Influence of static strain on viscoelastic phenomena associated with the glass–rubber transition of elastomers prepared from poly(neopentylglycol adipate)

Ricardo Diaz-Calleja
Laboratorio de Termodinámica de la ETSII, Universidad Politécnica de Valencia, Valencia, Spain

and Evaristo Riande and Julio Guzmán
Instituto de Plásticos y Caucho (CSIC), Madrid-28006, Spain

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Dynamic loss tangent measurements performed on poly(neopentylglycol adipate) networks in the temperature range −140 to −10°C show the existence of a well defined α absorption, associated with the glass–rubber transition, and a β absorption in the glassy region which is presumably caused by molecular motions in which the bulky neopentyl residue intervenes. The results obtained from dynamic deformations of small amplitude, superimposed on strained networks, indicate that the intensity of the loss tangent associated with the α transition tends to increase with the static deformation. The free volume interpretation of the experimental results gives a good account of the α relaxation for both unstrained and strained networks. Moreover, the analysis of the glass–rubber transition in terms of Eyring theory suggests that in the present system the compensation law holds.

(Keywords: polyester networks; glass transition; static strain; loss tangent; compensation law)

INTRODUCTION

In an earlier work[1], the influence of static strain on the dynamic properties of several aromatic polyesters was studied. The results obtained indicated that the position of the peak associated with the glass transition shifts to lower temperatures with increasing static strain. Since in other systems[2] an increase in the apparent glass transition with elongation occurs, the changes in this parameter can be considered as a result of two competing and opposite effects[3]: the increase in free volume and the decrease in conformational entropy caused by the static strain. If the conformational effects (increasing T_g with decreasing conformational entropy) are larger (lower) than the volume effects (decreasing T_g with increasing free volume) the glass transition temperature increases (decreases) with increasing elongation.

An important issue in the analysis of the glass–rubber transition of polymeric networks that needs to be elucidated is whether the free volume interpretation of the viscoelastic mechanisms involved in the transition holds for strained networks. Fractional free volumes (f_g) calculated at T_g for amorphous uncrosslinked polymers from the dependence of the relaxation times on temperature seem to be consistent with those calculated independently from a free volume analysis of the dependence of relaxation times on pressure and dilution with solvent[4]. Since an analysis of the influence of static strain on the fractional free volume is still lacking, in this work we have determined the value of this parameter for elongated poly(neopentylglycol adipate) networks. In addition, a semiquantitative description of the changes that take place in the apparent T_g with the static strain was performed by relating the activation parameters to the variations that occur in the relaxation spectra of strained networks.

EXPERIMENTAL

Preparation of poly(neopentylglycol adipate) networks

Hydroxyl-terminated poly(neopentylglycol adipate) (PNA) chains were obtained in toluene solution by reaction of neopentylglycol and adipic acid, using *p*-toluene sulphonic acid as catalyst. Details of the polymerization reaction are given elsewhere[5]. A fraction of number-average molecular weight 5500 was crosslinked at 80°C with 2,4-bis(*p*-isocyanate benzyl) phenyl isocyanate for two days. The networks were extracted with chloroform and the value of the sol fraction was found to be 0.07. The glass transition temperature of the networks, measured with a DuPont TMA apparatus at a heating rate of 5°C min^{-1}, amounted to −38°C.

Dynamic experiments

Viscoelastic dynamic experiments were conducted on unstrained rectangular strips, cut from the network sheets, with a DMTA apparatus at four frequencies (0.33, 1, 3 and 10 Hz), over the temperature range −115 to 15°C. The measurements proceeded from low to high temperatures at a heating rate of 1°C min^{-1} and the precise position of the peaks was determined by the method of frequency multiplexing. The same strip was stretched on the experimental equipment until an

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elongation ratio $\lambda = 1.88$ was reached and then it was permitted to relax at temperatures well above T_g. Then the elongated strip was quenched in liquid nitrogen and the viscoelastic experiments were performed. Before the experiments were begun, the strips were dried in a vacuum oven at 50°C, in order to remove traces of humidity.

