Studies of Relaxation Phenomena in Polymers. II. The Behavior of Simple Polymers in their Main Transition Region

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Synopsis

In an earlier paper,[1] a "new" viscoelastic function, $\log J_2 = g\{\log J_1\}$, was defined. For polymers, the linear viscoelastic behavior of which is characterized by "simple segment movements" in their main transition regions, the following general properties are found: (1) The local maxima of the function for different polymers fall along a straight line width the slope approximately equal to 1.1. (2) A characteristical general shape is noticed for the function after shifting along the straight line and reducing the J_1 compliance as regards the "frozen in" compliance J_{10}. (3) J_1 reflects the storage and J_2, the loss mechanisms of the system. The relation J_2/J_1 is an expression for the average retardation time.

INTRODUCTION

In an earlier paper,[1] a new viscoelastic function was defined, its relations to the complex compliance were developed, and special equipment for direct measurements was described. The function $\log J_2 = g\{\log J_1\}$, where J_1 and J_2 are the compliances at the time $(\zeta/2 + 2n\zeta)$ for an odd,

$$n \to \infty$$

periodic, square function and an even, periodic, triangular function, respectively, with periods of 2ζ showed characteristic shapes for viscoelastic spring and dashpot models. The sum of J_1 and J_2 at $\zeta/2$ agreed very well with the creep compliance at the same time.

In noncrystalline polymers, a dispersion region, which is often very distinct, appears directly above the glass point. This transition is usually called the α-transition, the main transition, or the glass–rubber transition. The accepted molecular explanation for many years has been that it originates from large-scale conformational rearrangements of the polymer chain backbone, the chain segment movements.

Transition mechanisms of the same type also appear in the amorphous regions of semicrystalline polymers, but in this case are disturbed by hindrance in the neighborhood of the crystallites.

In the following, the function $\log J_2 = g\{\log J_1\}$ has been studied in the linear viscoelastic region for a series of polymers listed with references in Table I.

TABLE I
Studied Polymers[a]

Polymer no.	Polymer	Reference
1.	PVC	b
2.	PVC 10% dioctyl adipate (DOA)	b
3.	PVC 60% dimethylthianthrene (DMT)	2
4.	PVC-gel 90% (DMT)	2
5.	PVAc	b
6.	PVAc	3
7.	PVAc 50% tri-m-cresyl phosphate	4
8.	PMA	4
9.	PIB	5
10.	PMP	b
11.	CN-gel diethyl phtalate	6
12.	NR	7
13.	NR	8
14.	NR	9
15.	SBR	10
16.	UR	11

[a] Polymer numbers refer to Fig. 1.
[b] From direct measurements; polymers specified in Table II.

TABLE II
Polymers Studied by Direct Measurements of J_1 and J_2

Polymer	Procedure
1. PVC (KemaNord AB, R 45) $\bar{M}_w = 130\ 000$	Specimens are made by postforming sheets, calendered 15 min at 140°C. The postforming is made by pressing a bent slice of the sheet into a cylindric mold at 150°C for about 15 min, followed by very gradual cooling for about 4 hr down to room temperature. After being fixed in the measuring equipment, the specimens are heat treated at about 110°C for more than 4 hr, followed by very gradual cooling.
2. PVC + 10% DOA (KemaNord AB)	Polymer, preparation of specimens, and heat-treating procedure as in 1.
5. PVAc $\bar{M}_w = 55\ 000$	Specimens made by compression molding at 125°C fr 2 hr, followed by gradual cooling to room temperature for about 8 hr. Specimens heat treated at 60°C for about 4 hr.
10. PMP (ICI, RT 18)	Specimen made by compression molding at 250°C for 2 hr, followed by gradual cooling to room temperature for about 8 hr. Specimens heat treated at 100°C for about 4 hr.

