Pressure Dependence of Molecular Motion in Some Elastomers

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ABSTRACT: Molecular motion has been investigated in natural rubber, polyisobutylene, poly-*cis*-butadiene, and an ethylene–propylene copolymer, using methods of pulsed nuclear magnetic resonance, over a pressure range of 1–680 atm and at temperatures from −125 to +100°. Enthalpies and volumes of activation have been determined and are examined in terms of simple models of thermally activated transitions. The pressure dependence of nmr relaxation in these elastomers is compared with information from the literature on viscoelasticity and dielectric relaxation.

Molecular motion in polymers has been studied by a variety of techniques, but there have been relatively few studies in which the pressure has been a variable. Nuclear magnetic resonance (nmr) spectroscopy has shown itself to be useful for studying relaxation processes of polymers in certain portions of the frequency spectrum. With the notable exception of Nolle's study of polyisobutylene,[1] these measurements have been carried out at atmospheric pressure. We report here some studies of the effects of pressure and temperature on molecular motion in some elastomers, as observed by measurement of the proton magnetic relaxation in these substances over a pressure range of 1–680 atm and at temperatures from −125 to +100°. The elastomers studied were natural rubber, polybutadiene, polyisobutylene, and an ethylene–propylene copolymer.

Experimental Section

Measurements were made of the proton spin-lattice relaxation time, T_1, at a radiofrequency of 30 MHz. The pulsed nmr apparatus has been described briefly elsewhere.[2] The pulses were 1–3 μsec in length and the recovery time of the receiving circuit following a pulse was about 15 μsec. The time T_1 was found by the null method of Carr and Purcell.[3] The pressure equipment has also been described.[4] In this work the temperature range was extended well beyond that used previously. For this reason, we used dibromotetrafluoroethane as the hydraulic fluid, rather than carbon disulfide. The experiments were restricted, for convenience, to quite low pressures; the upper limit was 680 atm (10,000 psi).

Some measurements of the coefficients of thermal expansion and volume compressibility were also carried out on these compounds. The apparatus was made available through the courtesy of our colleague, Dr. S. Matsuoka. The features of this apparatus have been described elsewhere.[5] The measurements involved pressures up to 7000 atm and temperatures over the range 25–120°.

The sample of Hevea rubber consisted of gum crepe stock. The polybutadiene was provided through the courtesy of Dr. Gerald Kraus, Phillips Petroleum Co., and contained ~95% *cis*-1,4 sequences. The polyisobutylene was obtained through the cooperation of Dr. Donald Beeson, Esso Research and Engineering Co., and had a molecular weight of about 1.3 × 10⁶. The ethylene–propylene elastomer was a 1:1 copolymer, with highly random monomer sequences, and was received through the courtesy of Dr. Emmanuel G. Kontos, Uniroyal Research Center.

T_1 **Measurements.** A representative set of T_1–pressure data, taken on polybutadiene, is shown in Figure 1. Similar

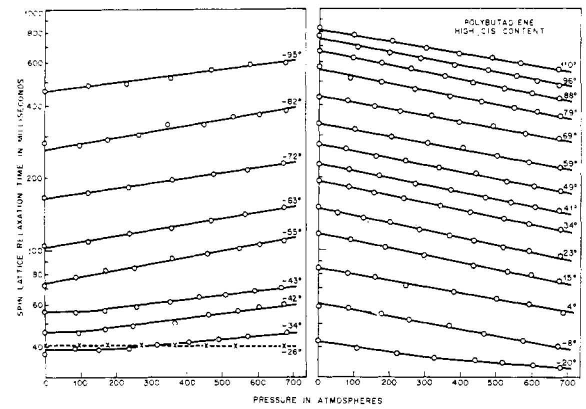

Figure 1. Pressure variation of the nmr spin–lattice relaxation time in poly-*cis*-butadiene at various temperatures.

