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Quantifying Changes in the High-Frequency Dynamics of Mixtures by Dielectric Spectroscopy†

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Additives to polymeric materials can lead to appreciable changes in the rates of relaxation and reaction in these mixtures that can profoundly alter material properties and function. We develop a general theoretical framework for quantifying changes in the “high-frequency” relaxation dynamics of mixtures based on classical transition state theory, in conjunction with mathematical statements regarding the dependence of the entropy ($S^+$) and enthalpy ($E^+$) of activation of the high-frequency relaxation time on diluent mass fraction, $x_w$. Specifically, we deduce a general classification scheme for diluents based on a consideration of the sign of the differential change in $S^+$ and $E^+$ with $x_w$. Two of these classes of diluents exhibit a transition from plasticization to antiplasticization (defined specifically as a speeding up or slowing down of relaxation relative to the pure system, respectively) upon varying temperature through an “antiplasticization” temperature, $T_{anti}$. Extensive dielectric relaxation measurements on polycarbonate (PC) as a function of temperature and diluent (Aroclor) concentration are utilized to illustrate our theoretical model, and we focus particularly on the Arrhenius “$\beta$” dielectric relaxation process of these mixtures. Many aspects of our scheme for quantifying changes in the high-frequency dynamics of mixtures are rationalized by our mixture model. In particular, we show that the dilution of PC by Aroclor is consistent with a theoretically predicted (one of the two antiplasticization mixture classes mentioned above) transition from antiplasticization to plasticization with decreasing temperature. We briefly compare our findings from dielectric measurements with those from elastic incoherent neutron scattering and dynamical—mechanical measurements, providing further evidence for the antiplasticization-to-plasticization transition phenomena that we observe in our high-frequency dielectric measurements.

I. Introduction

The introduction of solvents and nanoparticle additives to biological and synthetic polymeric materials can have a tremendous impact on the processing characteristics, functioning, and stability of diverse materials. Currently, the investigation of this phenomenon is particularly active in connection with the preservation and modification of the aesthetic properties of foods, the preservation of tissues and drugs, and with studies aimed at understanding toxicity effects arising from environmental exposure to additives that disrupt natural biological function. In synthetic polymers, there is active research relating to the enhancement of the mechanical stability of polymer films, the control of the gas permeability of polymeric films and bulk materials, as well as in the development novel nanocomposite materials. Given this diverse activity, there is evidently a need for a theoretical framework for understanding and controlling basic property changes in these complex mixtures (e.g., tensile strength, stiffness, heat distortion, elongation, impact strength, gas permeability, reaction rates, etc.).

In the present work, we investigate this general problem using the synthetic polymer polycarbonate (PC) and the diluent Aroclor 1260 (a commercial name for polychlorinated biphenyl mixture with 60% chlorine); this is a classical model system in which large dilution-induced changes in mechanical properties have been well documented.1 Such synthetic model mixtures are advantageous in initial studies aimed at developing a framework for these property changes since the molecular structure (mass, side groups) can be tuned with considerable control,2 allowing us to explore how molecular properties influence dynamical—mechanical properties. We choose dielectric spectroscopy as our primary experimental methodology because it is readily available in many academic and commercial laboratories and because this methodology can access the relatively high-frequency regime describing the local segmental dynamics of the polymer.

Although our experimental focus is on the relatively high-frequency “$\beta$” or “secondary” dielectric relaxation process of PC, we are concerned with using this data in developing a general method for quantifying how molecular additives influence alter high-frequency relaxation processes in liquids. We restrict our attention to relaxation process that do not involve highly cooperative or intermittent molecular motions, and which correspondingly exhibit relaxation times having a nearly Arrhenius temperature dependence. This choice is not overly restrictive since most high-frequency relaxation processes in condensed materials appear to satisfy this relationship over a wide temperature range. We develop a framework for describing changes in the high-frequency dynamics of mixtures based on a simple transition state theory framework, which is consistent with Arrhenius temperature-dependent relaxation times.$^{3,4}$

Our previous study of high-frequency dielectric relaxation in mixtures of trehalose and glycerol$^{4,5}$ was aimed at understanding antiplasticization in model trehalose—glycerol mixtures as a process relevant to protein preservation and, in this specific context, we defined the ratio $\theta$ of the high-frequency relaxation
time for the mixture $\tau_{\text{(mixture)}}$ to the one of “pure” species $\tau_{\text{(pure)}}$ as a basic quantity for investigation.\textsuperscript{5}

$$\theta = \frac{\tau_{\text{(mixture)}}}{\tau_{\text{(pure)}}}$$

(1)

The slowing down of the high-frequency dynamics by an additive is a defining characteristic of “antiplastization”,\textsuperscript{5} while speeding up of the dynamics characterizes “plasticization”.\textsuperscript{5} (Notably, this phenomenon is not generally correlated to changes in the low frequency fluid dynamics such as the zero shear viscosity and the glass transition temperature, although the addition of additives changes this aspect of the fluid dynamics, as we shall discuss below.) Thus, we refer to a mixture as “plasticized” if the “antiplasticization parameter” obeys the relation $\theta < 1$ and “antiplasticized” for $\theta > 1$. The temperature where $\theta = 1$ defines the “antiplasticization temperature”, $T_{\text{anti}}$, where the additive makes no change in the fluid relaxation time. Evidently, $T_{\text{anti}}$ is some kind of compensation temperature where the mixture is “ideal” in some sense and we show how this quantity can be estimated in our modeling section. In most polymer fluids (at least to the extent such things have been investigated),\textsuperscript{5} antiplasticization is found well below the glass transition temperature, $T_g$. This is a “normal” trend in cases where antiplastization is observed.\textsuperscript{5,6}

