

A CONSTRAINT DYNAMICS APPROACH TO RUBBER ELASTICITY

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ABSTRACT

The coupling model of relaxation is applied to crosslinked rubber, with a connection drawn between the dynamics of network junctions and statistical mechanics derived rubber elasticity theory. The suggestion that unifying concepts must underlie dynamical models and thermodynamic theories is shown to be supported by analyses of recent ^{31}P NMR spectroscopy measurements by Shi, Dickinson, MacKnight and Chien¹ on polytetrahydrofuran networks and of our mechanical relaxation data on stretched and unstretched polycarbonate.

INTRODUCTION

The classical approach to rubber elasticity considers only the chain entropy and internal energy contributions to the elastic energy of a network. Any effect of intermolecular interactions is ignored, based on the idea that such interactions are independent of the chain configurations and thus do not modify the stress. The deviation of experimental results from the predictions of classical theory, as exemplified by the strain dependency of the elastic modulus (defined as the ratio $\sigma/(\lambda - \lambda^{-2})$, where σ is the stress and λ the extension ratio), has led to refinements which take into account the effect of interactions among the network chains. In the Flory description,²⁻⁴ the intermolecular interactions reduce the configurations available to the network chains by constraining the network junctions. The reduced effectiveness of these constraints upon deformation gives rise to a strain dependent elastic modulus.

Rubber elasticity theories restrict their concerns to the properties of the network in mechanical equilibrium. However, experimental studies reveal analogies in the behavior of elastomers and polymer melts. These similarities (which necessarily are observed away from mechanical equilibrium since polymer melts exhibit no equilibrium stress) include (i) their large elastic recoil,⁵ (ii) a separability of time and strain dependencies,^{6,7} and (iii) anomalously high hysteresis for reversing strain deformations.⁸⁻¹⁰ Based on these similarities, it has been proposed¹¹ that polymer melts and elastomers exhibit universal mechanical behavior, at least at strains below full extension of the network mesh. Certainly the similarities in the behavior of melts and networks bespeak a connection between elastic and dynamic properties, suggesting that unifying concepts may underlie thermodynamic theories and dynamical models. Indeed, there have been a number of attempts to describe network elasticity through analysis of the network dynamics.¹²⁻¹⁴

By providing information on the dynamics of networks, recent experimental advances reinforce the idea that the microscopic motions and the elastic properties can be usefully interrelated. For example, quasielastic neutron scattering measurements probe the motions of the network crosslinks.^{15,16} In end-linked polydimethylsiloxane it was observed that the junctions diffuse on the same time scale as the network chains, although the spatial extent of the cross-link motion is reduced by intermolecular constraints.¹⁶ Recent molecular dynamics simulations have also added new insight, for example, by demonstrating the existence of local constraints on the network chains at strand lengths less than the molecular weight

necessary for chain entanglements.¹⁷ More recently ³¹P NMR spin-lattice relaxation measurements on a series of polytetrahydrofuran (PTHF) networks with tris(4-isocyanatophenyl) thiophosphate junctions has been carried out,¹ in order to study junction dynamics and their dependencies on crosslink density and diluent concentration. These less conventional techniques (as far as the study of rubber elasticity is concerned) provide information that is consistent with existing rubber elasticity models, yet demonstrates that a void exists. There is a conspicuous absence of theories which specifically describe the junction dynamics. The new experimental findings invite a new approach from a totally dynamic point of view; mechanical equilibrium properties can be considered as only a special or limiting case (albeit a very important one).

The restrictions on the configurations available to the crosslink junctions of a network, arising from its presence in dense phase, govern the mechanical properties of elastomers. These constraints also give rise to intermolecular correlations and cooperativity of the junction motions, and hence can be described by a model of constraints dynamics. The close connection between the elasticity of networks and junction dynamics has, in fact, been illustrated through a comparison of the predictions of a model for constraints dynamics with the constrained junction model of Flory.¹⁸ The model for constraint dynamics (henceforth referred to as the coupling model) was previously shown to successfully describe terminal and segmental relaxations in polymers.¹⁹⁻²² and, more recently, has been used to obtain a connection between molecular structure and viscoelastic properties.²³ In this paper we outline the manner in which the coupling model, previously restricted to relaxation, can be applied to the elastic response of networks. The adequacy of this extension of the model is demonstrated by a comparison of mechanical relaxation of deformed and undeformed polymers and by analysis of recent ³¹P NMR spin-lattice relaxation data.¹

