer II is significantly higher and implies that the average T_1 values of the carbons in the terminal blocks of the chain are longer than the average for the molecule. Furthermore, because of the high average molecular weight of polymer II, more than just a few terminal carbon atoms must have T_1 greater than the average to account for this significant increase in ρ.

In two separate experiments similar isotopomeric triblock PS polymers III and IV were prepared with considerably lower average molecular weight as was indicated by the T_1 measurements of the aromatic carbons. Both III and IV were deuterated in the central portion in the methine position to the extent of about 65% and 60%, respectively. The T_1 data are summarized in Table IV. In both instances ρ is significantly higher than the value for an undeuterated polymer of comparable molecular

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Table IV
^{13}C T_1 of Aromatic and Methine Carbons in Low Molecular Weight PS Polymers III and IV at 30 °C in ms

type (PS)	ortho, meta	para	methine	ρ
III	152	131	133	1.01
IV	143	128	124	0.97

weight, i.e., below or close to 0.85.

The temperature studies on all polymers reported in this work showed that T_1 increased with temperature, implying that higher T_1 values are associated with lower effective correlation times. This fact and the higher ρ values associated with the undeuterated terminal portions in both the low and high molecular weight selectively deuterated polymers are consistent with a monotonic decrease in τ_{eff} from the central to the terminal portions. This monotonic decrease cannot be limited to a few terminal units since the higher ρ values are associated with relatively long terminal portions. It is rather surprising that the terminal segments of the high molecular weight PS-II polymer have higher ρ and T_1 values than the terminal segments of the lower molecular weight polymers of Table IV. A similar fact is revealed by comparing Tables II and III, which show that polymer chains in the lower molecular weight range (17 500–35 000) have shorter T_1 values than terminal chains that are of comparable length but are contained in the high molecular weight PS-II polymer. Since the average methine T_1 of the high molecular weight PS-I polymer remains near the asymptotic value (about 106 ms), the middle segments must have shorter T_1 that balance the increased T_1 of the terminal segments.

It would first appear from the T_1 data that the terminal segments of the higher molecular weight polymers have greater flexibility than in the low molecular weight polymers. However, another and perhaps more reasonable explanation is that the orientational degrees of freedom of the interior segments of the high molecular weight polymer contribute to the larger T_1 of the terminal segments. The shorter T_1 of the interior segments would still have to be explained in terms of the additional constraints in their motion as the molecular weight increases.

A more definitive interpretation would require measurements of T_1 at more positions along the chain and analysis of the data in terms of a motion model[7-9] that accounts for the internal degrees of freedom. Such studies are being initiated in our laboratory using fractions of selectively deuterated polymers with very narrow molecular weight distributions and making accurate determination of the extent of deuteration in each molecular weight fraction.

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Registry No. Polystyrene, 9003-53-6.

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Effect of Bead Movement Rules on the Relaxation of Cubic Lattice Models of Polymer Chains

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ABSTRACT: Monte Carlo computer simulations of the relaxation of cubic lattice models of polymer chains have been performed in order to study the effect of the two-bead crankshaft motion on the terminal relaxation time. Chains of lengths 11–59 bonds were studied, with and without excluded volume. In the absence of excluded volume the longest relaxation time of the chain approximately obeys the Rouse scaling law, $\tau \sim N^2$. In the presence of excluded volume the scaling exponent is increased slightly to 2.13. These results differ from those obtained previously by Kranbuehl and Verdier. Reasons for this difference are discussed.

Introduction

The study of the relaxation of cubic lattice models of polymer chains using Monte Carlo techniques was initiated by Verdier and Stockmayer.[1] The technique has been developed and applied to new problems primarily by Verdier and Verdier and Kranbuehl.[2] Probably the most interesting and important aspect of these conceptually and computationally simple simulations is their ability to explore the effects of excluded volume on the relaxation of polymer chains. Since the chain is modeled as a random walk on a cubic lattice, the excluded volume effect is easily incorporated by studying the self-avoiding walk. Indeed this has been a major focus of the work of Verdier and Verdier and Kranbuehl.[3] The original results of these workers showed a dramatic and surprising effect of excluded volume on the terminal relaxation time of the chain.

The best way to summarize the results of the Monte Carlo studies of lattice models with and without excluded volume is through scaling relations.[4] In the absence of excluded volume the longest relaxation time of the chain (τ) varies with chain length as predicted by the Rouse model;[5] that is

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