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Adi Eisenberg[ab]; Shogo Saito[ac]
[a] Department of Chemistry, University of California, Los Angeles, California [b] McGill University, Montreal, Canada [c] Japan Electrotechnical Laboratory, Tokyo, Japan

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Molecular Flow and Lanthanum-Catalyzed Bond Interchange in Sodium Phosphate Polymers*

ADI EISENBERG† and SHOGO SAITO‡

Department of Chemistry
University of California
Los Angeles, California

SUMMARY

It is observed that sodium phosphate polymers, in which some of the Na^+ ions have been replaced by La^{3+} ions, are subject to both simple molecular flow and to bond interchange in the glass transition region. These two relaxation mechanisms are separated, and their relative contributions to the shear viscosity are calculated. It is shown that the bond-interchange mechanism is subject to an activation energy of ca. 50 kcal, while that of the molecular flow is of the order of 200 kcal at T_g + 30°C; the latter is of the WLF form. It is further shown that the La^{3+} ions act as cross-links, at least at low concentrations, and that bond interchange occurs at the site of the La^{3+} ions rather than at random along the polymer chain.

INTRODUCTION

A wide range of inorganic ionic glasses possess many of the structural characteristics of the classical organic polymers, particularly with regard to linearity of the backbone chain. These materials include not only the well-explored polyphosphates [1-6], but presumably also the silicates over a wide range of compositions [7, 8], and possibly also vanadates and arsenates [9]. When

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† Present address: McGill University, Montreal, Canada.

‡ Present address: Japan Electrotechnical Laboratory, Tokyo, Japan.

subjected to stress, the noncrystalline linear organics relax (in the absence of chemical degradation) by a simple molecular-flow mechanism [10, 11]; occasionally bond interchange is encountered, for instance in the polysulfides [10] or the polyurethanes [12], but in these materials it occurs far above the glass transition temperature. By contrast, some linear inorganic glasses have been found in which bond interchange is a major contributing relaxation mechanism in the glass transition region [13], and in which the bond-interchange process is catalyzed by specific cations. It is therefore of interest to inquire to what extent the relative contributions of these two mechanisms can be determined if their relaxation times are comparable and, furthermore, if any ideas can be gained about the kinetic parameters and the mechanism of the bond-interchange process. In this paper, specifically, we wish to report a study of lanthanum-catalyzed bond interchange in a linear sodium phosphate polymer, in which a preliminary study [13] has shown that both mechanisms were present. An attempt is made not only to determine the relative contribution (for instance to the viscosity) of each of the mechanisms, but also to find out whether lanthanum catalyzes the reaction directly or only indirectly by increasing the glass transition temperature. Furthermore, the techniques will be described not only for quantitative estimations mentioned above, but also for a very rapid determination of the existence of two simultaneous mechanisms in the flow region.

The materials employed here consisted of polymeric sodium phosphate $(NaPO_3)_x$ to which various amounts of $[La(PO_3)_3]_x$ were added. The samples may thus be regarded as counterion copolymers, since the backbone remains identical with only the relative counterion concentrations varying. The concentrations of lanthanum, expressed as $(3La/P) \times 100$ to indicate the percentage of repeat units neutralized by the lanthanum, were 6.0, 10.5, 15.3, 22.5, 30.3, and 39.0. Higher concentrations were too difficult to prepare by our techniques; the method of preparation, incidentally, was described elsewhere [14], and consisted in adding to the $NaPO_3$ melt enough $LaPO_3$ and P_2O_5 to achieve the desired compositions. A predetermined amount of excess P_2O_5 had to be added to compensate for losses due to volatilization. The viscoelastic properties of the 22.5% sample were described in a preliminary fashion before [13], as were also the flass transition temperatures of all the samples [14]. The glass transition values are also listed in Table 1.

Before concluding the introduction, it is advisable to review very briefly preceding work done on the viscoelastic properties of polymers subject to multiple relaxation mechanisms, as well as previous solution studies of phosphates in the presence of lanthanum.

The high-frequency dynamic behavior of polymers possessing various side groups and exhibiting a multiplicity of transitions and relaxations has been the subject of a recent symposium (see Ref.

[13]). Prior to that, Ferry and co-workers [15] investigated the viscoelastic properties of a series of methacrylates and found that in certain regions time-temperature superposition did not apply due to side-chain motion occurring with an activation energy different from that of the main chain. They were able to separate these two types of motions and to determine the activation energies and relaxation spectra due to each. To distinguish the two, they referred to backbone motion as the α mechanism, while the side-chain motion was called the β mechanism.

In a completely unrelated development, Bamann [16] showed that lanthanum hydroxide promotes the hydrolysis of α-glyceryl phosphate; subsequently, Butcher and Westheimer [17] investigated the promotion of the hydrolysis of phosphate esters by lanthanum hydroxide gel and found a more than thousandfold increase in the rate. They also proposed a mechanism for the reaction which, however, involves water.

The last two investigations mentioned above, in addition to the known effect of transition metal ions in accelerating some biologically important phosphate reactions, prompted us to choose the $NaPO_3$-$La(PO_3)_3$ system for our first investigation of bond interchange in polyanionic inorganic glasses in which simple molecular motion was probably also important. For the sake of simplicity, relaxation by molecular (diffusional) flow, which leaves the backbone intact, will be referred to as the α mechanism in accordance with the usage proposed by Ferry et al., while the bond-interchange reaction, owing to its chemical nature, will be referred to as the χ mechanism.

EXPERIMENTAL RESULTS AND INTERPRETATIONS

Phenomenology of Multiple Mechanism Relaxation and Separation of the Mechanisms

All the primary experimental data were obtained by the technique of stress relaxation. Since the primary curves (before shifting) show no unusual features, they will not be reproduced here. The characteristics of multiple relaxation do become evident, however, when an attempt is made to construct a master curve [10]. It is observed that while in the glassy and transition regions the behavior is completely normal, in the flow region superposition is impossible. This manifests itself in a number of ways, two of which can serve as indicators of multiple mechanism relaxation, provided the material is in the region of linear viscoelasticity.

One of the noteworthy characteristics of these materials that was found was the nonlinearity of the plot of the shift factor, (a_t), versus the maximum relaxation time, (τ_m), as shown in Fig. 1. The shift factor here refers to the horizontal shift needed to bring into coin-

Table 2

3La/P	E_m[a], dynes/cm^2 × 10^7	M_c × 10^2 (from E_m)	[C], moles/cm^3 × 10^{-4} (from composition)	[C], moles/cm^2 × 10^{-4} (from M_c)	Efficiency,[b] %
6	3.0	125	4.65	1.00	21.5
10.5	4.8	78	8.32	1.60	19.2
15.3	9.1	41	12.1	3.05	25.2
22.5	11	34	17.4	3.68	21.2
30.3	15	25	23.1	5.00	21.6
39	13	29	29.2	4.32	14.8

[a] Average value for "ultimate Maxwell element."

