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Viscoelastic Relaxation Mechanism of Inorganic Polymers. V: Counterion Effects in Bulk Polyelectrolytes

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Synopsis

The viscoelastic properties of an inorganic anionic polymer were studied as a function of the counterion. It is shown that as the counterion strength (expressed, for instance, by the ratio of charge to internuclear distance between cation and oxygen anion) increases, the distribution of relaxation times narrows in an approximately linear manner. A small effect of the molecular weight is also observed on the narrowing of the relaxation spectrum, but the latter is much smaller than the former.

It is known that ionic forces change the properties of polymeric materials profoundly (*1–7*); for instance, the glass transition temperature of one system can be raised by as much as 530°C. In spite of this the quantitative effects of these forces on the viscoelastic behavior have not yet been explored extensively. In organic polymers the introduction of ionic groups is possible only within rather narrow limits, since the materials become unmanageable with increasing ionic strengths; it is therefore necessary to resort to inorganic materials in order to obtain a quantitative idea of the effects involved. The polyphosphates represent perhaps the best system of a completely ionic polymer (every repeat unit carries one change) in which the counterion can be varied at will and in which preparation of homogeneous amorphous samples presents no difficult problems. Furthermore, the polyphosphates, being

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* Contribution No. 1894.

linear ionic polymers, represent an excellent bridge between the linear nonionic organic polymers on one hand and the highly cross-linked ionic inorganic glasses on the other, so that a study of those polymers may improve our understanding of the interrelation of these two large families of materials.

In this work the results of a study of the viscoelastic properties of a series of anionic polyphosphates as a function of counterion strength will be reported. The study is limited to monovalent and divalent cations (Na^+, K^+ and Ca^{2+}) in various proportions, the glass-transition temperatures of the materials ranging from 210 to 520°C (5). The results of a study involving a trivalent cation (La^{3+}) will be reported separately, because in that instance it was found (*6*) that the relaxation mechanism of the polymer changed from simple molecular flow encountered in pure $(NaPO_3)_x$ (*7*) to a superposition of this mechanism and bond interchange upon addition of even a small percentage of lanthanum. Some results, however, will be reported here insofar as they have a bearing on the present discussion. Specifically, the attempt is made here to see to what extent cation strength (expressed, for instance, by the ratio of the cation charge to the internuclear distance between cation and oxygen anion on the phosphate chain) affects the width of the spectrum of relaxation times, the constants of the WLF equation, and other parameters that characterize the viscoelastic properties of a material in the absence of mechanistic complications represented by bond interchange or by drastic changes in the structure of the materials.

Before proceeding it is advisable to review briefly the results of relevant studies that preceded the present work. In addition to the work on partially or completely neutralized copolymers of organic acids (*1–3*) with nonionizable monomers, it was shown that lithium perchlorate could be dissolved in organic polyethers (*4*) with an attendant rise in the glass-transition temperature. With regard to the polyphosphates, their solution properties have been studied extensively in several laboratories (*8–11*). The glass transitions in sodium phosphate polymers were studied both as a function of the chain length (*12*) and as a function of the ionic strength (5), the latter work demonstrating a linear relation between the glass transition and the ratio of the cation charge to the internuclear distance between cation and oxygen. A study of the viscoelastic properties of sodium phosphate polymers as a function of the molecular weight showed that the behavior of these polymers is quite similar to that of nonionic materials, except that the dependence of the maximal relaxation time (*13*) on molecular weight below the critical entanglement region was considerably higher, the exponent of the molecular weight being between 2 and 3, in contrast to the range of 1 to 2 encountered in nonionic polymers. Finally, a study of "polysalt," a stoichiometric adduct of poly(styrene sulfonate) and poly(vinylbutyltrimethylammonium), a polyanion–polycation complex, should be mentioned (*14*). It was found that a single master curve could express the relaxation of the material as a function of swelling, electrolyte concentration, temperature, etc.

EXPERIMENTAL TECHNIQUES

Sample Preparation

The details of the sample preparation technique have been given elsewhere (*5*). In brief, it consisted of preparing dehydrated polymeric glassy $NaPO_3$ or $Ca(PO_3)_2$ or crystalline KPO_3, mixing appropriate amounts to obtain the desired copolymers, heating, and pouring into molds. The molded samples were further ground (*7*) into prisms of precise dimensions.

