

Influence of Chain Length on the α - β Bifurcation in Oligomeric Glass Formers

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A series of oligo(propylene glycol) dimethyl ethers has been investigated using dielectric spectroscopy in order to relate features of the glass transition dynamics to the number of monomer units N in the chain. The results show that (i) when scaled with the glass transition temperature, the β relaxations systematically become faster for larger N whereas the α relaxations display nearly identical temperature evolutions, i.e., the α - β bifurcation shifts towards shorter times for larger N , (ii) the bifurcation scenario displays a crossover in behavior at $N \sim 10$ monomer units, signaling the transition from oligomeric to polymeric behavior, and (iii) the β relaxation has a cooperative nature.

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The liquid-glass transition is an important unresolved phenomenon in condensed matter physics [1]. The main feature of the glass transition is the rapid increase in viscosity and the slowing down of the main relaxation, the α relaxation, as the temperature is decreased towards T_g . The α relaxation time τ_α displays a non-Arrhenius temperature dependence, which is considered to be a direct consequence of the cooperative nature of this relaxation process [2]. In addition to the primary α relaxation, a secondary so-called β relaxation normally exists. This relaxation process typically shows an Arrhenius temperature dependence of its relaxation time, i.e., $\ln(\tau_\beta) \sim 1/T$. At some temperature, $T_{\alpha\beta}$, well above T_g , the α and β relaxations merge and form one effective process.

In addition to the α - β bifurcation, several dynamical peculiarities are found in the region $\sim T_{\alpha\beta}$; for instance: (i) a decoupling of translational and rotational molecular motion [3], (ii) a significant change in the temperature behavior of τ_α [4], and (iii) a sharp change in the behavior of the α relaxation strength [5]. These coinciding features demonstrate that the supercooled liquid undergoes qualitative changes in its dynamics in the temperature range $\sim T_{\alpha\beta}$. Within an energy landscape picture, this is often envisaged as a transition from “landscape influenced” to “landscape dominated” relaxation [6]. The structure of the landscape becomes important below $T_{\alpha\beta}$, which in turn coincides with the onset of strong cooperative motions and dynamical clustering [2]. Thus, important aspects of the glass transition process appear at this crossover between different dynamical regimes and the region around $T_{\alpha\beta}$ is hence of fundamental importance for the understanding of glassy dynamics.

It is known that the molecular structure directly influences the dynamics of the glass transition [7]. It is therefore of great interest to systematically investigate the relation between the α - β relaxation scenario and molecular structure. The present work constitutes such a study for linear molecules, where the length of the chains is

varied. In order to investigate the relationship between glassy dynamics and chain length, a system lacking strong intermolecular interactions acting through the chain ends is required. Hence, we have chosen to study a homologous series of propylene glycol based dimethyl ethers, $\text{CH}_3\text{-O-}[\text{CH}_2\text{-CH}(\text{CH}_3)\text{-O}]_N\text{-CH}_3$, including samples corresponding to $N = 1, 2, 3, 7, 17$, and 34 , where N corresponds to the peak molecular weight. We have further included the hydroxyl capped polymer poly(propylene glycol), PPG, with $M = 4000$ ($n \approx 69$) as a good approximation of the polymeric behavior for the dimethyl ethers, since the influence of the end groups is marginal at such high M [8,9]. All samples were measured over a broad frequency (10^{-2} – 10^7 Hz) and temperature range using a high resolution dielectric spectrometer (Novocontrol Alpha). Asymmetric (Kohlrausch-Williams-Watts-type) and symmetric (Cole-Cole) response functions [9,10] were fitted to the primary and secondary relaxation peaks, respectively. The inset to Fig. 1 shows representative raw data for the trimer together with the fits to the dielectric loss ϵ'' as a function of frequency and temperature.

