Dynamical heterogeneity in binary mixtures of low-molecular-weight glass formers

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Homogeneous diethyl phthalate/phenylphthalain-dimethylether (DEP/PDE) mixtures have been investigated by means of broadband dielectric spectroscopy. Contrarily to the widespread view that homogenous binary mixtures should give rise to a single glass transition, the mixture displays two dynamics giving rise to two glass transitions. Such a finding can be rationalized invoking the self-concentration concept that relies on the localized nature of the glass transition phenomenon. In such a way, the analogy with miscible polymer blends, for which this concept has been introduced, is highlighted. A model based on the combination of the Adam-Gibbs (AG) theory of the glass transition and the self-concentration concept resulted to be fully predictive once the only unknown variable, namely, the glass-former specific parameter (α) connecting the characteristic length for the glass transition to the configurational entropy, is extracted applying the model itself to DEP/toluene and DEP/PDE solutions highly concentrated, respectively, in DEP and PDE. The α parameter obtained in such a way allows the precise determination of the most probable relaxation time even for those DEP/PDE mixtures displaying a strong overlap of the dielectric response. The model incorporating the self-concentration concept to the AG theory also provides the characteristic length scale for the glass transition for both DEP and PDE.

Such a length scale was found to be on the order of 1–1 nm. This is comparable to that obtained for other glass formers.

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I. INTRODUCTION

Mixtures of liquids with negligible interactions are known to display properties intermediate between those of the pure liquids. This is particularly true for thermodynamic properties, such as volume or enthalpy, and can be promptly tested performing standard density or calorimetric measurements. Apart from these properties, a common belief is also that mixtures of glass-forming liquids display a single glass transition temperature \(T_g\) intermediate between those of the pure glass formers. However, such a belief has already been disproved for (quasi)athermal miscible polymer blends [1–10]. These glass-forming systems display two \(T_g\)’s arising from the presence of two well distinguishable segmental relaxation processes. Also numerous cases displaying the presence of two primary relaxations have been reported for mixtures of low-molecular-weight glass formers [11–13]. For miscible polymer blends this striking result, long debated within the scientific community [14–16], is now widely recognized to be due to self-concentration effects, arising from the localized nature of the glass transition phenomenon. In particular, when a volume is centered on the basic structural unit of one of the polymers of a given blend, the effective concentration \(c_{\text{eff}}\) will be in general larger than the macroscopic one. This generates a relaxation that is closer to that of the pure component than would be expected from a pure mixing rule of the dynamics of the pure components of the blends.

An essential ingredient that has been invoked to explain self-concentration effects is the presence of chain connectivity in polymer blends [16]. Certainly, chain connectivity enhances these effects as it imposes that at least two neighbors of the structural unit under examination are made of the same polymer even in highly diluted blends [17]. Some authors have, therefore, asserted that self-concentration can be an issue of importance only for polymer blends and only marginally for mixtures of low-molecular-weight glass formers [18,19]. At the same time, it is also well established that in miscible polymer blends the typical length scale for segmental relaxation arising from self-concentration arguments is of the order of the Kuhn segment [16], i.e., about the typical intermolecular distance. Such a limited length suggests that, though to a less extent, self-concentration can be of significant importance also for mixtures of low-molecular-weight glass formers. This conjecture has been demonstrated to be highly consistent with recent experiments on the dynamics of diluted low-molecular-weight polychlorinated biphenyl (PCB54) in 1,4 polybutadiene (PB) [20]. The results in this work clearly indicate that PCB54 dynamics decouples from that of PB. This can be interpreted according to self-concentration arguments, being, according to this interpretation, the effective concentration in the volume relevant for PCB54 dynamics larger than the macroscopic one, i.e., larger than zero being PCB54 highly diluted in PB. The role of self-concentration was later confirmed investigating the dynamics of PCB54/toluene mixtures, namely, a system composed of two components displaying very different mobilities [21]. These mixtures actually display two well-separated dynamics as expected from self-concentration arguments.