JUNCTION DYNAMICS

The coupling model^{19,24,25} is an attempt to provide a unifying picture of the constraint dynamics of relaxation phenomena in dense phase. Motion of any moiety in a dense packed system is governed by constraints originating from intramolecular and intermolecular interactions with other groups. The essence of the coupling model can be summarized as follows. At short times each moiety relaxes independently, the dynamic constraints not having built up to an extent sufficient to impede the motion. In this short time regime, the relaxation rate τ_0^{-1} can be expressed in terms of transitions of independent moieties. As an example, in certain cases it is appropriate to model τ_0^{-1} as a thermally activated process, *i.e.*,

$$\tau_0^{-1} = \tau_x^{-1} \exp(-E_a/RT), \quad (1)$$

where E_a and τ_x^{-1} can be identified as an energy barrier and attempt frequency, respectively. However, beyond a (temperature insensitive) time scale, t_c , the average relaxation rate of the moieties will be slowed down by the dynamic constraints. From general physical principles,^{19,24,25} it was found that the averaged relaxation rate $W(t)$ assumes the form

$$W(t) = \tau_0^{-1}(t/t_c)^{-n}, \quad t > t_c, \quad (2)$$

where the coupling parameter, n , is a positive number less than unity. As a consequence, the normalized correlation function that describes the relaxation of a macroscopic variable will have the stretched exponential form

$$C_c(t) = \exp-(t/\tau^*)^{1-n}, \quad (3)$$

where

$$\tau^* = [(1 - n)t_c^{-n}\tau_0]^{1-n}. \quad (4)$$

From experimental data on amorphous polymers^{19,20} t_c is deduced as having a magnitude between 10^{-12} and 10^{-11} s. Recent neutron scattering experiments and computer simulations provide direct evidence for the existence of a temperature independent crossover time with this order of magnitude.^{26,27}

Particularly for amorphous polymers, the coupling model has provided numerous predictions which have been experimentally verified.²⁸ In addition, a number of anomalies—otherwise without explanation—have been shown^{21,22} to be a natural consequence of constraint dynamics or intermolecular cooperativity as described by the coupling model. From the demonstrated generality of the model, it is clear that a polymer network is another dense system, the dynamics of which should be well described by the coupling model. Flory modeled the effects of restrictions imposed by neighboring chains on the fluctuations of network junctions, deriving an expression for the modification of the elastic stress for a network of phantom chains. Analogously, the coupling model (when applied to junctions in polymer networks) uses the dynamics of the constraints on junctions to model the slowing down of the motions of the network junctions caused by interactions with neighboring chains, and thus obtain the modification of the correlation function of relaxation of junctions for a network of phantom chains, $C_{ph}(t)$. From the idea that phantom chains are able to freely pass through one another, we expect that $C_{ph}(t)$ has an exponential time dependence, $\exp[-(t/\tau_0)]$, where at temperatures sufficiently above T_g , the time independent junction relaxation time can be well approximated by the Arrhenius temperature dependence of Equation (1), in which E_a is the true microscopic conformational energy barrier to motion of junctions in the phantom network model. Following the general physical principle behind the coupling model, the junction constraints will modify $C_{ph}(t)$ to $C_c(t)$ as given by Equations (2) and (3). The coupling parameter, n , determines both the nonexponentiality of the constraints-modified correlation function, and the correlation time τ^* . In particular the temperature dependence of τ^* is modified to