The function $\log J_2 = g\{\log J_1\}$ has been measured with a special equipment,[1] and in order to be able to make a reasonably rapid study of a large number of polymers, the function has also been calculated from dynamic data, in accordance with the relationships pointed out in the paper mentioned above, for a number of polymers. To avoid the uncertainties of
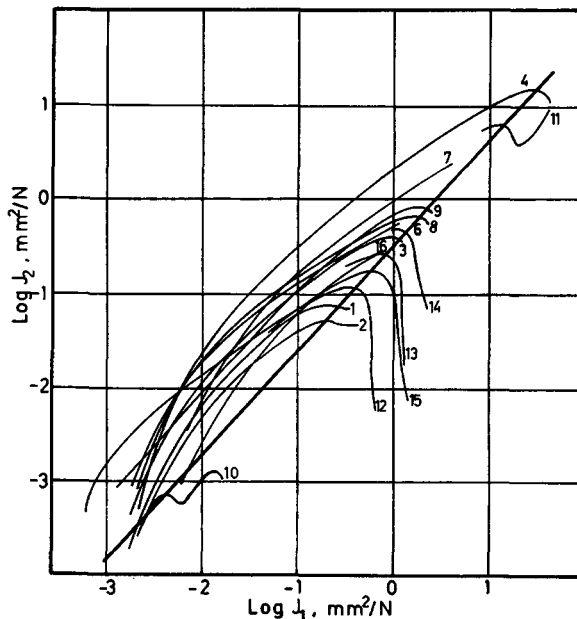
Fig. 1. Viscoelastic function $\log J_2 = g\{\log J_1\}$ for some polymers, specified in Table I.

the "method of reduced variables," especially when superimposed transition mechanisms occur, the calculations have been based on unshifted data, when available. Thus, J_1 and J_2 are in general studied as functions of temperature at constant time.

In Figure 1, the function $\log J_2 = g\{\log J_1\}$ has been plotted for the polymers in Table I. The curves cover mainly the glass transition regions of the polymers and show essentially the same form as the curve for the Burgers model.[1] In noncrystalline polymers with monosubstituted carbon atoms, usually only one transition mechanism occurs in the main transition region. Thus, in this respect, the conditions for the method of reduced variables to be valid are fulfilled. In this case, the graphs of the compliance function $\log J_2 = g\{\log J_1\}$ will be identical whether they have been calculated from the original frequency characteristics of the complex compliance or from master curves. This is shown in Figure 2. As may be expected, the agreement is very good.

It is of interest to notice that the maxima of all the curves in Figure 1 fall with good accuracy along the straight line:

$$\log J_2 = a \log J_1 - b \tag{1}$$

where $a \approx 1.1$ and $b \approx -0.52$ (mm²/N). In Figure 3, some of the curves in Figure 1 have been shifted along the straight line until the maxima coincide or, in some cases, until the regions of the curves near the maxima coincide. From these curves, a general function, $\log J_2 = g_{\alpha 0}\{\log J_1\}$, can be derived from the relation

$$\log J_2 = g_{\alpha 0}\{\log(J_1 + J_{10})\} = g_\alpha\{\log J_1\} \tag{2}$$

where J_{10} is the value of J_1 in the region where the main transition mechanism is "frozen in." The function $\log J_2 = g_{\alpha 0}\{\log J_1\}$ is drawn in the figure.

In different polymers, the main transition mechanism—the chain segment movements—differ, partly owing to the distribution of retardation times and the position of the retardation spectrum along the time axis and partly owing to the distribution of the spectral compliance magnitudes.
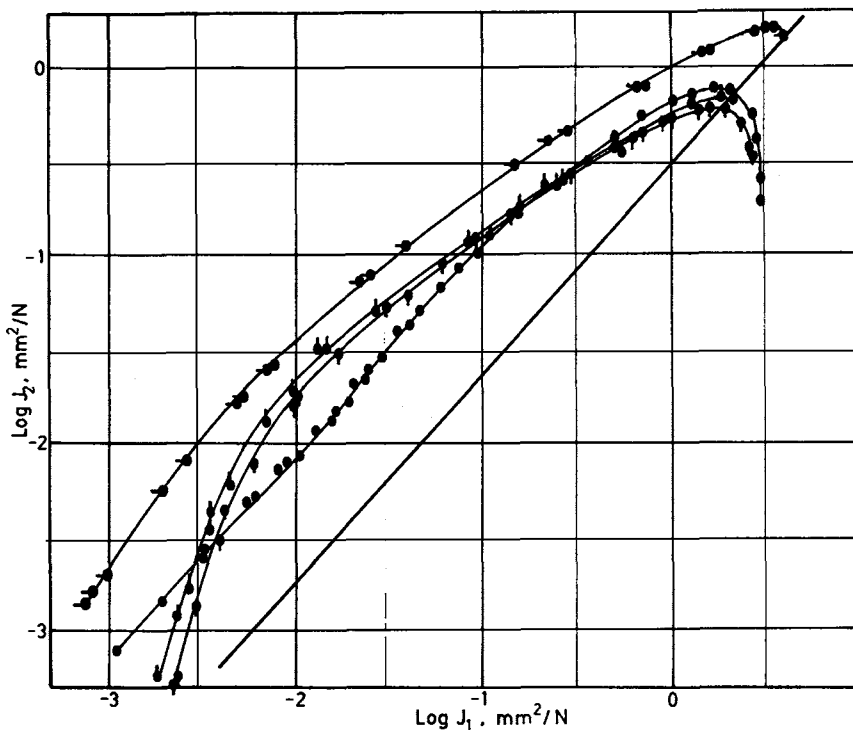