A detailed description and discussion of the experimental procedure and the subsequent analysis can be found in [9]. We will here concentrate on results concerning the relaxation times (as calculated from the α peak frequencies f_p by $\tau = 1/2\pi f_p$) of the two processes. Figure 1 shows the relaxation time data for all investigated samples plotted vs inverse temperature. A marked feature is the large shift of the α relaxation times and accordingly the glass transition temperature with molecular weight. Both the α and the β relaxations become slower with increasing M .

In Fig. 2 the same relaxation time data are plotted vs T_g/T , where T_g is defined as the temperature where the α relaxation time reaches 100 s. The most striking features are the collapse of the α relaxation data and the systematic variation of the β relaxation with M . The strong variation with M of the temperature dependence of the α relaxation observed for the corresponding hydroxyl end-capped system [9,11] is not observed here. The relaxation times of the

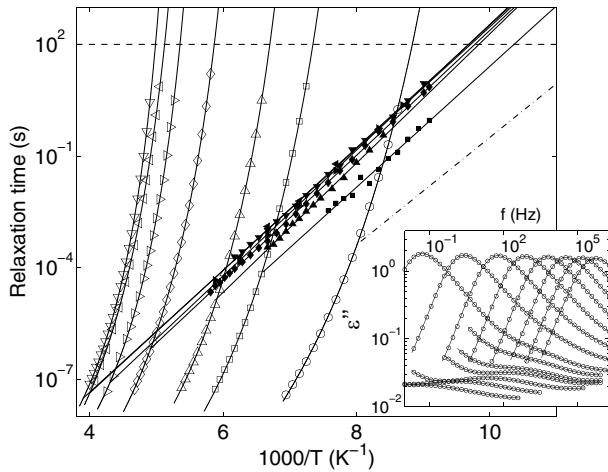


FIG. 1. α and β relaxation times vs inverse temperature. The data include $N = 1$ (\circ), 2 (\square), 3 (\triangle), 7 (\diamond), 17 (\triangleright), 34 (\triangleleft), and 69 (∇), where the unfilled symbols indicate τ_α and the filled symbols τ_β . The solid lines are the results of the data fitting described in the text. The dash-dotted line indicates τ_β for the monomer, obtained from a scaling analysis as described in [12]. The inset shows the dielectric loss ϵ'' vs frequency for the trimer at $T = 110, 122, 134, 146, 148, 150, 152, 156, 160, 164, 168, 172, 176,$ and 180 K, respectively. The result of the data fit, described in the text, is shown in solid lines.

α processes, τ_α , are well described by Vogel-Fulcher-Tammann (VFT) functions [6] over a large frequency range, as seen by the fits to the α relaxation data shown in Fig. 1. The β relaxations, on the other hand, are well described by Arrhenius temperature dependencies. At low temperatures, the β processes show up as loss peaks well separated from the α response in all samples except for the monomer. The monomer instead displays a so-called excess wing, which we in a separate publication [12] show is due to a β relaxation merged with the α process. In a scaling analysis, described in detail in [12], the β relaxation could be located also for this sample and in agreement with the higher N samples, it follows an Arrhenius behavior (see the dash-dotted line in Fig. 1). Thus, all samples show a secondary β relaxation, with a relaxation time following an Arrhenius temperature dependence, i.e., $\tau = \tau_0 \exp(E_a/kT)$, where τ_0 is a typical molecular vibrational time scale and E_a is an activation energy. The activation energies for all samples are in the range $\sim 0.29\text{--}0.34$ eV. The values of τ_0 , in turn, are all in the range $\sim 10^{-15}\text{--}10^{-14}$ s, which agrees well with a time scale typical of molecular vibrations.

