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On the [^{13}C]T$_1\rho$ behavior of some elastomers

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Summary

The temperature dependencies of the [^{13}C]T$_1\rho$ NMR relaxation behavior of poly(butyl acrylate), *cis*-polyisoprene, polychloroprene, and *cis*-polybutadiene have been studied. The temperature dependence of the relaxation time for each elastomer follows the WLF equation.

Introduction

The relationship derived by Williams, Landel, and Ferry (1) (i.e., the WLF equation) gives a ratio of the relaxation time at a given temperature, T, to that at the glass transition temperature, T_g, for a polymer in the range of T_g to $T_g + 100$:

$$\ln(\nu_1/\nu_0) = C_1(T - T_g)/ [C_2 + (T - T_g)]$$

where ν_1 is the frequency of motion at any particular temperature and ν_0 is the frequency at T_g. The free volume at T_g arises as a fundamental constant for polymers. The molecular motions in polymers and linear hydrocarbons are driven by the availability of free volume (1). C_1 and C_2 were initially considered to be universal constants with values of 17.44, and 51.6, respectively. Subsequent work demonstrated that they vary from polymer to polymer (2).

High resolution ^{13}C NMR has been used for studying the structure, miscibility, intermolecular interactions, and morphology of both compatible and two phase polymer blends (3). The miscibility of the interphase regions of multiphase polymer blends has been investigated in recent years by the measurement of spin-lattice relaxation (T_1), spin-spin interactions (T_2), and spin-lattice relaxation in the rotating frame ($T_1\rho$) using solid-state Nuclear Magnetic Resonance (NMR) spectroscopy (4,5). The [H]T$_1\rho$ values are primarily sensitive to molecular motions in the 10-50 kHz region; many of the molecular motions which occur in polymers lie within the mid-kilohertz range (6). Thus, [H]T$_1\rho$ measurements are useful in probing polymer microstructure and chain dynamics (7).

Sometimes spin diffusion (exchange of spin energy between neighboring nuclei) complicates [H]T$_1\rho$ measurements leading to loss of details on the molecular motions. This can be overcome by measuring [^{13}C]T$_1\rho$. As the ^{13}C atoms are less abundant (1.1 %) than protons, the probability of finding two ^{13}C atoms close enough to each other to be involved in an energy transfer is very small. Thus, the phenomenon of spin diffusion, which causes a transfer of energy from one atom to another can be effectively avoided by the measurement of [^{13}C]T$_1\rho$. Molecular motions are expected to contribute to the [^{13}C]T$_1\rho$ relaxation. Also, molecular motions are responsible for the dynamic properties of polymers and affect their behavior. The temperature dependence of [^{13}C]T$_1\rho$ in the region of T_g to T_g + 100°C was studied for some elastomers. Because the molecular motions in

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polymers are driven by the availability of free volume (1), it is expected the [^{13}C]T$_1\rho$ relaxations of the backbone carbon atoms should also depend on the free volume available, which in turn depends on the temperature.

Dekmezian et al. (8) have studied the average correlation time for segmental motion versus temperature behavior for a set of amorphous polymers, semi-crystalline polymers, and a series of ethylene-vinyl acetate copolymers. They found that the correlation time depends on the temperature according to the WLF equation (1). The C_1 and C_2 parameters were found to be in the range of 11 - 17 and 40 - 70, respectively, depending on the nature of the polymer. Laupretre et al. (9), and Spyros et al.(10) have studied the correlation times obtained from the ^{13}C relaxation data of several amorphous and semi-crystalline polymers and have found that these data also obey the WLF equation. To our knowledge the temperature dependencies of [^{13}C]T$_1\rho$ of elastomers have not been correlated with the WLF constants. In this report the temperature behaviors of [^{13}C]T$_1\rho$ for a set of elastomers are presented.

Experimental Methods

Materials: Poly(butyl acrylate) was synthesized using emulsion polymerization techniques. *Cis*-polyisoprene, polychloroprene, and *cis*-polybutadiene were obtained from Aldrich and used as received.

NMR Measurement: The solid-state ^{13}C NMR spectra were obtained using cross-polarization, magic-angle sample spinning, and dipolar-decoupling (CP/MASS/DD) (3) on a General Electric GN 300 spectrometer operating at a carbon frequency of 75.47 MHZ. A carbon magnetization is first established by using a cross-polarization procedure. After turning off the proton field, the carbon spins are held in the rotating field for a variable period of time. This was followed by the sampling of carbon magnetization while simultaneously decoupling the protons (3). Sixteen different spin lock times were used for the determination of each relaxation time. The [^{13}C]T$_1\rho$ of the backbone methylene carbons of the elastomers were monitored. The [^{13}C]T$_1\rho$ values are calculated from the negative inverse of the slope of graphs of ln(magnetization) versus the variable length spin lock time. The Hartman-Hahn condition was set with an adamantane sample spinning at a speed of 2500 ± 100 Hz, by adjusting the power level for the protons and carbons to maximize the signal for adamantane. A magnetic field strength of 50 kHz was used for the matched spin lock cross polarization transfer. Approximately 200 μL of the samples were spun at a speed of 2400 ± 100 Hz at the magic angle; 128 scans were required for each [^{13}C]T$_1\rho$ relaxation time. At least 1024 data points were acquired for each experiment. The acquisition time for each spectrum was 20.48 ms; the data were zero-filled once before processing.

