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α-relaxation and the excess wing in polychlorinated biphenyls

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Dielectric spectra were obtained on three polychlorinated biphenyls, having glass temperatures T_g differing by up to 48 deg. The shapes of the α-relaxation peaks were the same for all samples, as were the T_g-normalized temperature dependences of the relaxation times. The characteristic temperatures at which the relaxation times deviate from a Vogel-Fulcher dependence were also equivalent ($T_B \sim 1.14\,T_g$). However, the prominence of the high-frequency "excess" wing, while present in the spectra for all materials, was markedly different. This lack of correlation between the α relaxation and the excess wing suggests the two phenomena are distinct.

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I. INTRODUCTION

The frequency-dependent dielectric loss $\varepsilon''(\nu)$ of glass forming materials is dominated by the structural (or α) relaxation, which slows down dramatically upon cooling toward the glass temperature. In addition, $\varepsilon''(\nu)$ spectra often reveal a second relaxation [the Johari-Goldstein (JG) process[1]], sometimes resolvable as a higher-frequency peak. However, if the relaxation times for the structural and secondary processes are nearly equal, it can be difficult to observe a distinct second peak, especially if its intensity is weak. Recently, much effort has been devoted to the study of so-called "type-A" glass formers, such as glycerol and propylene carbonate.[2–5] These lack a secondary peak in their dielectric loss spectra, but exhibit an excess intensity at high frequency. This excess wing can be described by a power law $\varepsilon''(\nu) \sim \nu^{-b}$, distinct from the power law for the high-frequency flank of the α relaxation, $\varepsilon''(\nu) \sim \nu^{-\beta}$ ($b < \beta$). It is an open, if much debated, question whether this excess wing is an intrinsic part of the α relaxation, or merely an unresolved JG secondary process. By JG process, we refer to relaxations that can arise solely from intermolecular processes,[6] and thus can exist even in rigid molecules.[1] This definition does not distinguish between processes involving the entire molecule or only part of it, as long as the motion is "governed" by intermolecular interactions.

By an appropriate scaling, the peak and wing measured at various temperatures can often be superposed onto a single master curve.[7] Such scaling suggests that the two features of the spectra are components of the same structural relaxation mechanism. Theoretical models[8,9] offer support for this interpretation. On the other hand, the notion that the excess wing is actually an unresolved secondary relaxation underlies interpretation of various experimental studies.[10–12] Moreover, physical aging has been shown to cause emergence of a nascent peak at frequencies associated with the excess wing.[3,4] The implication is that a weak, close-lying secondary process is masked by a dominant structural relaxation. Indeed, it has been argued that the absence of an observable secondary relaxation is caused by a narrow structural relaxation peak, with consequently similar temperature dependence.[13]

Clearly, more information is necessary to resolve this issue. One approach toward better understanding is to compare the properties of different glass formers exhibiting an excess wing in their dielectric loss.

II. EXPERIMENTAL

Herein, we describe results on polychlorinated biphenyls (PCB), in which modification of the chemical structure, while not affecting the nature of the α relaxation, strongly influences the high frequency wing. These amorphous liquids, referred to herein as PCB42, PCB54, and PCB62, have 42%, 54%, and 62% by weight chlorine, respectively. All PCB are mixtures of biphenyls containing one to nine chlorines per molecule; the presence of various homologs suppresses crystallization. The primary species in PCB42 is trichlorobiphenyl, in PCB54 is pentachlorobiphenyl, and in PCB62 is heptachlorobiphenyl.

Dielectric measurements were carried out over 13 decades of frequency (10^{-4}–10^{9} Hz), using an IMass time domain dielectric analyzer, a HP4284A LCR meter, and a HP4291A impedance analyzer.

From the dielectric data, we determine glass temperatures [defined as $\tau_{\max}(T_g)=100$ s], $T_g=221$ K for PCB42, $T_g=248$ K for PCB54, and 269 K for PCB62.

III. RESULTS AND DISCUSSION

In Fig. 1 are displayed the frequencies of the maximum in the dielectric loss, $\nu_{\max}$, as a function of inverse temperature, the latter normalized by T_g of the respective PCB. Notwithstanding a difference of as much as 48 K in glass temperature, the materials have equivalent temperature dependences over the entire measurement range.