Stress Relaxation Studies and Molecular Weight

These experimental details also have been reported elsewhere, as was the design of the instrument with which the experiments were performed (*7*).

EXPERIMENTAL RESULTS

The stress relaxation master curves (*15*) for the sodium-potassium copolymers with T_g as the reference temperature for each sample are shown in Fig. 1; the distribution of relaxation times for the same samples are shown in Fig. 2. Only the first approximation is shown here (*15*), since it had been found before that within experimental error for these materials the second approximation offers no significant improvement. Finally, Fig. 3 shows the shift factors (*15*) for the same samples, plotted as $\log a_T$ versus $T - T_g$, the dotted line being a plot of the WLF equation (*16*) with universal constants.

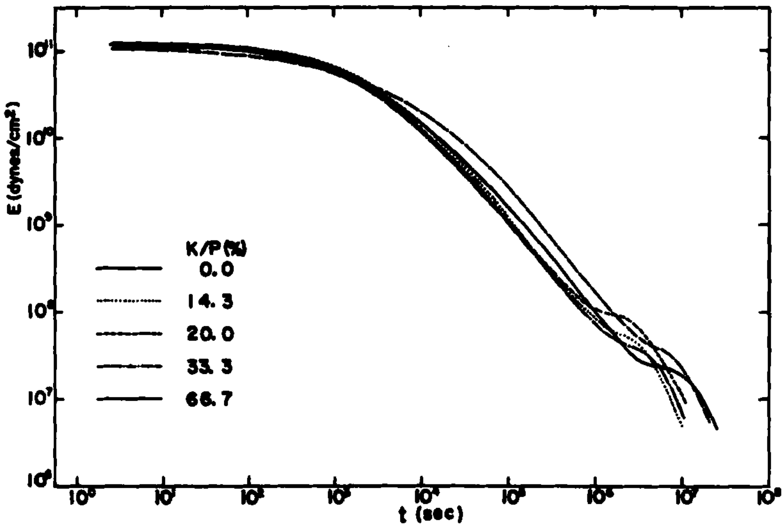

FIG. 1. Stress relaxation master curves for $NaPO_3$-KPO_3 copolymers.

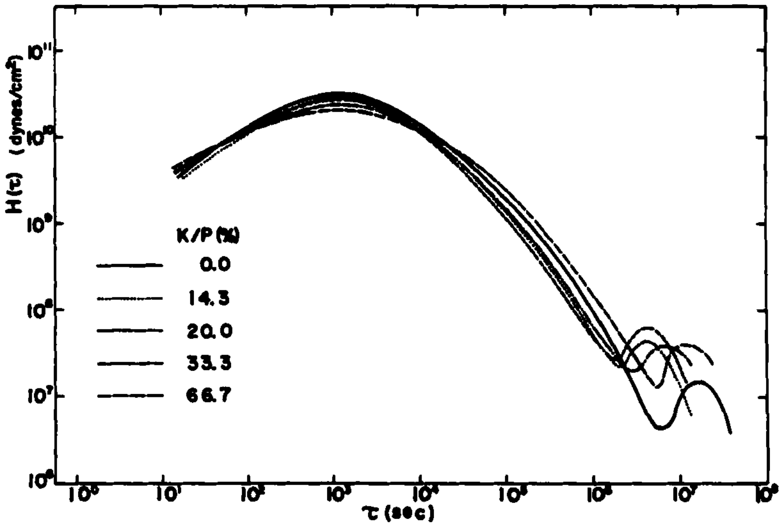

FIG. 2. Distribution of relaxation times in stress relaxation for $NaPO_3$-KPO_3 copolymers.