Our previous investigation of trehalose—glycerol\textsuperscript{5} mixtures confirmed this expected trend, indicating antiplasticization in the low temperature glass state based on high-frequency (“$\beta$”) dielectric relaxation measurements and plasticization at more elevated temperatures (below $T_g$). This result was also confirmed qualitatively by independent incoherent neutron scattering and spectroscopy measurements (see ref 5 for discussion), and recently this effect has also been confirmed by atomistic molecular dynamics simulations.\textsuperscript{7,8} The novelty of our previous work\textsuperscript{5} is the high level of quantification of the change in the high-frequency dynamics that was achieved by dielectric spectroscopy, the precise identification of the temperature where the change plasticization to antiplasticization occurs upon cooling, and the theoretical framework developed to explain these changes in the high-frequency mixture relaxation time of trehalose as a function of diluent (glycerol) concentration and temperature. Extending these measurements and the corresponding theoretical framework\textsuperscript{5} to PC/Aroclor mixtures led us (fortuitously) to the first quantitative observation of the opposite situation: plasticization in the low temperature glass regime and antiplasticization at higher temperatures. These observations obviously provide a challenge for theoretical explanation, and we show below that a generalization of our former theoretical treatment\textsuperscript{5} naturally explains these opposing antiplasticizing trends with temperature.

Of course, not all high-frequency relaxation processes, involving relatively local molecular motions, compared to those involved in structural ($\alpha$) relaxation, will be shifted in the same way by additives, and only some of these relaxation processes can be expected to be of direct relevance in connection with observable mechanical properties and the physics of glass-formation. This situation requires the comparison of the selected high-frequency relaxation process, and its changes with dilution, with independent mechanical measurements and other high-frequency measurements that provide insight into the stiffness of the material to establish the predictive significance of observed changes in the “high-frequency” dielectric measurements. Accordingly, we briefly compare our dielectric measurements with incoherent neutron scattering and mechanical relaxation measurements to characterize and compare how the antiplastization effect is exhibited in these measurements.

Of course, some differences (e.g., the precise value of the antiplasticization temperature) are expected because of the very different frequency ranges explored in these relatively “high-frequency” measurements. Thus, while all our measurements below exhibit a common trend in the transition between plasticization and antiplasticization as the temperature is varied, there are quantitative differences in the exact compensation or antiplasticization temperature, etc. (Evidently, there is some uncertainty in the specification of the antiplasticization temperature, but there is no uncertainty in the determination of $T_{\text{anti}}$ of a particular relaxation process.)

The complementary neutron and viscolelastic measurements further remind us that the term “high-frequency” relaxation is relative, and it is always possible to define even higher frequency relaxation processes in condensed phases of matter. Our dielectric measurements specifically focus on the Johari–Goldstein ($JG$) or “$\beta$-relaxation” process that is conspicuously and generally observed in glass-forming liquids in dielectric and calorimetric measurements in a frequency range higher than the $\alpha$-relaxation process and for a temperature range where those relaxation processes can be resolved from each other.\textsuperscript{5,10} Very high-frequency (“fast”) relaxation processes (typically in the range of $10^{-12}$ s to $10^{-9}$ s) are often studied in glass-forming liquids in connection with small-scale density fluctuations in dynamic neutron scattering measurements, and computational limitations often limit molecular dynamics simulations to this time regime. Importantly, the $JG$ ($\beta$-relaxation) process has been shown to be directly linked in phenomenology to the $\alpha$-relaxation process.\textsuperscript{10} Although there is no general agreement on the exact nature of the local molecular motions responsible for the dielectric $\beta$-relaxation process, this “secondary” relaxation process is commonly interpreted in terms of the elementary local collective motions from which the larger scale collective motions associated with the $\alpha$-relaxation process are comprised.\textsuperscript{10} The dielectric $\beta$-relaxation process is thus an obvious candidate for quantifying the freezing of the high-frequency dynamics of fluids.

II. Materials and Measurements

A. Materials. Poly(Bisphenol A carbonate) (PC) with an average molecular mass of 64 000 g/mol was purchased from Aldrich Chemicals Co. and dissolved in dichloromethane (DCM) to obtain a 10% solution by relative polymer mass. Then, Aroclor 1260 was added to the solutions at mass fractions $x_w$ of 0.05, 0.1, 0.15, 0.2, relative to the PC. These solutions were left to evaporate the DCM in air at room temperature for 12 h. The samples were then kept under vacuum at $T = 505$ K for another 12 h to ensure solvent removal. After this time, the samples were formed by melt pressing at $T = 473$ K for a few minutes. This strategy resulted in samples having a thickness of about 0.07 mm to 0.09 mm.

B. Differential Scanning Calorimetry (DSC). DSC measurements were performed on the TA Instruments DSC Q1000 analyzer. All samples were analyzed in the temperature range from 303 to 523 K with the heating/cooling rate of 10 K/min. An appreciable step, indicating the glass transition temperature, $T_g$, has been observed for all the samples. The standard uncertainty of the method was about 5%.

C. Dielectric Spectroscopy. The film samples were placed between parallel gold-plated flat electrodes (Novocontrol) and measured in a frequency range between 0.1 Hz and 1 MHz using an Alpha-A High Performance Frequency Analyzer from Novocontrol Technologies. The measurements have been performed in a temperature range between 153 and 483 K. All the
experiments have been performed under isothermal conditions, and the standard uncertainty of the method was about 10%.