[b] Assumes front factor of 1; if front factor is smaller, efficiency is greater.

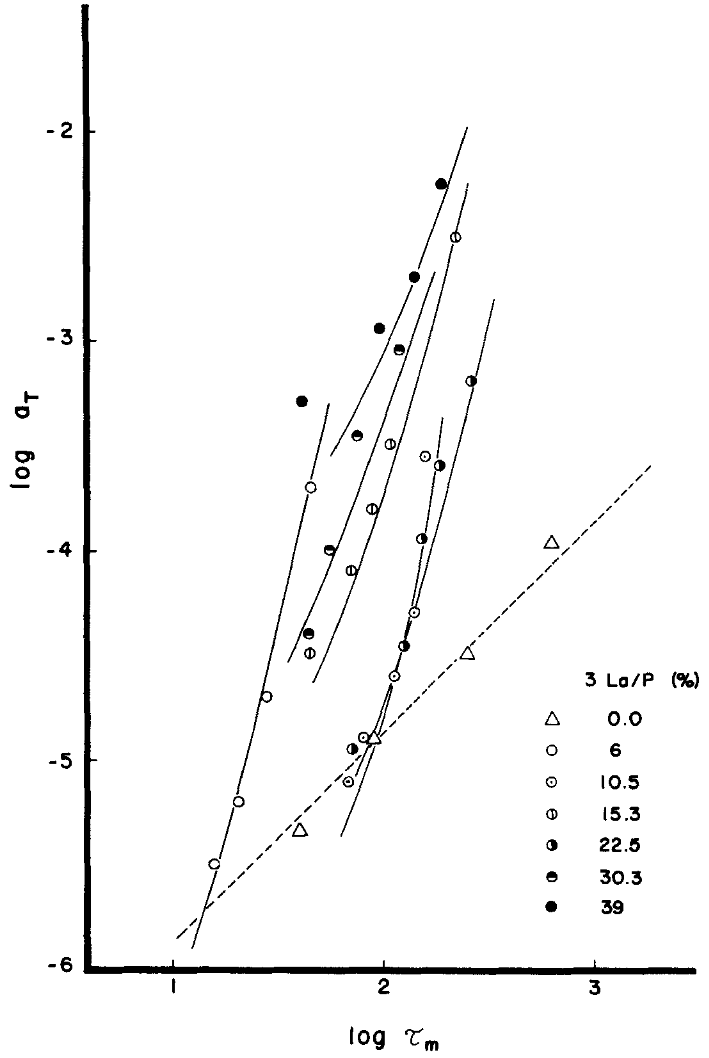

Fig. 1. Shift factor versus maximum relaxation time (sec) for Na^+-La^{3+} phosphate counterion copolymers.

cidence the stress relaxation curves obtained at various temperatures, with the curve obtained at T = T_g used as the reference, while the maximum relaxation time (τ_m) refers to the "equivalent ultimate Maxwell element" and is obtained from a plot of log E versus time. If only one mechanism is operative, then the plot should be linear with a slope of 45°, since the short-time (≈ 10 sec) and long-time (≈ 1000 sec) behavior are governed by the same kinetic factors. On the other hand, if more than one mechanism is present, each of which is subject to different kinetic parameters, then the short-time relaxation behavior (related to a_t if superposition is attempted in the short-time region) should be subject to different kinetic parameters than the long-time relaxation behavior (related to τ_m), and therefore linearity is not to be expected.

As is clearly seen in Fig. 1, the line for pure sodium phosphate is linear, indicating the presence of only one relaxation mechanism, or possibly of two mechanisms with identical kinetic parameters, which is highly unlikely; a previous investigation [6], as a matter of fact, failed to reveal any indication of a mechanism other than α in pure sodium phosphate. On the other hand, upon addition of varying amount of lanthanum, marked deviations from linearity are observed, as will be discussed later; the slope of these plots is related to the ratio of the activation energies of the two processes, while the curvature is related to the change in the activation energy with temperature for the α mechanism, which, in turn, can be expressed by the WLF equation [18].

Another very significant characteristic of multiple mechanism relaxation is the pronounced change of the shape of the spectrum of relaxation times with temperature. As was pointed out in the preliminary publication [13], with increasing temperature the relaxation spectrum not only shifts to short time values, but a dip appears and deepens, indicating increased separation with temperature of those parts of the spectrum due to the different mechanisms. The high temperature or long-time part of the spectrum consists, for all practical purposes, of a single line; i.e., it is Maxwellian. The change of the spectrum with temperature reflects itself in the failure of time-temperature superposition, which can be seen in Fig. 2a for the 30.3% sample in stress relaxation and in Fig. 2b upon recalculation of the relaxation data into creep compliance by the methods suggested by Tobolsky and Aklonis [19]; that recalculation was performed because, as was indicated by Ferry et al. [15], if a material is subject to two mechanisms, then the observed creep compliance is a sum of the creep compliances due to the individual mechanisms. Following Ferry et al.'s procedure, we ascribe the lower envelope of points on the creep master curve (obtained by superposing the curves obtained at short times) to one of the mechanisms, while any deviation is ascribed to the second mechanism. This is also shown in Fig. 2b; it is particularly noteworthy that the calculated points due to second