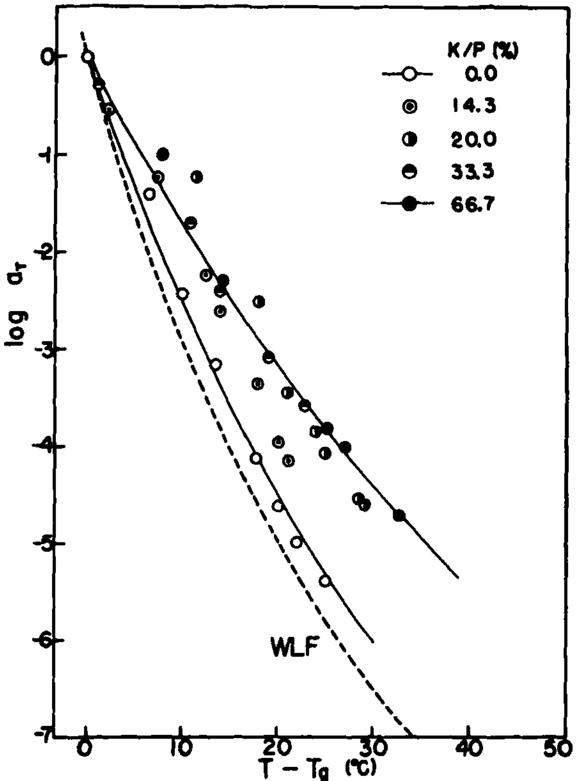

FIG. 3. Time-temperature shift factors for $NaPO_3$-KPO_3 copolymers. The dashed line is the WLF equation with universal constants.

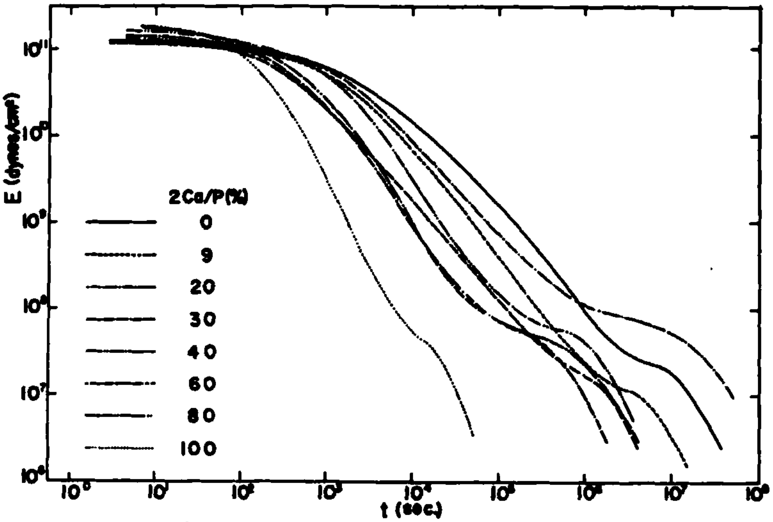

FIG. 4. Stress relaxation master curves for $NaPO_3$-$Ca(PO_3)_2$ copolymers.

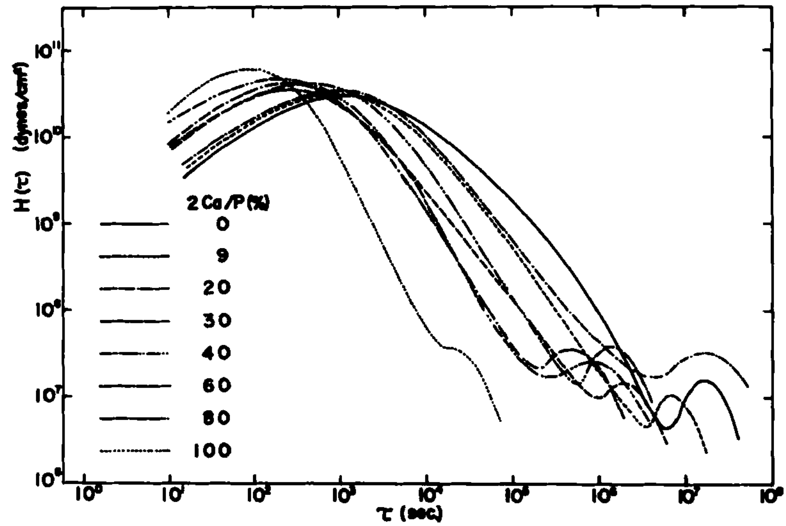

FIG. 5. Distribution of relaxation times in stress relaxation for $NaPO_3$-$Ca(PO_3)_2$ copolymers.