Fig. 2. Comparison of function $\log J_2 = g\{\log J_1\}$ determined partly from master curves, partly from unshifted complex compliance: (-●) PVC-gel, $J_i \times 10^{-1}$, from master curve and from unshifted curves at 30, 100, and 500 Hz; (●) PMA, from master curve and from unshifted curves at 100 and 1000 Hz; (●) PIB, from unshifted curves at 70, 100, and 200 Hz; (●) PVAc, from unshifted curves at 30, 100, 300, and 500 Hz, and from master curve. Data taken from references shown in Table I.

For polymers characterized by small hindrances to the chain segment movements, i.e., by "simple segment movements," the experimental results reported above show that the function $\log J_2 = g\{\log J_1\}$, fixed in the log J_2/J_1 plane by the straight line in eq. (1), assumes a characteristic shape independent of the chosen combination of time–temperature.

The relation J_2/J_1 is proportional to the retardation time of the Kelvin model,[1] and J_1 and J_2 are measures of the parts of the supplied energy which are stored and lost, respectively. For the generalized Kelvin model,

$$J_2/J_1 = \frac{2 \sum_i \tau_i/\zeta \, f(\zeta/\tau_i)}{\sum_i f(\zeta/\tau_i)} \qquad (3)$$

where

$$f(\zeta/\tau_i) = 2 \, Je_i \left\{ 1/2 + \sum_{n=0}^{N_{odd}} (-1)^{n+1} e^{-(2n+1)\zeta/2\tau_i} \right\}.$$

Thus, the relation J_2/J_1 in eq. (3) in proportional to the average retardation time in accordance with

$$J_2/J_1 \sim \sum_i \tau_i \frac{J_{1i}}{J_1} \qquad (4)$$

where J_{1i} is the value of J_1 adherent to the retardation time τ_i. (The relation in eq. (4) agrees in principle to the relation J''/J' between the corresponding complex quantities.)

Thus, the function $\log J_2 = g_{\alpha0}\{\log J_1\}$ gives the variation of the average retardation time $\bar{\tau}$ throughout the main transition, independently of the combination of time–temperature.

The time or temperature dependence of the system can then be described with the aid of the average retardation time $\bar{\tau} \sim J_2/J_1$ as a function of time
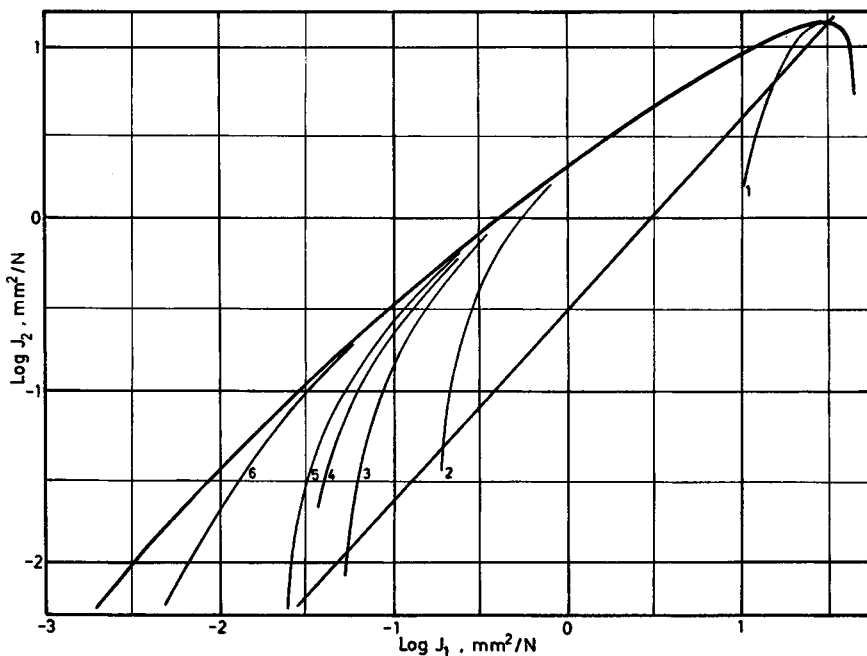