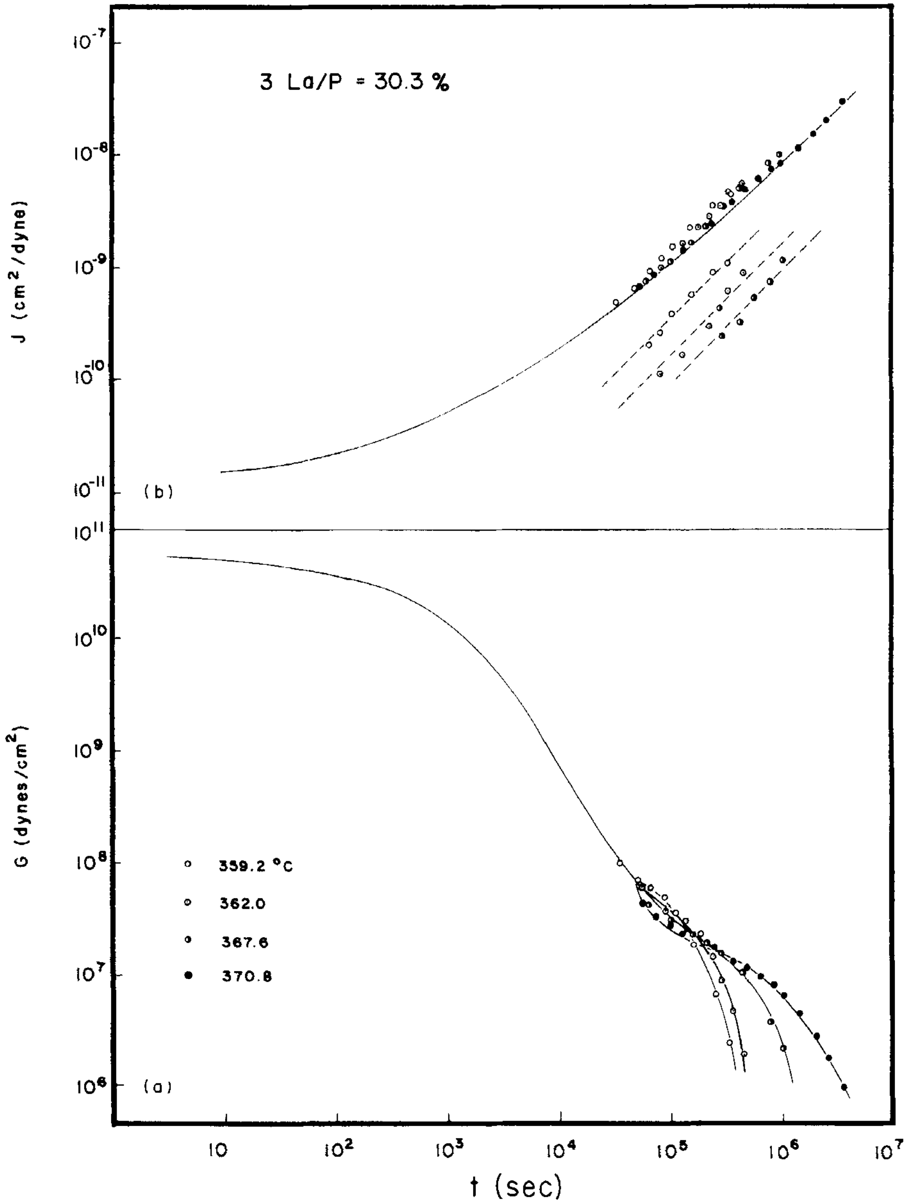

Fig. 2. (a) Stress relaxation master curve for the 30.3% sample. Log $G_r(t)$ versus log t. (b) Creep compliance master curve for the 30.3% sample. Log J(t) versus log t.

mechanism fall on a straight line of a slope of 45° on a log J versus log t plot, indicating that only irrecoverable compliance is involved here. This feature, coupled with the activation-energy arguments to be presented in the next section, suggest that the lower envelope of points is due to the α mechanism, while the deviations are due to the χ mechanism.

Activation Energies of the Two Processes and Identification of the Mechanisms

An attempt will now be made to determine the activation energies of the two processes, since the identification of the mechanism is based to a large extent on this factor: a study of all the stress relaxation curves has revealed that within experimental error time-temperature superposition is valid above a modulus of 10^8 dynes/cm^2, and that the shift factors are of the WLF form. These shift factors (a_t) are shown in Fig. 3; it should be pointed out that the shift factors for the stress relaxation curves are, as might be expected, identical to those of the compliance curves, an example being shown in Fig. 4. Since these shift factors are of the WLF form, we can determine the constants of the WLF equation

$$\log a_T = C_1(T - T_g)/C_2 + T - T_g)$$

and the constants are listed in Table 1. Also in the same table are the values of the activation energy for the process (α) which is governed by these shift factors, calculated for $T = T_g + 30$.

The method of determining the activation energy for the second mechanism is the following. As can be seen in Fig. 2b, the deviations of the individual curves in the high compliance region from the lower envelope of points is quite large; on a plot of the stress relaxation modulus, this discrepancy appears even larger, as can be seen from Fig. 2a (the lower envelope of points on the compliance curve corresponds to the highest stress relaxation curve). Thus we can be quite sute that the maximum relaxation time τ_m (obtained from a plot of log E versus time), while containing some contribution from the first mechanism (tentatively identified as α, see discussion below), will reflect primarily the second, or χ, mechanism. Therefore, a plot of log τ_m versus 1/T should give the activation energy for that process. The plots are shown in Fig. 5, plotted both as log τ_m versus 1000/T and versus (1000/T) — (1000/T_g); the significance of the second plot will be discussed later. Over the narrow temperature range over which the τ_m values can be obtained, the plots are practically linear, the activation energy averaging ca. 50 kcal, much lower than for the first mechanism. It should be pointed out that in the case of sulfur cross-linked with arsenic, linearity in the plot of log τ_m versus 1000/T is observed over four orders of magnitude of τ_m, supporting the linearity observed here.