Figures 4, 5, and 6 reproduce the same data for the $NaPO_3$-$Ca(PO_3)_2$ systems, Fig. 4 showing the stress relaxation master curves, Fig. 5 reproducing the distribution of relaxation times, and Fig. 6 giving the shift factors for the various samples.

Finally, Table 1 gives the degrees of polymerization, $\bar{P}_n$, for the

TABLE 1

Degrees of Polymerization and Calculated Constants[a] for the WLF equation (*16*) and Derived Values of the "Fractional Free Volume" f_g and the Free Volume Expansion Coefficient α_f for $NaPO_3$-$Ca(PO_3)_2$ Copolymers

			Constants			
100 × 2 Ca/P	$\bar{P}_n$	T_g, °C	C_1	C_2	f_g	α_f, × 10^4
0	—	287	21	75	0.021	2.8
9	161	290	24	132	0.018	1.4
20	174	300	23	125	0.019	1.5
30	126	315	31	277	0.014	0.5
40	112	330	33	303	0.013	0.4
60	91	380	32	302	0.014	0.5
80	—	430	30	382	0.015	0.4
100	48	520	22	270	0.020	0.7

[a] $\log a_T = -C_1(T - T_g)/(C_2 + T - T_g)$.

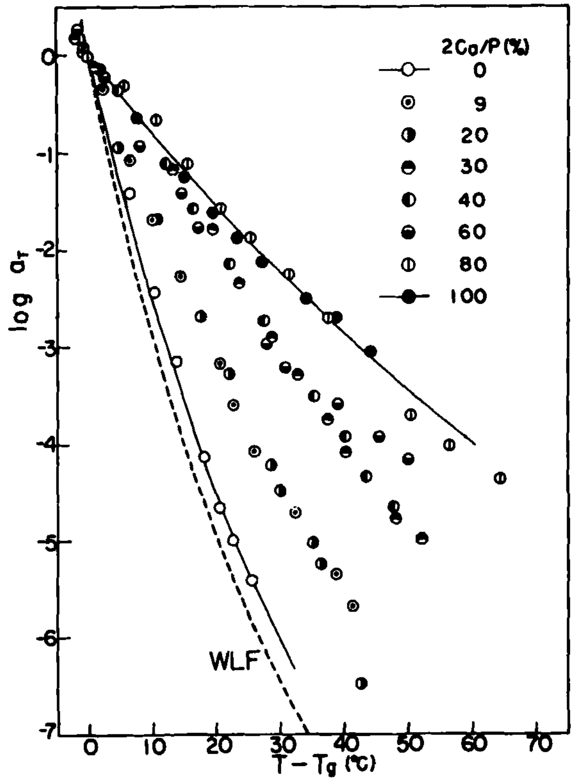

FIG. 6. Time-temperature shift factors for $NaPO_3$–$Ca(PO_3)_2$ copolymers. The dashed line is the WLF equation with universal constants.

$NaPO_3$–$Ca(PO_3)_2$ samples for which these were measured. The technique of intrinsic viscosity was employed, using the procedures and constants given by Strauss et al. (*8,17*). Table 1 also gives other data, which will be discussed.

DISCUSSION

The Stress Relaxation Master Curves

In Figs. 1 and 4 a pronounced inflection point or incipient plateau can be observed at a modulus of about 10^7 dynes/cm^2. Since this value lies near the lower limit of detectability for the sample geometries that had to be employed here, the accuracy in the position of this plateau is not very high. The plateau itself, however, is believed to be real and to reflect molecular entanglements just like those encountered in organic materials.

The Distribution of Relaxation Times

As can be seen from Figs. 2 and 5, the distribution of relaxation times narrows appreciably with increasing Na^+ content in the Na^+–K^+ copolymers and with increasing Ca^{2+} content in the Na^+–Ca^{2+} copolymers. This can be due to one of two possible causes or to a combination of both: a decrease of the molecular weight or an increase in the three-dimensional character of the material upon the increase in concentrations indicated above, that is, an increase in electrostatic interactions between chains.