$$\tau^* = \tau_\infty^* \exp[-E_a^*/RT], \quad (5)$$

where

$$\tau_\infty^* = [(1 - n)t_c^{-n}\tau_\infty]^{1/(1-n)}, \quad (6)$$

and

$$E_a^* = \frac{E_a}{1 - n}. \quad (7)$$

By examining Equations (5) and (6) we see that the degrees of modification of the preexponential and the activation energy, from the phantom network values to the constrained values, are proportional to n . Typically τ_∞ is of the order of 10^{-13} to 10^{-14} s. This, together with $10^{11} < t_c^{-1} < 5 \times 10^{11}$ s⁻¹, indicate that the ratio τ_∞/t_c is much less than unity. Hence, both $\log(\tau_\infty/\tau_\infty^*)$ as well as the ratio E_a^*/E_a increase with n or the severity of constraints, and both quantities vanish at $n = 0$. Higher crosslink densities and crosslink functionality will enhance the strength of the intermolecular constraints and consequently n . On the other hand, with the addition of diluent the junctions become increasingly isolated from the neighboring chain segments, so that the strength of the intermolecular constraints, and hence n , decrease. Such a decrease of n with diluent concentration, as also seen for the local segmental motion²⁹ in amorphous polymers and in the terminal motion of barely entangled polymer solutions,³⁰ has similarly been explained by a reduction of intermolecular constraints and hence of the coupling parameter. In fact, in these cases the experimental data gave direct evidence of the decrease of n with diluent concentration.^{29,30}

COMPARISON WITH EXPERIMENTAL RESULTS

³¹P NMR SPECTROSCOPY

Until recently, little experimental information existed concerning the relaxation dynamics of junctions in a polymer network; however, new insight has been provided by the solid state ³¹P NMR spin-lattice relaxation measurements of Shi, *et al.*¹ on a series of polytetrahydrofuran networks. The relaxation properties of the *tris*(4-isocyanatophenyl) thiophosphate junctions were characterized in networks with strand molecular weights ranging from 250

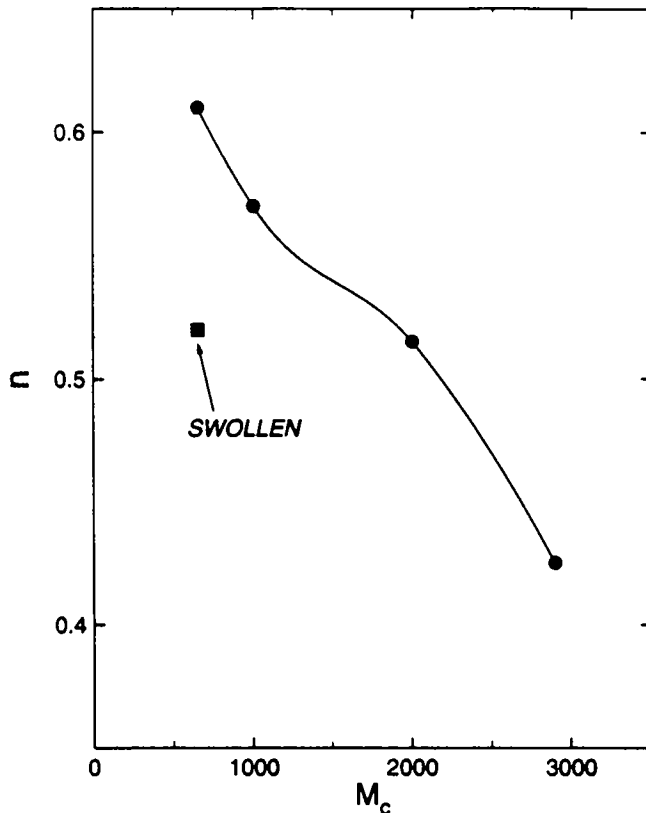


FIG. 1.—The coupling parameter of junction dynamics, n (filled circles), obtained by taking the average of the two values determined by Shi *et al.* from their ^{31}P NMR data using cross and direct polarizations¹ for four polymer networks with different molecular weights between crosslinks, M_c . The filled square is the corresponding coupling parameter obtained in a similar manner for a swollen sample with $M_c = 650$. The smooth curve drawn through the data points is a visual aid only.

to 2900. The dominant mechanism for ^{31}P nuclear spin relaxation was identified to be chemical shift anisotropy. The spin-lattice relaxation times measured over a wide range of temperatures were fitted by spectral density functions derived from the appropriate Fourier transforms of the stretched exponential correlation function given previously (Equation (3)), with τ^* assumed to have the Arrhenius temperature dependence of Equation (5). From these fits Shi *et al.*¹ obtained the coupling parameter n , the apparent preexponential factor τ^* , and the apparent activation energy E_a^* for the networks of different crosslink densities, both neat and diluted. The coupling parameter was found to increase with decreasing molecular weight between crosslinks and, at constant crosslink density, decrease with the addition of diluent. Averages of the values of the coupling parameter determined for each sample from ^{31}P spin-lattice relaxation data by two parallel methods (cross polarization and direct polarization), are plotted in Figure 1. These results are in accord with expectations based on the coupling model.

