Fine Structure of the Glass Transition in Amorphous Polymers: Slight Shoulder in the Shear *H* Spectrum at the *L* Peak

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ABSTRACT: A slight shoulder in the shear relaxation spectrum (*H*) at the relaxation time for the main maximum of the retardation spectrum (*L*) was detected for three amorphous polymers: polystyrene, poly(vinyl acetate), and a slightly vulcanized natural rubber. This finding is discussed in terms of a distinctive manifestation of different molecular modes across the glass (main) transition.

I. Introduction

There is an increasing interest in the complexity of the main transition of amorphous polymers and in a distinctive manifestation of different molecular modes across the main (α) dispersion zone. Since 1986, Ngai, Plazek, and collaborators have collected evidence that the main transition consists of at least three types of modes (in the sequence of increasing times): local segmental motion, sub-Rouse modes, Rouse modes.[1−3] An extensive review is given in ref 4. Seen from a slightly different view, this phenomenon was called fine structure of the main or glass transition;[5−7] see also refs 8−11. In this series of papers, the names for the mode sequence were chosen as proper glass transition, confined flow zone, and hindering zone by entanglements. Rouse modes could not be identified in the main transition of these polymers.

Important aspects in this field are the sequence of corresponding lengths (including the characteristic length of the proper glass transition), a "general scaling law" (i.e., a supposed dispersion law connecting longer relaxation times with longer mode lengths across the whole main transition), the different mode sensitivity of different activities (such as shear modulus, T_1-like NMR times, dielectric and heat capacity spectroscopy, shear compliance, and others[12]), and the encroachment problem.[2]

The latter refers to the observation[13] that at least the longest modes of the main transition have some other WLF equation than the shorter modes; their traces in the Arrhenius diagram encroach because the longer modes have a *smaller* Vogel temperature. This is explained as a necessary effect caused by short-mode preaveraging of the effective energy landscape for the longer modes.[14] A consequence of encroaching on the shear relaxation curves is some spreading (divergence) of the individual curves in certain frequency (or time) regions of master curve constructions; in general, encroaching leads to thermorheological complexity,[14] which is discussed by Ngai et al. in terms of his coupling model.[1,3,4]

It seems to be interesting to find further criteria for the independence of the modes participating in the main transition. It is suggested to use peculiarities of the "complementary" shear spectra at the time location of the main (large) peaks of the shear relaxation spectra, *H*, and the shear retardation spectra, *L*. This means there is a slight shoulder in *L* at the *H* peak (as found by Plazek[15,16] and which is now confirmed[17]) and, inversely, a slight shoulder in *H* at the main *L* peak (this work).

In general, the main *H* and *L* peaks are separated by three or four decades in time. This follows from the $G^*J^* = 1$ relation in the case of large G' ratios between the glassy zone ($G' \approx$ GPa) and plateau zone ($G' \approx$ MPa). (G^* and J^* are the dynamic shear modulus and the compliance, respectively.) This fact does not mean, however, that the two peaks are necessarily the manifestation of one uniform, underlying process, similar to mechanical spring−dashpot models of viscoelasticity. Instead, the fluctuation dissipation theorem (FDT) shows[14] that, without any time or frequency shifts, the relaxation times are identical to the corresponding times in the molecular correlation functions and that the probing frequencies of periodic linear-response experiments are identical to the frequencies in the spectral densities of these molecular correlations. That is, a slight shoulder, for example, in *H* at the main *L* peak means that the shear modulus is also sensitive to the modes that are responsible for the log G' wing between the main transition zone and the rubbery plateau zone etc. This "ω identity"[14] aspect of the FDT is the general theoretical precondition for a discussion of any distinctive manifestation of different molecular modes detected by linear-response methods and allows one to interpret the small shoulders as criteria for such independent modes.

By the way, the consideration of the *H* and *L* spectra (instead of G^* or J^* directly) uses an amplification effect due to the effective differentiation linked with the calculation of *H* and *L* from experimental G^* or J^* values. Modern programs such as CONTIN[18] or NLREG (nonlinear regularization)[19] enlarge the certainty of this differentiation by orders of magnitude.

The aim of this paper is to show, by means of careful mechanical modulus experiments and data evaluation, that in several amorphous polymers a slight shoulder in the shear relaxation spectrum *H* can be detected exactly at the relaxation times where the main peak in the shear retardation spectrum *L* is. This finding can be added to the others which enlarge the evidence for a real fine structure of the main transition with rather independent components.

