

Studies of Relaxation Phenomena in Polymers. IV. Superimposed Transition Mechanisms in Polymethacrylates

JAN-FREDRIK JANSSON, *Department of Polymer Technology,
The Royal Institute of Technology, Stockholm, Sweden*

Synopsis

The existence of superimposed transition mechanisms in the " T_g region" of polymethacrylates has been indicated by several authors including Ferry and co-workers, who also have tried to separate the mechanisms. Using the general properties of the viscoelastic function $\log J_2 = g_\alpha \{\log J_1\}$ and a simple weighting model, the α - and β -mechanisms have been separated. The viscoelastic function $\log J_2 = g_\beta \{\log J_1\}$ is determined and is found to coincide both where different polymethacrylates are concerned and for the calculated as well as the directly measured data.

INTRODUCTION

In a paper from 1955, Hoff, Robinson, and Willbourn¹ indicate experimentally, by dynamic-mechanical measurements in a torsion pendulum at constant frequency and various temperature, the existence of superimposed loss mechanisms in a series of polymethacrylates at temperatures around the glass point. Hoff ascribed these loss mechanisms to side group motions. The possibility of side group motions being coupled to the movements of the main chain in polymethacrylates has been discussed theoretically by Koppelman,^{2,3} in terms of the "Platzwechsel" concept of Müller.⁴ Andrews and Hammack⁵ suggested that this secondary transition mechanism is caused by the interaction between the dipoles of the ester groups in accordance with the association-dissociation theory of Andrews.⁶

In a series of papers from 1957-1959, Ferry and co-workers⁷⁻¹¹ have studied this transition mechanism by dynamic-mechanical measurements and also have tried to separate it from the main transition mechanism. A number of other authors have also reported studies of such mechanisms in polymethacrylates.¹²⁻²² In the studies of such coupled mechanisms, dielectric, dilatometric, and other methods have been used, and most of these works are summarized by McCrum, Read, and Williams²³ and Ferry.²⁴

USE OF FUNCTION $\log J_2 = J_\alpha \{\log J_1\}$ FOR SEPARATION OF α - AND β -MECHANISMS FOR POLYMETHACRYLATES

As has been mentioned previously, the β -transition of polymethacrylates is associated with coupled elementary mechanisms in the main chains and voluminous side groups. The elementary mechanisms, i.e., the segment movements in the main chain and rotations of the side groups, are dependent on each other and movements in one of them require movements in the other.^{2,3}

It is therefore reasonable to expect increasing mechanical losses, especially in the temperature-frequency (time) region where the segment movements, which need higher activation energy than the rotation of the side groups, "freeze in," i.e., in the region around the glass point of the polymer. This corresponds very well with experimental experience^{1,22} and with the "Platzwechsel" concept³ and means that

$$\tan \delta = \frac{J''}{J'} \geq \tan \delta_\alpha = \frac{J''_\alpha}{J'_\alpha} \quad (1)$$

It is also reasonable that the voluminous side groups through steric hindrance provide an increased resistance to deformation, i.e., higher modulus. Like the effects of the mechanical losses, this must especially be visible in the region around the "freezing point" of the α -mechanism and means that

$$|J^*| = (J'^2 + J''^2)^{1/2} < |J_\alpha^*| = (J'^2_\alpha + J''^2_\alpha)^{1/2} \quad (2)$$

The resultant of the superposed 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. Hence,

$$\log J_2 \equiv \log \{f_2(J_{2\alpha}, J_{2\beta})\} = g \{\log J_1\} \equiv g \{\log [f_1(J_{1\alpha}, J_{1\beta})]\} \quad (3)$$

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 observed curves by Jansson.²⁵

The problem at this point is to find the coupling functions f_1 and f_2 for the two mechanisms. Until further experience in the shape of the function $\log J_2 = g \{\log J_1\}$ concerning superimposed transition mechanisms is obtained, the possibility of separating the two processes is limited to determining a relative weighting.

Based on experimental and theoretical experience, the following coupling functions are assumed:

$$f_1(J_{1\alpha}, J_{1\beta}) = \frac{J_{1\alpha} J_{1\beta}}{J_{1\alpha} + J_{1\beta}} = J_1 \quad (4)$$

and

$$f_2(J_{2\alpha}, J_{2\beta}) = J_{2\alpha} + J_{2\beta} = J_2 \quad (5)$$

where $J_{1\beta}$ and $J_{2\beta}$ include a weighting factor taking into account the relative influence of each process.