D. Neutron Scattering. The incoherent neutron scattering experiments were performed at the NIST Center for Neutron Research on the high flux backscattering spectrometer (HFBS), located on the NG2 beamline. The standard uncertainty of the method was in order of 1%. This spectrometer utilizes cold neutrons with a wavelength of 6.271 Å and probes motions over a reciprocal space range of 0.25 Å$^{-1}$ and Q < 1.75 Å$^{-1}$. The 0.8 μeV full width at half-maximum energy resolution of this spectrometer means motions slower than 200 MHz appear as static and contribute to the elastic scattering. The HFBS spectrometer was operated in the “fixed window mode”, where the sample was ramped at 1 K/min from approximately 50 K to a final temperature that was well above the $T_g$ of the PC/ Aroclor mixtures. The decrease in the intensity of the elastic scattering peak was recorded as a function of $T$ and $Q$. For elastic incoherent scattering, the $Q$ dependence of this elastic scattering is often approximated with the Debye–Waller factor:

$$I_{mc\text{-elastic}}(Q) \propto \exp \left( -\frac{1}{3} Q^2 \langle u^2 \rangle \right)$$

Within this model, based on a harmonic oscillator, the slope of $\ln(I_{mc\text{-elastic}}(Q))$ versus $Q^2$ is equal to $\langle u^2 \rangle/3$. While most atomic motions in soft condensed matter are admittedly anharmonic, this approximation has been found to be practically useful in characterizing the dynamics in both synthetic$^{11-15}$ and biological$^{16-20}$ macromolecules.

E. Dynamical Mechanical Analysis (DMA). DMA of the films was performed on a TA Instruments DMA Q800 analyzer in tensile mode using clamps for thin film samples. The standard uncertainty of the method was about 10%. All samples were analyzed at a frequency of 1 Hz over a temperatures range from 133 to 470 K with a heating rate of 2 K/min.

III. Results

Figure 1 illustrates the imaginary part of permittivity $\varepsilon''$, as a function of temperature, in the frequency of 60 kHz, for pure PC (squares) and its mixtures with Aroclor with the weight fractions $x_w = 0.05$ (circles), 0.1 (upward pointing triangles), 0.15 (downward pointing triangles), and 0.2 (diamonds). Two relaxation peaks are observed. A prevalent $\alpha$-relaxation process at higher temperatures and a $\beta$-relaxation process at lower temperatures are apparent, and the insets provide enlargements of these peaks. Qualitatively, we see a progressive shift in Figure 1 of both relaxation processes to lower temperatures with dilution, consistent with plasticization in the low temperature glass state, and we quantify this trend below.

We contrast our observations with previous ones on the addition of tris(2-ethyl)phosphate (TOP) to PC over a similar temperature range. In this system, the $\beta$-relaxation peak, observed by DMA, shifts to higher temperatures, while $T_g$ decreases.$^{21,22}$ This corresponds to classic antiplasticization (slowing down of the high-frequency relaxation despite the reduction of the glass transition temperature) in the glassy state. Plasticization of the high-frequency dynamics has also been qualitatively observed both by dielectric spectroscopy and DMA in nearly the same temperature range with the addition of TOP to tetramethylbisphenol A polycarbonate (TMBA-PC),$^{23}$ in accord with our observations. Previous work has established trends in the observation of plasticization or antiplasticization in the low temperature glass state with variation in the additive structure and interaction.$^{20}$ The physics of this counterintuitive change in fluid dynamics has been explored recently in molecular dynamics simulations,$^{24-27}$ where the effect is attributed to the consequences of the modification of fluid molecular packing by the additive.

A firm assignment of a transition from plasticization to antiplasticization with temperature cannot be determined from Figure 1, since this relaxation process (i.e., peak in dielectric spectra as a function of temperature at fixed frequency) is only observed in the low temperature glass state.

A. High-Temperature Relaxation. Although our main purpose in the present work is to characterize the change in the high-frequency dynamics of the reference system (PC) through the addition of diluent (Aroclor), it is important to characterize how the long-time $\alpha$-relaxation associated with cooperative molecular motions and the glass-formation become modified by the diluent. Of course, the effects of diluents on the $\alpha$-relaxation dynamics in polymers have been exhaustively studied in previous work so we concentrate only on some of the essential aspects of these changes relevant to the current study. In particular, we examine how the diluent modifies the temperature dependence of the $\alpha$-relaxation time, $\tau_\alpha$, and thus the fragility of glass-formation, and we also determine the variation of the glass transition temperature $T_g$ with the concentration of Aroclor based on DSC.

The results obtained from dielectric measurements, for each relaxation process, have been analyzed in term of Havriliak–Negami (HN) relationship (eq 3),$^{28}$ which applies to high-frequency condensed matter relaxation processes with remarkable universality.$^{29,30}$ The general HN relaxation function,$^{28}$

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (\omega\tau_N)^{\alpha/\beta}}$$

is a natural candidate for characterizing dielectric data of glassy materials. In eq 3, $\omega = 2\pi f$, $\varepsilon^*$ is the relative complex dielectric permittivity, $\varepsilon^* = \varepsilon' - j\varepsilon''$, $\varepsilon_\infty$ denotes the asymptotic value of the permittivity at high frequency, $\Delta\varepsilon$ is the dielectric strength, $\tau_N$ is the relaxation time of the dielectric process, and $\alpha$ and $\beta$ ($0 < \alpha, \beta \leq 1$ and $0 < \alpha, \beta \leq 1$) are the “shape” or fluid “memory” parameters that describe the symmetric and asymmetric broadening of the dielectric function. We note that when
$\beta = 1$, the HN relaxation function becomes the Cole–Cole function,\textsuperscript{29–31} which describes materials exhibiting a broad and symmetric distribution of relaxation times. This kind of relaxation process is usually observed for relatively “local” relaxation in macromolecules in comparison to long time $\alpha$-relaxation, exhibiting a nonsymmetrical and a much narrower peak (see Figure 1 insets). We refer to the relative slow $\alpha$ and fast $\beta$ relaxation times as $\tau_\alpha$ and $\tau_\beta$, respectively. It has been shown that the relaxation time obtained from fitting to the HN equation depends on the values of parameters $\alpha$ and $\beta$.\textsuperscript{32} For this reason, another definition of relaxation time: $\tau = 1/(2\pi f_{\text{max}})$, where $f_{\text{max}}$ indicates the frequency in which $\varepsilon''$ has its maximum, is often used, and this definition is implemented in our study.