The apparent activation energy E_a^* is also found to increase significantly with higher crosslink density and, at constant crosslink density, decrease with the addition of diluent. Again, in Figure 2 we have plotted the averages of the E_a^* values determined by the two NMR methods. The product $(1 - n)E_a^*$, obtained by using the experimentally determined values of the coupling parameter (Figure 1) and the apparent activation energy (Figure 2), is for all samples essentially constant, =26.2 kJ/mole. This constancy is predicted by the coupling model, since the product, being the true microscopic energy barrier, E_a , to motion

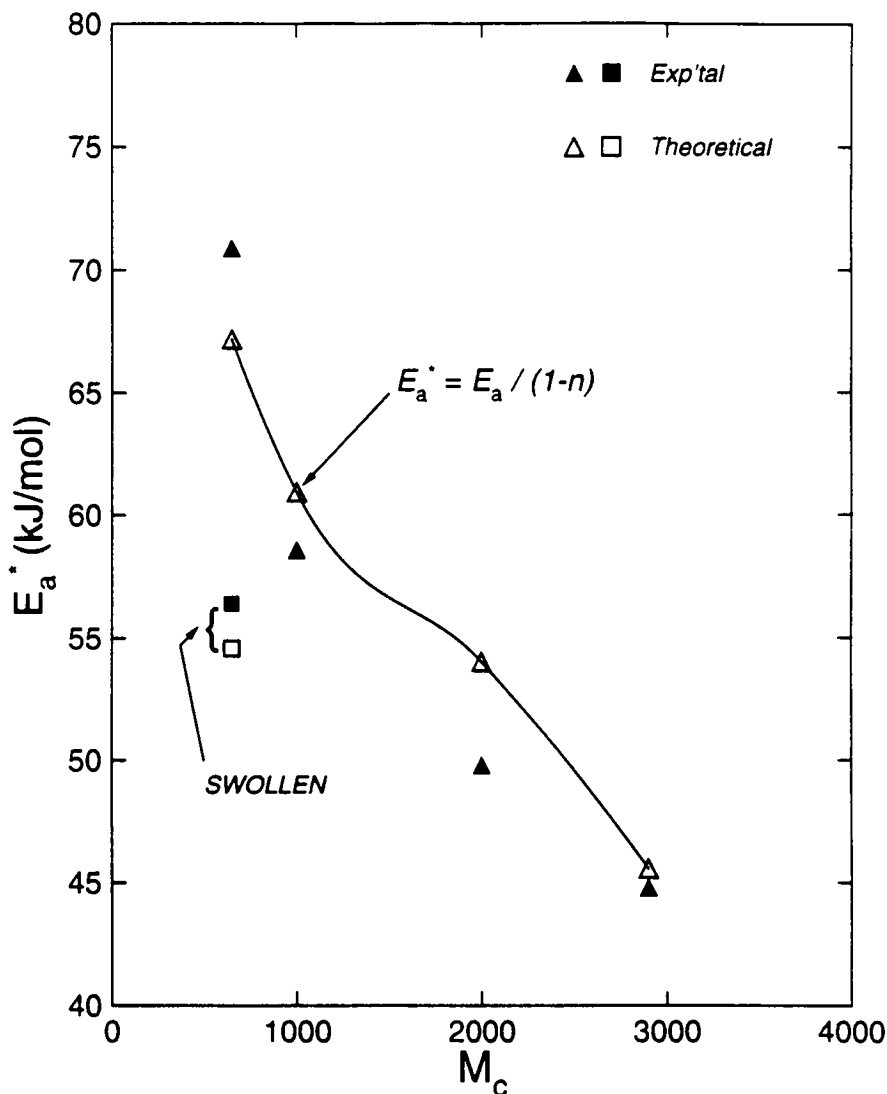


FIG. 2.—Filled triangles represent the apparent activation enthalpy, E_a^* , obtained by averaging the two values determined by Shi *et al.*¹ from their ³¹P NMR data using direct and cross polarizations for four polymer networks. Filled square is E_a^* for the swollen polymer network having $M_c = 650$. The corresponding unfilled symbols are the theoretical predicted values of the coupling model calculated by the equation $E_a^* = E_a / (1 - n)$ using a constant $E_a = 26.2$ kJ/mol and the coupling parameters for the same five network polymers given in Figure 1. A smooth curve has been drawn through the calculated points to guide the eyes.