THEORETICAL

According to Fox and Flory[6], the specific volume v can be considered a linear function of temperature:

$$v = v_0 + \alpha_f (T - T_\infty) \qquad (1)$$

where T_∞ is the temperature at which the free volume would be zero, were it not for the formation of the glassy state, and α_f is the expansion coefficient. On the other hand, the relaxation time τ_i, associated with the viscoelastic mechanism i, is related to the free volume by the Doolittle equation[7]:

$$\log \tau_i = A + (B/\ln 10)/\phi \qquad (2)$$

where $\phi = (v - v_0)/v_0$ is the relative free volume and A and B are empirical constants. The substitution of equation (1) into equation (2) leads to the Vogel equation[8]:

$$\log \tau_i = A + (m/2.303)/(T - T_\infty) \qquad (3)$$

By assuming that all the relaxation mechanisms have the same temperature dependence, the shift factor $a_T = \tau_i/\tau_{i,0}$, where $\tau_{i,0}$ is the relaxation time at the reference temperature T_0, is given by

$$\log a_T = A' + (m/2.303)/(T - T_\infty) \qquad (4)$$

In this equation

$$A' = -(m/2.303)/(T_0 - T_\infty) \quad \text{and} \quad m = Bv/\alpha_f \qquad (5)$$

The parameters of the Doolittle equation, ϕ and T_∞, are related to m by[9]:

$$m = (B/\phi)/(T - T_\infty) = (B/\phi_g)/(T_g - T_\infty) \qquad (6)$$

where ϕ_g is the relative free volume at T_g. Although the values of B for polymer systems are not exactly known, the values of ϕ and ϕ_g are customarily calculated from equation (6) assuming $B = 1$.

Recently[10] it has been proposed that the temperature dependence of an activated process such as mechanical and dielectric relaxations can be described in terms of the rate theory of Eyring[11], so that the frequency associated with the relaxations is:

$$\omega = (kT/h)\exp(\Delta S^\ddagger/k)\exp(-\Delta H^\ddagger/kT) \qquad (7)$$

where h and k are the Planck and Boltzmann constants, respectively. The interest of this equation lies not only in the thermodynamic consequences that will be discussed below, but also in that it predicts a linear relationship between the activation enthalpy and entropy, the so-called compensation law[12-15]. The term 'activation entropy' is associated with complex relaxations such as the glass transition where cooperative intramolecular motions and intermolecular interactions are involved[16]. In the equation of Eyring the possibility that the relaxation involves a wide distribution of relaxation times is excluded, in opposition to the Vogel equation where the existence of that distribution is a basic assumption. However, this difficulty can be avoided by using non-exponential decay functions such as those of Williams and Watts[17] and Jonscher[18]. According to the theory[19]:

$$\Delta H^\ddagger = \Delta V^\ddagger / K\beta \qquad (8)$$

$$\Delta S^\ddagger = \Delta V^\ddagger \alpha' / \beta \qquad (9)$$

where α' and β represent the thermal expansion and compressibility coefficients, respectively, and K is a constant whose value is believed to be 4. Combining equations (8) and (9) gives

$$\Delta H^\ddagger / \Delta S^\ddagger = (\alpha K)^{-1} \qquad (10)$$

This means that the theory of Eyring applied to relaxation processes predicts the existence of a second-order thermodynamic transition. Since the glassy state is a metastable state, it seems clear that the glass transition cannot be considered a true thermodynamic transition. In spite of this, attempts have been made[20] to justify such a possibility on the basis of the equation of Ehrenfest[21]. The most important conclusion of the theory is that both the activated entropy and enthalpy, in addition to the activated volume, are the principal parameters that determine the glass transition temperature.

In increasing the elongation it is expected that $\Delta V^\ddagger$ decreases and $\Delta S^\ddagger$ increases. If the former effect overcomes the latter, T_g will decrease, but if the opposite occurs, T_g will increase. Moreover, if the compensation law holds, a variation of $\Delta S^\ddagger$ will produce a change of the same sign in $\Delta H^\ddagger$.

RESULTS AND DISCUSSION

An elongated crosslinked network at equilibrium may be considered a new material with anisotropic properties. In order to study the effects of the static strain on the relaxation viscoelastic spectrum, it is essential that crystallinity is not developed in the strained networks. Although the uncrosslinked polymer crystallizes from the bulk, crystallinity vestiges were not detected by calorimetry in the unstrained networks kept at 15°C for several weeks. Moreover, crystallinity was apparently not developed in the strained networks, even for values of the elongation ratio as large as 3.5 and temperature as low as 15°C[5]. This behaviour suggests that the crosslinked points hinder the crystallization of the networks.

