

Studies of Relaxation Phenomena in Polymers. III. Superimposed Transition Mechanisms in Polyisobutylene and Poly(vinyl Acetate)

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Synopsis

Based on the general properties of the function $\log J_2 = g_\alpha \{\log J_1\}$, discussed in earlier papers,^{1,2} the existence of two superimposed dispersion mechanisms in the glass-rubber transition of polyisobutylene (PIB), and poly(vinyl acetate) (PVAc) is discussed. A simple weighting model is used for separation of the two mechanisms. For the interpretation of the β -mechanism, in PIB, the following facts are taken into account: (a) The loss maximum of the β -mechanism appears in a zone where only very reduced segment movements occur. (b) The methyl side groups in PIB require special conformations of the main chains before they can rotate. (c) The apparent activation energy for the β -mechanism is approx. 20 kcal/mole. Thus, for PIB the following interpretations for the α - and β -mechanisms are proposed: (1) The α -mechanism is due to simple segment movements. (2) The β -mechanism appearing in the " T_g region" is due to coupled movements between the main chain and methyl side groups. The ester groups of poly(vinyl acetate) need a lot more space for their rotations than the carboxy groups of poly(methyl acrylate) and can be expected to give considerable steric hindrance. It is therefore reasonable to suppose that a transition mechanism similar to the β -mechanism of polymethacrylates will appear in the "freezing" region of poly(vinyl acetate). The analysis of the β -mechanism is made using the same separation method as for polyisobutylene.

INTRODUCTION

In earlier papers,^{1,2} the general properties of the function $\log J_2 = g_\alpha \{\log J_1\}$ were discussed for a series of polymers, the linear viscoelastic behavior of which was dominated by only one molecular mechanism in their main transition region, i.e., simple segment movements.

Divergences from the general shape of the function may be expected to be rather common both for polymers in which the segment movements are disturbed by steric hindrance, stiff groups in the main chains, hindrances in the neighborhood of crystallites, and other regions with a high degree of ordered structure and with large secondary forces between different chains or parts of the same chain, and for polymers with superimposed transition mechanisms, e.g., coupled movements between the main chains and large side groups, decomposition of "widely spaced entanglements," or "untrapped entanglement," etc.

In the following, an analysis is made of the divergences from the general shape of the function for the case of polyisobutylene and poly(vinylacetate).

SUPERIMPOSED TRANSITION MECHANISMS IN THE MAIN TRANSITION REGION OF POLYISOBUTYLENE

In a paper from 1953, Fitzgerald, Gerandine, and Ferry³ report dynamic mechanical measurements on polyisobutylene at temperatures between -45° and $+100^\circ\text{C}$ and frequencies between 30 and 5000 Hz. The studied polymer had a molecular weight of 1.35×10^6 , weight-average from measurements of viscosity.

The curves of the loss factor $\tan \delta$ as a function of temperature at constant frequency show, besides a broad maximum in the main transition region, a shoulder or secondary maximum in the low-temperature side of the main peak. By changing the temperature, both transitions are shifted by about the same amount. Thus, their apparent activation energies are almost the same. It is reasonable to assume that this secondary transition is due to steric hindrance from the methyl side groups.

In the following, an attempt is made to find a more detailed explanation of the superimposed transition mechanisms and to separate them. Herein, it is assumed that the general properties of the function $\log J_2 = g_\alpha \{\log J_1\}$ are valid for the explanation of simple segment movements, the α -mechanism, of polyisobutylene.

The compliances J_1 and J_2 have been calculated in accordance with the interrelations pointed out by Jansson¹ from complex compliance at frequencies between 70 and 600 Hz taken from Fitzgerald et al.³ The function $\log J_2 = g \{\log J_1\}$ is plotted in Figure 1 at five different frequencies together with the functions $\log J_2 = g_{\alpha 0} \{\log J_1\}$. A significant divergence is seen at low temperatures or short times from the general shape pointed out by Jansson.² However, at high temperatures or long times (well above the "glass point"), the shape of the function coincides completely with the properties of the general function² $\log J_2 = g_{\alpha 0} \{\log J_1\}$ and gives a "freezing-in compliance" of $J_{10} \approx 3 \times 10^{-2} \text{ mm}^2/\text{N}$. From this point of view, it is reasonable to assume that the shoulder in $\tan \delta$ derives its origin from a superimposed secondary transition mechanism.