Fig. 3. Function $\log J_2 = g\{\log J_1\}$ for (1) PMP; (2) Hypalon; (3) PMA; (4) NR; (5) PVAc; (6) PVC-gel, after shifting the functions along the line $\log J_2 = 1.1 \log J_1 - 0.52$. The thick continuous line represents the function $\log J_2 = g_{\alpha0}\{\log J_1\}$.
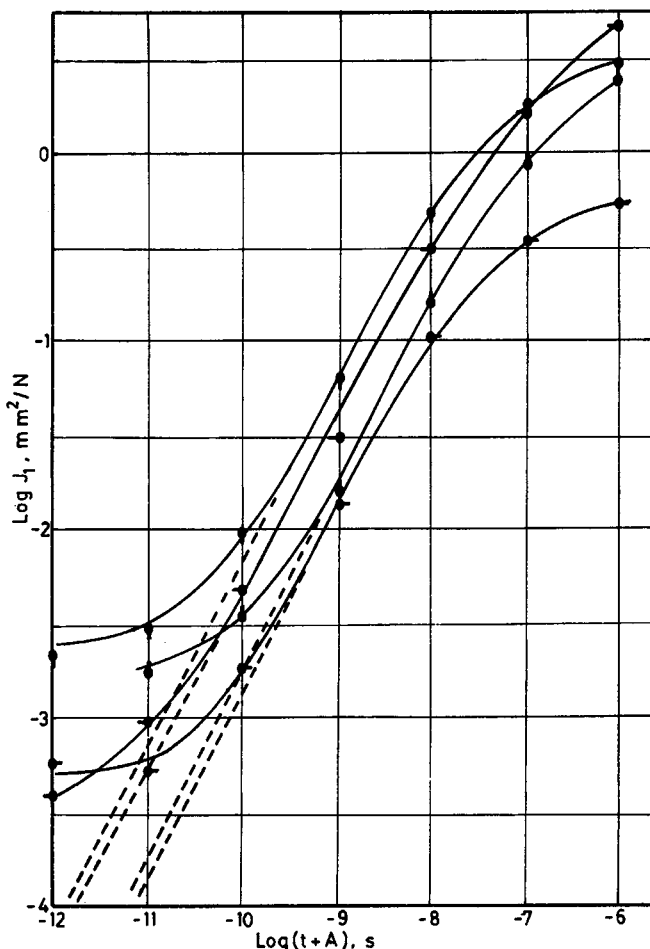
Fig. 4. Function $J_1(t)$, for: (⚫) PVAc, $A = -4, J_{10} = 1.5 \times 10^{-3}$; (⚫-) NR, $A = 0$, $J_{10} = 5 \times 10^{-4}$; (⚫) PMA, $A = -8, J_{10} = 2.5 \times 10^{-3}$; (-⚫) PVC-gel, $(J_1 \times 0.1)$ $A = 0, J_{10} = 3 \times 10^{-3}$.   Dashed curves correspond to $J_1 - J_{10}$.

and temperature, respectively.   Phenomenologically, the main transition can be described with the aid of the "frozen in" compliance J_{10}, the equilibrium compliance J_e, and the time and temperature variation of the average retardation time $\bar{\tau}$.   In connection herewith, it is essential to notice that the slope of the straight line in eq. (1) differs from 1.

In Figures 4 and 5, the compliances J_1 and J_2 are drawn as functions of time at constant temperature as calculated from the master curves of the complex compliance in accordance with the method developed by Jansson.[1] For short times, J_1 approaches J_{10} and log J_2 varies linearly.   In Figure 4, J_1 has been reduced as regards J_{10} in accordance with eq. (2), after which a linear relation between log $(J_1 - J_{10})$ and log t is observed for short times.