The temperature dependence of the storage modulus at 1 Hz and of the loss tangent at several frequencies are given for the unstrained network in *Figures 1* and *2*, respectively. In the latter figure two peaks, α and β, located respectively in the high- and low-temperature region, appear. As expected, the position of the maximum of the α peak, centred at -28.9°C at 1 Hz, is frequency-dependent in the sense that it shifts to lower temperature with decreasing frequency. Since the glass transition temperature of the network is -38°C, the α peak can be considered to be associated with cooperative motions of

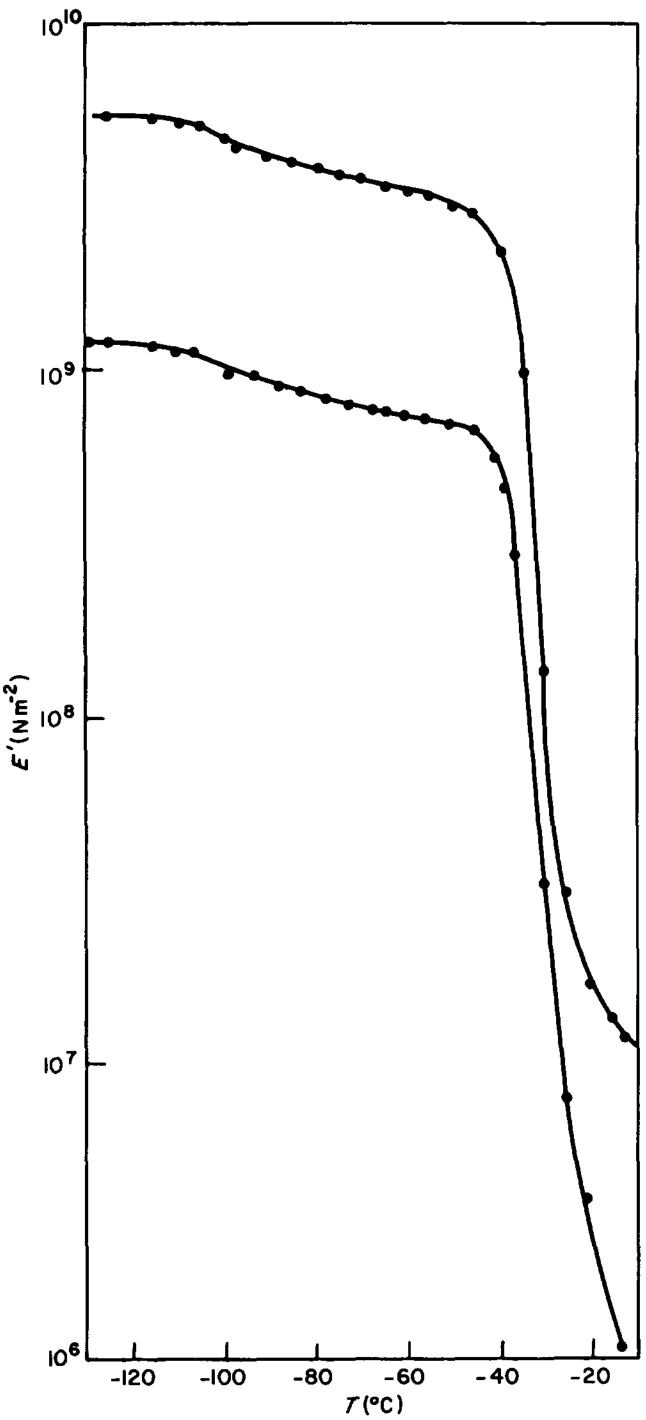

Figure 1 Storage modulus as a function of temperature for poly(neopentylglycol adipate) networks: upper curve, $\lambda = 1.88$; lower curve, $\lambda = 1$

the skeletal bonds and therefore to the glass transition of the polymer.

In the glassy region an asymmetric absorption centred at −80°C is found whose shape suggests it to be the result of two overlapping peaks, although this possibility has not been confirmed by the results obtained at the lowest frequency used in the experiments.

Time-dependent mechanical deformations of small amplitude were superimposed on a sample under a static deformation $\lambda = 1.88$. As can be seen in *Figure 1*, the real part of the complex relaxation modulus is much higher than that corresponding to the unstrained network. In the stretched sample the position of the maximum of the glass transition peak (*Figure 3*) shifts to lower temperatures ($T_{\max,\alpha} = -32.5$°C), suggesting that the volume effects overcome the entropic effects. The fact that the maximum of the α peak is higher in the strained network than in the unstrained one suggests that more active segments are present in the former case than in the latter.

The shape of the β peak is similar to that obtained for the unstrained sample. The apparent activation energy associated with the β transition, obtained from the Arrhenius plot, amounts to 22 kcal mol^{-1}. The fact that the value found for this activation energy is significantly higher than that reported for the peak of other aliphatic polyesters (~ 15 kcal mol^{-1})$^{22-24}$ suggests that molecular motions of the bulky neopentyl residue intervene in the β relaxation of PNA chains that must overcome higher potential barriers than the methylene groups of their polyester counterparts. A summary of the principal viscoelastic characteristics of both the strained and unstrained networks is shown in *Table 1*.