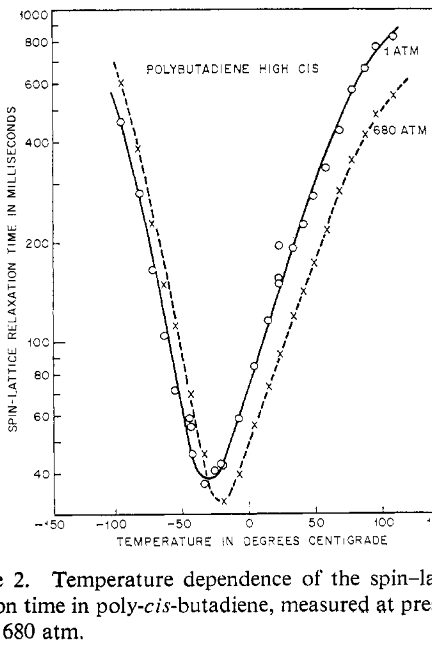

Figure 2. Temperature dependence of the spin–lattice relaxation time in poly-*cis*-butadiene, measured at pressures of 1 and 680 atm.

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[1] A. W. Nolle and J. J. Billings, *J. Chem. Phys.*, **30**, 84 (1959).

[2] W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 10 (1964).

[3] H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

[4] J. E. Anderson and W. P. Slichter, *J. Chem. Phys.*, **44**, 1797 (1966).

[5] S. Matsuoka and B. Maxwell, *J. Polym. Sci.*, **32**, 131 1958).

behavior was found with the other elastomers. In these semilogarithmic plots of T_1 *vs.* pressure, it is seen that the isotherms are linear at temperatures removed from the temperature of the T_1 minimum. As is shown in Figure 2, a pressure change from 1 to 680 atm causes a pronounced shift in the T_1–temperature curve.

Similarly, Figure 3 shows the temperature dependence of T_1 in natural rubber at two pressures. The low-temperature minimum is ascribed[6,7] to the rotation of the substituent methyl groups about the C–C bond. This motion seems insensitive to pressure. This result is reasonable, for one would not expect the constraints to motion of the pendant CH_3 group to be appreciably changed by the modest pressures used here. Similar behavior has been observed for methyl rotation in solid *n*-alkanes.[4] The high-temperature minimum arises from the reorientations of main-chain segments.[6,7] This relaxation is produced by the same molecular processes that develop at the glass temperature, T_g, as the substance is warmed from the glassy state. Here, however, the motions are relatively high in frequency, $\sim$30 MHz, and the temperature of the relaxation is correspondingly higher than T_g.[8] This process is clearly affected by the application of pressure, as would be expected. The displacement of the T_1–temperature curve by pressure is smaller on the low-temperature side of the T_1 minimum than on the high-temperature side. As with polybutadiene, the isotherms in graphs of log T_1 *vs.* pressure are linear at temperatures removed from the T_1 minimum.

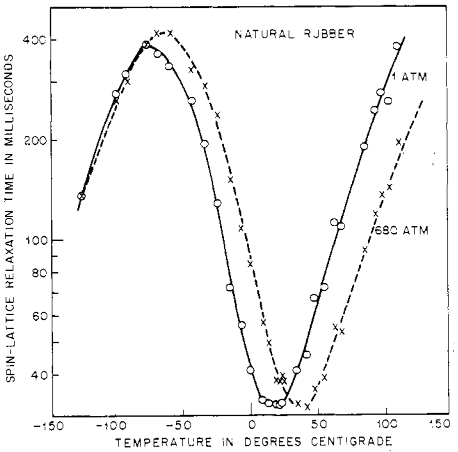

Figure 3. Temperature dependence of the spin–lattice relaxation time in natural rubber, measured at pressures of 1 and 680 atm.

The behavior of the ethylene–propylene copolymer, Figure 4, is qualitatively similar to that of natural rubber. In polyisobutylene, Figure 5, the application of pressure is seen to influence not only the main-chain relaxation but also the relaxation at lower temperature, ascribed to rotation of the methyl groups. This observation is in keeping with earlier conclusions[7,9] that there is effectively an interlocking of the closely spaced CH_3 groups in this polymer which causes the T_1 minimum to occur only at relatively high temperature. This steric hindrance is relieved by the onset of main-chain motion, and since this latter motion is constrained by external pressure, the methyl rotation in polyisobutylene is found to be sensitive to pressure.