In Figure 2, $\log J_1$ and $\log J_2$ are plotted as functions of temperature at $2.5 \times 10^{-3} \text{ s}$ and $4.15 \times 10^{-4} \text{ s}$. The J_1 curve corresponding to the α -mechanism is the dashed line.

The J_2 curve is linear or almost linear at low temperatures.

From Figures 1 and 2, from the general properties of $\log J_2 = g_\alpha \{\log J_1\}$, and from data for the complex compliance it can be concluded that the secondary process gives an increase in both mechanical losses and stiffness of the polymer. Using the subscript α for the main transition process and β for the secondary mechanism, this can be written

$$\begin{aligned} J_1 + J_2 &\leq J_{1\alpha} + J_{2\alpha} \\ J_2/J_1 &\geq J_{2\alpha}/J_{1\alpha} \\ J_1 &\leq J_{1\alpha}; J_2 \geq J_{2\alpha} \end{aligned} \quad (1)$$

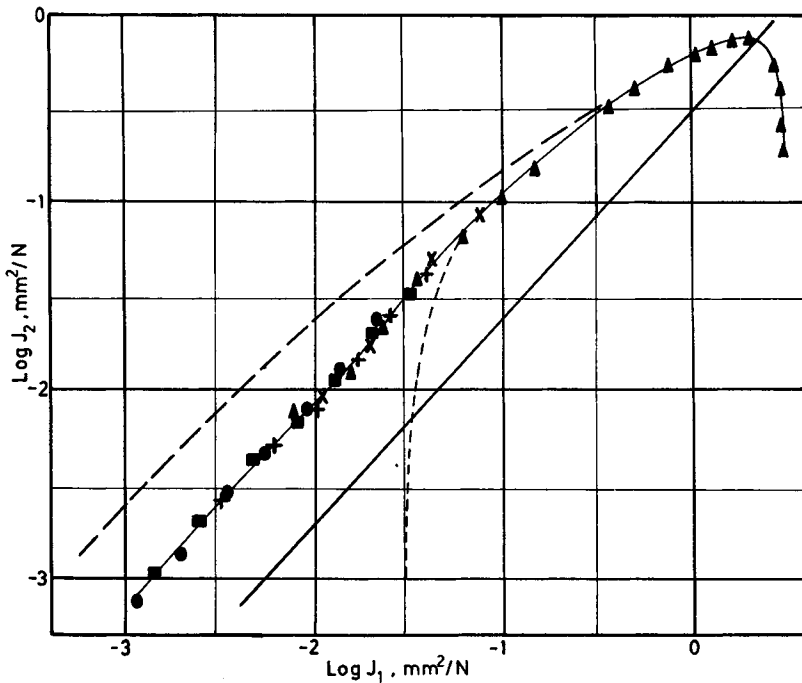


Fig. 1. Function $\log J_2 = g\{\log J_1\}$ for PIB: (—) $\log J_2 = g_{\alpha 0}\{\log J_1\}$; (---) $\log J_2 = g_{\alpha}\{\log J_1\}$; (X) 3.6×10^{-3} sec; (▲) 2.5×10^{-3} sec; (+) 1.25×10^{-3} sec; (■) 8×10^{-4} sec; (●) 5.5×10^{-4} sec.

Furthermore, the α -mechanism dominates at high temperatures or long times while the β -mechanism dominates at low temperatures or short times. This means that

$$J_{1\beta} \approx J_1 \ll J_{1\alpha} \text{ and } J_{2\beta} \ll J_2 \approx J_{2\alpha} \quad (2)$$

at low temperatures, and

$$J_1 \approx J_{1\alpha} \ll J_{1\beta} \text{ and } J_2 \approx J_{2\alpha} \gg J_{2\beta} \quad (3)$$

at high temperatures.