It is customary to fit the temperature dependence of $\nu_{\max}$ to the Vogel-Fulcher (VF) equation,[14,15] $\log_{10}(\nu_{\max})=A+DT_0/(T-T_0)$, where T_0 is the Vogel temperature and A and D are constants. Deviation from the VF equation can be assessed from plots of the derivative function (the so-called Stickel plot[16]). In the inset of Fig. 1, we plot the quantity $\phi=[-d\log_{10}(\nu_{\max})/d(T_g/T)]^{-1/2}$ versus T_g/T. The derivative with respect to normalized temperature T_g/T is used to allow comparison of the three materials. A linear plot is obtained for a VF dependence (Arrhenius behavior would yield a constant). It is evident from Fig. 1 that the low-temperature data conform to one VF relation, up to a temperature T_B

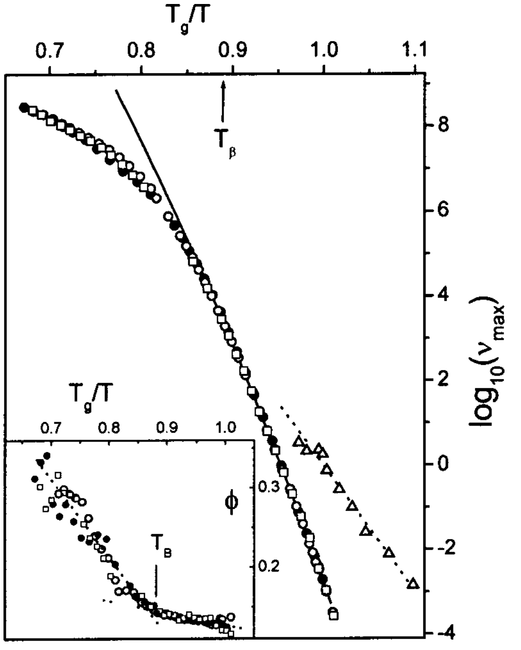

FIG. 1. Peak frequency of the dispersion in the dielectric loss versus reciprocal temperature normalized by T_g for PCB42 (●), PCB54 (□), and PCB62 (○). The fit to the VF equation for $T < T_B$ is shown as the solid line for PCB62; fits for the other two materials are practically indistinguishable and not reported for clarity. For PCB42, the peak frequency of the secondary relaxation deduced from fitting to Eq. (1) is also shown (△), along with an Arrhenius dependence (dashed line). The inset shows the function $\phi = [-d\log_{10}(\nu_{max})/d(T_g/T)]^{-1/2}$ versus T_g/T for all the materials (The dotted lines are guides for the eye).

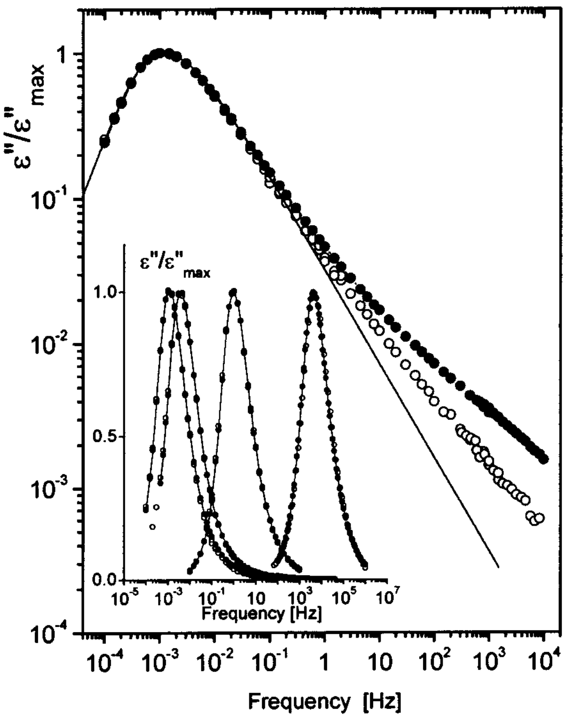

FIG. 2. Dielectric loss spectra, normalized to their maximum, for PCB42 at $T = 220.2$ K (●) and PCB62 at $T = 268.1$ K (○). The frequencies are as measured. The solid line is an extrapolation of the primary peak, demarcating the deviation at high frequency. For PCB54 (omitted for clarity), this excess intensity falls between that for these two samples. In the inset are the dielectric loss spectra (same symbols), normalized to their respective maxima without any frequency shift. For PCB42 the temperatures are (from left to right): 220.2, 222.2, 231.7 and 249.1 K. For PCB62 the temperatures are (from left to right): 268.1, 270.1, 281.6, and 304.2 K.

$\sim 1.14\,T_g$, beyond which the data begin to deviate. The three PCB behave identically in this regard.