In this work, we present relaxation data measured by means of broadband dielectric spectroscopy (BDS) for diethyl phthalate/phenylphthalain-dimethylether (DEP/PDE) mixtures, a system mainly interacting via van der Waals forces and displaying strong dynamic contrast, the \(T_g\) of the components being very different \((T_g^{\text{DEP}}=183\,\text{K} \text{ and } T_g^{\text{PDE}}=290\,\text{K})\). Similarly to PCB54/toluene mixtures, also these mixtures display two main relaxational processes with
strongly super-Arrhenius temperature dependence. These two processes have been attributed, respectively, to the α relaxation, namely, that associated to the glass transition, of DEP and PDE. In this case the two relaxational processes are much less separated than in the case of PCB54/toluene mixtures [20] as a consequence of the smaller dynamical contrast. This allows avoiding those typical nonequilibrium effects observed in mixtures of both polymeric and nonpolymeric glass formers [21,22]. Finally, the dynamics of both components of the mixtures are described through a model presented by us for polymer blends [23,24] and recently extended to mixtures of low-molecular-weight glass formers [20,21] combining the Adam-Gibbs theory of the glass transition with the self-concentration concept. The model relies on the fitting of only one parameter \( \alpha \), namely, that connecting the characteristic length of the structural relaxation to the configurational entropy. As the dynamics of the two components of the mixture are somewhat overlapped, the precise identification of the most probable relaxation time and, consequently, the fitting of the data with the model are in some cases not straightforward. This is particularly true for the dielectric response of DEP/PDE mixtures with relatively high DEP content. Therefore, the glass-former specific parameter \( \alpha \) was determined applying the model to mixtures where the dielectric response is dominated by the component for which this parameter is required. Since PDE possesses a dielectric strength significantly larger than that of DEP, PDE’s \( \alpha \) parameter can be easily obtained fitting the model to dielectric relaxation data of PDE/DEP solutions with high PDE content. On the other hand, DEP’s \( \alpha \) parameter was determined applying the model to DEP/toluene solutions highly concentrated in DEP. Once \( \alpha \) is obtained for both DEP and PDE, the prediction of the component dynamics in DEP/PDE mixtures can be straightforwardly performed. Such a procedure was analogous to that recently employed to predict the component dynamics of polyisoprene/polyvinylethylene (PI/PVE) blends [8]. Furthermore, the knowledge of the \( \alpha \) parameter of the two components of the mixtures allows the prediction of the most probable relaxation time related to DEP even for those mixtures highly concentrated in PDE, where DEP contribution to the dielectric response is masked by the significantly more prominent signal related to PDE.

II. EXPERIMENTAL

Diethyl phthalate (DEP) and phenylphthalein dimethyl ether (PDE) were purchased, respectively, from Aldrich and Polymer Source, Inc. Both samples were used as received. Homogeneous DEP/PDE solutions were prepared mixing thoroughly the two species. DEP and PDE were found to be miscible at all concentrations. Homogeneous DEP/toluene mixtures were also prepared in a similar manner. The solutions were subsequently poured on the bottom electrode of a liquid sample cell. Teflon spacers were added to avoid short circuit of the so-obtained dielectric capacitor. Solutions containing the following DEP/PDE weights ratio were investigated: 90/10, 80/20, 70/30, 20/80, and 10/90 wt/wt %. DEP/toluene solutions with the following weights ratios were investigated: 90/10, 80/20, and 70/30 wt/wt %.

Dielectric measurements were carried out on all aforementioned mixtures and on pure DEP and PDE using a high precision dielectric analyzer (ALPHA, Novocontrol GmbH) over a wide frequency range \( (3 \times 10^2 - 10^6 \text{ Hz}) \). A Novocontrol Quatro cryosystem for temperature control with a precision of \( \pm 0.1 \text{ K} \) was employed in all measurements. Measurements were performed in a wide temperature range in isothermal steps from the lowest temperature. Our dielectric measurements on pure DEP and PDE were compared with those already reported in the literature [25–27]. General agreement between the former and latter measurements was found for both glass formers.