It is characteristic feature of high-frequency relaxation processes that the relaxation time has an Arrhenius temperature dependence, and our measurements indeed indicate that our dielectric $\beta$-relaxation time $\tau_\beta$ obeys the relationship\textsuperscript{33,34}

$$\tau_\beta = \tau_\alpha \exp\left(\frac{E^+}{RT}\right)$$ \hspace{1cm} (4)

where $E^+$ is the $\beta$-relaxation activation energy, $R$ is the gas constant, and $\tau_\alpha$ is the $\beta$-relaxation time prefactor. A characteristic features of $\tau_\alpha$ from dielectric $\beta$-relaxation measurements is that it is commonly observed to correspond to an extremely small time scale in the range (10$^{-13}$ s to 10$^{-18}$ s),\textsuperscript{33} and below we consider some arguments that have been made to rationalize this phenomenon.

In contrast to $\beta$-relaxation, the long-time segmental structural relaxation time $\tau_\alpha$, associated with the large-scale collective molecular motion that accompanies glass-formation,\textsuperscript{34,35} is characteristically non-Arrhenius\textsuperscript{7,9} and Figure 2 illustrates estimates of the temperature dependence of $\tau_\alpha$ obtained from our dielectric relaxation measurements. The symbols represent data determined by fitting to the HN equation and the lines are fits to the Vogel–Fulcher (VF) relation,\textsuperscript{36}

$$\log \tau_\alpha = \log \tau_0 + \frac{D_f T_0}{T - T_0}$$ \hspace{1cm} (5)

where the $\alpha$-relaxation time prefactor $\tau_0$ typically has an order of magnitude $\tau_0 \sim O(10^{-13}$ s), $T_0$ is the VF temperature where the relaxation time extrapolates to an infinite time, and the dimensionless “fragility parameter” $D_f$ provides a measure of how much the relaxation deviates from an Arrhenius relation. Fluids that exhibit VF temperature of structural relaxation have been termed “fragile” and $D_f$ is accordingly often taken as a quantitative measure of the “fragility” of glass-formation.\textsuperscript{17,37} Sometimes the fragility parameter is alternatively defined as $K = 1/D_f$, which increases as the fragility of the glass-formation increases.\textsuperscript{15,17,38}

The glass transition temperature $T_g$ is another basic characterization parameter of glass-forming liquids, and for completeness we also consider this quantity as a function of dilution, even though our focus in the present paper is on the high-frequency relaxation processes. The DSC estimates of $T_g$ for our mixtures shown in Figure 3 indicate a linear decrease of $T_g$ with an increasing diluent concentration, and the inset presents the corresponding variation of $D_f$, obtained by fitting the data.
in Figure 2 to the VF relation, eq 5. As in the case of \( T_g \), the fragility parameter \( D_f \) also progressively decreases with an increasing Aroclor concentration. This means that the fragility of PC of the glass-formation increases upon dilution by Aroclor, a situation opposite to our previous findings for the addition of glycerol to trehalose. Enhanced fragility upon dilution has also been observed in the addition of trehalose to water and upon the addition of water to glycerol, an effect that has potential ramifications to the preservation of biological materials in aqueous media.

B. Plasticization—Antiplasticization Transition in PC/Aroclor. As mentioned before, the relaxation peaks in dielectric data presented in Figure 1 indicate plasticization in the glass state since both peaks are shifted to lower temperatures. More generally, introducing an additive should shift the \( \beta \)-relaxation peak time to a lower or higher value at a fixed temperature, corresponding to plasticization or antiplasticization, respectively. This definition allows us to consider plasticization versus antiplasticization as a function of temperature. Accordingly, Figure 4 shows the variation of \( \tau_\beta \) for PC diluted by Aroclor obtained by fitting our dielectric data to the HF equation. We admit that the PC secondary relaxation peak is somewhat weak and broad and that our frequency range is limited, which restricts the temperature range of our observations to a range of about 50 K. Nevertheless, we find that the Arrhenius curves for \( \tau_\beta \) intersect at a common point, allowing us to estimate the antiplasticization temperature, \( T_{\text{anti}} \approx 260 \) K. At this temperature, the effect of the additive on the relaxation time evidently becomes inverted. We also observe that the curves rotate in a clockwise direction, indicating that the Aroclor causes PC to become plasticized at low temperatures (as evident in Figure 1), while it is predicted to become antiplasticized at higher temperatures (but still comparable to \( T_g \)). Unfortunately, our current experimental setup can not access the frequency range required to directly observe this plasticization—antiplasticization transition in PC/Aroclor. However, we have observed the full antiplasticization—plasticization transition in glycerol—trehalose mixtures. In this case (inset in Figure 4), the rotation direction of the Arrhenius curves is inverted from the present observation on Aroclor—PC mixtures. The other inset in Figure 4 shows the \( T \) dependence of \( \theta \) for Aroclor-PC mixtures, providing a different perspective on the same phenomenon, and this representation was also considered in our trehalose—glycerol study. The crossing pattern of Arrhenius curves shown in Figure 4 has been reported before for the conductivity of both inorganic and organic semiconducting materials with impurities. In this context, this crossing relation is referred to as the Meyer—Neldel rule.