of junctions in a phantom network, is not dependent on intermolecular interactions or constraints, and hence should be independent of crosslink density and dilution. It is worthwhile to point out that 26.2 kJ/mol is of the correct magnitude for the intramolecular conformational energy barrier of polymers with structure similar to the PTHF network junctions. We have calculated E_a^* by Equation (7) using the experimentally determined coupling parameters (Figure 1) and a constant value of $E_a = 26.2$ kJ/mol. The results (Figure 2) indicate good agreement with the experimental values of E_a^* for five samples of different crosslink densities and diluent concentrations.

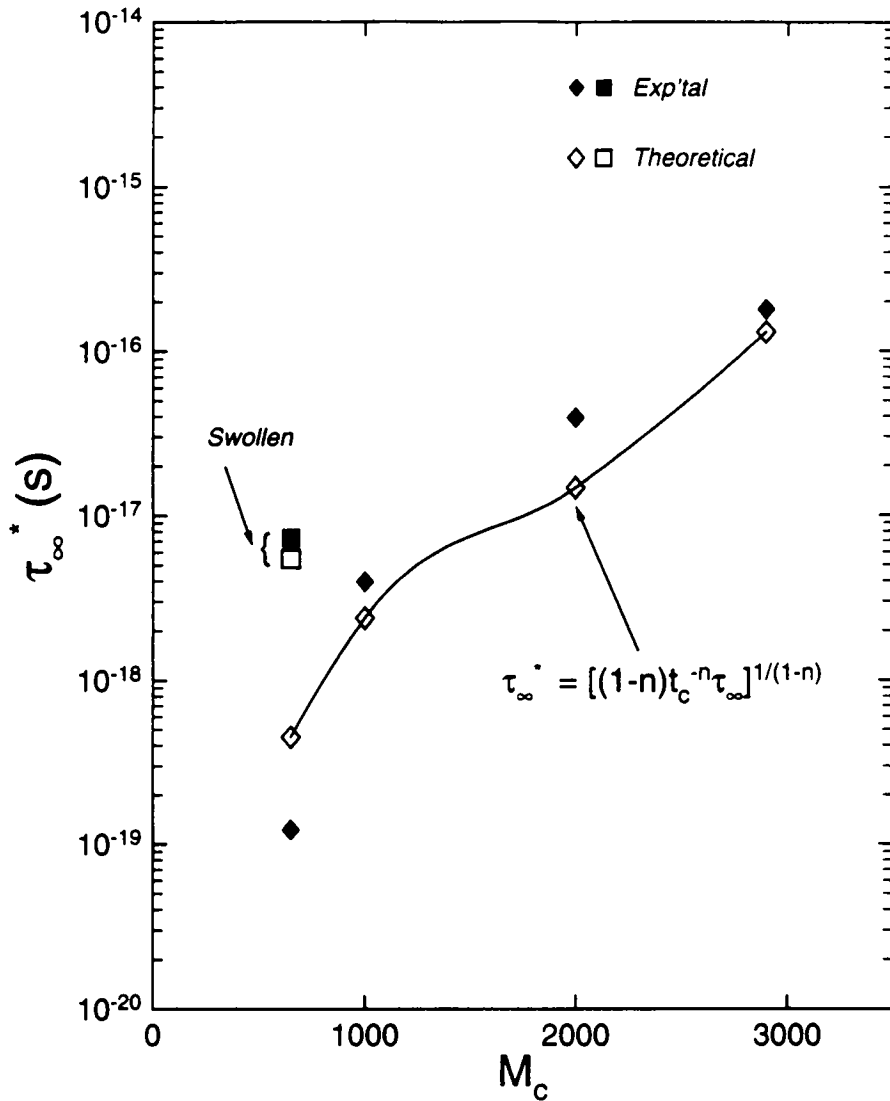


FIG. 3.—Filled diamonds are the apparent pre-exponential, τ_{∞}^* , determined by Shi *et al.* from their experimental data¹ for the four polymer networks by cross and direct polarizations respectively. Filled square is τ_{∞}^* for the swollen polymer network with $M_c = 650$. The corresponding open symbols represent the theoretical predictions of the coupling model calculated by the equation indicated in the figure using constant values of $\tau_{\infty} = 1.5 \times 10^{-14}$ s and $t_c = 4 \times 10^{-12}$ s independent of M_c and diluent concentration. The coupling parameters used here are taken from the data in Figure 1. For clarity a smooth curve is drawn through the calculated points.

The analysis of the ^{31}P NMR data¹ also yielded unphysically short values of the apparent pre-exponential (10^{-16} to 10^{-19} s); moreover, the τ_{∞}^* decrease dramatically with higher crosslink density (see Figure 3). The experimental values for τ_{∞}^* in this Figure are the geometric mean of the values obtained by the two NMR methods. These anomalous properties of τ_{∞}^* can be explained by Equation 6 of the coupling model. We use the experimentally determined coupling parameters, along with a value for the cross-over time, $t_c = 4 \times 10^{-12}$ s, as suggested by neutron scattering experiments and molecular dynamics simulations.^{26,27} The prefactor, τ_{∞} , corresponds to relaxation of junctions of a phantom network. Thus, its value should be independent of intermolecular interaction and hence of crosslink density and diluent con-

centration. Since τ_α has not been determined directly by experiment, it is taken to be an adjustable (albeit constant) parameter.