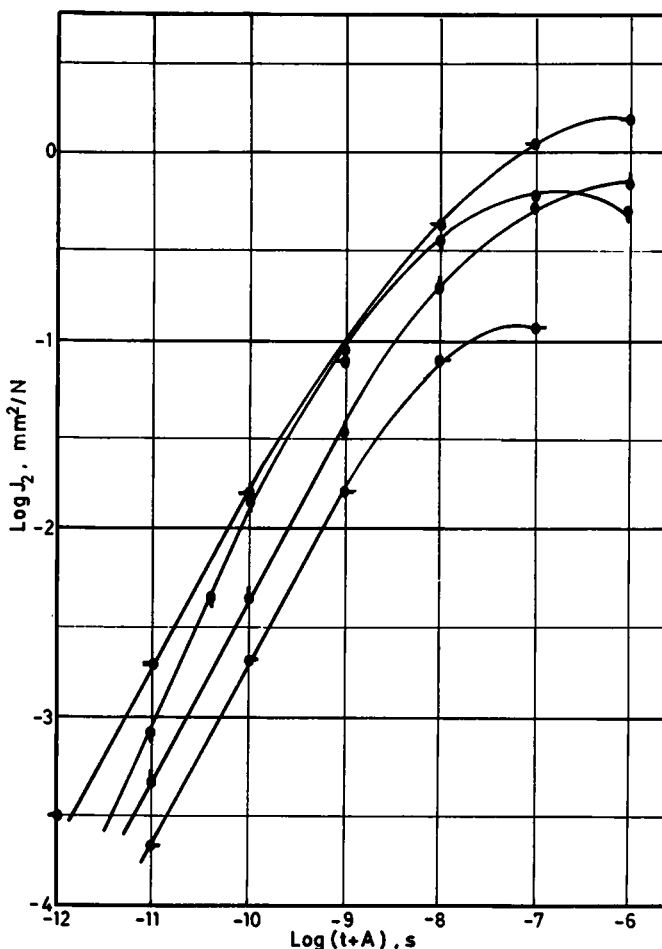In Figures 6 and 7, log J_1 and log J_2 are plotted against temperature at

Fig. 5. Function $J_2(t)$ for: (⬤) PVAc, $A = -4$; (⬤) NR $(J_2 \times 10)$, $A = 0$; (⬤) PMA, $A = -8$; (-⬤) PVC-gel $(J_2 \times 0.1)$ $A = 0$.

constant time. Even in this case, J_1 is reduced as regards J_{10}, after which both log $(J_1 - J_{10})$ and log J_2 vary linearly with temperature in the examined region.

The above linear relations in the "freezing in" region may be looked upon as a consequence of the chain segment movements described in the molecular theories of Tobolsky-Aklonis-Du Pré[12] for damped torsional oscillations in small segments of 3 to 4 units in length.

CONCLUSIONS

In order to evolve the mechanical spectroscopy and find new methods of studying the rise of nonlinear viscoelasticity, a new viscoelastic compliance function, log $J_2 = g\{\log J_1\}$, has been developed, having the following properties in the linear viscoelastic region:
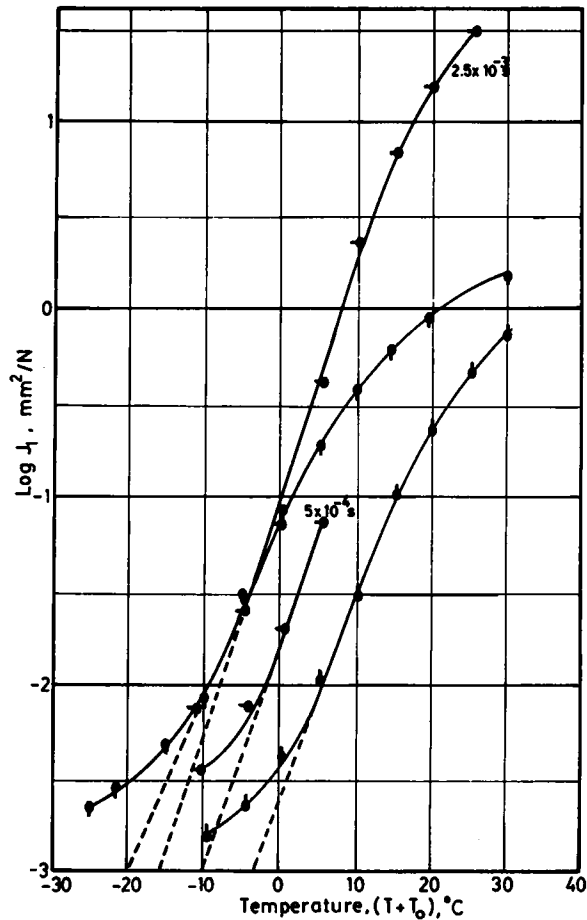
Fig. 6. Function $J_1(T)$ for: (-●) PVC-gel, $T_0 = 0$; (●) PMA, $T_0 = -50°C$; (●) PVAc $T_0 = -60°C$.   Dashed curves correspond to $J_1 - J_{10}$.