Calorimetric measurements were carried out by means of the differential scanning calorimeter (DSC-Q2000) from TA-Instruments. These were performed on pure PDE and DEP in temperature modulated mode with an average heating rate of 0.15 K/min and amplitude of 0.5 K. Different oscillation frequencies were investigated and the so-obtained specific heats were extrapolated to zero frequency in order to obtain quasistatic values of the specific heat itself. Standard calorimetric measurements were also performed on all DEP/PDE mixtures with a heating rate of 10 K/min.

III. RESULTS

Figure 1 displays standard calorimetric measurements for all investigated mixtures and for pure DEP and PDE. Clearly the specific-heat jump marking the glass transition lays in between that of the pure components for all DEP/PDE mixtures. The most prominent feature of DSC plots is the presence of a single specific-heat jump. The average \( T_g \) of all systems, determined as the temperature corresponding to half of the heat capacity change, is presented in the inset of Fig. 1 as a function of DEP concentration. The error bars correspond to the \( T_g \) range. Interestingly, a broader \( T_g \) range is displayed by DEP/PDE mixtures in comparison to the pure components.

The dielectric response of all DEP/PDE mixtures and that of pure DEP and PDE is displayed in Fig. 2, where the loss part of the dielectric permittivity is reported as a function of the frequency at 223 K for pure DEP and DEP/PDE mixtures.
with 70, 80, and 90 wt % DEP (upper panel) and at 303 K for pure PDE and DEP/PDE mixtures with 10 and 20 wt % DEP (lower panel). The following observations can be done from the analysis of the figure: (i) DEP/PDE mixtures with relatively high DEP content (upper panel) exhibit two prominent relaxational processes, whereas both DEP and PDE present only one, apart from the much weaker secondary relaxation process; (ii) mixtures with relatively high PDE content (lower panel) present only one relaxational process with dielectric strength increasing with increasing PDE content; (iii) the relaxational process showing up at relatively high frequency increases its strength with DEP concentration, whereas the relatively slow relaxational process gets stronger when DEP concentration is lowered.

Figure 3 displays the dielectric response of DEP/toluene mixtures and that of pure DEP as a function of the frequency at 188 K for DEP/toluene mixtures with the following wt/wt %: 100/0 (circles), 90/10 (triangles), 80/20 (squares), and 70/30 (diamonds). The inset shows the dependence on DEP wt % of the dielectric strength of the process related to DEP (circles) and PDE (triangles).

In order to extract the most probable relaxation time related to each process and, therefore, get more insight about the associated molecular motion, the spectra were fitted through a sum of Havriliak-Negami (HN) functions plus a direct current (dc) conductivity contribution. This for the relative complex dielectric permittivity ($\varepsilon^*$) in the frequency domain ($\omega$) reads [28]

$$
\varepsilon^*(\omega) = -\frac{i\sigma_{dc}}{\varepsilon_0\omega} + \varepsilon_\infty + \sum_{k=1}^{n} \frac{\Delta\varepsilon_k}{1 + (i\omega\tau_{HN,k})^{\alpha_{HN,k}}} \tau_{HN,k},
$$

where $\tau_{HN}$ is the HN relaxation time, $\varepsilon_\infty$ is the high frequency limit value of the dielectric constant, $\Delta\varepsilon$ is the dielectric strength of the relaxation process, $\alpha_{HN}$ and $\gamma_{HN}$ are the shape parameters of the HN function describing, respectively, the symmetric and asymmetric broadening of the complex dielectric permittivity, $\sigma_{dc}$ is the dc conductivity, and $\varepsilon_0$ is the vacuum permittivity.