The sample size was chosen to minimize radio-frequency field inhomogeneities. Cooling of the sample for the variable temperature measurements was achieved by passing the dry spinning air through a heat exchanger coil immersed in liquid nitrogen. Fine tuning of the temperature was achieved by using the heater provided with the 7 mm Doty Scientific, Inc., NMR probe. Temperatures above room temperature were achieved by using the heater alone. Temperatures in the range of 170 K - 370 K could be achieved. The temperature near the sample was measured using a thermocouple gauge; approximately 15 minutes were allowed for the sample to come into thermal equilibrium.

Results and discussion

The WLF equation was fit to the $[^{13}C]T_1\rho$ relaxations of poly(butyl acrylate), *cis*-polyisoprene, polychloroprene, and *cis*-polybutadiene with a linear least squares procedure. The glass transition temperature of these polymers fall in the range of -85°C to -55°C. For each polymer, $(T - T_g)$ is plotted versus $-(T - T_g)/\ln(a_T)$ (where $a_T = \nu_1/\nu_0$) as shown in Figure 1. The C_1 and C_2 values are obtained from the slope and intercept of these plots, respectively. The $[^{13}C]T_1\rho$ relaxation times of the backbone carbons obey the WLF equation over the temperature range of T_g to $T_g + 100$. The R^2 values are in the range of 0.88 - 0.92 for each fit. The error bars for the C_1 and C_2 values are estimated to be in the range of ± 2, and ± 4, respectively. The large values of $[^{13}C]T_1\rho$ are difficult to measure reliably at higher temperatures and account for the large errors in the WLF constants derived from the NMR data. The experimentally measured values of $[^{13}C]T_1\rho$ agree well with the values of $[^{13}C]T_1\rho$ obtained from the WLF equation (Figure 1). Table 1 presents a sample set of raw data obtained for polybutadiene; Table 2 summarizes the values of C_1 and C_2 obtained from the literature and from this study.

Table 1: The Variation of $[^{13}C]T_1\rho$ as a Function of Temperature For *cis*-Polybutadiene

Temperature (K)	**$[^{13}C]T_1\rho$ (ms)**
188	0.012
208	4.00
228	133
248	471
258	790
270	2.0×10^3

The results obtained from the NMR study are close to those reported in the literature. It can be concluded that the values obtained from the $[^{13}C]T_1\rho$ measurements are comparable to those values obtained from mechanical relaxation measurements in detecting molecular motions.

Conclusions

Thus, it was found that the temperature dependence of $[^{13}C]T_1\rho$ of some elastomers follows the WLF equation. The results indicate that $[^{13}C]T_1\rho$ relaxation measurements are useful in detecting molecular motions.

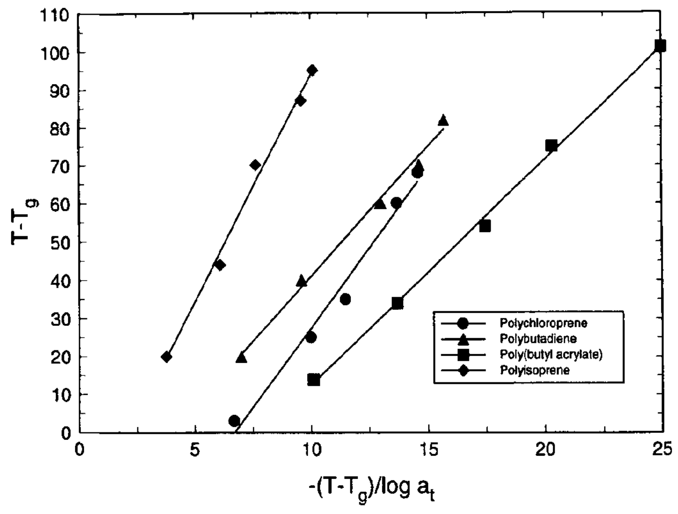

Figure 1: T - T_g versus -(T - T_g)/log(a_t) for polychloroprene, cis-polybutadiene, poly(butyl acrylate), and polyisoprene. The negative of the intercept gives C_2 while the slope yields C_1. The reasonable linear least squares fits confirm that the [^{13}C]$T_1\rho$ values follow the WLF equation.

Table 2: The WLF Constants Reported in the Literature and Experimentally Measured Using [^{13}C]$T_1\rho$ Relaxation Measurements

Sample	Literature Values [+*]		Values from ^{13}C NMR Relaxation measurements	
	C_1	C_2	C_1	C_2
Polychloroprene	13.1	58.6	10 ± 2	52 ± 4
cis-Polybutadiene	11.3	60.0	10 ± 2	58 ± 4
Poly(butyl acrylate)	13.8	53.5	16 ± 2	49 ± 4
cis-Polyisoprene	12.9	56.3	14 ± 2	54 ± 4

[*] Average values for polymers are C_1 = 17.44 and C_2 = 51.6

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