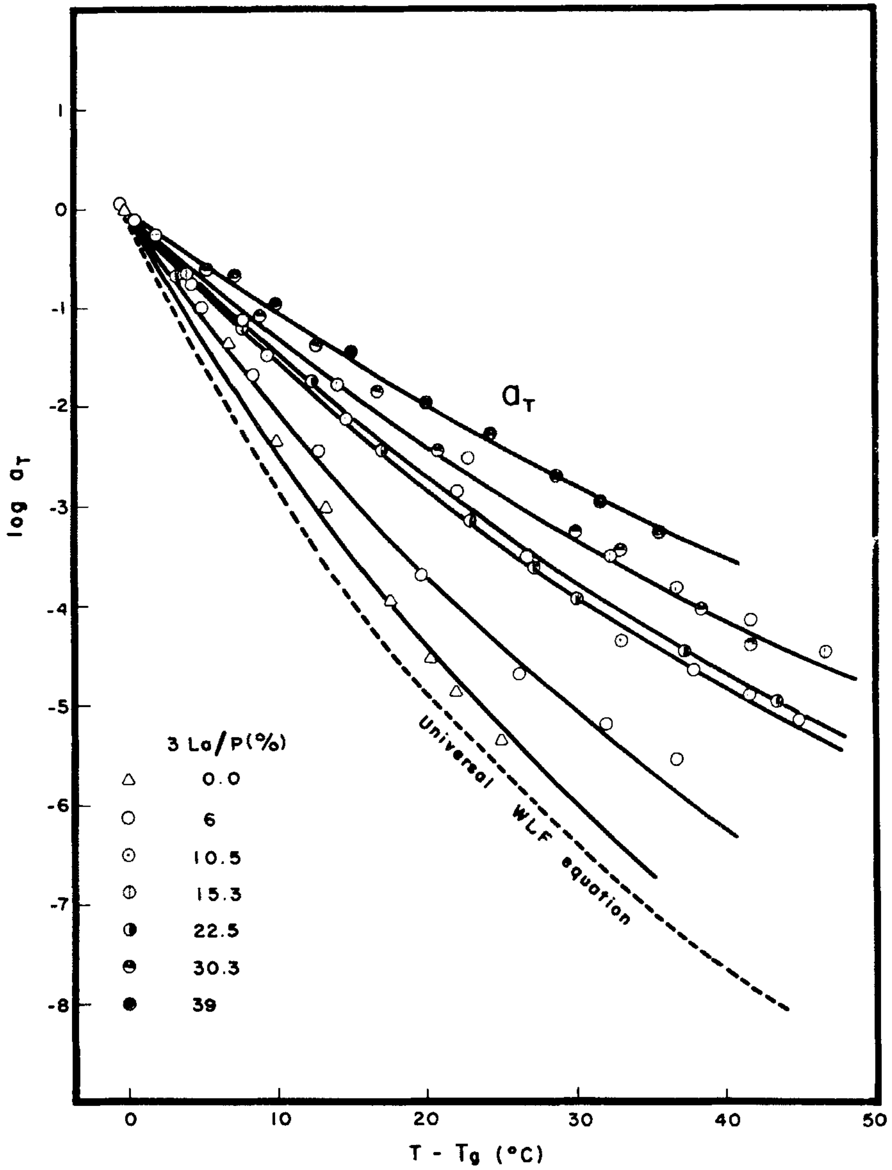

Fig. 3. Shift factors for all samples. The lines are computed from constants in Table 1. Log a_t versus $T - T_g$.

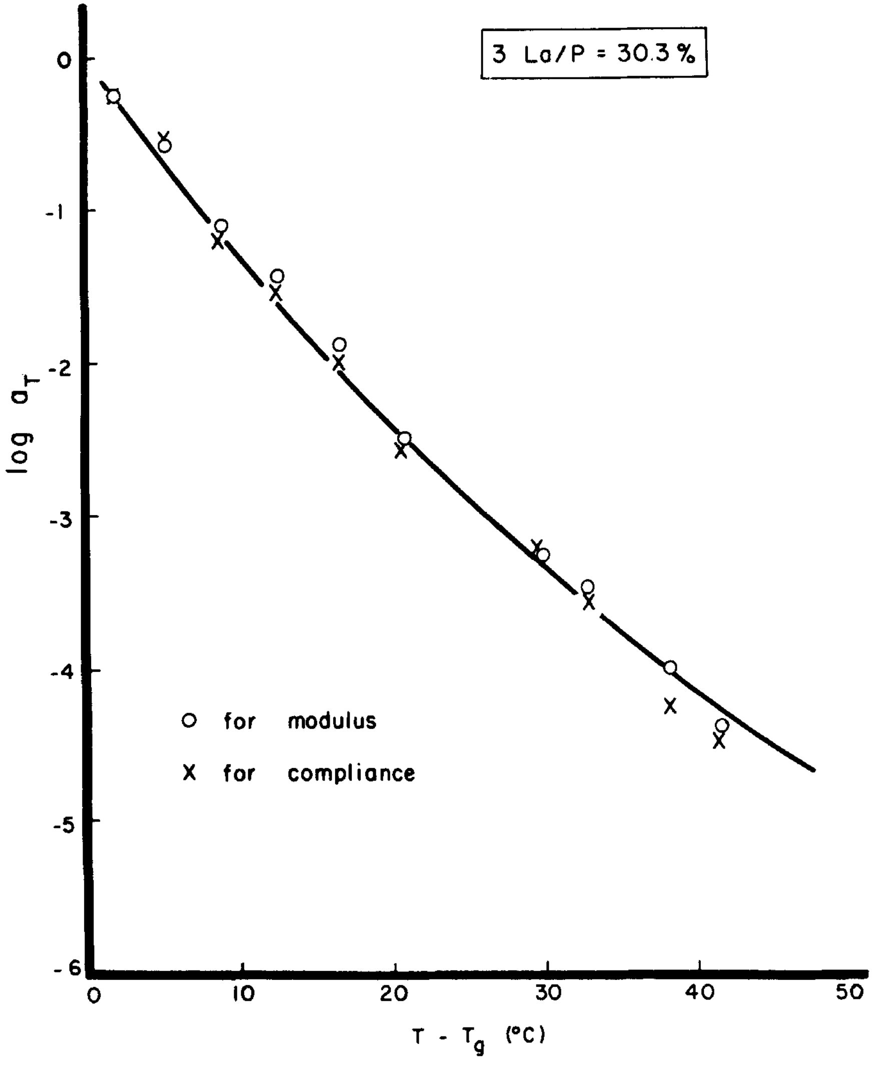

Fig. 4. Comparison of shift factors for stress relaxation and creep. Log a_t versus $T - T_g$.