The first possibility emerges from the fact that a decrease in the number-average chain length below about 200 units has been observed to lead to a decrease in the width of the relaxation spectrum in $NaPO_3$ homopolymer (see below). The second emerges from a prediction made by Tobolsky (*18*), who showed that a three-dimensional polymer should have a narrower relaxation-time spectrum than one that is encountered in the case of a linear material. Indeed, a very narrow (single-line) spectrum was observed in the case of a low-molecular-weight glass (*19*), a model "three dimensional" material. This concept might be applicable here also, because, as has been pointed out previously in connection with glass-transition studies in ionic polymers (*5*), an increase in the average value of q/a, where q is the cation charge and a is the internuclear distance between the cation and the oxygen, leads to an increase in the glass-transition temperature as a result of an increase in both the barrier to internal rotation and the "hole-formation energy" or interchain energy, as defined in the Gibbs–Di Marzio theory (*20*). An increase in the Na^+ concentration in the Na^+–K^+ copolymers or an increase in the Ca^{2+} concentration in the case of the Na^+–Ca^{2+} system leads to an increase in the average value of q/a, since the q/a values for the pure materials are 0.37 for K^+, 0.42 for Na^+ , and 0.84 for Ca^{2+}. The increase in the interchain energy makes the interchain forces more significant in relation to the primary backbone bonds and tends to give the polymer an increased three-dimensional character, which might reflect itself in the width of the spectrum of relaxation times.

Before attempting the correlation between the width of the spectrum and either the q/a value or the molecular weight it is necessary to find a quantitative measure of the width of the relaxation spectrum. This is done by the following means. On a plot of $H(\tau)$ versus log τ a perpendicular is dropped from the point at which $H(\tau)$ reaches the maximum down to the log τ axis. Halfway between the maximum and the log τ axis a line is drawn parallel to the axis,

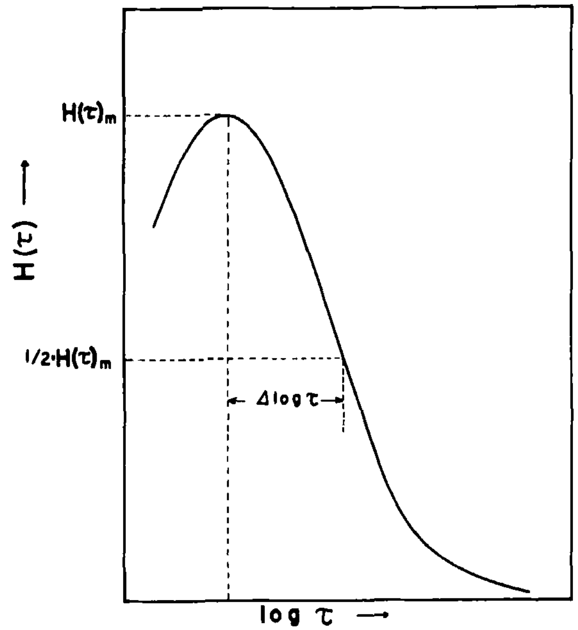

FIG. 7. Illustration of the method used for determining Δ log τ.

and the length of the line between the perpendicular and the intersection with the $H(\tau)$ plot at high τ values is taken as a measure of the width of the relaxation spectrum; it is called Δ log τ. The entire half-width is not taken, because the error in $H(\tau)$ is greatest at the short τ side. An illustration of the method of obtaining Δ log τ is shown in Fig. 7, and the plot of Δ log τ versus q/a is given in Fig. 8, indicating a practically linear relationship between these two variables. It should be pointed out that the point at $q/a = 0$ was obtained from a previous study of the polyphosphoryl dimethylamides (*21*) and is believed to be applicable to the correlation given above, at least approximately, because the backbone is identical, the "side chains" being —$O^{-}Na^{+}$ in the case of the ionic