The fits through Eq. (1) to experimental data are satisfactory with one HN function for pure PDE, DEP, and DEP/PDE mixtures with 10 and 20 wt % DEP, and two HN functions for DEP/PDE mixtures with 70, 80, and 90 wt % DEP. The inset of Fig. 2 displays the dielectric strength of both peaks showing up for DEP/PDE mixtures as well as the dielectric strength of the main relaxational process related to pure PDE and PDE dynamics as a function of DEP concentration. As seen in the inset, the dielectric strength of the two processes varies between zero and the dielectric strength of pure PDE and PDE, respectively, and depends linearly on DEP concentration. This result provides strong indication that the relatively slow process should be assigned to PDE relaxation in the mixture, whereas the one showing up at relatively high frequency to DEP relaxation in the mixture. In addition, these two processes display super-Arrhenius temperature dependence as shown in Fig. 4 where the decimal logarithm of the relaxation time corresponding to each relative maximum of the dielectric permittivity is displayed as a function of the inverse temperature. This means that the two processes detectable in DEP/PDE mixtures should be attributed to the $\alpha$ relaxation of each component in the mixture. This remarkable result is reminiscent of that found for toluene and its intrinsically lower dielectric strength compared to DEP.
The electric spectrum of DEP/PDE mixture is analogous to that one for each component of the blend. In particular, the distribution. In the upper inset the miscible polymer blends that also display two relaxations, one for each component of the blend. In particular, the dielectric spectrum of DEP/PDE mixture is analogous to that found for PI/PVE blend.

Figure 5 displays the temperature dependence of the decimal logarithm of the structural relaxation time of all DEP/toluene mixtures together with that of pure DEP and toluene. As already discussed when presenting dielectric spectra of DEP/toluene mixtures, the presence of toluene provokes the acceleration of the dynamics of DEP in comparison to that of pure DEP.

### IV. APPLICATION OF THE AG-SC MODEL

Inspired by the analogy between the dynamics of DEP/PDE mixtures and those of miscible polymer blends, we have combined self-concentration concept [16], already widely exploited to describe the component dynamics of miscible polymer blends, with the Adam-Gibbs (AG) theory to the glass transition [29]. Details about the application of the self-concentration concept within the AG theory (AG-SC model) can be found in Refs. [8,20,21,23,24]. The application of the AG-SC model to the dynamics of binary mixtures relies on the evaluation of the configurational entropy and of the parameter $C$ of the AG equation as a function of the effective concentration to calculate the component relaxation time as [8,20,21,23,24,29]

$$
\tau = \tau_0 \exp \frac{C(\phi_{eff} - \phi_s)}{TS_{ex}(\phi_{eff})}.
$$

Here the configurational entropy, experimentally inaccessible until very recently [30], has been replaced by $S_{ex}$, i.e., the entropy of the supercooled liquid in excess to that of the corresponding crystal. Such an assumption relies on the approximate proportionality between excess and configurational entropy. The soundness of this proportionality has been recently proved by several approaches [31–34]. $C$ and $S_{ex}$ are calculated as a linear combination of the same properties of the pure components through the effective concentration in the volume relevant for dynamics. The assumption of ideal mixing between DEP and PDE is justified considering that mixtures of van der Waals liquids generally display deviations from ideality smaller than a few point percentage of the total thermodynamic property [35]. The effective concentration, i.e., the concentration experienced by the relevant volume for segmental relaxation, is related to the self-concentration by [16] $\phi_{eff} = \phi_s + (1 - \phi_s)\phi$, where $\phi_{eff}$, $\phi_s$, and $\phi$ are, respectively, the effective, the self, and the macroscopic concentrations.