IV. A Simple Model of Additive-Induced Changes in High-Frequency Dynamics

A. Formal Application of Transition State Theory to the Dynamics of Mixtures. High-frequency relaxation processes characteristically exhibit an Arrhenius temperature dependence, so we may profitably adopt the Eyring transition state theory framework to estimate \( \theta \). In particular, we may formally write \( \theta \) within transition state theory as

\[
\theta = \exp(\delta G_m^*/RT) \tag{6}
\]

where \( \delta G^+ = G_{\text{mixture}}^+ - G_{\text{pure}}^+ \) and \( G_{\text{mixture}}^+ \) and \( G_{\text{pure}}^+ \) are activation free energies of the high-frequency relaxation process under investigation in the fluid mixture and in the pure liquids, respectively. The activation free energy is then

\[
G^+ = E^+ - TS^+ \tag{7}
\]

where \( E^+ \) and \( S^+ \) are the enthalpies and entropies of activation so that the change in the activation energy upon dilution \( \delta G_{\text{mixture}}^+ \) can be decomposed into enthalpic contributions:

\[
\delta G_{\text{mixture}}^+ = \delta E_{\text{mixture}}^+ - T\delta S_{\text{mixture}}^+ \tag{8}
\]

Transition state theory implies that \( \theta \) is defined as

\[
\theta = \frac{\tau_{\text{mixture}}}{{\tau_0}} = \frac{\tau_{\text{mixture}}}{{\tau_0}} \exp(E^+/RT) \tag{9}
\]

where \( E_{\text{mixture}}^+ \equiv E_{\text{m}}^+ \) and \( E_{\text{pure}}^+ \equiv E_0^+ \) are the observed activation energies of the mixture and the pure solvent, respectively, and \( \tau_{\text{mixture}} \equiv \tau_{\text{m}} \) and \( \tau_{\text{pure}} \equiv \tau_0 \) are the corresponding relaxation time prefactors. We then identify \( \delta E_{\text{m}}^+ \) and \( \delta S_{\text{m}}^+ \) as

\[
\delta E_{\text{m}}^+ = E_{\text{m}}^+ - E_0^+ \tag{10}
\]

\[
\exp(-\delta S_{\text{m}}^+ /R) = \frac{\tau_{\text{m}}}{\tau_0} \tag{11}
\]

The problem of determining the change in the high-frequency relaxation time \( \tau_B \) (more generally, the reaction rate in a chemical reaction context) then devolves to a consideration of the separate concentration dependencies of \( \delta E_{\text{m}} ^+ \) and \( \delta S_{\text{m}}^+ \).

It is natural to assume, within this mean field theoretical description of the fluid dynamics, that the molecular species are homogeneously mixed and that \( \delta E_{\text{m}}^+ \) and \( \delta S_{\text{m}}^+ \) are analytic functions of concentration. We then formally expand \( \delta E_{\text{m}}^+ \) and \( \delta S_{\text{m}}^+ \) in a Taylor series in the concentration \( x_w \) of the diluting species,

\[
E_{\text{m}}^+ = E_0^+ + \left( \frac{dE_{\text{m}}^+}{dx_w} \right) x_w + O(x_w^2) \tag{12}
\]

\[
S_{\text{m}}^+ = S_0^+ + \left( \frac{dS_{\text{m}}^+}{dx_w} \right) x_w + O(x_w^2) \tag{13}
\]

where \( O \) denotes the order of magnitude. When the concentration of the diluting species is small, which is often a defining feature of “diluent", a truncation of these series should be adequate, leading to the approximate relations

\[
\delta E_{\text{m}}^+ = \left( \frac{dE_{\text{m}}^+}{dx_w} \right) x_w, \quad \delta S_{\text{m}}^+ = \left( \frac{dS_{\text{m}}^+}{dx_w} \right) x_w \tag{14}
\]

Similar formal arguments were made by Eyring and co-workers in the context of estimating the viscosities of fluid mixtures, who also suggested that the linear concentration terms \( \delta E_{\text{m}}^+ \) and \( \delta S_{\text{m}}^+ \) are the enthalpies and entropies of activation of some local binary mixtures at low temperatures, is characterized by heterogeneity, and the measured relaxation rates reflect an averaging over this local structure. Molecular relaxation processes, even relatively...
high-frequency processes, intrinsically involve cooperative molecular motion, as well as structural heterogeneity. Experimental studies of high-frequency (‘$\beta$’) relaxation processes in polymers have established that the apparent activation energy $E^\ast$ for such high-frequency processes depend strongly on chain molecular mass, but that these changes in $E^\ast$ saturate for a modest number of backbone atoms, and this phenomenon has reasonably been interpreted in terms of the local motion of groups of atoms defining the statistical segments of the polymer chains. While the recognition of the existence of coarse-grained dynamical units within the polymer allows for a rationalization of the observed $E^\ast$, on the basis of extensions of original arguments relating $E^\ast$ to the intermolecular cohesive energy, it is difficult to estimate the prefactor associated with these high-frequency molecular relaxation processes. This prefactor is coupled with entropic changes that occur through the hierarchical molecular rearrangement events involved in molecular displacements in the condensed state.

Experimentally, one can obtain the activation energy, $E^\ast$, and the pre-exponential factor $\tau_0$ from the Arrhenius temperature dependence of relaxation times (see eq 4). As we defined in our previous paper, the pre-exponential factor of mixture and of the pure liquid are described by the relation

$$\tau_{am/\tau_0} = \exp(\delta S^\ast_{m/\tau_0} K\tau R) = \exp(\delta S^\ast_{m/\tau_0} K\tau)$$ \hspace{1cm} (15)

$$[S^\ast_{m}] \equiv \lim_{x_w \to 0}(\delta S^\ast_{m/\tau_0} K\tau R) = (dS^\ast_{m/\tau_0} K\tau) / R$$ \hspace{1cm} (16)

Equations 8 and 13 imply that $\theta$ should have a general exponential concentration dependence at low-to-moderate concentrations of additive,

$$\theta = \exp(Ax_w)$$ \hspace{1cm} (17)

where $A$ is correspondingly defined as

$$A = (\delta E^\ast_{m/\tau_0} K\tau R) - (\delta S^\ast_{m/\tau_0} K\tau R) = ([E^\ast_{m}] / T) - [S^\ast_{m}]$$ \hspace{1cm} (18)

$$[E^\ast_{m}] = \lim_{x_w \to 0}(\delta E^\ast_{m/\tau_0} K\tau R_w) = (dE^\ast_{m/\tau_0} K\tau R) / d(T)$$ \hspace{1cm} (19)

The parameters $[S^\ast_{m}]$ and $[E^\ast_{m}]$ are “virial coefficients” for the entropy and enthalpy of activation. In our previous work, we denoted $[S^\ast_{m}]$ by $\tau_{am}$, where the sign convention is notably opposite that of the current definition.

