SEGMENTAL AND CHAIN DYNAMICS IN POLYMERS

DYNAMICS IN POLYMERS

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Abstract. All polymers exhibit a breakdown of time-temperature superpositioning in the softening zone, where both local and global chain modes contribute to the measured dynamic response. This differing behavior of the two modes is also seen in the volume and pressure dependences of the respective relaxation times. Nevertheless, the superposition of local segmental and global chain modes can be achieved by expressing the relaxation times as a function of the product of temperature, $T$, times specific volume, $V$, with the latter raised to a constant $\gamma$. Moreover, the value of $\gamma$ is the same for the two modes. These experimental facts reveal that the relative contribution of temperature and volume is the same for the two modes, although their response to either variable differs; that is, while having the same functional form, the combined effect of $T$ and $V$ on the respective modes is different.

Keywords: segmental relaxation, structural relaxation, chain modes, global motion

1. Breakdown of Time-Temperature-Pressure Superpositioning

It has been known for at least 40 years that polymers are thermorheologically complex\textsuperscript{1,2}. This breakdown of time-temperature superpositioning transpires not only in mechanical measurements, but is also apparent in dielectric spectra\textsuperscript{3} and

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Ironically, one of the most dramatic manifestations of the phenomenon is observed in a polyisobutylene NBS standard. Measurements in the 1950’s on this very sample in laboratories around the world were instrumental in the development and acceptance of the idea of time-temperature superpositioning in polymers. The thermorheological complexity of polymers is most evident in the transition zone, where the local modes change more strongly with temperature than do the chain modes. At temperatures sufficiently above $T_g$, the respective $T$-dependences become parallel. This is seen in data on atactic-polypropylene in Fig. 1, obtained using several different spectroscopies.

![Figure 1. Segmental relaxation times (hollow symbols) and shift factors for the terminal (chain) relaxation times (solid symbols) for atactic polypropylene measured by various spectroscopies.](image)

The different response to pressure of the two modes is seen in dielectric measurements at elevated pressure, as first shown by Floudas and coworkers, wherein the local segmental motion has a larger activation volume. When combined $T$- and $P$-dependences are converted to $V$-dependences, the results are the same – a stronger variation of the segmental mode in comparison to the chain modes. This is illustrated in Figure 2 for polyoxybutylene.
One interesting aspect of this universal behavior of polymers is the absence of its recognition in most textbooks of polymers science. Commonly, ostensibly satisfactory master curves are shown for polystyrene or another polymer, along with a description of the time-temperature superposition principle. However, invariably there is no mention of the failure of $t-T$ superpositioning whenever local and global modes both contribute (e.g., in the glass transition zone). This error likely arises from expectations drawn from theory. Both the Rouse\textsuperscript{10} and reptation\textsuperscript{11} models of polymer dynamics express the chain relaxation times with expressions whose only $T$-dependence is the ratio $\zeta/T$. $\zeta$ is the local, monomeric friction coefficient, which is identified with the friction coefficient describing local segmental motions.

The fallacy of master curves that span the viscoelastic spectrum from the glassy zone to the terminal flow regime is demonstrated in Figure 3, showing an ostensibly accurate master curve for high molecular weight 1,4-polyisoprene. Due to the paucity of data points in the transition zone, the various isotherms appear to superpose. However, as seen in the inset,
there is a marked change in the shape of the loss tangent in the transition zone, revealing the thermorheological complexity.

![Figure 3. Master curve of the mechanical storage and loss moduli for 1,4-polyisoprene ($M_w=500$ kg/mol). The inset shows the loss tangent in the transition zone, where thermorheological complexity is evident.]

### 2. Scaling of Relaxation Times

The local segmental relaxation times of polymers (and correspondingly the structural or $\alpha$-relaxation times of molecular liquids) superpose when plotted versus $TV^\gamma$, where $\gamma$ is a material constant$^{12,13,14}$. The scaling exponent $\gamma$ is usually determined empirically by shifting $\tau$ measured under isothermal and/or isobaric conditions. It can also be calculated from $PVT$ measurements using the relation $\gamma = -T/\alpha$, where $\alpha$ is the volume expansion coefficient at constant $\tau$. With some assumptions $\gamma \sim \gamma_G^{15,16}$, where $\gamma_G$ is the Grüneisen parameter.
quantifying the anharmonicity of the vibrational motions. This $TV^\gamma$ scaling is illustrated in Figure 4 for polyoxybutylene\textsuperscript{17}.