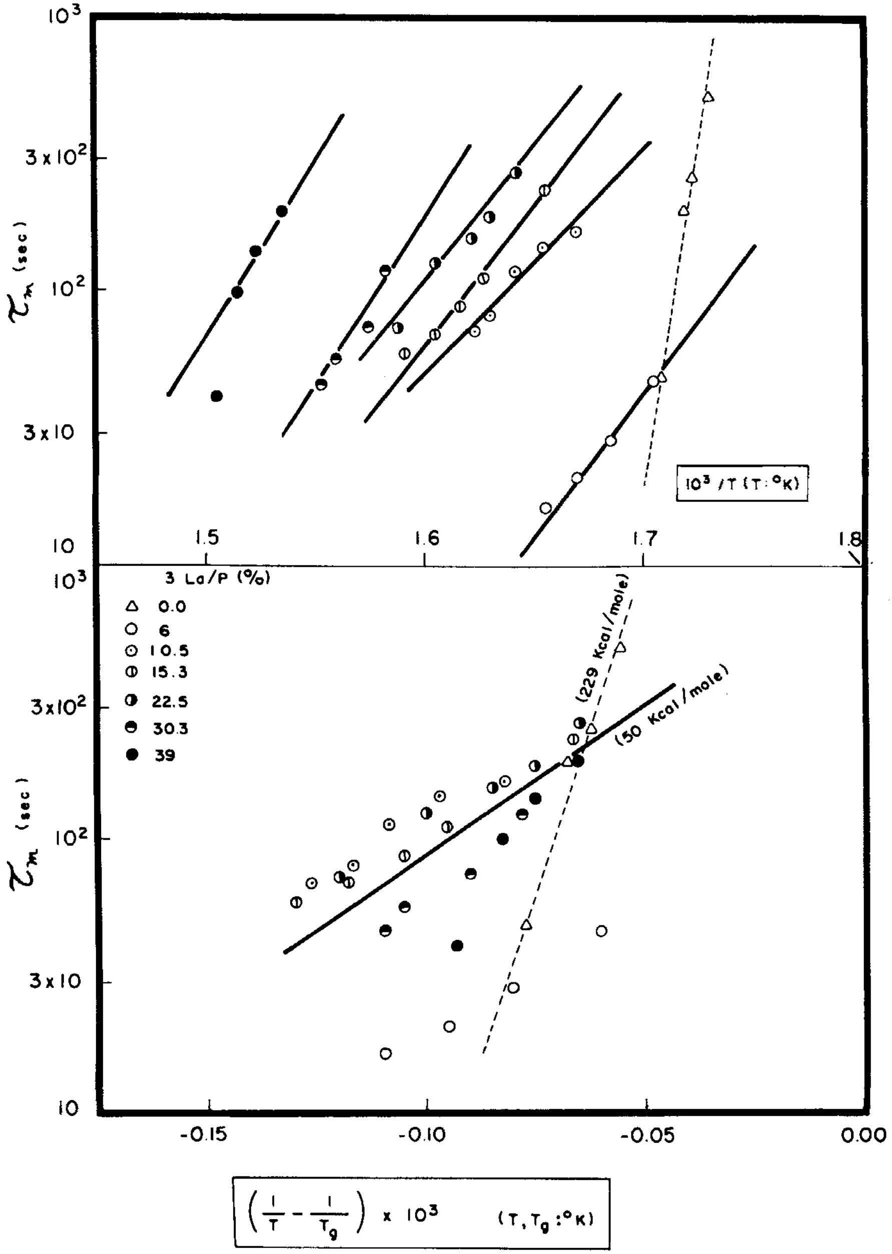

Fig. 5. Maximum relaxation time (log τ_m) versus 1000/T and versus (1000/T) − (1000/T_g).

There is one other method of determining the activation energy for the second process. From the compliance curves due to the χ mechanism, we can calculate the viscosity as a function of temperature. A plot of the viscosity as a function of temperature ($\log \eta$ versus 1/T) shown in Fig. 6 shows a much higher activation energy than 50 kcal. This is not surprising, however, because for a relaxation mechanism of the type encountered here, $\eta = G\tau$, where τ is the relaxation time and G the shear modulus of the system. Since it is the relaxation time which gives a direct clue as to the kinetics and activation energy of the processes, it is more meaningful to obtain the activation energy from a plot of $\log \eta_\chi/E_m$ (or G_m), the modulus corresponding to that mechanism. These plots, shown in Fig. 7, indicate again an activation energy of ca. 50 kcal, the value of the relaxation time being much higher, however. One possible reason for this will be given later.

We are now ready to attempt the identification of the two mechanisms. This identification is based on the following points.

1. The shift factors corresponding to the first mechanism are of the WLF form, giving an activation energy for the process at $T = T_g + 30$ ranging from 150 to 230 kcal, values typical of the α mechanism in linear organic polymers.
2. The shift factors and activation energies for the first mechanism are very much in line with those observed for pure sodium phosphates, in which no evidence for bond interchange has been found.
3. The activation energy for the second mechanism is ca. 50 kcal.
4. The variation of the maximum relaxation time with temperature indicates that the rate constant is of the Arrhenius type.
5. The compliance resulting from the second mechanism is strictly irreversible, as shown by the linearity of the difference plot in Fig. 2b and the slope of 45°.

Therefore, the first mechanism is identified as α mechanism, while the second is assigned to the χ mechanism. The linearity of the $\log \tau_m$ versus 1000/T or $(1000/T) - (1000/T_g)$ plots is believed to be particularly significant, indicating that the size of the reacting group does not change with temperature, in contrast to molecular motion (the α mechanism), which is governed by the WLF relation. The second plot indicates that the glass transition temperature is a reference temperature, with the rates of interchange for all materials being identical at identical reduced temperatures, at least within experimental error.

Relative Contribution to Viscosity of Each of the Mechanisms

Before attempting to separate quantitatively the effect of the two mechanisms on the viscosity, it should be recalled that in doing so an experimental creep compliance curve is subtracted from the lower envelope of points, the deviation being ascribed to the χ mechanism.

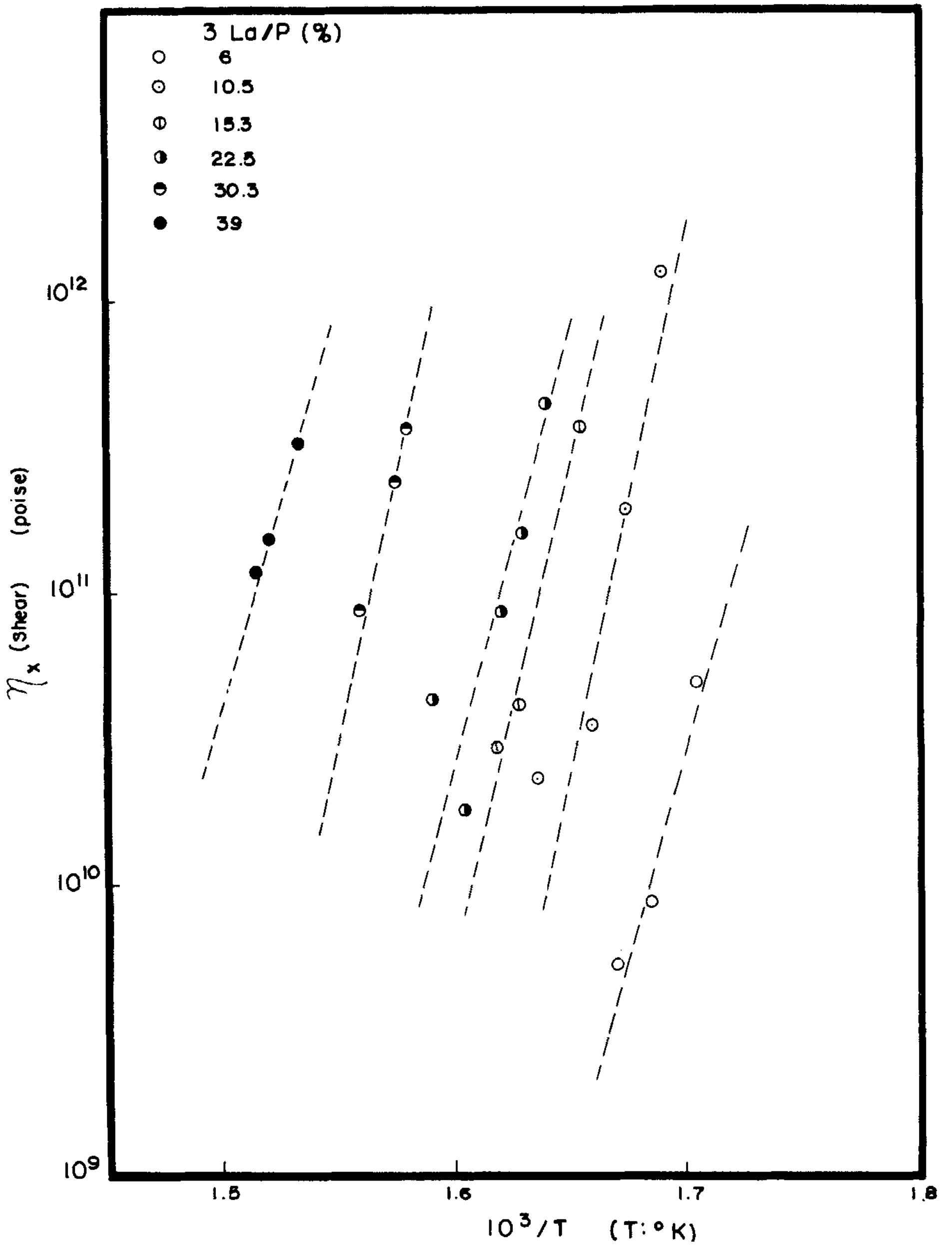

Fig. 6. Viscosity (log η) versus 1000/T and versus (1000/T) — (1000/T_g).