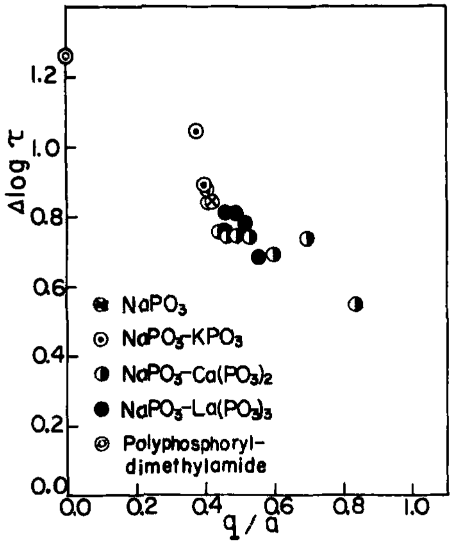

FIG. 8. Dependence of Δ log τ on cation strength, expressed by ratio of charge q to internuclear distance a between cation and oxygen; q/a values not corrected for molecular weight.

sodium polyphosphates and —$N(CH_3)_2$ in the nonionic case. The latter is probably somewhat larger than the former, so that the observed linearity down to $q/a = 0$ may be fortuitous; the trend, though, is clear.

It should be stressed, however, that superimposed on this q/a effect is the effect of molecular weight. The change of the spectral width with molecular weight is not large and is shown in Fig. 9 (with an enlarged Δ log τ scale) for pure $NaPO_3$ terminated by hydroxyl groups and for a 1:1 $NaPO_3$-KPO_3 copolymer. As can be seen, the effects are comparable in these materials. The linearity, however, may be fortuitous or due to the small range of molecular weights that is accessible. In any case, since the effect is not large, and since the range of molecular weights shown in Table 1 also is small, the effect of molecular weight on Δ log τ was not incorporated in the data plotted in Fig. 8.

The Possibility of Bond Interchange

Bond interchange has been observed in the case of $La(PO_3)_3$-$NaPO_3$ copolymers (6), whereas none was observed in pure $NaPO_3$

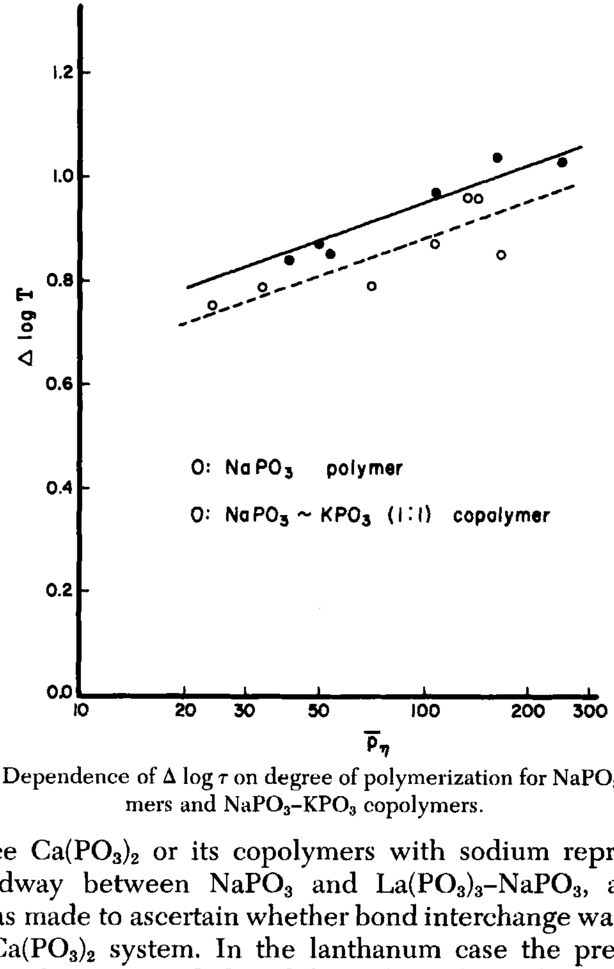

FIG. 9. Dependence of Δ log τ on degree of polymerization for $NaPO_3$ polymers and $NaPO_3$-KPO_3 copolymers.