The calculated τ_α^* , using $\tau_\alpha = 1.5 \times 10^{-14}$ s, are found to be in good agreement with the experimental values obtained for all five samples, as shown in Figure 3. The trends of a rapid decrease of τ_α^* with crosslink density and an increase upon dilution are reproduced. This agreement supports the idea of employing the coupling model to describe the junction dynamics of networks.

EFFECT OF DEFORMATION

In Flory's constrained junction model of elasticity, elongation alleviates the restrictions of junctions from neighboring segments,²⁻⁴ in that the "domain" of the constraints extends along the stretch direction. The elastic behavior of the network thus becomes more phantom-like at higher elongations, in agreement with experiment.^{9,31-33} We anticipate that this alleviation of the constraints on the junctions by elongation will be manifested in the junction dynamics. If this is the case, the coupling model predicts a decrease of n with extension, along with corresponding changes in relaxation time τ^* , apparent activation enthalpy E_a^* , and apparent prefactor τ_α^* (as expected from Equations (5), (7) and (6), respectively).

In lieu of experimental data such as the ³¹P NMR technique¹ on deformed elastomers, we can employ mechanical relaxation measurements. These must be carried out, however, on a deformed polymer in the glassy state in order to avoid relaxation of the deformation. A comparison of the stress relaxation modulus to that obtained on an isotropic sample can reveal changes in the network dynamics associated with elongation.

Stress relaxation measurements were made on an amorphous bisphenol A polycarbonate (BPA-PC) before and after it was elongated to the point of yielding. The drawing was done at a mean strain rate of 10^{-6} s⁻¹ to an extension ratio of 1.70. A specimen was then taken from the necked region for the stress relaxation measurements. The results, obtained at both 0.1% and 0.2% extension, are shown in Figure 4 for both the stretched and the undeformed samples.

The elongated BPA-PC sample exhibited a roughly 45% increase of the short time ($t = 0.1$ s) value of its relaxation modulus. After normalizing by this short time value, it can be seen (Figure 5) that the stress relaxation rate of the elongated polymer is faster than that of the undeformed sample. When the two sets of relaxation data are fitted to the Kohlrausch stretched exponential relaxation function (cf. Equation (3)),

$$E(t) = E_0 \exp\left[-(t/\tau^*)^{1-n}\right], \quad (8)$$

we find for the undeformed sample: $E_0 = 2.43$ GPa, $n = 0.86$ and $\tau^* = 7 \times 10^{10}$ s, and for the stretched specimen: $E_0 = 3.54$ GPa, $n = 0.77$ and $\tau^* = 4 \times 10^7$ s.