The resultant of the superimposed α - and β -mechanisms is assumed to be the combination of the two general functions, $\log J_2 = g_{\alpha}\{\log J_1\}$ describing the α -mechanism and $\log J_2 = g_{\beta}\{\log J_1\}$ for the β -mechanism:

$$\begin{aligned} \log J_2 &= \log\{f_2(J_{2\alpha}; J_{2\beta})\} \\ &= g\{\log J_1\} \equiv g\{\log[f_1(J_{1\alpha}; J_{1\beta})]\} \end{aligned} \quad (4)$$

where the functions f_1 and f_2 give the coupling between the superimposed processes and the shape of $\log J_2 = g_{\alpha}\{\log J_1\}$ is assumed to agree with the curves shown by Jansson.² The problem is to find the coupling functions f_1 and f_2 for these mechanisms. Until further experience is obtained regarding the shape of the function $\log J_2 = g\{\log J_1\}$ in the presence of superimposed transition mechanisms, the possibility of separating the two processes is limited to determining a relative weighting.

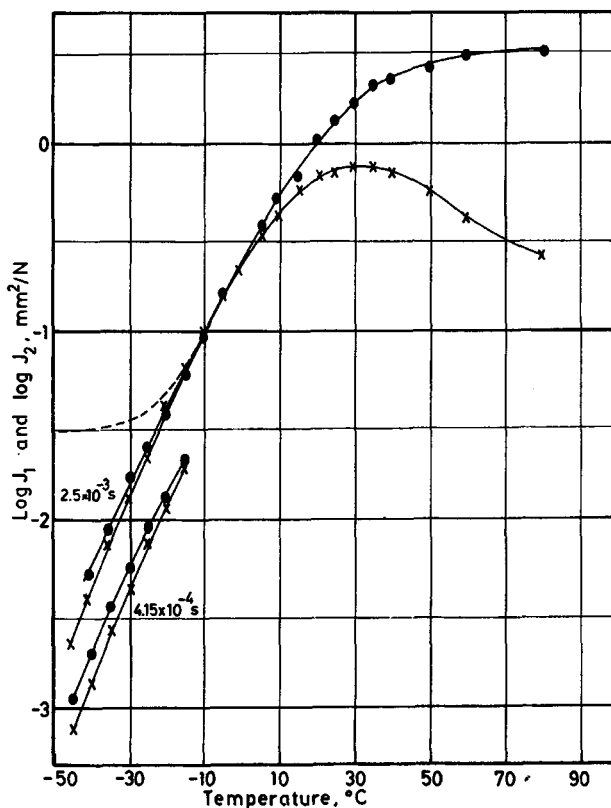


Fig. 2. Functions $J_1(T)$ and $J_2(T)$ for PIB: (●) $J_1(T)$; (×) $J_2(T)$.

Based on the experimental experience mentioned above, the following simple mathematical model is assumed for the combination of the two superimposed dispersion mechanisms

$$J_2 = J_{2\alpha} + J_{2\beta}$$

and

$$\frac{1}{J_1} = \frac{1}{J_{1\alpha}} + \frac{1}{J_{1\beta}} \quad (5)$$

where the α - and β -components contain a weighting factors which takes into account the active molecular fractions involved in each process. The small deviations from linearity in the J_2 curve cannot be utilized for calculation of $J_{2\beta}$ which is much smaller than J_2 or $J_{2\alpha}$ ($J_{2\beta\max} < 5 \times 10^{-4} \text{ mm}^2/\text{N}$).

Figure 3 shows $\log J_{1\alpha}$, $\log(J_{1\alpha} - J_{10})$, and $\log J_{1\beta}$ at 2.5×10^{-3} , 8.3×10^{-4} , and 4.15×10^{-4} sec, calculated in accordance with eq. (5). $\log(J_{1\alpha} - J_{10})$ varies linearly with temperature, which is consistent with the general characteristics pointed out by Jansson.² This supports the separation model used.