DETERMINATION OF $\log J_2 = g_\alpha \{ \log J_1 \}$

From experimental experience, it can be concluded that the function $J_{1\beta}$ and $J_{2\beta}$ reach observable magnitude only around the "freezing point" of the α -mechanism. Thus, by using the characteristic general shape of $\log J_2 = g_\alpha \{ \log J_1 \}$, it is possible to find the function corresponding to the α -mechanism from that part of the curve of $\log J_2 = g \{ \log J_1 \}$ where the influence of the β -process is negligible. This gives an indication of the presence of the superimposed mechanism and a value for the "glass compliance," J_{10} , of the α -process but does not immediately make it possible to extrapolate the $J_{1\alpha}$ and $J_{2\alpha}$ curves toward lower temperatures or shorter times. However, such an extrapolation can be performed either by using the empirically noted linear relation between $\log J_{2\alpha}$ and temperature around the freezing point or the linear relation between $\log J_{1\alpha}$ and $\log J_{2\alpha}$ and logarithmic time in the same region.

Figures 1 and 2 show $\log J_1$ and $\log J_2$ as functions of temperature partly for poly(ethyl methacrylate), poly(*n*-butyl methacrylate), poly(*n*-hexyl methacrylate), poly(*n*-octyl methacrylate) and poly(*n*-dodecyl methacrylate) at 2.5×10^{-3} sec calculated, in accordance with the formulas given by Jansson,²⁶ from the complex compliance taken from unshifted data from Ferry and co-workers,⁷⁻¹¹ partly for poly(ethyl methacrylate) at 20 sec from direct measurements by the equipment previously described.²⁵ The differences in position along the temperature axes are due to the differences in time, and the divergences in shape are due to the differences in average

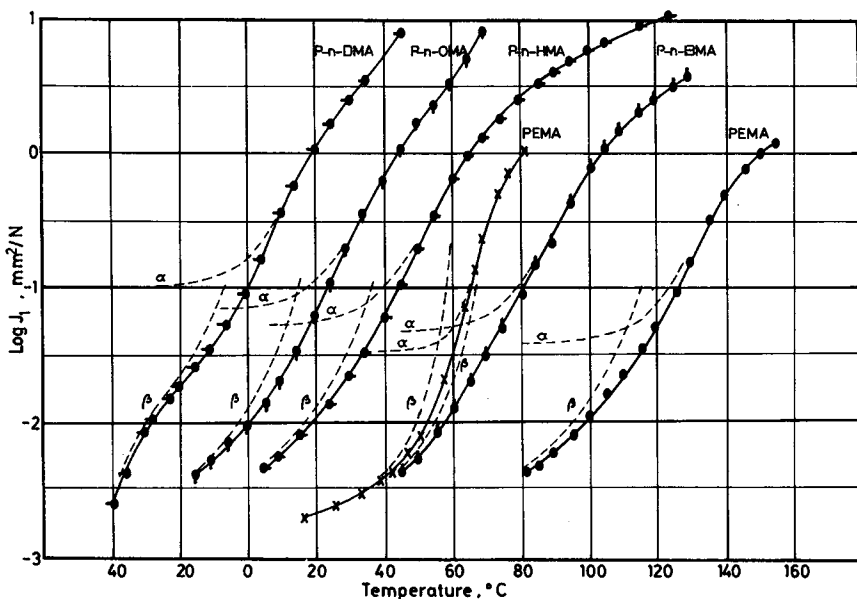


Fig. 1. Function $J_1(T)$ for some polymethacrylates at 2.5×10^{-3} and 30 sec: dashed curves correspond to the separated functions $J_{1\alpha}$ and $J_{1\beta}$; (—X—) from direct measurements.