II. Experimental and Data Evaluation

Three amorphous polymers were investigated: A commercial poly(vinyl acetate) (PVAC) with a broad distribution of molecular weights obtained from BUNA AG, a polystyrene standard (PS-700-M) with a narrow distribution purchased from Waters GmbH, and a natural rubber (NR) weakly vulcanized with 1.8 phr sulfur kindly provided by Continental

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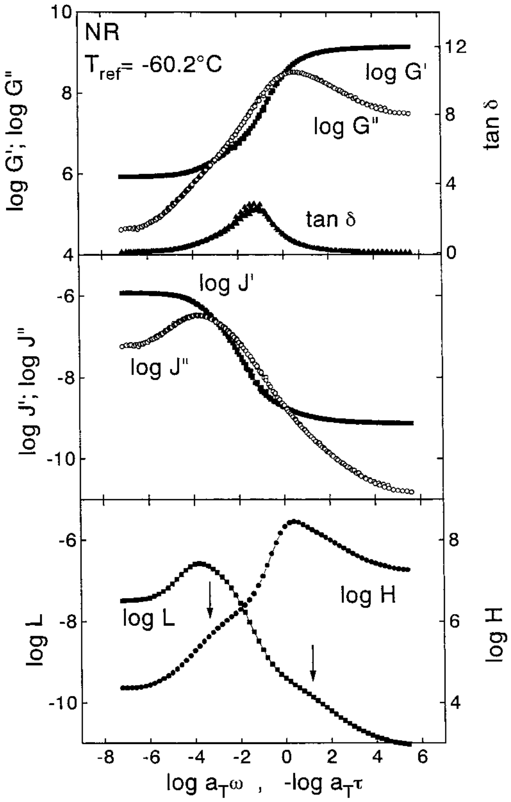

Figure 1. Master curves for shear modulus (log G', log G''), loss tangent (tan δ), and shear compliance (log J', log J'') for NR. Also shown are the corresponding $H(\tau)$ and $L(\tau)$ spectra ($\omega\tau = 1$). The arrows label the slight shoulders. Units are Pa for H and G^*, 1/Pa for L and J^*, and rad/s for ω.

Table 1. Molecular Weights and Glass Transition Temperatures for the Three Polymers Investigated

	M_w (kg/mol)	M_w/M_n	T_g (°C)	M_c (kg/mol)
PS	706	1.05	101	
PVAC	560	3.7	38	
NR			−62	≈ 5

AG. The PVAC sample was carefully dried in vacuum (36 h, 105 °C) and measured under an inert N_2 atmosphere. The PS and NR samples were measured as obtained.

The samples are characterized in Table 1. The glass transition temperatures (T_g) were calculated by an equal-area construction from DSC measurements in a Perkin-Elmer DSC7. Average molecular weights (M_w) and polydispersities (M_w/M_n) were determined by GPC calibrated with polystyrene standards. The average molecular weight between two cross-links, M_c, in the NR sample was calculated from dynamic shear measurements in the rubbery plateau.

Dynamic shear (modulus) measurements were made in a RDA II instrument from Rheometrics (frequency range: 0.01−100 rad/s, temperature range: 41.5−150.2 °C for PVAC and 101.7−129.6 °C for PS; frequency range: 0.1−100 rad/s, temperature range: −20 to −72 °C for NR). The samples were annealed (equilibrated with respect to the main transition) in the apparatus for 900 s for PVAC and PS-700-M and 300 s for NR. The strain amplitude was 0.2% in the case of PVAC and PS and <0.5% for NR. Stripes of about 25 × 10 × 1.5 mm^3 were used with the fixed clamp at the top, and the signals were detected by a FRT (force rebalance transducer). Additional high-temperature measurements for PVAC were performed in a DSR instrument from Rheometrics with parallel plates (frequency range: 0.0001−100 rad/s, temperature range: 77.9−150.2 °C, sample diameter: 20 mm, sample thickness: 2−3 mm).

The master curves for G', G'', J', J'', and tan δ were calculated with the Rheometrics RHIOS 4.22 program, using only horizontal shifts. The H and L spectra were calculated with the very effective NLREG program by Weese and Honerkamp,[19] checked iteratively by inversion routines.

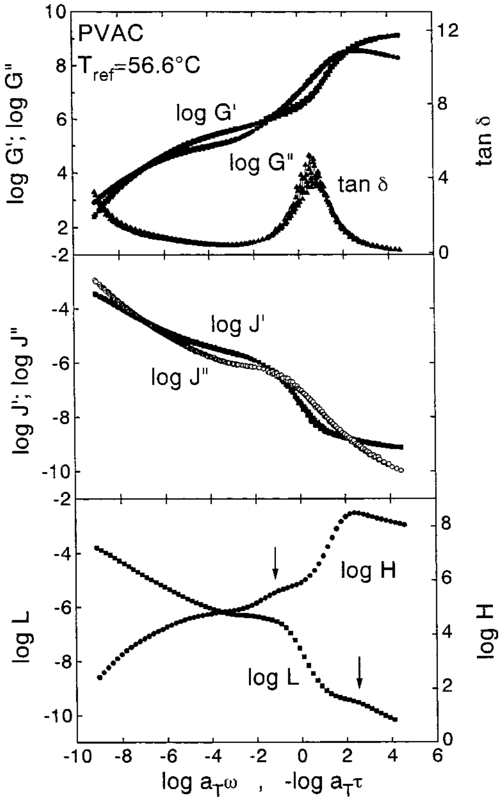

Figure 2. Master curves and spectra for PVAC.