A dependence of $\theta$ on concentration consistent with eq 17 has been observed for numerous condensed phase systems, and some representative examples are indicated in Figure 5 to give some appreciation of the generality of the effect (see also Section IV.B). These examples include solvent reorientational relaxation in polymer solutions, dielectric relaxation in a sugar–alcohol mixture, and the rate of a classical chemical reaction in a solvent mixture. The figure panels are described as follows: (a) Schematic dependence of $\theta$ on concentration in mixtures exhibiting a plasticization–antiplasticization transition as a function of temperature. The figure illustrates the common physical situation, where antiplasticization occurs upon cooling and where the slope in this type of plot progressively decreases as the temperature is decreased. (b) Mean solvent reorientation time $\tau_r$ for Aroclor 1248 (polychlorinated biphenyl mixture with 48% chlorine) in polymer solutions normalized by its value in a neat solvent $\tau_0$, versus polymer concentration in grams per mole × 100. Four different polymers are shown at two temperatures: poly(styrene, poly(isopropylene, poly(1,2-butadiene), and poly(1,4-butadiene)). (c) Dielectric relaxation time data for trehalose diluted by glycerol at five different temperatures. The data indicate the ratio of relaxation time of a secondary dielectric relaxation process of a trehalose–glycerol mixture relative to its value for pure trehalose. (d) The dependence of the rate constant of the Diels–Alder reaction of methyl vinyl ketone with cyclopentadiene in aqueous solutions on the addition of organic cosolvents. This figure shows the Diels–Alder rate constant of the mixture $k_m$ with the organic cosolvent relative to the pure aqueous solution $k_0$ (see also refs 47 and 48).

It is evident that the signs of $[E^\ast_{m}]$ and $[S^\ast_{m}]$ in eq 18 determine whether antiplasticization ($\theta > 1$) or plasticization ($\theta < 1$) is observed and whether a transition between these behaviors should occur as the temperature is varied from high to low $T$. In particular, if $[E^\ast_{m}]$ and $[S^\ast_{m}]$ have opposite signs, then no transition from plasticization to antiplasticization occurs, while, if the quantities have the same signs, then there is a compensation temperature $T_{anti}$ defined by $A = 0$ and $\theta = 1$ in eqs 17 and 18. This allows us to estimate the “antiplasticization temperature” $T_{anti}$ explicitly as

$$T_{anti} = (dE^\ast_{m/\tau_0} K\tau R_w) / (dS^\ast_{m/\tau_0} K\tau R)$$ \hspace{1cm} (20)

As noted in our previous work, the transition from antiplasticization to plasticization can occur under two distinct conditions corresponding to where ([E^\ast_{m}], [S^\ast_{m}]) obey the sign relations (+, +) or (−, −). Physically, these mathematical conditions correspond to whether antiplasticization is observed at low temperatures (as usually the case) or whether it is observed at high temperatures. These qualitatively different patterns in the change of the rate of relaxation (or reaction kinetics) with diluent are readily recognized graphically, and the change in the rate of molecular relaxation rates with dilution can be classified into 10 different classes of behavior, of which the four relevant cases are schematically illustrated in Figure 6. Equations 16 and 17 imply that the Arrhenius curves for log($\tau$) versus 1/$T$ should rotate counter-clockwise about a fixed point (the antiplasticization temperature, $T_{anti}$) when the plasticization-to-antiplasticization transition occurs upon cooling (case I in Figure 6). In the opposite case, the predicted plasticization effect should occur upon cooling, and this rotation should occur in the clockwise direction (case II; see data presented in the following sections). In the next two cases, although the lines rotate, $T_{anti}$ formally occurs for a negative temperature (cases III (counter-clockwise) and IV (clockwise rotation); not presented in the figure for simplicity) so that compensation does not occur for a finite $T$. There are also cases where no antiplasticization–plasticization compensation effect exists. When $[S^\ast_{m}]$ (or the entropy of activation) changes while $[E^\ast_{m}]$ remains constant, the Arrhenius curves for $\tau$ become translated either down or up, corresponding to a uniform decrease or increase of $\tau$, respectively (cases V and VI, see ref 49). Correspondingly, when $[S^\ast_{m}]$ is constant and $[E^\ast_{m}]$ changes, only the slope of the curves changes, and no transition occurs (cases VII and VIII). Finally, there are cases where both $[S^\ast_{m}]$ and $[E^\ast_{m}]$ change and are proportional, but where these quantities have the opposite sign so that there is no condition where compensation can occur (cases IX and X). This situation has been termed “anti-compensation.”

B. Plasticization–Antiplasticization Transition and Entropy–Enthalpy Compensation. Since our previous work on trehalose–glycerol mixtures, we have realized that our observation of a plasticization–antiplasticization transition with temperature is actually a special case of a more general phenomenon termed “entropy–enthalpy compensation.” The compensation condition $\theta = 1$ indeed means that the enthalpy and entropies of activation change by dilution compensate each other. Our analysis indicates that, while this phenomenon may be common,
it is not universal. For example, the catalytic behavior of some proteins and catalysts revolve around their acting to shift $\theta$ to uniformly larger values, corresponding to case V of Figure 6.