The isotherm curves showing the frequency dependence of the loss tangent ratio ($\tan\delta/\tan\delta_{\max}$) were used to study the influence of the free volume in the α relaxation process. Taking the isotherm corresponding to −30°C as the reference for the unstrained network, the temperature–frequency reduction of the relaxation curves

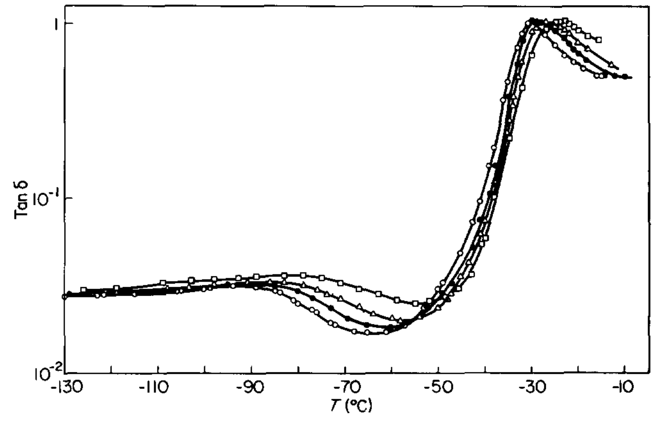

Figure 2 Loss tangent as a function of temperature for poly(neopentylglycol adipate) networks at several frequencies: □, 10 Hz; △, 3 Hz; ●, 1 Hz; ○, 0.3 Hz

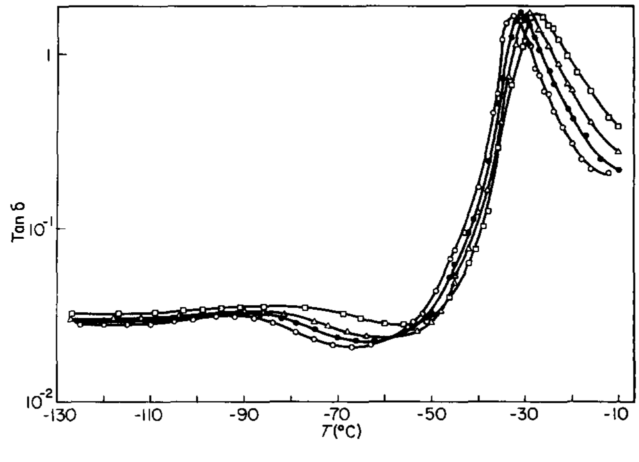

Figure 3 Loss tangent as a function of temperature for poly(neopentylglycol adipate) networks under static elongation: □, 10 Hz; △, 3 Hz; ●, 1 Hz; ○, 0.3 Hz

Table 1 Summary of viscoelastic results for unstrained and strained networks at 1 Hz

	α relaxation		β relaxation		
Network	$T_{\max}$ (°C)	$\tan\delta_{\max}$	$T_{\max}$ (°C)	$\tan\delta_{\max}$	E_a (kcal mol^{-1})
Unstrained	−30.6	1.09	−89	0.032_8	22±1
Strained	−32.5	1.74	−89	0.032_2	22±1

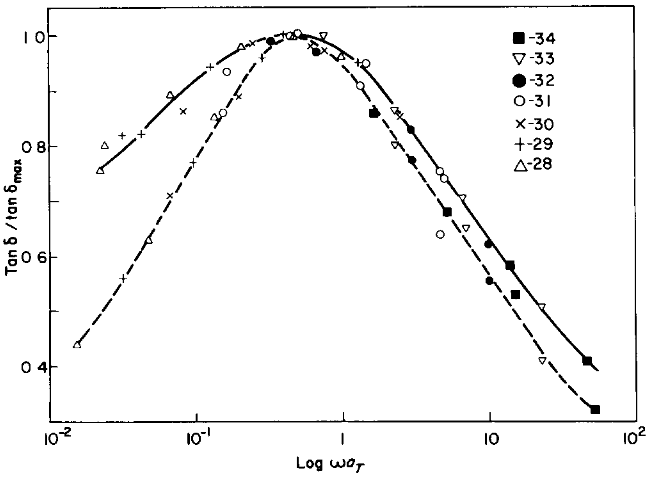

Figure 4 Master curve for the loss tangent of unstrained (full curve, $\lambda=1$) and strained (broken curve, $\lambda=1.88$) poly(neopentylglycol adipate) networks

results in the master curve shown in *Figure 4*. As can be seen in *Figure 5*, fitting of the experimental shift factors a_T to equation (4) requires use of the value of $T_\infty=-90$°C, for which the plot of log a_T vs. $1/(T-T_\infty)$ is a straight line. Since the dilatometric T_g for the unstrained network is −38°C, a value of 0.020 is obtained for the fractional free volume, in fair agreement with the value reported for this parameter in most systems[4]. Moreover, by considering that $\alpha_f=(\phi_g/B)/(T_g-T_\infty)$, the value of the expansion coefficient is $3.8\times10^{-4}K^{-1}$. This value also seems to support the free volume interpretation of the α relaxation, since it is of the correct magnitude for a thermal expansion coefficient.