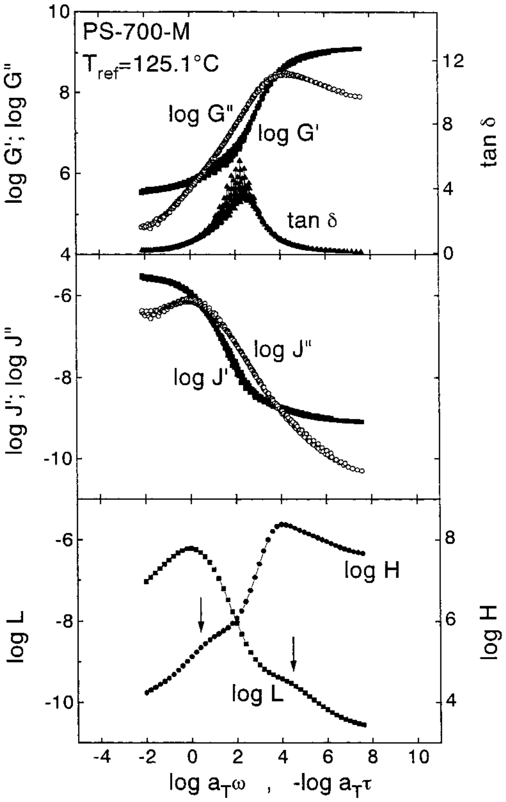

Figure 3. Master curves and spectra for PS-700-M.

III. Results

Figures 1−3 show the full set of $G'(\omega)$, $G''(\omega)$, tan $\delta(\omega)$, $J'(\omega)$, and $J''(\omega)$ master curves obtained for the three polymers, completed by the relaxation ($H(\tau)$) and

Table 2. Frequency Position (rad/s) of Main Peaks and Shoulders in the *L* and *H* Spectra Determined by a Double Tangent Construction

	$\log \omega_{H_\text{peak}}$	$\log \omega_{L_\text{shoulder}}$	$\log \omega_{L_\text{peak}}$	$\log \omega_{H_\text{shoulder}}$
PS	3.88	4.60	0.21	0.57
PVAC	2.16	2.70	−0.90	−1.16
NR	0.17	1.02	−3.22	−3.30

retardation ($L(\tau)$) spectra ($\tau = 1/\omega$). The arrows label Plazek's slight shoulder in the *L* spectrum and, as found in all three polymers, the new slight shoulder in the *H* spectrum. All shoulders (with an uncertainty less than one decade) are located at the frequency of the complementary main peak of *L* and *H*, respectively; see Table 2.

The master curves of tan δ for all three polymers show data spreading (divergence) at the top and left (low frequency) flank of the peak. This indicates thermorheological complexity[4] and, perhaps, a certain independence of the modes between the main *H* and *L* peaks. The shear exponent (steepness index = largest slope of d log G'/d log ω) is rather similar for the three polymers used (1.22 for PVAC, 1.21 for PS, and 1.12 for NR) and neither G' and G'' nor J' and J'' are (even approximately) parallel in the central part of the main transition. No distinctive parts with an index 0.67 or 0.50 (Rouse modes) could be detected.

Additionally, an effort to prove the existence of the slight *H* shoulder was tried by differentiating each $G'(\omega)$ isotherm by a five-point method. As is well known, log(dG'/d log ω) with $\omega\tau = 1$ can be considered as a first approximation for log *H*. A shoulder in the log(dG'/d log ω) isotherms would prove that it is a local phenomenon, not resulting from nonlocal properties of the evaluation program or the frequency temperature shifts.[17] Figure 4 shows some examples for the log(dG'/d log ω) isotherms. For NR, the shoulders can be seen with the naked eye. For PVAC, the shoulders are indicated at several isotherms. For PS-700-M, no clear hint to a peculiarity can be observed in the single isotherms. Nevertheless, the NLREG program results in a distinct shoulder in the master *H* spectrum for all three polymers, demonstrating the ability of its procedure to densify the experimental information.