Fits of ν_{max} to the VF equation for $T < T_B$ are included in Fig. 1 for PCB62 (solid line); fits for the other two materials are hardly distinguishable. Departure from Arrhenius behavior can be quantified by a steepness index (or fragility), defined as $m = -d\log(\nu_{max})/d(T_g/T)|_{T=T_g}$. For all three materials, we find $m = 63$. This falls within the range of glycerol ($m = 53$) and propylene carbonate ($m = 90$),[17] two glass formers having an excess wing but no distinct secondary relaxation.

Fragility is known to correlate with the breadth of the α relaxation.[18,19] In the inset of Fig. 2 are shown spectra for PCB42 and PCB62 obtained at four temperatures, each normalized to the maximum in $\varepsilon''(\nu)$. No shift along the frequency axis was necessary, since each sample was measured at respective temperatures yielding the same ν_{max}. It can be seen that the spectra superimpose well, consistent with their equal fragilities.

Figure 2 shows the dielectric loss for PCB42 at $T = 220.2$ K. Evident at high frequency is a transition from the high-frequency power law of the α relaxation to a second power law associated with the excess wing. Superimposed on this is the dielectric loss of PCB62 measured at $T = 268.1$ K. The two spectra differ at high frequencies, the wing for PCB62 being much weaker. In measurements at lower temperature (not shown) the excess wing becomes more apparent in the spectrum of PCB62. The spectrum for PCB54 at $T = 247.2$ K (having approximately the same peak frequency of those in Fig. 2) shows intermediate behavior, with an excess wing intensity that falls intermediate to the other samples. A distinct secondary peak is never observed for any of these materials.

This comparison of the dielectric spectra demonstrates the absence of any direct correlation between the α relaxation and the excess wing. In Fig. 3, we attempt to rescale the spectra onto a single master curve, using the approach proposed by Dixon *et al.*[7] In this plot the abscissa is $(1/w)(1/w+1)\log_{10}(\nu/\nu_{max})$ and the ordinate $(1/w)\log_{10}(\varepsilon''\nu_{max}/\nu\Delta\varepsilon)$, where w is the (Debye-normalized) width at half maximum and $\Delta\varepsilon$ is the dielectric strength. The failure of the scaling procedure is evident for the three materials. This is expected, since the scaling parameters are derived only from the α relaxation, which is essentially the same for the three PCB, while their respective excess wings have different properties.

An alternative approach is to consider the spectrum as the superposition of two relaxations. This presumes not only distinct processes, but also an absence of mutual interaction.[20,21] As shown in Fig. 4, the dielectric loss spectra for PCB42

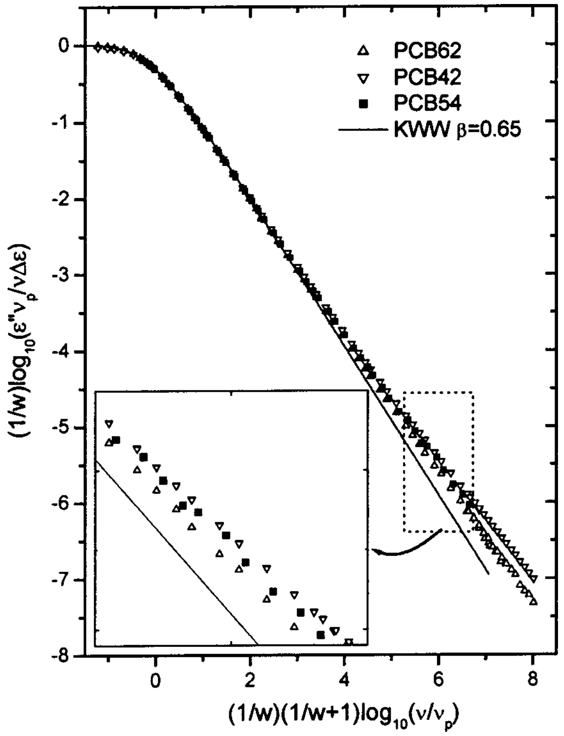

FIG. 3. Scaling of the dielectric loss spectra, as proposed by Dixon *et al.*,[7] for PCB42 at $T=220.2$ K, PCB62 at $T=268.1$ K, and for PCB54 at $T=246$ K. The solid line is a stretched exponential fit with $\beta=0.65$. The inset shows a partial enlargement revealing the different behavior of the three PCB's. The spectra for PCB54 was only measured over a more limited frequency range.