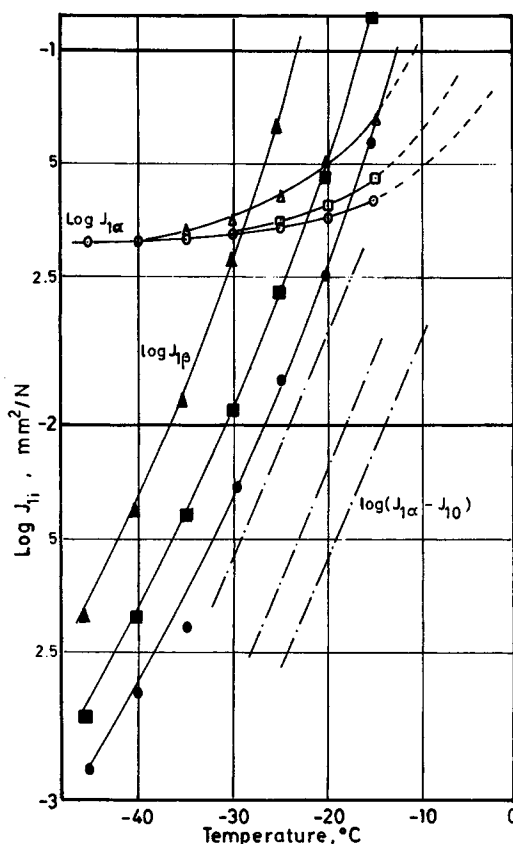


Fig. 3. Functions $J_{1\alpha}(T)$, $J_{1\beta}(T)$, and $J_{1\alpha}(T) - J_{10}$ for PIB: (▲) 2.5×10^{-2} sec; (■) 8×10^{-4} sec; (●) 5.5×10^{-4} sec.

From the curves in Figure 3, the apparent activation energy has been determined in the usual way. This gives 26 kcal/mole for the α -mechanism, which agrees with values assembled by McCrum, Read, and Williams,⁴ and 21 kcal/mole for the β -mechanism.

Conclusions

Based on the general properties of the function $\log J_2 = g_\alpha\{\log J_1\}$, the existence of two superimposed dispersion mechanisms has been indicated for the glass-rubber transition of polyisobutylene. A simple weighting model for the coupling of the J_1 and J_2 functions of the mechanisms has been used for the separation of the processes.

The general shape of the function $\log J_2 = g_\alpha\{\log J_1\}$ has indicated the presence of the α -mechanism (simple segment movements), whereas divergences from the general shape of $\log J_2 = g_\alpha\{\log J_1\}$ in the " T_g region" have indicated the β -mechanism.

The coupling model agrees with experimental experience, but its derivation from molecular theory has not yet been achieved.

The apparent activation energy of the α -mechanism is 26 kcal/mole and of the β -mechanism, 21 kcal/mole at about -20°C . The loss compliance $J_{2\beta}$ of the β -mechanism is much smaller than for the α -mechanism in the overlapping region, and it has not been possible to calculate it.

For the interpretation of the β -mechanism, the following facts may be taken into account: (a) The loss maximum of the β -mechanism appears in a zone where only very reduced segment movements can occur. (b) The methyl side groups in polyisobutylene are so voluminous that they require special conformations of the main chains before they can rotate. (c) The apparent activation energy of approx. 20 kcal/mole is of the same size as that for the coupled transition mechanism between the main chain and side groups for polymethacrylates.

Based on these facts, the following interpretations for the α - and β -mechanisms are proposed:

1. The α -mechanism. The dispersion mechanism dominating the viscoelastic behavior in the high-temperature or long-time region of the main transition region of polyisobutylene is due to simple segment movements.

2. The β -mechanism. The superimposed mechanism in the " T_g region" of polyisobutylene is due to coupled movements between the main chain and methyl side groups in analogy with the case of other polymers with disubstituted carbon atoms in their main chains, e.g., polymethacrylates. The possibility for side group motions being coupled to the movements of the main chain have been discussed theoretically by Koppelman^{5,6} in terms of the "Platzwechsel" concept of Müller.⁷

The elementary mechanisms, i.e., the segment movements in the main chain and the rotation of the side groups, are mutually dependent, and movements in one of them require movements in the other. Thus, it is reasonable to expect increasing mechanical losses, especially in the temperature-frequency (time) region where the segment movements, which need higher activation energy compared with the side group rotation, "freeze in", i.e., in the region around the glass point of the polymer. This explanation corresponds very well with experimental experience of polyisobutylene as well as with the obtained increase in stiffness, which is reasonable also to assign to the coupled movements.