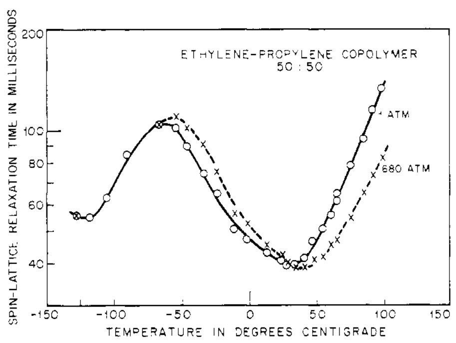

Figure 4. Temperature dependence of the spin–lattice relaxation time in an ethylene–propylene 1:1 copolymer, measured at pressures of 1 and 680 atm

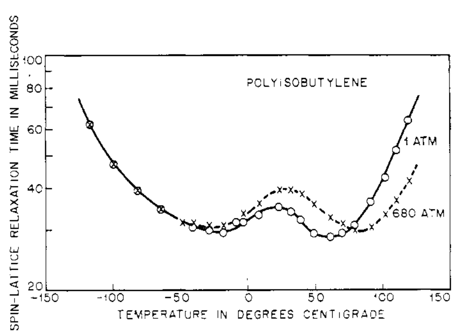

Figure 5. Temperature dependence of the spin–lattice relaxation time in polyisobutylene, measured at pressures of 1 and 680 atm.

Pressure Dependence of the Glass Temperature. Considerable interest has surrounded the transition between glassy and rubbery behavior in polymers. As McCall has shown,[8] the characteristic relaxation processes for a given polymer are described by essentially the same temperature coefficient for all experimental methods. The pressure dependence of the glass temperature, dT_g/dP, has been studied much less. However, O'Reilly[10] has tabulated this coefficient for a number of materials measured by several methods. He has also shown that $dT_g/dP \sim TV\Delta\alpha/\Delta C_P$ for most of the substances reported. Here $\Delta\alpha$ and ΔC_P are, respectively, the discontinuities in thermal expansion and specific heat at the transition. It was also found[10] that $dT_g/dP \sim 0.025°/\text{atm}$, although the values ranged between 0.016 and 0.044°/atm for the substances listed. The significance of these apparent correlations is still unsettled,[11,12] but measurement of the coefficient dT_g/dP is clearly a matter of interest.

Table I lists values of dT_g/dP measured in the present work from the shift in the temperature of the T_1 minimum upon application of hydrostatic pressure. The table also lists values for two of the elastomers from O'Reilly's survey.[10] The coefficient for rubber in the present work is

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(6) H. S. Gutowsky, A. Saika, M. Takeda, and D. E. Woessner, *J. Chem. Phys.*, **27**, 534 (1957).

(7) W. P. Slichter and D. D. Davis, *J. Appl. Phys.*, **35**, 3103 (1964).

(8) D. W. McCall, Polymer Research Group Conference, Moretonhampsted, England, April 1964; Proceedings, Second Materials Research Symposium, National Bureau of Standards, Gaithersburg, Oct 1967.

(9) J. G. Powles and K. Luszcynski, *Proc. Phys. Soc.* (London), **74**, 408 (1959).

(10) J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962), and references contained therein.

(11) M. Goldstein, *J. Chem. Phys.*, **39**, 3369 (1963).

(12) G. Gee, *Polymer*, **7**, 177 (1966).

Table I

Pressure Shift of Glass Temperature

	Pressure shift, deg/atm	
	This work	Ref 10
Rubber	0.029	0.024
Polybutadiene	0.013	
Polyisobutylene	0.035	0.024
E-P copolymer	0.010	

nearly the same as that found in other measurements. The coefficient for polyisobutylene, however, is much greater than in other measurements made at lower temperatures and frequencies. One can only conjecture on these differences. Perhaps the consistency with rubber is fortuitous. On the other hand, the variability with polyisobutylene may be related to the considerable steric hindrance that occurs among the substituent methyl groups[7,9] and may be associated with the sluggishness of segmental motion that is seen[13] in viscoelastic properties of this polymer. This steric hindrance should become progressively less important at the higher temperatures, but conversely it ought to be rather sensitive to external pressure. The coefficient dT_g/dP is seen in Table I to be relatively small for polybutadiene and the ethylene-propylene copolymer. We know of no related experiments to compare with these results.