A correlation was recently suggested [13,14] between the location of the α - β bifurcation and the fragility [15], connecting a lower fragility to a smaller value of the ratio T_g^β/T_g . From the Arrhenius plot of our data, shown in Fig. 2, it is clear that even though we observe only minor changes in fragility for the investigated samples, the variation of T_g^β/T_g is strong. It is thus clear that at least in an

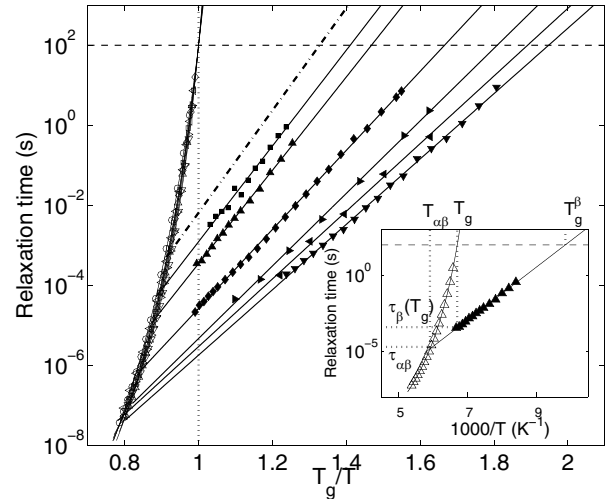


FIG. 2. α and β relaxation times vs inverse temperature normalized by T_g . The symbols are the same as in Fig. 1. The inset shows data for the trimer together with the definition of a number of characteristic temperatures, $T_{\alpha\beta}$, T_g , T_g^β , and time scales, $\tau_\beta(T_g)$ and $\tau_{\alpha\beta}$, used in the analysis and further described in the text.

oligomeric system like this with a high degree of connectivity, there can be strong variations in the location of the α - β bifurcation, without any strong variations in fragility. This implies that the recently proposed relation between the behavior of the α - β bifurcation and the fragility [13,14] may not be universal.

In order to investigate the α - β bifurcation behavior more quantitatively, we choose to study a range of related parameters, described and defined in the inset to Fig. 2. T_g^β is defined as the temperature where the β process reaches 100 s. As signatures of the α - β bifurcation, we have used either the β relaxation time at T_g , $\tau_\beta(T_g)$, the relaxation time at the extrapolated crossing of the α and β relaxations, $\tau_{\alpha\beta}$, or alternatively the corresponding temperature, $T_{\alpha\beta}$.

Figure 3 shows the variation with chain length of T_g and T_g^β . It is clear from Fig. 3 that even though the β relaxation behavior appears to approach that of the polymer in a gradual fashion, T_g^β changes rapidly with M only for the three lowest M samples. This is clearly seen also in the behavior of $\tau_\beta(T_i)$ (see inset to Fig. 3), where T_i is an arbitrary temperature within the β relaxation range. A rough extrapolation of the β relaxation behavior with a linear function for the lowest M data shows that for M below ~ 250 , corresponding to $\sim 3\text{--}4$ monomer units or $\sim 12\text{--}15$ backbone atoms, there is a strong speed up of the secondary process. We see from the smooth and considerably more stretched out behavior of T_g vs M that the M dependence of the β relaxation cannot be explained on the same footing as that of the α relaxation. A reduced density, and accordingly an increased free volume, due to higher

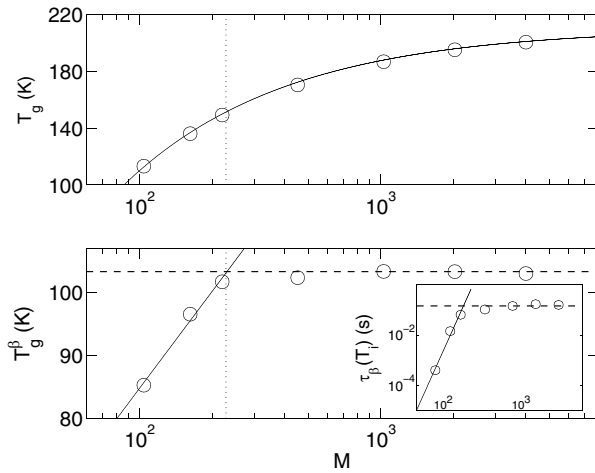


FIG. 3. The upper panel shows T_g vs M and the lower panel shows T_g^β vs M . The inset in the lower panel shows $\tau_\beta(T_i)$ vs M , where $T_i = 133$ K. The dashed lines mark the values for the polymer. The solid lines are guides to the eye.

importance of chain ends for shorter chains can thus not be the main origin of the observed effect.