It is important to note that the temperature at which the stress relaxation measurement were made are about one hundred degrees below the glass transition temperature. Hence, this stress relaxation cannot be unambiguously related to the local segmental relaxation. The relaxation parameters n and τ^* , determined by fitting $E(t)$ to Equation (8) may not be identified with those of the local segmental motion responsible for the glass transition. The actual coupling parameter of local segmental motion in BPA-PC determined by measurements near T_g is about 0.65,³⁴ which is smaller than the value n_α obtained here. Nevertheless, the stress relaxation data clearly indicate a reduction of the intermolecular dynamic constraints and hence their effects on the retardation of the relaxation—see Equation (2)—after the sample has been subjected to large macroscopic deformation.

The reduction of dynamic constraints corresponds to a decrease in the coupling parameter which in turn (Equation (10)) shifts τ^* to much shorter times. This is equivalent to an increase in the molecular mobility of the deformed sample. These conclusions bear strong similarities to those made by Flory concerning the effect of elongation on the elasticity of networks. Elongation is expected to alleviate the restrictions on the junctions from neighboring segments. The network becomes more phantom-like; the junctions have higher mobility at higher elongations.

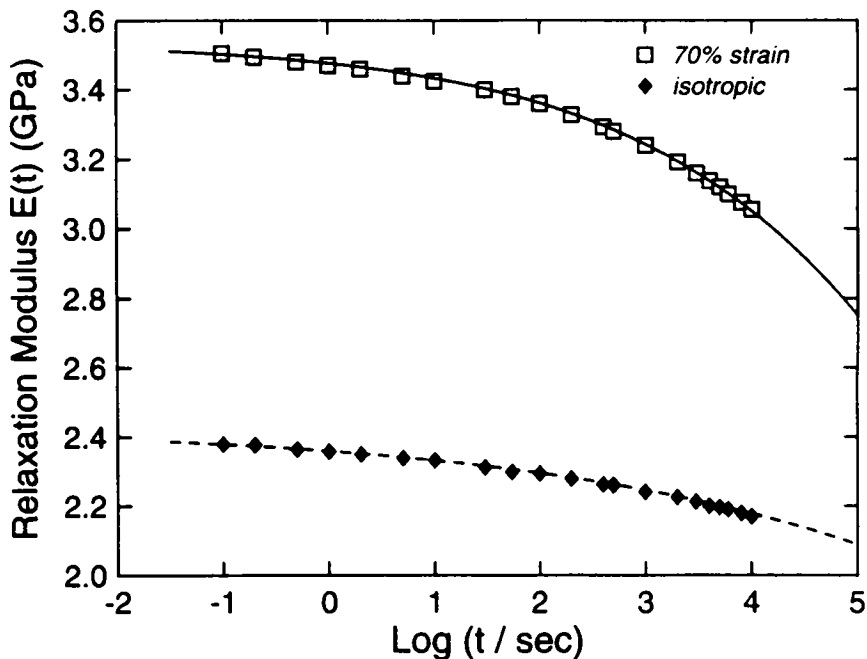


FIG. 4.—Tensile stress relaxation of isotropic and stretched ($\lambda = 1.70$) BPA-PC at 33°C plotted against time. The dashed curve is a fit to the data of the isotropic sample using Equation (8) with $n = 0.86$, $\tau^* = 7 \times 10^{10}$ sec, and $E_0 = 2.43$ GPa. The fit to the elongated sample (solid curve) corresponds to Equation (8) with $n = 0.77$, $\tau^* = 4 \times 10^7$, and $E_0 = 3.54$ GPa.