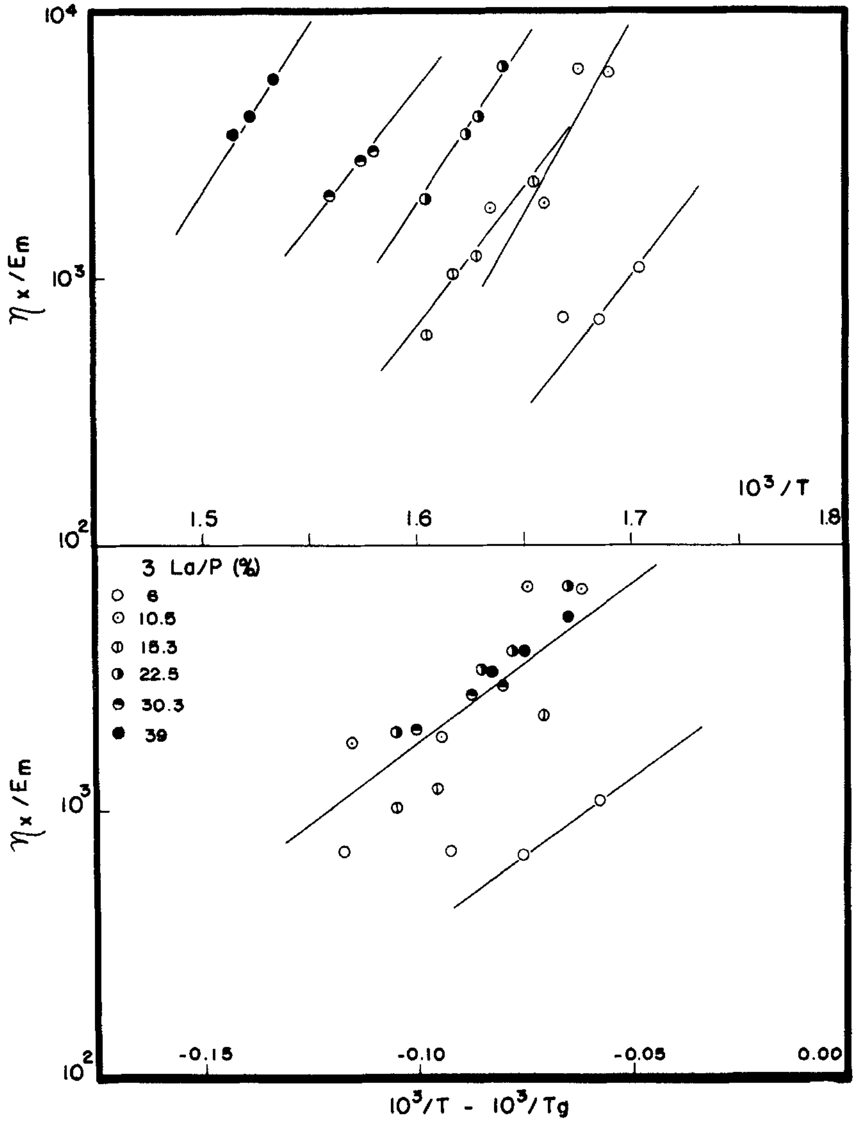

Fig. 7. Log (η_x/E_m) versus $(1000/T) - (1000/T_g)$.

This works very well for all curves except those obtained at the highest temperatures. The highest temperature curve still reflects the χ mechanism, because with our experimental techniques, we could not reach high enough temperatures or low enough moduli to obtain a curve in which the α mechanism predominates. To obtain the viscosity due to the χ mechanism, we simply resort to the subtracted curves, but for the α mechanism we need the complete α curve, which we do not have, at least not for the longest times, which have the highest influence on the viscosity. Therefore, although we can obtain the viscosity due to the χ mechanism (η_χ) and the total viscosity (η_{total}) as a function of temperature, we cannot obtain η_α with any degree of precision. Incidentally, η_{total} is obtained simply from the relationship

$$\eta = \int_0^\infty H(\tau)\, d\tau$$

An example of such a separation is shown in Fig. 8 for the 15.3% sample.

As a result of the fact that we do not have the complete α-mechanism curve, it is probable that the viscosity due to the α mechanism is somewhat underestimated, and thus that due to the χ mechanism also. The inaccuracy in the value of the viscosity may have caused the discrepancy in the values of τ_m obtained by the two methods.

It is interesting to observe that the total viscosity is lower than that due to either the α or the χ mechanism alone. This is quite understandable, because if two independent flow mechanisms are accessible to the sample, the resulting viscosity should be lower than either of the two alone, a situation analogous to the total resistance of two resistors connected in parallel.

Having addressed ourselves to the problem of the detection of the presence of multiple mechanisms, their activation energies, and the determination of their relative contributions to the viscosity, we can now attempt to answer some detailed mechanistic questions, such as:

1. Does the La^{3+} serve as a cross-link?
2. Does it serve as a bond-interchange catalyst (this question is relevant because the bond interchange above T_g might be due to the increase of T_g with increasing La^{3+}) and, if so, what is the detailed mechanism of interchange; do bonds interchange at random or only at the cross-links?

We shall now attempt to answer these questions within the limits of the experimental data.