1.   The local maxima of the curves for different polymers fall along a straight line, with the slope approximately equal to 1.1

2.   A characteristical general shape of the curve $\log J_2 = g_{\alpha 0}\{\log J_1\}$ is noticed after shifting the curves along the straight line and reducing the J_1 compliance as regards the "frozen in" compliance J_{10}, independently of whether the curves are plotted at constant time and varying temperature or vice versa.

3.   The relation J_2/J_1 is an expression for the average retardation time, and the general shape of $\log J_2 = g_{\alpha 0}\{\log J_1\}$ gives its variation throughout the main transition.

4.   At least for linear viscoelastic systems, J_1 reflects the storage and J_2 the loss mechanisms of the system.

5.   It is most likely that the function $\log J'' = h\{\log J'\}$, in the complex plane, will give similar results as the $J_1 - J_2$ function.   The argument for developing the new function is therefore to get a method of character-
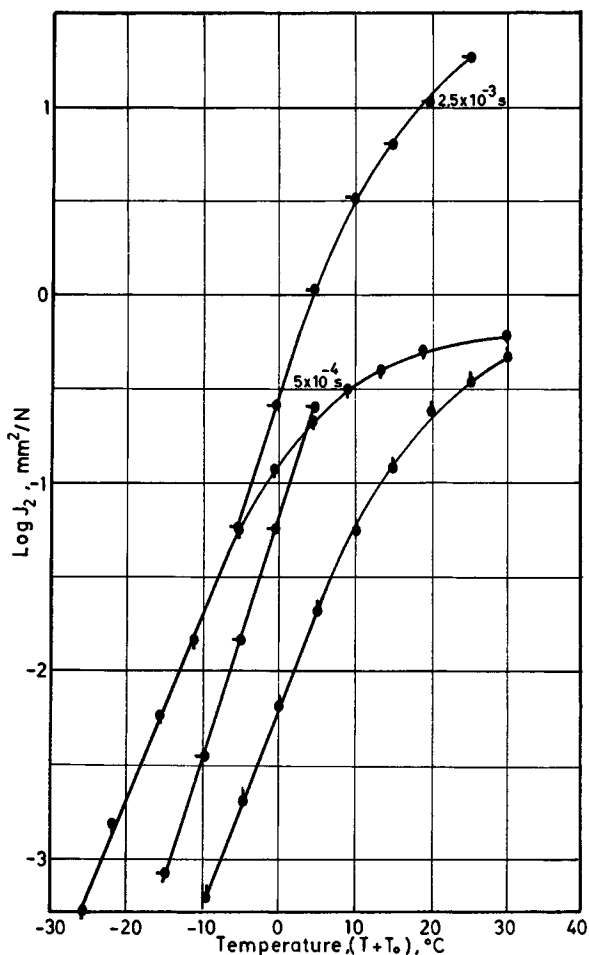
Fig. 7. Function $J_2(T)$ for: (-●) PVC-gel, $T_0 = 0$; (●) PMA, $T_0 = -50°C$; (●) PVAc, $T_0 = -60°C$.

izing, comparable to the complex compliance, which contrary to this can be extended to the nonlinear viscoelastic region.

6. The general properties are valid for polymers characterized by "simple segment movements" in their main transition. It is reasonable to expect divergences from these properties for polymers containing long, stiff sequences in their main chains, bulky side groups, etc., or for semi-crystalline polymers and for polymers with other types of heterogeneous structure. It seems most likely that the divergences of these types are rather common in polymers.

References

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