were fit to a superposition of the Havriliak-Negami[22] (HN) and Cole-Cole[23] (CC) functions

$$\varepsilon''(\nu)=\mathrm{Im}\left[\Delta\varepsilon_{HN}\frac{1}{[1+(i2\pi\nu\tau_{HN})^{1-\alpha_{HN}}]^{\beta_{HN}}}+\Delta\varepsilon_{CC}\frac{1}{1+(i2\pi\nu\tau_{CC})^{1-\alpha_{CC}}}\right]. \tag{1}$$

in which τ_{HN} and τ_{CC} are relaxation times, $\Delta\varepsilon_{HN}$ and $\Delta\varepsilon_{CC}$ relaxation strengths, and α_{HN}, β_{HN}, and α_{CC} shape parameters. The individual contributions of the two processes are indicated in Fig. 3 by the dashed and dotted lines, respectively. The frequency of the secondary peak obtained from the fitting ($\nu_{\max}=1/2\pi\tau_{CC}$) is displayed in Fig. 1 (open triangles). Given the large width and weak intensity of the secondary relaxation, the fitting procedure becomes problematic at the higher temperatures. To corroborate these results, we also analyzed the data by simply subtracting the high-frequency contribution from the α relaxation, to obtain the maximum of the resulting intensity. These results were in substantial agreement with the relaxation times deduced from the fitting procedure.

The temperature dependence of the secondary relaxation is Arrhenius, at least over the limited temperature range. By extrapolating to higher temperature, we determine a merging temperature (at which the two relaxation times become equal) $T_\beta=1.12T_g$. This value is very close to the characteristic temperature T_B ($\sim 1.14T_g$) associated with the change of dynamics. A similar correlation is known for glass formers exhibiting distinct secondary relaxations,[24,25] thus supporting identification of the excess wing in PCB as a submerged secondary relaxation. Consistent with this interpretation is the fact that extrapolation to high temperature yields an unphysically high value of $\tau_\beta \sim 10^{-20}$ s (faster than phonon frequencies). This indicates that the process cannot reflect intramolecular motions, since these would continue to be activated up to high temperatures ($T>T_B$). The secondary process in PCB is intermolecular, and thus merges with the α relaxation at higher temperatures.

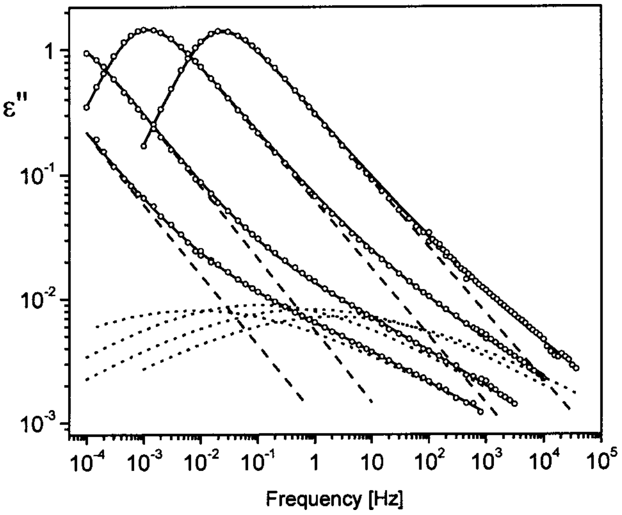

FIG. 4. Dielectric loss for PCB42 (○) at four temperatures (from left to right): 225.2, 220.2, 214.2, and 206.2 K. The solid lines represent the best fit to Eq. (1), with the dashed and dotted lines representing the respective HN and CC contributions.

An understanding of the origin of the secondary relaxation in glass formers remains a subject of debate, and definitive identification of the observed phenomena is not yet possible. Vogel *et al.*[26] have proposed that the secondary relaxation involves molecular axis rotations that subtend only a small angular range. Following this idea, it is tempting to conclude that an increased number of chlorine atoms alters the intramolecular interaction hindering such motion, with consequent decrease of the intensity of the secondary process. This interpretation would account for the results described herein.

IV. CONCLUSIONS

In conclusion, we have presented dielectric data on three PCB, having substantially different glass temperatures. The T_g-normalized temperature dependences of their structural relaxation times are the same. Moreover, similar to the behavior of other glass formers such as glycerol and PC, the dielectric loss spectra exhibit an excess wing at low temperature. While the dynamics of the α relaxation (peak shape and value of T_B/T_g) were essentially identical for the three PCB, the nature of their respective excess wings was quite different. This lack of correlation between the two phenomena is hard to reconcile with an interpretation as components of the same structural relaxation process. Nevertheless, while our results are consistent with identification of the excess wing as a submerged secondary relaxation, this does not imply that the wing is completely ''decoupled'' from the structural relaxation. The present results, clarifying the nature of the excess wing, can guide further experimental and theoretical work, directed toward a fuller understanding of this phenomenon.

ACKNOWLEDGMENT

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