We examine this entropy–enthalpy compensation phenomenon in some detail for our diluted PC measurements in Figure 7. The insets show the Aroclor concentration dependence of the apparent activation energy $E^+$ and log($\tau_\infty$). The figures reveal that the concentration dependence of $E^+$ and $S^+$ is linear at least in the investigated range of concentrations. In Figure 7, we also observe that log($\tau_\infty$) $\propto$ $S^+$ varies in near proportionality to $E^+$. This is a classic entropy–enthalpy compensation plot, and Table 1 enumerates some other particular systems where this effect has been observed. We see that this ("repeatedly discovered") phenomenon is found rather frequently in both the chemical reaction kinetics and the relaxation dynamics of condensed phases (both liquids and solids), and this phenomenon even arises in heterogeneous gas phase catalysis. Liu and Guo provide an extensive review of entropy–enthalpy compensation, including many further examples and discussion of the issues these observations raise. Entropy–enthalpy compensation is evidently at the heart of the plasticization–antiplasticization transition.

Figure 5. (a) Concentration dependence of $\theta = \tau_{\text{mixture}}/\tau_{\text{pure}}$ under various temperature conditions. Schematic concentration dependence of $\theta$ in a system exhibiting antiplasticization. There are two classes of antiplasticizers, corresponding respectively to an increase or decrease of the slope indicated with cooling (see text for explanation). (b) Solvent rotational relaxation time for Aroclor 1248 as a function of polymer concentration at various constant temperatures (figure reprinted with permission from ref 44). (c) Dielectric relaxation time of trehalose diluted by glycerol at various temperatures; concentrations given in glycerol weight fraction. (d) Kinetics of reactions in aqueous solutions of organic fluids (figure reprinted with permission from ref 45).

Figure 6. Schematic indication of different classes of plasticization–antiplasticization. Thick solid lines represent pure systems, and the other lines indicate curves obtained progressively increasing the concentration of the additive (lowest concentration = solid line; intermediate concentration = dashed line; highest concentration = dotted line). See text for further description.
Quantifying Changes in High-Frequency Dynamics

Figure 7. Prefactor from Arrhenius function versus activation energy for different PC–Aroclor mixtures. The insets present log(τ) and $E_m$ for mixtures with corresponding Aroclor concentrations.

Although a full molecular understanding of entropy–enthalpy compensation can be expected to involve subtle many-body effects, Dyre52 and Vainas53,54 have provided valuable qualitative insights into this difficult problem. For example, Dyre notes that, if the relaxation process involves an exponential distribution of barrier heights, reflecting the local structural heterogeneity of the disordered material, then atomic displacements becomes correspondingly intermittent. He then notes that this situation leads to a relaxation process in which the entropy and enthalpy of activation of structural relaxation exhibit compensating changes and to a corresponding power law relaxation associated with the intermittent molecular displacements. Our observation of HN relaxation and entropy–enthalpy compensation in our β dielectric relaxation measurements are both qualitatively consistent with Dyre’s heuristic arguments. Vainas has also provided some insight into this ubiquitous phenomenon by exactly solving a model of relaxation on a hierarchical lattice (Cayley tree) in which the activation entropy is precisely tunable in terms of lattice geometry. Vainas’ model exactly leads to entropy compensation with the VF temperature, where local relaxation “freezes”. This suggests an interesting possible direct connection between the entropy–enthalpy compensation phenomenon and the physics of glass-formation for the high-frequency dynamics studied in the present work.

We emphasize that our recognition that the antiplasticization–plasticization transition in our dielectric relaxation measurements corresponds to enthalpy–entropy compensation within transition state theory does not really explain this phenomenon. Enthalpy–entropy compensation has been characterized as one of the most general, but least theoretically understood phenomenon of the physical chemistry of liquids.51 While it certainly makes sense heuristically that a stronger enthalpic interaction in the transition state can reasonably be expected to lead to a reduced magnitude of the activation entropy because of the more constrained motions in the transition state,55,56 it is difficult to translate this qualitative reasoning into any kind of precise theoretical predictions for $T_{anti}$.

V. Evidence for Plasticization–Antiplasticization Transition from Neutron Scattering and Mechanical Measurements

Antiplasticization by a diluent is also characterized by material stiffening, despite the contrary general trend of a reduction of $T_\alpha$ with the addition of molecular additives. It should then be possible to observe this phenomenon in high-frequency dynamics measurements such as neutron or X-ray scattering through measurements of the Debye–Waller factor or through direct mechanical properties measurements such as the storage modulus of the diluted polymeric material ($G'$). Notably, the rheological measurements normally involve a much lower frequency regime than the neutron and secondary relaxation dielectric measurements that include the α-relaxation processes associated with cooperative segmental motions, as well as much slower relaxation processes associated with large-scale chain motions so that comparisons to high-frequency dielectric measurements must be performed appropriately. Despite these different frequency ranges, a tendency toward stiffening with dilution can be expected in conjunction with antiplasticization in these measurements. We are concerned in this section with confirming that these changes are at least qualitatively consistent with the dielectric measurements, given the greatly different frequency ranges explored in these “high-frequency” measurements.

A. Neutron Scattering. In Figure 8, we illustrate the $T$ dependence of the average mean squared hydrogen atom displacement $\langle u^2 \rangle$ in our PC material diluted by Aroclor. For our samples below $T_g$, but above the dielectric antiplasticization temperature $T_{anti} \approx 260$ K, we observe that the average slope describing the $T$ dependence of $\langle u^2 \rangle$ becomes reduced with increasing Aroclor concentration. Within a simple harmonic localization model, this slope can be described as being inversely proportional to a molecular “force constant” $\kappa$.

$$\langle u^2 \rangle = \frac{\langle k_B T \rangle}{\kappa}$$ (21)

and we plot $\kappa$ based on this simple approximation (made in the temperature range of 200–350 K) in the figure inset. We thus infer a progressive local stiffening of the polymeric material in the temperature range $T > T_{anti}$, despite the fact that the addition of Aroclor causes an appreciable drop in $T_g$. This trend is consistent with antiplasticization behavior and with the high-frequency dielectric relaxation time data shown in Figure 4. However, the neutron data does not reveal an overt transition to plasticization in the low temperature glass state, an effect clearly indicated by the dielectric data in Figure 1. (At very low temperatures, the neutron scattering data is noisy, and it is frankly difficult to resolve any clear trend.) We also note that the side-group (methyl group, in particular) rotations give a large contribution to $\langle u^2 \rangle$ so that simplistic interpretation of $\langle u^2 \rangle$ as a measure of local material “stiffness” must be made with due caution; neutron measurements by themselves provide an inconclusive measure of plasticization or antiplasticization. References 60–62 discuss issues that arise from methyl rotation effects that arise in relation to interpreting dynamic neutron scattering measurements.