La^{3+} as a Cross-Linking Agent

If La^{3+} acts merely to increase the glass transition temperature, then the "rubbery" modulus of the material should not necessarily

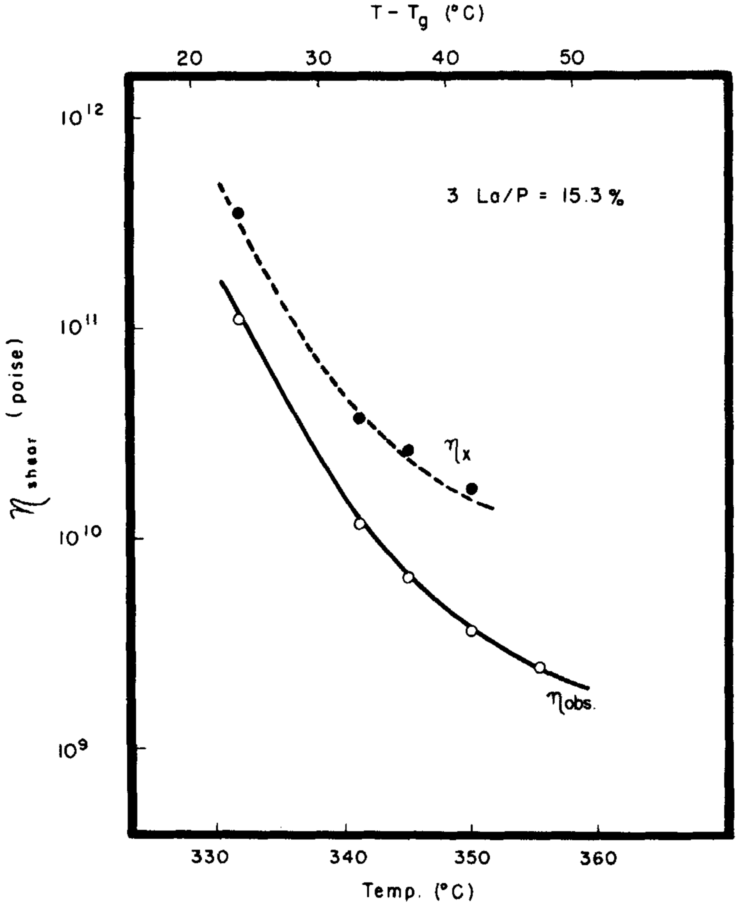

Fig. 8. Relative contributions to the viscosity of the mechanisms and the total viscosity of the 15.3% sample. Log (poise) versus $T - T_g$.

change; if, on the other hand, it does cross-link the material, then the rubbery modulus should change in a manner predicted by the kinetic theory.

Unfortunately the materials do not have a sufficiently well-developed rubbery modulus for use in calculations. We therefore resort to the equivalent "ultimate Maxwell element" from which the maximum relaxation time was computed, and utilize the modulus corresponding to that ultimate element for subsequent computations. Table 2 lists these moduli, as well as a number of other values described below. Now if La^{3+} ions act as cross-links, then the E_m values should be directly proportional to their concentration, c, since both E_m and c are inversely proportional to the molecular weight between cross-links, M_c. The former relationship is due to the kinetic theory of rubber elasticity ($E_m = \Phi\, 3\rho RT/M_c$, where Φ is the front factor, ρ is the density, and R the gas constant), and the latter to simple stoichiometry ($c = \rho/2M_c$) for trifunctional cross-links. A plot of E_m versus c is shown in Fig. 9, both for La^{3+} and for Ca^{2+}, indicating that both ions act as cross-links, at least at low concentrations and only for the "ultimate Maxwell element."

It is now interesting to inquire about the efficiency of these cross-links; i.e., does every La^{3+} act as a cross-link or are some lost, for instance in forming loops along the same chain? Although we cannot answer the question unequivocally, we can obtain a rough guide by comparing the value of c calculated from the overall composition with that calculated from the kinetic theory, i.e., that value of c which would ideally be needed to give the experimental E_m (assuming $\Phi = 1$). These two values of c are also given in Table 2, as well as their ratio, expressed as per cent efficiency. The efficiency value ranges around 20%, implying that either only one out of five La^{3+} ions forms an effective cross-link, or that the front factor is ca. 0.2. At present, no decision can be made as to which of

Table 1

3La/P, %	T_g, °C	C_1	C_2	ΔH_α, kcal/mole[a]	ΔH, kcal/mole[b]
0.0	287	21	75	229	230
6	294	20	88	207	48
10.5	298	16	93	164	37
15.3	308	15	104	150	47
22.5	315	15	88	165	45
30.3	329	15	104	160	56
39	353	17	153	154	57

[a] ΔH_α, apparent activation energy (at T_g + 30°C) calculated from C_1 and C_2.

[b] ΔH, apparent activation energy from τ_m.

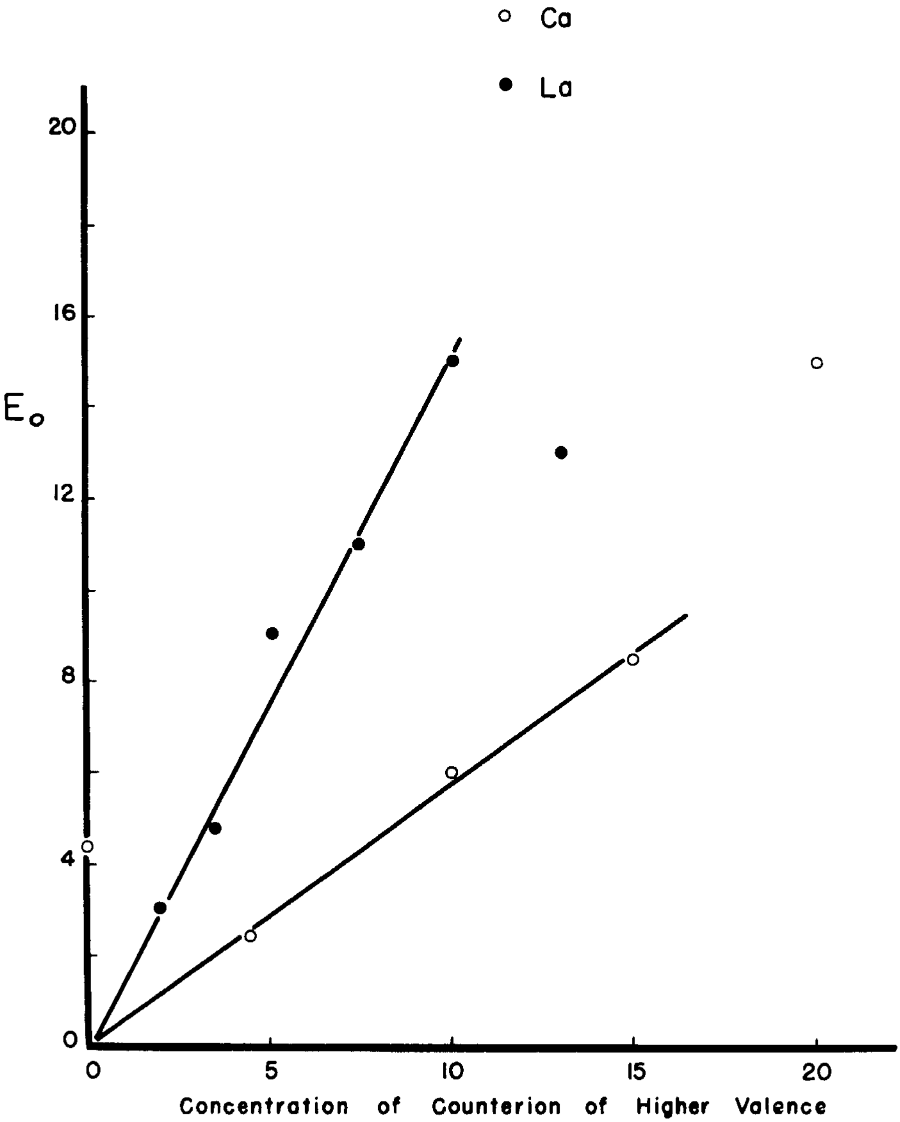

Fig. 9. Modulus corresponding to ultimate Maxwell element (E_m) versus concentration Ca^{2+} or La^{3+} in a region of low concentration.

these two possibilities is the correct one, although a front factor of 1 is possible in view of the occurrence of bond interchange and the resultant ability of the chains to assume their "unperturbed" conformations.