Relaxation Time as a Function of *T* and *P*. Williams[14] has examined the dielectric relaxation of polymers in this transition region in terms of the variables frequency, temperature, pressure, and volume. He has discussed the Arrhenius model, the transition state theory, and the free volume model in terms of these variables. The frequency range of the nmr experiments, however, is much narrower than in dielectric or viscoelastic measurements. We therefore limit ourselves to a phenomenological description in terms of the simple model of an activated process, in which the motion is characterized by a single correlation time, τ_c. The correlation time is represented in the usual way by eq 1,

$$\tau_c = \tau_c{}^0 \exp(\Delta F^*/RT) \tag{1}$$

where ΔF^* is the free energy of activation. Since the spin-lattice relaxation process is governed by the molecular motions, T_1 should depend on τ_c. Indeed, according to elementary theory for simple systems,[15] eq 2a and 2b hold

$$T_1 = C_1\tau_c \tag{2a}$$

for $\omega_0\tau_c \gg 1$ (slow motion) and

$$T_1 = C_2/\tau_c \tag{2b}$$

for $\omega_0\tau_c \ll 1$ (rapid motion). Here ω_0 is the nmr frequency, and C_1, C_2 are factors that depend on the internuclear distances and on certain constants. C_1 and C_2 do not involve temperature and pressure explicitly but may depend on these parameters implicitly through variation in the internuclear distances. With the low pressures used in these studies, one would not expect change in bond distances to be a factor in the pressure dependence of T_1. Rather, the pressure effects should mainly reflect changes in the constraints to motion. If we assume that C_1, C_2 and also the preexponential term $\tau_c{}^0$ are independent of temperature and pressure over the limited range of these parameters in this work, we can define ΔH^*, the enthalpy of activation (eq 3), and ΔE^*, the internal energy of activation (eq 4).

$$\Delta H^* = \pm R\left[\frac{\partial \ln T_1}{\partial(1/T)}\right]_P \tag{3}$$

$$\Delta E^* = \pm R\left[\frac{\partial \ln T_1}{\partial(1/T)}\right]_V \tag{4}$$

Here, the plus and minus signs depend on whether the measurement is made, respectively, in the limit of slow or rapid molecular motion.

The activation energy at constant volume, ΔE^*, is important because it is a measure of constraints to motion other than those involving lattice expansion. However, it is a difficult quantity to measure directly, since the condition of constant volume is hard to achieve when the temperature is being varied. The relation between ΔH^* and ΔV^* (eq 5) can be obtained mathematically.

$$\Delta H^* = \Delta E^* + RT^2\left(\frac{\partial \ln T_1}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V \tag{5}$$

The factor $RT(\partial \ln T_1/\partial P)_T$ has the dimensions of a volume. Through eq 1 and 2, it is the activation volume, ΔV^*, for the relaxation. The factor $T(\partial P/\partial T)_V$ is the thermal pressure, P_t. Therefore, eq 5 may be written

$$\Delta H^* = \Delta E^* + P_t\Delta V^* \tag{6}$$

From the definitions of the thermal expansion coefficient, $\alpha = (1/V)(\partial V/\partial T)_P$, and the isothermal compressibility, $\beta = -(1/V)(\partial V/\partial P)_T$, it follows that $P_t = T(\alpha/\beta)$.

Table II lists values of ΔH^*, ΔV^*, and ΔE^* for the four elastomers studied, together with the data on α and β used to calculate the values of P_t for eq 6. Values of α and β for most of these elastomers have not been reported previously. The thermal expansion and compressibility of rubber have been measured with high precision by Wood and Martin.[16] Our value of α for rubber at room temperature compares quite well with theirs (6.5×10^{-4} deg^{-1}), but our value of β is about 13% smaller than that found by Wood and Martin. The apparatus in our experiments was not designed to measure compressibilities, and therefore this disparity is not surprising. Presumably, the values of β for the other three elastomers are too small by a fraction comparable to that found with rubber. The thermal pressure has been measured directly for a natural rubber vulcanizate[17] and for a low molecular weight polyisobutylene.[18] The values given in Table II appear to be about 20% higher than those found by direct measurement, but we use the present results for the sake of internal consistency.