The β relaxation is often assumed to be noncooperative and thus local. On the contrary, this study shows that it can in fact have a cooperative nature, since it changes rapidly with N for short chains. A similar conclusion has recently been drawn for a gel system consisting of cross-linked triols of varying complexity [16,17]. The result is also in accord with some previous suggestions for the origin of the β relaxation in PPG [18,19]. Furthermore, the activation energy of the β relaxations found in our system (0.29–0.34 eV) supports an interpretation in terms of cooperative movements. The activation energy necessary for rotation of a small lateral group is normally less than ~ 0.16 eV and conformational changes are usually characterized by activation energies below 0.1–0.2 eV [20,21]. Thus, the β relaxation should involve an entity more difficult to move than a lateral group or a single backbone bond. This conclusion is also consistent with the fact that β relaxations are found in glass formers lacking intramolecular degrees of freedom [22].

A salient feature of Fig. 2 is the clear trend observed for the bifurcation of the α and β relaxations. Approaching T_g from above, the longer the chains are, the sooner the separation of the primary and secondary relaxations occur; i.e., the bifurcation is found at gradually higher temperatures relative to T_g . Figure 4 shows $T_{\alpha\beta}/T_g$ plotted vs $\log_{10}(M)$. We note the monotonical increase of the ratio with increasing M for the oligomers. A qualitatively similar behavior has been observed both for a variation of chain length in strongly hydrogen bonded systems [23,24], and for the triol based gel system mentioned above [16]. Hence, the observed trend of an increasing $T_{\alpha\beta}/T_g$ with growing molecular complexity appears to be a feature of some generality in glass forming systems.

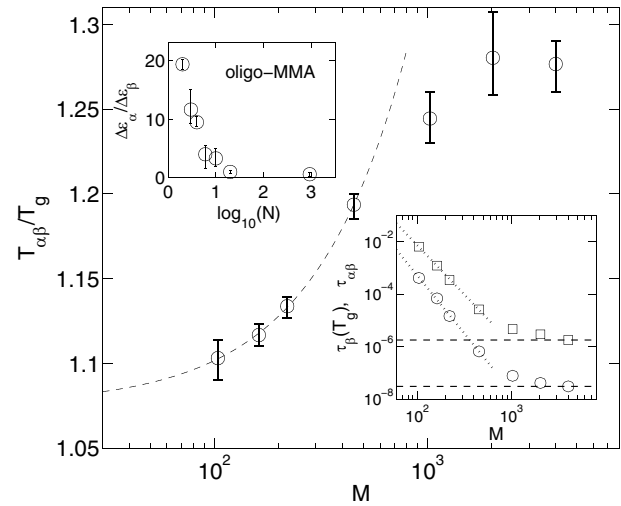


FIG. 4. Variation of $T_{\alpha\beta}/T_g$ with $\log_{10}(M)$. The dashed line is the result of a fit with a linear function to the four lowest M data points. The right inset shows a log-log plot of $\tau_\beta(T_g)$ (circles) and $\tau_{\alpha\beta}$ (squares) vs M , respectively. The dotted lines are power-law fits to the low- M data and the dashed lines mark the polymer values. The left inset shows the ratio between the strength of the α relaxation $\Delta\epsilon_\alpha$ and β relaxation $\Delta\epsilon_\beta$ vs chain length N for a series of oligo-methyl methacrylates.