(7). Since $Ca(PO_3)_2$ or its copolymers with sodium represent an area midway between $NaPO_3$ and $La(PO_3)_3$-$NaPO_3$, a careful study was made to ascertain whether bond interchange was present in the $Ca(PO_3)_2$ system. In the lanthanum case the presence of bond interchange was deduced from the failure of time–temperature superposition to apply over a relatively wide region of the modulus and from the fact that the shift factors and the maximum relaxation times had drastically different temperature dependencies or activation energies. The difference in activation energies is due to the fact that the shift factors (in those regions where time–temperature superposition does apply) reflect the temperature dependence of "normal" molecular motions which leave the backbone intact, whereas the maximum relaxation time reflects chemical bond interchange. In "normal" polymers, on the other hand (those in which bond interchange is completely absent) both the shift factors and the maximum relaxation times reflect the same molecular processes and have the same temperature dependence, at least to a very good approximation. It should be recalled here that Plazek has shown (22) that the shift factors for viscosity and for recoverable compliance, although quite similar (both being of the WLF form), are not identical; their difference, however, is much smaller than that due to bond interchange versus molecular flow. Thus, if a log–log plot were made of the shift factors a_t against the maximum relaxation times τ_m, a line with a slope of about 1 should result; if bond interchange is encountered, however, the slope should be

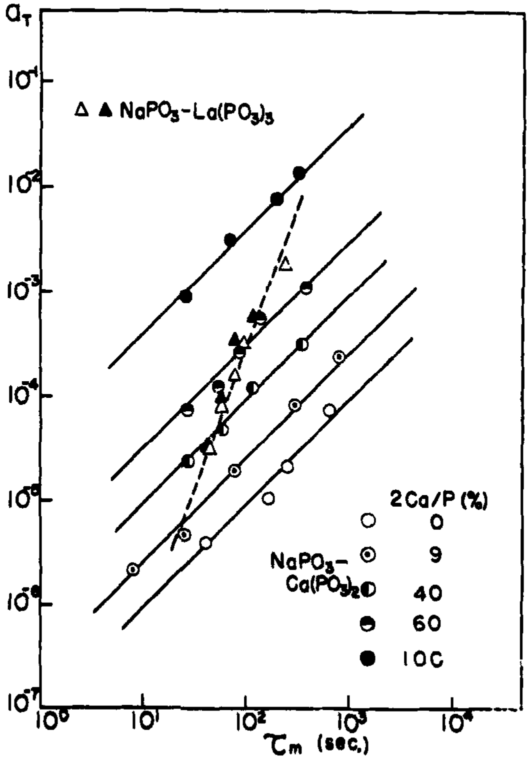

FIG. 10. Plot of shift factors a_T and maximum relaxation times τ_m, illustrating the absence of bond interchange in the NaPO$_3$–Ca(PO$_3$)$_2$ copolymers (slope = 1) and the presence of bond interchange in the NaPO$_3$–La(PO$_3$)$_3$ copolymers (slope > 1).

drastically different, the difference reflecting the differences in the activation energies for the two processes. Figure 10 shows a plot of log a_t versus τ_m for the $NaPO_3$–$Ca(PO_3)_2$ copolymers, giving a slope of 1 over the whole range of compositions. By contrast, the plot for the two $La(PO_3)_3$–$NaPO_3$ samples shows a different slope, indicating the presence of two different mechanisms in those materials. The dashed line does not imply linearity over very wide ranges of τ_m; it merely illustrates the drastic change in slope.

WLF Parameters

A study of Figs. 3 and 6 reveals the interesting fact that the shift factors in $NaPO_3$ can be fitted by means of constants very similar to those of the "universal" WLF equation, the deviations increasing with increasing Ca^{2+} or K^+ content. No reasonable explanation of the phenomenon can be offered at this time. Further as Table 1 (which also gives the various WLF parameters for the Ca^{2+} system) reveals, both f_g and α_f (where f_g is the fractional free volume at T_g and α_f is the "free volume expansion coefficient") go through a minimum in the region in which about half the backbone charges are neutralized by the Ca^{2+}. Since this minimum was observed in this work (in which it was calculated from the shift factors) in the study of the glass transitions (5), in which $T_g\Delta\alpha$ was determined experimentally (where $\Delta\alpha$ is the difference between the cubic expansion coefficients above and below T_g), and in V_0 (equivalent to f_g but calculated from the Gibbs-DiMarzio theory) (5) it is believed to be physically real. It has, incidentally, also been observed in the case of conductivities of borates and silicates (23) when two counterions were present in equimolar concentrations. No explanation of this phenomenon can be given at present beyond that already presented in work on glass transitions (5).

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