B. Mechanical Measurements. An antiplasticization–plasticization effect of PC with the addition of Aroclor is an established effect in mechanical measurements, giving greater confidence in the qualitative validity of the antiplasticization effect suggested by the dynamic neutron measurements. Since there have been many previous studies of this phenomenon in this classical model system, we only briefly illustrate this effect here. In Figure 9, we show the storage modulus at a fixed
frequency ($f = 1 \text{ Hz}$) as a function of temperature for our pure and diluted PC samples. The figure shows that the addition of Aroclor to PC leads to a softening (plasticization) of the material well below the antiplasticization temperature $T_{\text{anti}}$, which was determined from the dielectric measurements (vertical dotted line), and a stiffening (antiplasticization) of the material at higher temperatures than $T_{\text{anti}}$. This trend reverses again for temperature well above $T_g$, where plasticization is again observed, reflecting the downward shift of $T_g$ with Aroclor addition. Although the inversion temperature between plasticization and antiplasticization in the mechanical measurements is not very sharply defined, the qualitative trend observed in these measurements is quite consistent with changes in the dynamics indicated by the dielectric and neutron scattering measurements. We note that the relatively low and fixed frequency of these mechanical measurements makes the apparent antiplasticization temperature occur at an appreciably lower temperature ($\approx 40 \text{ K}$ lower) than the antiplasticization temperature estimated in the $\beta$ dielectric relaxation measurements (see Figure 4). Nonetheless, an overall stiffening of the mixture in the glassy state well below $T_g$ can be observed as a result of the antiplasticization of the high-frequency relaxation dynamics of the polymer material through the addition of Aroclor, while at higher temperatures, plasticization is found. Similar observations have been made before for PC diluted by different Aroclors having a range of molecular masses ($5460, 1254, 1232$), where the molecular mass is found to influence quantitative aspects of the antiplasticization effect, such as the particular value of $T_{\text{anti}}$.

VI. Conclusions

We further develop a theoretical framework for characterizing how the high frequency of fluids becomes modified upon the addition of fluid and nanoparticle additives. The framework indicates that there are eight distinct patterns of behavior that should occur. Two of these patterns involve the cases where antiplasticization (slowing down of the system dynamics) or plasticization (speeding up of these dynamics) always occurs regardless of the temperature. The other two cases correspond to the cases where a transition from plasticization to antiplasticization occurs upon varying $T$. While the case of a transition from plasticization to antiplasticization upon cooling appears to be the more common situation experimentally in diluted polymer melts, we observe the opposite case in our measurements on PC diluted by Aroclor. We also find that the fragility of glass-formation progressively increases with the addition of Aroclor, a trend opposite to our previous experience with mixtures of trehalose diluted by glycerol. Apart from the main applications of antiplasticization to materials processing enhanced abrasion resistance of films in photographic and laser printer films and food and drug preservation, our approach to quantifying the changes in the high frequency of diluted fluids should provide a powerful metric for understanding and controlling property changes related to dynamics and reaction processes in a wide range of mixtures, including the important case of aqueous solutions where alcohols, polymers, and salts additives can have an appreciable effect on the dynamics without any clear thermodynamic explanation. The combination of our theoretical framework with dielectric spectroscopy or other methods that allow for probing the high frequency in a routine

![Figure 8](image-url) Figure 8. Quasi-elastic neutron scattering data as a function of temperature; pure PC (a), mixtures with Aroclor mass fraction, $x_w$: 0.05 (b), 0.1 (c), 0.15 (d), and 0.2 (e), and pure Aroclor (f). Inset presents the effective force constant $k$ as a function of Aroclor concentration; the values are obtained from fitting for $T = 200$–$350 \text{ K}$.  

![Figure 9](image-url) Figure 9. Storage modulus from DMA measurements: pure PC (a), mixtures with Aroclor mass fraction, $x_w$: 0.05 (b), 0.1 (c), 0.15 (d), and 0.2 (e).
Quantifying Changes in High-Frequency Dynamics

Complex fluids, such as polymer melts, are often characterized by high-frequency molecular relaxation processes that can be identified by a variety of experimental methods. Future work should consider the extent to which the changes in the high frequency dynamics depend on the relaxation process examined. It is evidently important that the changes in the high frequency dynamics determined by our method correspond to property changes of interest in the diluent modified material (e.g., gas permeability, and stiffness) so that the high-frequency measurements inform about these property measurements, as well as other high-frequency domain measurements. This question requires further consideration.

In future work, we also plan to investigate whether the inverted trends in fragility changes with additive, seen in adding glycerol to trehalose and Acorol to PC, are related to the corresponding inversion in the antiplastization—plasticization transitions with temperature. Simulation has recently indicated, in accord with the entropy theory of glass-formation developed by Dudowicz et al. that reducing packing frustration tends to reduce the fragility of glass-formation, so that the increase of fragility upon the addition of an additive can naturally be understood by an increase of the fragility of glass-formation. The addition of fullerenes to poly styrene polymer matrix has indicated an appreciable increase in the Debye—Waller factor in the low temperature glass state, pointing to an increased fragility of the nanocomposite, an effect that we expect is quite common. In the near future, we plan to check the attractive possibility that additives that enhance or disrupt the molecular packing of the pure fluid correspondingly lead to antiplastization and plasticization, respectively, in the glass state well below $T_g$. If this proves to be true, then it would provide a valuable design tool for the properties of diverse mixtures.

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