As seen in Fig. 1 the bifurcation behavior is generally related to a chain length variation of both the α - and β -relaxation times. Connectivity, as formed by bonds or strong correlations between molecules, imposes constraints. In consequence, individual molecular movements become more or less hindered, which in turn is reflected in an increased T_g . Apart from the T_g shift, however, we find (see Fig. 2) that the decoupling of α and β dynamics occurs at shorter times or correspondingly higher temperatures relative to T_g for longer chains. The observed bifurcation behavior can be viewed as a decoupling of cooperative dynamics. It then arises due to an interplay between cooperative contributions (generally with both intra- and intermolecular character) to the α and β relaxations.

We now turn to a quantitative investigation of the parameters characterizing the α - β bifurcation. The lower right inset to Fig. 4 shows the logarithm of both $\tau_{\alpha\beta}$ and $\tau_\beta(T_g)$ plotted vs $\log_{10}(M)$. We find a highly systematic variation with M for both parameters. In fact, the approximately linear dependence (in a log-log plot) at low M values suggests a power-law relation between the relaxation times and M . The variation of $T_{\alpha\beta}/T_g$ with M for low M values is in turn linear to a good approximation (see the dashed line in Fig. 4). Thus, a highly systematic M variation of the α - β bifurcation is observed for low M values. Interestingly, for all parameters related to the α - β bifurcation, $\tau_{\alpha\beta}$, $\tau_\beta(T_g)$, and $T_{\alpha\beta}/T_g$, the M variation observed for the low M molecules changes at $M \sim 700$ – 800 , corresponding to $N \sim 10$ monomer units. Increasing the chain

length further only leads to a smooth approach toward the M -independent scenario characteristic of high M polymers. Thus, in the perspective of glassy dynamics, the behavior typical for small molecular glass formers and oligomers turns into that of the polymer already for a molecular size corresponding to ~ 10 monomer units.

We have recently observed a distinct transition between oligomeric and polymeric dynamic behavior also for a very different chain length system consisting of oligo(methyl methacrylates) [9]. The dielectric relaxation dynamics of these oligomers changes abruptly in an M range corresponding to ~ 10 monomer units; the typical relaxation behavior of a low M system, with a strong α relaxation and a significantly weaker β relaxation, changes to the polymeric methyl methacrylate behavior with a β relaxation considerably stronger than the α process (see inset to Fig. 4). Some evidence for a change in behavior in the same chain length regime exists also for other oligomeric systems [25,26]. Is the observed change in dynamic behavior related to a change in molecular structure? Evidence for this is found in studies of molecular conformation, where for several polymer systems at a length of 5–10 monomer units, a change from an M dependent conformation to a conformational structure typical of the polymer was found (see references in [26]). Additionally, Gaussian coiling should be expected for M values of this order [27]. It is thus plausible that a preferred conformation is generally found for a chain length corresponding to ~ 10 monomer units and that this is reflected in a range of different dynamical features directly related to glassy dynamics.

In conclusion, we have found the following: (i) The fragilities are nearly identical while the β relaxations, when scaled with T_g , systematically move towards shorter relaxation times for higher molecular weights. The α - β bifurcation thus occurs at higher temperatures or correspondingly shorter timescales for higher M , which leads to a higher $T_{\alpha\beta}/T_g$ ratio for higher M . (ii) The variation of the α - β bifurcation with M is highly systematic for chains ≤ 10 monomer units and a number of characteristic parameters directly related to the bifurcation scenario such as $\tau_{\alpha\beta}$, $\tau_{\beta}(T_g)$, and $T_{\alpha\beta}/T_g$ display simple scaling. For higher M a smooth approach to the polymeric behavior is found and a chain length of $N \sim 10$ monomer units thus marks the onset of polymeric behavior. In the light of glassy dynamics, an oligomer thus becomes a polymer already at these very short length scales. (iii) The β relaxation for this system has a cooperative nature, just as the α relaxation. It is the interplay between the cooperative nature and the associated length scales of the relaxation processes that leads to the complex M -dependent variation

of the bifurcation behavior as found, e.g., in the behavior observed for $T_{\alpha\beta}/T_g$ in Fig. 4.

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