Isotherm curves for the strained network were superimposed in the way indicated above, taking the isotherm corresponding to −32°C as reference. The master curve obtained, shown in *Figure 4*, suggests that the viscoelastic mechanisms involved in the glass transition of the anisotropic network have the same temperature dependence. The plots of *Figure 5* indicate that fitting of the shift factors a_T to equation (4) also occurs for $T_\infty=-90$°C. Since the temperature associated with the maximum of the α peak shifts about −2°C with respect to that of the unstrained network, it was assumed that the dilatometric T_g of the strained network should lie in the vicinity of −40°C. Using this value, the fractional free volume ϕ_g/B amounts to 0.019, in close agreement with the value obtained for this quantity in the case of unstrained networks. Therefore, it seems that the free volume interpretation also gives a good account of the α relaxation of strained networks.

By assuming that the α relaxation is an activated process, the dynamic experimental results of *Figures 2* and *3* can also be interpreted in terms of the theory of Eyring[10,11]. The results obtained for the entropy and enthalpy of activation, with a correlation factor $\rho=0.9997$, are given in *Table 2*. It can be seen that an increase in the values of both parameters with static strain occurs. Since the changes that take place in the values of $T_{\rm comp}$ with elongation practically lie within experimental error (see the last column of *Table 2*), it can be concluded that the compensation law holds. Moreover, the value of the expansion coefficient estimated by equation (10) ($7.0\times10^{-4}\,{\rm K}^{-1}$) is similar to that obtained in an experimental way[5] using picnometry techniques ($7.2\times10^{-4}\,{\rm K}^{-1}$).

The increase in entropy of activation with increasing static strain, shown in *Table 2*, seems to be consistent with the decrease of conformational entropy caused by the orientation of the chains. The results of the table also suggest that the response to a small strain superimposed on the stretched network at $T>T_g$ will be hindered by the increase in the barriers of free energy involved in the relaxation processes. Finally, the increase in free volume with static strain will presumably decrease the activation volume $\Delta V^\ddagger$ and taking into account equation (10) the value of the compressibility factor will decrease.

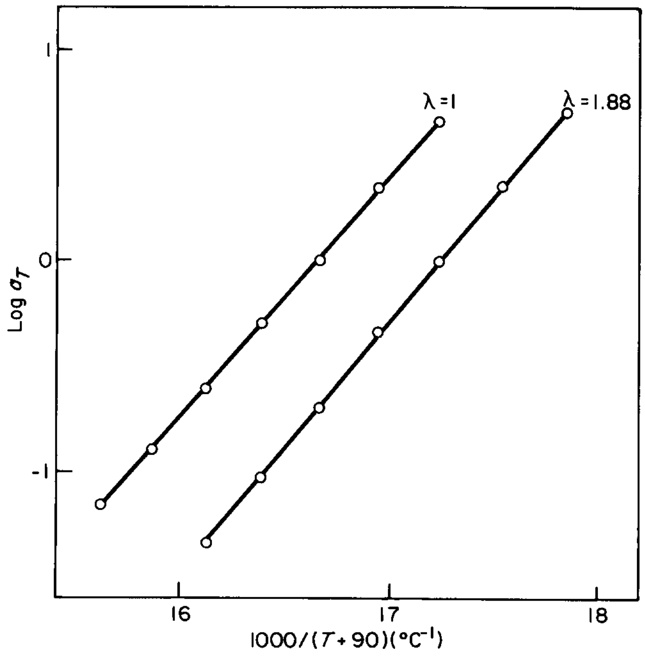

Figure 5 Plot of the logarithm of the shift factor a_T as a function of $1/(T+90)$; the temperature T is in °C

Table 2 Activation parameters ($\Delta H^\ddagger$ and $\Delta S^\ddagger$), compensation temperature (T_c) and thermal expansion coefficient for unstrained and strained networks

Network	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal mol^{-1})	$10^4\alpha'$ (K^{-1})	T_c (°C)
Unstrained	72±1	252±1	8.7±0.2	287±5
Strained	86±1	312±1	9.0±0.2	276±5

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