Apart from the relation between the relaxation time and the configurational entropy, the AG theory provides a connection between the number of basic structural units belonging to the cooperatively rearranging region (CRR) and the configurational (excess) entropy, $N = S_{ex}^{-1}$. Since the number of particles is proportional to the volume of the CRR, the characteristic length scale ($\xi$) can be related to the configurational entropy by

$$
\xi/2 = r_c = \alpha S_{ex}^{-1/3},
$$

where $r_c$ is the radius of the relevant volume for structural relaxation and $\alpha$ is a glass-former specific parameter assumed to be temperature independent. $\alpha$ can be evaluated through the fitting of experimental data exploiting the correlation between $r_c$ (or $\xi$) and $\phi_s$. This can be obtained through
simple geometric considerations involving the van der Waals radius [20,21].

In order to apply the aforementioned model, both the dynamic and thermodynamic parameters of the pure components of the mixture have to be determined. In particular, the excess entropy of the pure components has to be calculated through \( \Delta S_x(T) = \int_{T_m}^{T} \left( \frac{\Delta c_p(T)}{T} \right) dT \), where \( \Delta c_p(T) \) is the excess specific heat, \( \Delta c_p(T) = c_{p,melt}^{\text{crystal}} - c_{p,melt}^{\text{glass}} \), and was obtained through precise calorimetric measurements as described in the experimental section. In our approach, a linear form of the excess specific heat was employed: \( \Delta c_p(T) = a + bT \), where \( a \) and \( b \) are constants. Structural dynamics data for the glass formers relevant to our investigation, namely, pure DEP, PDE, and toluene were fitted through the AG equation to obtain the pre-exponential factor, the parameter \( C \), and the temperature where the relaxation time tends to diverge, identified with \( T_K \), i.e., the temperature where \( S_x \) related to the segmental relaxation extrapolates to zero. All parameters \( (a, b, \tau_0, C, T_K) \) for DEP, PDE, and toluene are listed in Table I. In this table, we also list the values of the van der Waals volume of DEP, PDE, and toluene evaluated employing the approach of Ref. [36].

As discussed in Sec. I, the AG-SC model can be first applied to DEP/toluene and DEP/PDE mixtures with high concentration of, respectively, DEP and PDE. This allows determining the material specific parameter \( \alpha \) of Eq. (3) for both DEP and PDE. In this case, due to the large concentration of the glass former for which \( \alpha \) is determined, the effect on the \( \alpha \) parameter arising from the presence of the other component of the mixture is minimized. Furthermore, the dielectric spectrum is dominated by the response of DEP, for DEP/toluene solutions with 70, 80, and 90 wt % DEP, and that of PDE, for DEP/PDE solutions with 80 and 90 wt % PDE. The solid lines in Fig. 4 (lower panel; those corresponding to crosses and hexagons) and Fig. 5 are the fits of the model to experimental data corresponding to the aforementioned mixtures. A single value of \( \alpha \) was found for DEP \( (\alpha_{\text{DEP}} = 31 \text{ J}^1/3 \text{ mol}_\text{DEP}^{-1/3} \text{ K}^{-1/3}) \), whereas the \( \alpha \) parameter of PDE was found to depend slightly on the concentration of PDE/PDE mixture, being equal to \( \alpha_{\text{PDE}} = 22 \pm 1 \text{ J}^1/3 \text{ mol}_\text{PDE}^{-1/3} \text{ K}^{-1/3} \) for the mixture with 80 wt % PDE and \( \alpha_{\text{PDE}} = 21 \pm 1 \text{ J}^1/3 \text{ mol}_\text{PDE}^{-1/3} \text{ K}^{-1/3} \) for the one with 90 wt % PDE. Extrapolation to pure PDE provides the intrinsic \( \alpha \) parameter of this glass former: \( \alpha_{\text{PDE}} = 20 \pm 1 \text{ J}^1/3 \text{ mol}_\text{PDE}^{-1/3} \text{ K}^{-1/3} \). All these values of \( \alpha \) are of the same order of magnitude as those obtained for other low-molecular-weight glass formers [20,21].