SUPERIMPOSED TRANSITION MECHANISMS IN THE MAIN TRANSITION REGION OF POLY(VINYL ACETATE)

In the previous section, the coupled movement of the main chains and side groups for polyisobutylene has been discussed. An analogous transition mechanism is also noticed in polymethacrylates.⁸⁻¹³ No phenomena of this type have been suggested for either poly(methyl acrylate)² or polypropylene.⁴ Thus, where polymethacrylates and polyisobutylene are concerned, the existence of the α -methyl groups is vital in order for the β -mechanism to occur.

It is, however, reasonable to expect similar coupled movements in polymers with monosubstituted carbon atoms in the main chain and side groups which are more voluminous than the carboxy groups in poly(methyl acrylate).

In the calculation of the function $\log J_2 = g\{\log J_1\}$ for poly(vinyl acetate) from complex compliance data taken from Williams and Ferry,¹⁴ a small deviation from the expected linear relation between $\log J_2$ and temperature can be seen, and it is also apparent as a small deviation from the general shape of the function $\log J_2 = g_\alpha\{\log J_1\}$. This deviation has been reproduced in additional direct measurements of the function $\log J_2 = g\{\log J_1\}$.

Figure 4 shows $\log J_1$ and $\log J_2$ as functions of temperature at time 30 sec in direct measurements for poly(vinyl acetate); and in Figure 5, the function $\log J_2 = g\{\log J_1\}$ is shown for the directly measured data as well as for the calculated data. In both cases, a "glass compliance" of about 1.8×10^{-3} mm²/N is obtained. The differences between the curves are

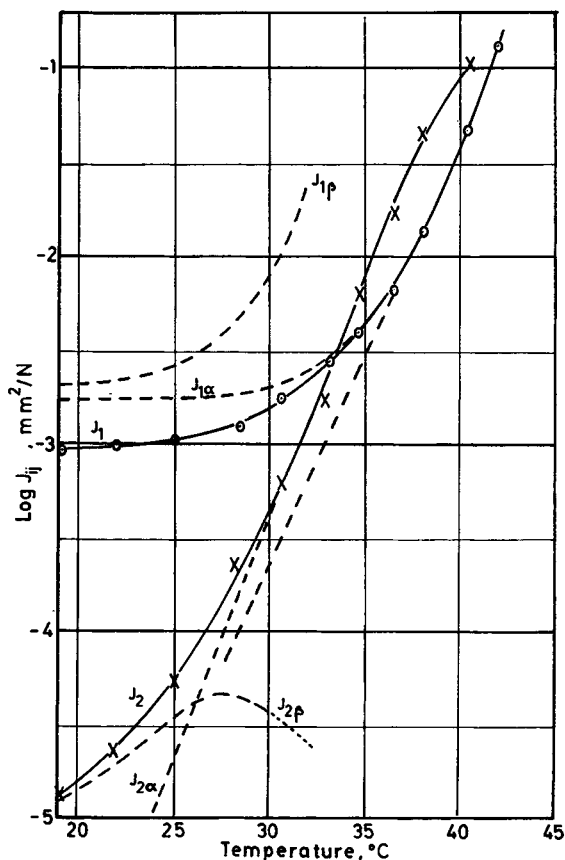


Fig. 4. Functions $J_1(T)$, $J_{1\alpha}(T)$, $J_{1\beta}(T)$, $J_{1\alpha}(T) - J_{10}$, and $J_2(T)$, $J_{2\alpha}(T)$, $J_{2\beta}(T)$ for PVAc from direct measurements at 30 sec.