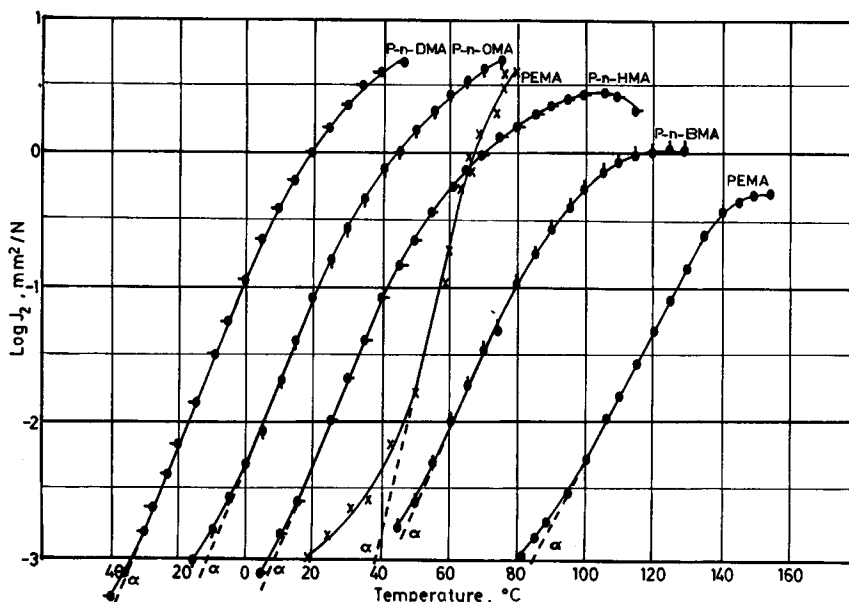


Fig. 2. Function $J_2(T)$ for some polymethacrylates at 2.5×10^{-3} and 30 sec: dashed curves correspond to the separated function $J_{2\alpha}(T)$; (—×—) from direct measurements.

molecular weight, molecular weight distribution, etc., are also and caused by the different shift factors of the superimposed transition mechanisms. The average molecular weight, \bar{M}_w , of Ferry's PEMA is 1.7×10^6 and of the directly measured polymer. In the figures, the corresponding α - and β -curves have also been plotted.

In Figure 3, the function $\log J_2 = g\{\log J_1\}$ has been plotted for the directly measured PEMA and for Ferry's polymer as calculated partly from unshifted data of the complex compliance and partly from Ferry's master curves. The divergence between the curves in the region where the β -mechanism is not negligible indicates the uncertainties of the method of reduced variables in the case of superimposed transition mechanisms.

The differences between the calculated and directly measured curves can be entirely expressed in terms of different materials, uncertainties in the calculation of the function from complex data, and different measuring equipments. Both materials give, as may be expected, the same "glass compliance" for the simple segment movements, approx. 4×10^{-2} mm²/N. In Figure 4, the function $\log J_2 = g_\beta\{\log J_1\}$ for the β -process is plotted as calculated in accordance with eqs. (4) and (5) from the linear extrapolation of $\log J_2$ toward lower temperatures in Figure 2 and the differences between the curve $\log J_2 = g_\alpha\{\log J_1\}$ (obtained from the part of the total curve of $\log J_2 = g\{\log J_1\}$ where the β -mechanism is negligible) and the total curve $\log J_2 = g\{\log J_1\}$ in Figure 3.

That the curves coincide both where the different polymethacrylates are concerned and for the calculated and directly measured data is obvious. P-*n*-DMA is an exception due to the crystallization of the long flexible side

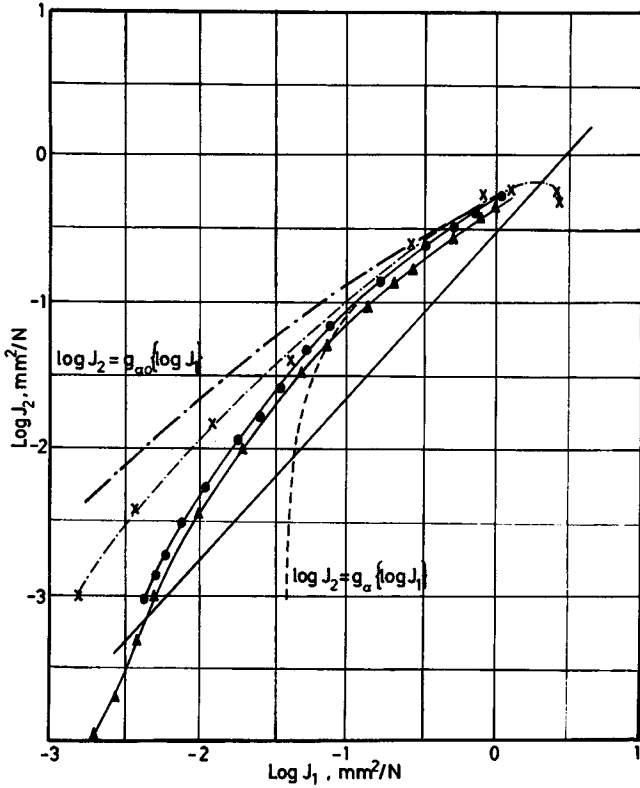


Fig. 3. Function $\log J_2 = g\{\log J_1\}$ for PEMA: (—x—) calculated from master curve; (—o—) calculated from complex compliance before shifting; (—Δ—) direct measurement.