The successful $TV^\gamma$ scaling of local segmental relaxation times raises the question of the behavior of the global motions: Do the relaxation times for the chain modes scale in the same fashion, and if so, what is the value of the scaling exponent? For polymers having a dipole moment parallel to the chain, these global dynamics are reflected in the dielectric normal mode, which is sensitive to the chain end-to-end vector. Included in Fig. 4 are the normal mode relaxation times measured for the polyoxybutylene. Note that these do indeed superimpose when plotted versus $TV^\gamma$; moreover, the value of $\gamma$ is the same for both relaxation modes. This surprising result appears to be generally valid, having been found as well for polypropylene glycol and 1,4-polyisoprene\textsuperscript{14,18}. 

\textbf{Figure 4.} Dielectric relaxation times for the local segmental (squares) and normal mode (circles) processes in polyoxybutylene as a function of the product $TV^\gamma$ with $\gamma=2.65$. Vertical shifting of the former to superpose at long times evidences the differing dependences on the scaled data.
3. Reconciling the Dynamics of the Local and Global Modes

The fact that the segmental and chain modes, which have different $T$, $P$, and $V$ dependences, both superimpose when expressed as a function of the $TV^\gamma$ using the same value of $\gamma$ deserves further consideration. In Fig. 4 the segmental relaxations times have been shifted vertically to superimpose at longer $\tau$ with the normal mode relaxation times. It is seen for polyoxybutylene (and also for polypropylene glycol and 1,4-polyisoprene) that there is a larger change in the segmental dynamics with change in $TV^\gamma$ than in the chain dynamics. This greater $TV^\gamma$-sensitivity mirrors the former’s stronger $T$, $P$, and $V$-dependences.

Since the exponent $\gamma$ reflects the contribution of volume relative to that from temperature to the dynamics, we can conclude that the relative effect of these two variables is the same for the two relaxation modes. However, this does not mean that the combined effect of $V$ and $T$ are the same; clearly, changes in $T$ and $V$ exert a stronger influence on the segmental dynamics. It is only that the apportionment of $\tau$ variations to $V$ and $T$ is the same for segmental relaxation as for the chain motions.

While the relaxation times for the local and the chain modes are functions of the same variable $TV^\gamma$ with the same $\gamma$, the functions per se are not the same. What can be said about the nature of the respective functions? According to the coupling model, measured properties such as the relaxation times for local segmental and chain motions are related to a primitive friction coefficient, $\zeta_0$ (primitive in that it is strictly non-cooperative intermolecularly). The characteristics of this primitive process, which serves as a precursor to the glass transition, suggests identification with the Johari-Goldstein secondary relaxation. The friction factor underlying the motions in dense phase are related to $\zeta_0$ by the fundamental equation of the coupling model, $\zeta \sim \zeta_0^{1/\beta}$, where $\beta$ is the Kohlrausch exponent describing the breadth of the relaxation function. This breadth is larger for local segmental motion than for the chain dynamics (since intermolecular cooperativity is stronger for the former); thus, any $T,P$, or $V$ dependences of $\zeta_0$ are amplified nonlinearly to a greater degree for the local segmental modes. This accounts for the stronger dependences on these variables of the local segmental relaxation times.

Implicit in this discussion is that $\zeta_0$ must be a function of $TV^\gamma$. This follows from the experimental fact that $\tau$ is a function of $TV^\gamma$, provided $\beta$ is constant over the range of $\tau$ under consideration.
4. Summary

The global dynamics is less sensitive to thermodynamic variables such as temperature, pressure, and volume than is the local segmental dynamics. This is a consequence of their different friction factors. Nevertheless, relaxation times for both processes can be superimposed when plotted as a function of $TV^\gamma$, where the material constant $\gamma$ is the same two modes. These seemingly contradictory results can be understood through consideration of the underlying, non-cooperative dynamics, which is expected to conform to the same $TV^\gamma$ scaling. This non-cooperative motion, which can be identified with the Johari-Goldstein relaxation, can be quantitatively related to the measured dynamic properties through application of the coupling model.

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References