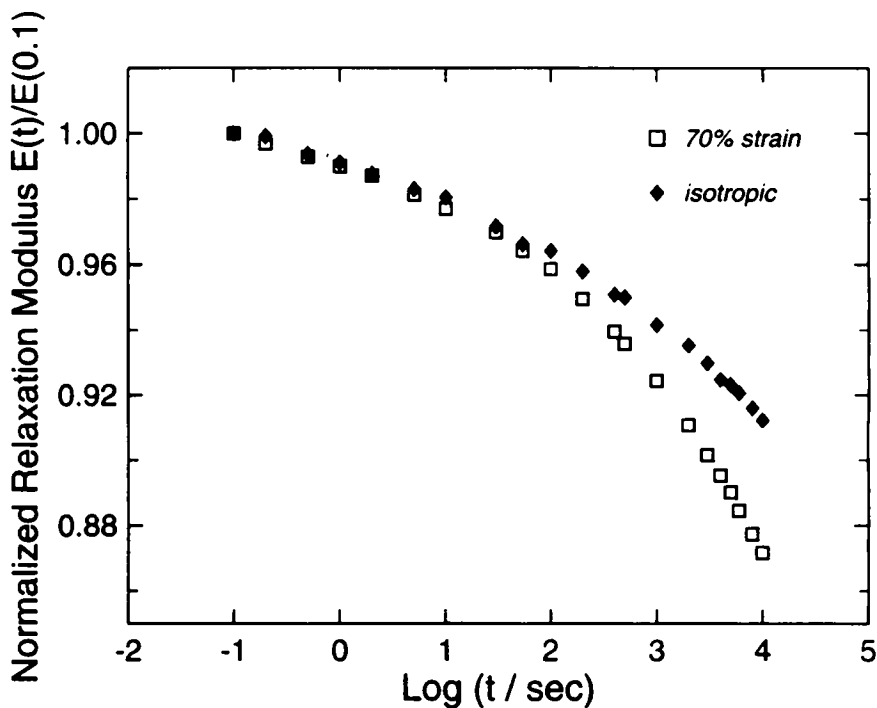


FIG. 5.—Tensile stress relaxation data normalized to its value at 0.1 s for the isotropic (filled diamonds) and the elongated (open squares) BPA-PC at 33°C.

The present experimental results are consistent with volume recovery and physical aging measurements on quenched BPA-PC,³⁵ wherein it was found that volume recovery after cold drawing was faster than in the absence of deformation. The stress relaxation and the volume recovery results may seem confusing in that they appear to be at odds with a decrease in specific volume after cold drawing (note that stretching the BPA-PC past the yield point increases its mass density). Pixa *et al.*³⁵ rationalize this apparent contradiction by assuming, first, that the volume decrease due to chain orientation affects only the occupied volume, and secondly that the free volume is increased by cold drawing. These are somewhat bold assumptions, which moreover cannot be easily verified given the difficulty of measuring both the free and occupied volumes.

The purpose of using the coupling model here is to incorporate the important factor of constraints (or cooperativity dynamics) in the structural relaxation of amorphous polymers; it does not necessarily imply a rejection of free volume concepts. Although free volume is not as fundamental a concept as a Hamiltonian description including interactions, it is still a useful concept provided intermolecular cooperativity is incorporated. In the framework of the coupling model, the "static mean field" part of the intermolecular interaction, conceptually analogous to the free volume, determines in combination with the conformational energy barrier of the chains the value of τ_0 in Equation (4). This mean field part of the intermolecular interaction should be distinguished from the dynamic part underlying the magnitude of the coupling parameter n in Equation (4). Thus, in the coupling model free volume effects are subsumed into τ_0 , while constraint dynamics are considered directly through Equations (3) and (4). Relaxation of drawn polymers in the glassy state provides an example of the interplay between the mean field and the dynamic aspects of intermolecular cooperativity in dense phase.

SUMMARY

New experimental methods, such as quasielastic neutron scattering, ³¹P NMR spectroscopy, and molecular dynamics simulations, are being applied to the study of networks. The insights provided by these techniques demonstrate a connection between rubber elasticity and dynamic properties, implying that unifying concepts must underlie thermodynamic theories and dynamical models. Available elasticity theories are largely restricted to thermodynamic and equilibrium properties. As exemplified herein by the coupling model, a new approach from a totally dynamics point of view is warranted; mechanical equilibrium can be considered as a special case. We have shown that the predictions drawn from the coupling model are in agreement with ³¹P NMR and mechanical relaxation results. Our current interest is to use the coupling model to derive constitutive equations, the *sine qua non* for predicting and characterizing the processing and mechanical properties of materials.

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