Site of the χ Mechanism

We must now inquire whether bond interchange occurs at random or whether La^{3+} is involved in the reaction. A priori we could assume that since glass transition temperature is raised in the La^{3+}-containing materials as compared to pure $(NaPO_3)_x$, the occurrence of bond interchange could be due only to this increase in temperature. After all, we know that bond interchange occurs rapidly enough in the melt (above ca. 650°C) to make the viscosity practically independent of the molecular weight. However, the work on $[Ca(PO_3)_2]_x$, the glass transition temperature of which is ca. 520°C, showed the absence of bond interchange in that material in the glass transition region and above; thus the slight increase in T_g of the La^{3+} systems cannot be held responsible for the bond-interchange reaction and the La^{3+} must be the catalyst.

Another line of reasoning can be followed to arrive at the same conclusion, the reasoning being based on the correlation of the relaxation time with the La^{3+} concentration. Again, we start with the consideration that bond interchange may occur either at random or at the cross-links, i.e., the sites neighboring the La^{3+}. How does each of these possibilities affect the maximum relaxation time, assuming that it alone reflects the χ mechanism? The rate of stress relaxation is directly proportional to the rate of interchange and also directly proportional to the chain length between cross-links; i.e., the fewer the network chains that support the stress, the faster the stress will relax at a constant rate of bond interchange. If bond interchange occurs at random, then the rate of interchange is independent of the $[La^{3+}]$ (since it is not a catalyst) but does depend on M_c. The latter, in turn, is inversely proportional to $[La^{3+}]$. Thus the rate of stress relaxation should be inversely proportional to $[La^{3+}]$. On the other hand, if bond interchange occurs at the site of the La^{3+}, then the rate of bond interchange should depend on $[La^{3+}]$, owing to its action as a cross-linking agent; thus, since the inverse proportionality to $[La^{3+}]$ due to its cross-linking effect still holds, the rate of stress relaxation should, if the catalytic action is first order, be independent of $[La^{3+}]$. Finally, it should be recalled that the rate of stress relaxation is related to the relaxation time by $df/dt = f(1/\tau)$, where f is the stress.

Before applying this relatively straightforward line of reasoning to the system under study, we must consider the effect of the proximity of the glass transition temperature on the process. While the bond-interchange process does contribute appreciably to the total viscosity even at the glass transition temperature, the transition itself is undoubtedly due to very short range motions of the chain which leave the backbone intact. Thus the glass transition can be regarded as a temperature at which the mobility of the chain segments is approximately constant. Therefore, in attempting to decide whether τ_m is or is not dependent on La^{3+}, we have to use the glass transition temperature as a reference temperature (as was pointed out before), since the mobility of a polyphosphate chain in a sample will depend much more on its distance from T_g than on its absolute temperature. Thus, rather than plotting log τ versus 1/T for samples of various $[La^{3+}]$, we plotted log τ versus $(1000/T) - (1000/T_g)$. This was shown in Fig. 5 and clearly indicates that within experimental error τ is independent of $[La^{3+}]$ (once the effect of $[La^{3+}]$ on T_g is removed), and that therefore bond interchange occurs at the La^{3+} sites.

Rate Constant for the Interchange Reaction

Having computed the activation energy of the interchange reaction and shown that it occurs at the site of the La^{3+}, it is of interest to compute the absolute rate constant for the reaction. The calculation of rate constants from stress relaxation data has been investigated extensively before for completely cross-linked rubbery materials for a wide range of possible cases [10, 20-23]; however, since we are not dealing with a rubbery material, we have to utilize the elastic modulus corresponding to the equivalent ultimate Maxwell element, which was taken before to represent the total chemical activity or bond-interchange contribution in the material. The assumptions that have to be made in the derivation include the following:

1. All the network chains are of uniform length.
2. The χ mechanism is a true bond-interchange process rather than an irreversible chain scission.
3. The "ultimate equivalent" Maxwell element reflects the entire χ mechanism.

Following the formalism of Tobolsky [10, 23], we set the number of chains supporting the stress at $t = 0$ to $n(0)$, the corresponding number at time t being $n(t)$. Again, considering only the "ultimate" element, we assume that the stress at any time is proportional to the number of chains that still support the stress, i.e., $n(t)/n(0) = f(t)/f(0)$, where f is the stress. The identical assumption is made in the case of rubbery materials. Since we know experimentally that the stress decays exponentially, in complete analogy to a first-order reaction, it is reasonable to set $-dn(t)/dt = kn(t)$, i.e., the rate of stress relaxation as proportional to the number of network chains still supporting the stress, k being the rate constant of the reaction. It should be borne in mind, however, that network interchange occurs continuously at a uniform rate, but that we detect by stress relaxation only the interchanges of those cross-links which still support the network and which existed since the imposition of stress, because cross-links reformed since then would be formed so as not to introduce any new net stress. Thus the absolute rate of interchange is given by the last equation for $t = 0$, since at that point each cut is effective.

Rewriting the last equation in the light of the preceeding one, we can say that $-df(t)/dt = kf(o)$, which, in its integrated form becomes $f(t) = f(o) \exp(-kt)$, which is the equation for Maxwellian decay. Thus $k = 1/\tau$, and the rate constant at the glass transition temperature for all materials of a high enough La^{3+} content is $k(T_g) = 1 \times 10^{-3}$ sec^{-1} and changes with an activation energy of ca. 50 kcal/mole.

It should be stressed that some assumptions have been made in the above derivation which make the results only first-order approximations. Assumption 1, i.e., a uniform chain network, could have been substituted by a most probable distribution of lengths, which would have introduced an additional correction factor [22], which is small compared to the inaccuracies inherent in the experiment and the other assumptions. Also, it is possible that a chain, once broken, does not necessarily reform in an unstrained state, but, unfortunately, no quantitative corrections can be made for this contingency since the degree of this frozen-in strain cannot be measured, owing to its randomness.

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