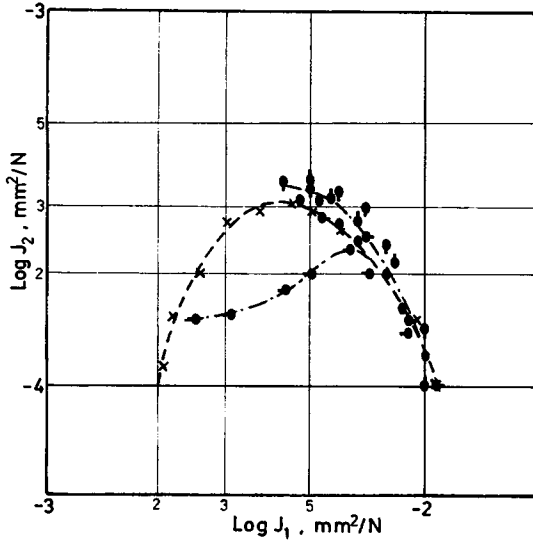


Fig. 4. Function $\log J_2 = g_{\beta}\{\log J_1\}$ for the β -mechanism in: (—o—) PEMA; (—●—) P-n-BMA; (—●—) P-n-HMA; (—●—) P-n-OMA; (—●—) P-n-DMA calculated from Ferry's data; (x) PEMA from directly measured data.

chains, which has also been observed by Ferry and co-workers¹¹ and Greenberg and Alfrey.²⁷ The directly measured curve gives a more complete picture of the function $\log J_2 = g_\beta \{\log J_1\}$.

It is reasonable to expect that the coupled movements between main chains and carboxy side groups in polymethacrylates are independent of the length of the side chains $-\text{CH}_2-\text{C}_n$ for temperature-time (frequency) combinations well above the freezing point for the carboxy side groups, -20°C at 1 c/s. Thus, the coincidence between the curves for different polymethacrylates is quite reasonable and can, together with the linear relation between temperature and $\log \{J_1 - J_{10}\}$ for the α -mechanism shown in Figure 1, be taken as an indication of the accuracy of this separation method.

These investigations are part of a research program on Mechanical Long Term Properties of Polymers supported by the Swedish Board for Technical Development (STU). The author would like to thank Professor Bengt Rånby for valuable discussions on the subject of this paper.

References

1. E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, *J. Polym. Sci.*, **18**, 161 (1955).
2. J. Koppelman, *Kolloid-Z.*, **144**, 12 (1955).
3. J. Koppelman, *Kolloid-Z., Z. Polym.*, **216-217**, 6 (1967).
4. F. H. Müller, Proc. 2nd Intern. Congr. Rheology, London, 1954, p. 38.
5. R. D. Andrews and T. J. Hammack, *J. Polym. Sci. B*, **3**, (1965).
6. R. D. Andrews, *J. Polym. Sci. C*, **14**, 261 (1966).
7. J. D. Ferry, W. C. Child, Jr., R. Zand, D. M. Stern, M. L. Williams, and R. F. Landel, *J. Colloid Sci.*, **12**, 53 (1957).
8. W. C. Child, Jr., and J. D. Ferry, *J. Colloid Sci.*, **12**, 327 (1957).
9. W. C. Child, Jr., and J. D. Ferry, *J. Colloid Sci.*, **12**, 389 (1957).
10. W. Dannhauser, W. C. Child, Jr., and J. D. Ferry, *J. Colloid Sci.*, **13**, 103 (1958).
11. S. F. Kurath, T. P. Yin, J. W. Berge, and J. D. Ferry, *J. Colloid Sci.*, **14**, 147 (1959).
12. W. Letherisich, *Brit. J. Appl. Phys.*, **1**, 294 (1950).
13. F. Bueche, *J. Chem. Phys.*, **20**, 1979 (1952).
14. F. Bueche, *J. Appl. Phys.*, **26**, 738 (1955).
15. K. Schmieder and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).
16. S. Iwaganagi and T. Hideshima, *J. Phys. Soc. Japan*, **8**, 365 and 368 (1953).
17. K. E. Deutsch, A. W. Hoff, and W. Reddish, *J. Polym. Sci.*, **13**, 565 (1954).
18. K. Sato, H. Nakane, T. Hideshima, and S. Iwaganagi, *J. Phys. Soc. Japan*, **2**, 413 (1954).
19. J. Hejbour, *Kolloid-Z.*, **148**, 36 (1956).
20. B. Maxwell, *J. Polym. Sci.*, **20**, 551 (1956).
21. R. D. Andrews, *J. Polym. Sci. C*, **14**, 261 (1966).
22. F. Boyer, Ed., *J. Polym. Sci. C*, **14**, 69 and 121 (1966).
23. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967.
24. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970.
25. Jansson, J.-F., *J. Appl. Polym. Sci.*, **17**, 2965 (1973).
26. Jansson, J.-F., *J. Appl. Polym. Sci.*, **17**, 2977 (1973).
27. S. A. Greenberg and T. Alfrey, *J. Amer. Chem. Soc.*, **76**, 6280 (1954).

Received January 2, 1973

Revised February 15, 1973