ΔV^* was found to depend markedly on temperature below the temperature of the T_1 minimum in each of the four elastomers studied. For example, the ΔV^* values for natural rubber ranged from zero to about 20 cm^3. With polybutadiene, ΔV^* increases from about 10 to about 20 cm^3 as the temperature is raised from -50 to $+50°$. It is not at all certain whether ΔV^* approaches a nearly constant value of

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(14) G. Williams, *Trans. Faraday Soc.*, **60**, 1548 (1964).

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(16) L. A. Wood and G. M. Martin, *J. Res. Nat. Bur. Stand.*, *A*, **68**, 259 (1964).

(17) G. Allen, G. Gee, D. Mangaraj, S. Sims, and G. J. Wilson, *Polymer*, **1**, 467 (1960).

(18) G. Allen, G. Gee, H. A. Lanceley, and D. Mangaraj, *J. Polym. Sci.*, **34**, 349 (1959).

TABLE II

THERMODYNAMIC DATA[a] AND ACTIVATION PARAMETERS

	α, deg^{-1} × 10^4	β, atm^{-1} × 10^5	P_t, cal cm^3	ΔH^*, kcal mol	ΔV^*, cm^3 mol	ΔE^*, kcal mol
Rubber	6.7	4.5	108	6.8	30	3.6
Polybutadiene	5.7	3.6	115	4.8	21	2.4
Polyisobutylene	5.2	3.7	100	6.0	20	4.0
E–P copolymer	6.0	5.4	79	5.9	20	4.3

[a] Measured at 23° (1 atm).

~20 cm^3 above the T_1 minimum, for the temperature span of the measurements was rather narrow and the scatter of the calculated values, owing to drifts in temperature during the course of pressure measurements, was something of a problem.

It is of interest to compare the ΔV^* values determined by different relaxation measurements. Nuclear magnetic relaxation is governed largely by the relative motion of neighboring magnetic nuclei. In contrast, viscoelastic measurements are sensitive to the motions of larger parts of the macromolecules, or of whole molecules. On the hypothesis that ΔV^* reflects the size of the basic relaxing unit, one might expect there to be differences in the ΔV^* values obtained by these two techniques. It is perhaps not surprising to find that nmr ΔV^* values are smaller than those determined by viscoelastic measurements. Allen, *et al.*,[17] found ΔV^* to decrease from about 100 to about 20 cm^3 with increase in temperature over the interval −10 to 55°. One would ordinarily expect the added volume needed for molecular reorientation to decrease as the lattice expands with increasing temperature, as has indeed been found in these viscoelastic experiments. The opposite trend that appears in our nmr measurements is not understood.

There is little information from other studies to compare with the values of ΔH^* and ΔV^* in Table II. In measurements of the viscous flow in polyisobutylene of very low molecular weight (~440) it was found by Allen and coworkers[18] that $\Delta H^* \cong 13$ kcal/mol at 25°. Powles[19] and Connor[20] have shown that the activation enthalpies yielded by nmr using an analysis that invokes a single correlation time[15] are lower than those given by dielectric measurements. It is of course implicit in comparisons between methods that corresponding motions are responsible for relaxation in each measurement. Such correspondence may not be the case in comparisons between nmr relaxation and viscous flow. Still it is clear that the neglect of a distribution of correlation times in nmr causes the values of activation enthalpies to be too small.

From the measured values of ΔH^*, ΔV^*, and P_t, we obtain ΔE^* for each elastomer by use of eq 6. The activation energy at constant volume is seen to be comparable to or greater than the $P_t\Delta V^*$ term in the enthalpy of activation. It would appear that lattice expansion has a relatively minor effect on nuclear relaxation in these polymeric systems. This situation differs from the behavior of some monomeric organic compounds, such as camphor and benzene, capable of molecular reorientation in the solid:[4] in them the lattice expansion term is a relatively large constituent of ΔH^*. Presumably the importance of the ΔE^* term for the elastomers reflects constraints imposed by the polymeric character of the molecules.

Acknowledgment. We are grateful to Dr. D. W. McCall for valuable discussions of this research and to Dr. S. Matsuoka for advice on the measurement of compressibility and thermal expansion.

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