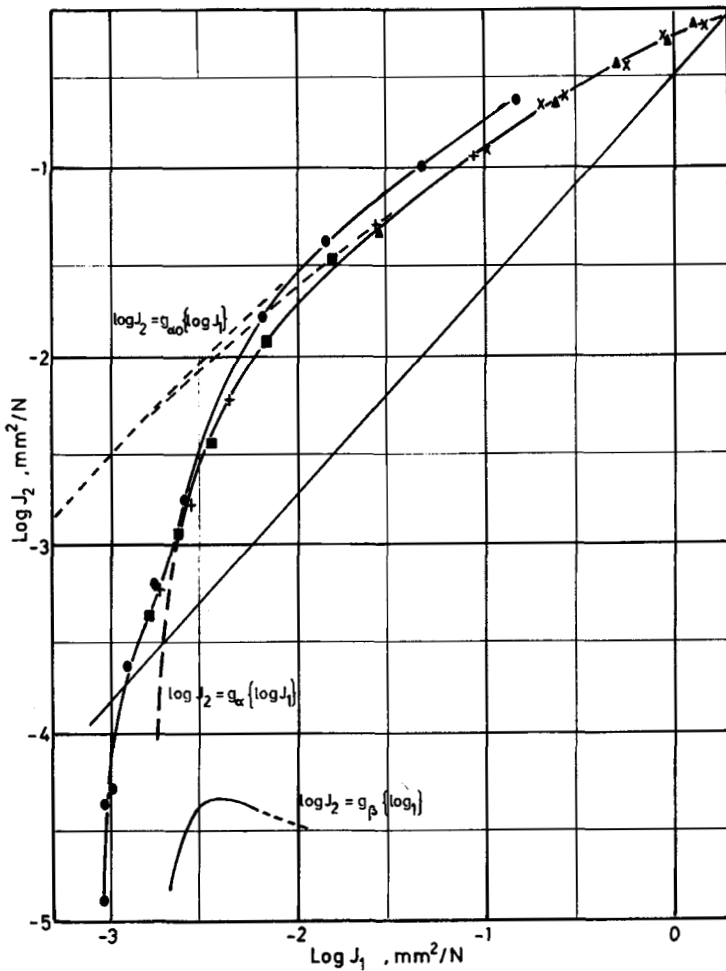


Fig. 5. Function $\log J_2 = g_i\{\log J_1\}$ for PVAc from direct measurements at 30 sec and calculated from complex compliance at: (X) 8.3×10^{-3} sec; (▲) 2.5×10^{-3} sec; (+) 8.3×10^{-4} sec; (■) 5×10^{-4} sec.

completely explicable in terms of the differences in the materials. Ferry's polymer has a molecular weight, \bar{M}_w , of 420,000, while the directly measured polymer has a molecular weight, \bar{M}_w , of 55,000. The curves show the influence of a secondary transition mechanism in the region where only small segment movements occur.

Schmieder and Wolf¹⁵ have observed, by dynamic mechanical measurements at 10 p/s, two secondary transition mechanisms with dispersion maxima at about -30° and -100°C . The peak at -100°C corresponds to the β -mechanism observed by Ishida, Matsuo, and Yamafuji¹⁶ in dielectric measurements and is attributed to side group movements. No dielectric equivalent has been observed for the peak at -30°C . It is therefore assumed to be caused by impurities.

The direct measurements are made at very low deformation rates, and therefore it is not likely that the observed divergences from the general shape of $\log J_2 = g\{\log J_1\}$ at temperatures above $+20^\circ\text{C}$ are caused by a presumptive dispersion at -30°C .

The ester groups of poly(vinyl acetate) need a lot more space for their rotations than the carboxy groups of poly(methyl acrylate) and can be expected to give considerable steric hindrance. It is therefore reasonable to suppose that a transition mechanism similar to the β -mechanism of poly-methacrylates will appear in the "freezing" region of poly(vinyl acetate).

Using the same separation method for analysis as in the case of polyisobutylene, eq. (5), a weighting has been made for the two mechanisms. The separated functions are drawn in Figure 4. After separation of the β -mechanism and reduction with the glass compliance J_{10} , $\log(J_{1\alpha} - J_{10})$ varies linearly with temperature in accordance with experimentally observed instances.² This can be taken as an indication of the accuracy of the separation method. The function $\log J_\alpha = g_\beta\{\log J_1\}$ is drawn in Figure 5.

It can be ascertained from the above discussion that in noncrystalline polymers with monosubstituted carbon atoms in the main chains, considerable steric hindrance, causing a severe coupling effect between main chain and side group movements, appears for side groups more voluminous than the ester groups in poly(vinyl acetate), while in polymers with disubstituted carbon atoms even two adjoining methyl groups give similar effects.

It is reasonable to expect a distinct influence from the steric effects due to a stereoregular structure. Studies of this type have, however, not yet been carried out.

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