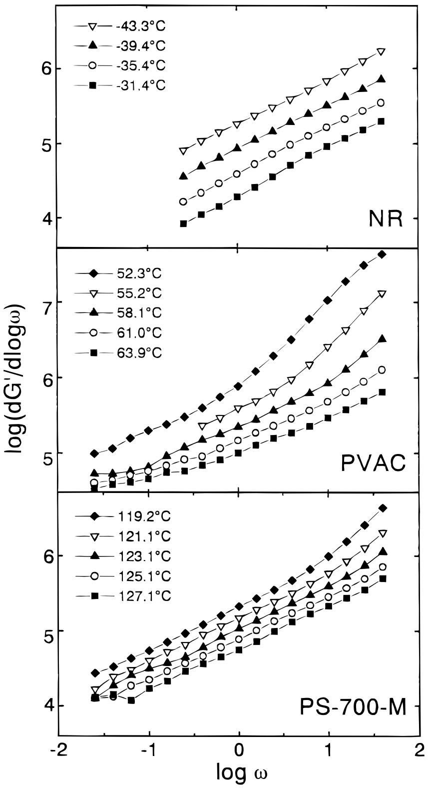

Figure 4. Five-point differentiation of all original isotherms of the dynamic storage modulus for the three polymers in the *H* shoulder region. Concerning the 55.2 °C isotherm, five points must be omitted because the G^* point at $\omega = 0.1$ rad/s was failed.

IV. Discussion

Let us now briefly discuss at a speculative level why we would like to prefer our fine-structure terms[6] as compared to the Ngai–Plazek terms[4] for the different modes across the main transition.

A. Local Segmental Motion ↔ Proper Glass Transition (Main *H* Peak, Slight *L* Shoulder). As indicated by a comparison with heat capacity and dielectric spectroscopy data,[11,17] both signals are at the time scale of the main *H* peak and of Plazek's slight *L* shoulder. Since both, the calorimetric and the dielectric signal, are usually connected with the glass-transition cooperativity and since the ω identity of the FDT does not allow any frequency shift in the molecular interpretation, we are forced to interpret this mode type as the cooperative movement of polymer segments (monomeric units), similar to cooperative movements of molecules in small-molecule glass formers (length scale about 2 nm). This corresponds to ref 4 always associating the local segmental motion with the proper glass transition, too.

B. Sub-Rouse Modes ↔ Confined Flow (Between the *H* and *L* Peaks). Let us use a crude argument: Assuming that in the case of sub-Rouse modes the entropy forces between the beads are modified by potential barriers between the C−C bonds, side groups, etc.; i.e., the forces are *stronger* than the entropy springs. Then we should expect that the maximal shear exponent d log G'/d log ω in the main transition should be *less* than 0.5 (as for Rouse modes). But in most cases, larger shear exponents are observed; as an extreme example, d log G'/d log ω = 1.45 and d log G''/d log ω = 0.97 for the PVAC investigated by Plazek.[15] Ideal Newton flow has the exponents 2 and 1, respectively. Our interpretation is, therefore, that the monomeric units, after they were mobilized at the proper glass transition, start to flow for longer times. The idealization is broken by the chain structure of the macromolecules and is spatially confined by the entanglements (length scale of entanglement spacing, d_E, about 7 nm).

C. Rouse Modes ↔ Hindering Zone (Main *L* Peak, Slight *H* Shoulder). There are amorphous polymers where a Rouse mode part at the main transition can directly be determined by shear, e.g., for poly(*n*-alkyl methacrylates) (alkyl = methyl to hexyl).[20,21] But this is rather an exception than the rule. The fate of Rouse modes when, by lowering the temperature, they encroach on the main transition is an interesting and unresolved question. An approach to this problem is planned for the future.[21] Since the hindering of Rouse modes by the entanglements can explicitly be detected by dynamic neutron scattering[22] for high frequencies above the $\alpha\beta$ splitting, it is not very probable that such a hindering should not occur for confined flow at low frequencies. The main *L* peak is, generally, a qualitative indication that a flowlike motion is hindered or stopped, here at the beginning of the rubbery plateau zone.

V. Conclusions

The existence of the slight shoulders in the shear retardation spectrum and the shear relaxation spectrum, respectively, the latter experimentally verified for the first time in this work, is an additional criterion for the independence and distinctive manifestation of different molecular modes across the main transition of amorphous polymers.

In the next papers of this series, the following problems will be discussed: (a) the length scales of the different modes between the characteristic length of the proper glass transition, $\xi_a \approx 3$ nm, and the entanglement spacing $d_E \approx 7$ nm; (b) sensitivity of different activities (including heat capacity spectroscopy and NMR times) to the different modes; and (c) the fate of the Rouse modes during encroaching, and, as a special example, the three shoulders in the L spectrum of polyisobutylene.

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