The knowledge of the \( \alpha \) parameter of both DEP and PDE allows the prediction of the component dynamics of the DEP/PDE mixtures with 70, 80, and 90 wt % DEP. These mixtures display a marked overlap of the dielectric response related to the two components and, in the case of DEP/PDE mixture with 70 wt % DEP, the dielectric contribution related to DEP is obtained with a relatively high degree of uncertainty (see Figs. 2 and 4). The employment of a mixing rule for the \( \alpha \) parameter of the pure components through the effective concentration to determine the \( \alpha \) parameter provides a quantitatively accurate description of the dynamics of both components in all mixtures. The employment of a mixing rule provides the \( \alpha \) parameter at any effective concentration as illustrated in the insets of Fig. 4, where the value of the average \( \alpha \) parameter as a function of the average effective concentration is displayed for both DEP and PDE [37]. In Fig. 4 the fits of the model to experimental data are shown by the solid lines. As can be observed, the model is able to accurately predict experimental relaxation times related to the dynamics of both PDE and DEP in the mixture. Furthermore, the prediction of DEP dynamics in DEP/PDE 70/30 wt/ wt %, where the dielectric contribution to the overall spectrum related to DEP dynamics is relatively weak and highly overlapped to that related to PDE, allows the precise determination of the most probable relaxation time, which would be otherwise ill defined (see error bars in Fig. 4). Finally, it is worth noticing that the employment of the macroscopic concentration would be unable to properly describe experimental data. This is due to the following two reasons: (i) introducing the macroscopic concentration in Eq. (2) would provide only one relaxation time at odds with the experimental evidence that two relaxational processes are present; (ii) the relaxation time provided by this procedure lays between the slow and the fast process and, therefore, does not correspond to any relaxational processes displayed by DEP/PDE mixtures (see arrows in the upper panel of Fig. 2).

Another important implication of the predictive power of the AG-SC model—one of the material specific \( \alpha \) parameters is known for the glass formers of the mixture under investigation—is the possibility of identifying the most probable relaxation time for the dynamics related to a component whose dielectric contribution to the overall response is either intrinsically weak or hidden by other relatively stronger contribution. The latter occurrence is actually taking place for DEP/PDE mixtures with 10 and 20 wt % DEP, where DEP’s contribution to the overall dielectric spectrum is not visible due to the much larger response related to PDE dynamics (see Fig. 2 lower panel). The predicted most probable relaxation for DEP’s component dynamics is indicated by the arrows in Fig. 2 and by the straight lines in the Arrhenius plot displayed in the upper panel of Fig. 4.
The knowledge of $\alpha$ allows the determination of the characteristic length scale for structural dynamics via Eq. (3) for both pure PDE and DEP in the mixture and the pure glass formers. The latter is plotted as a function of temperature in Fig. 6 for both DEP and PDE in all mixtures and equals about 12–20 Å (for the mixtures similar results are found) in agreement with that found for a large number of glass formers, both polymeric [8,10,16,19,17,23,24] and nonpolymeric [20,21]. From inspection of Fig. 5, one can conclude that DEP cooperative relaxation requires larger volumes in comparison to PDE. Such a conclusion is straightforwardly achieved also inspecting the typical length scale of pure PDE dynamics, which is somewhat larger than that of pure PDE dynamics: 16–20 Å for pure DEP vs 12–15 Å for pure PDE.

V. DISCUSSION

In the preceding section of the paper, we have shown that homogenous DEP/PDE mixtures, mainly interacting via weak van der Waals forces, display dynamical heterogeneity manifesting with the presence of two main dynamical processes (those associated with the $\alpha$ process). Such a phenomenology is nicely caught by the self-concentration concept. This is based on the localized nature of the structural relaxation in glass-forming liquids as discussed in Sec. I. The effect of self-concentration has been first introduced to describe the dynamics of miscible polymer blends [16]. However, in this case it has been often remarked that such effects should be relevant only for polymer blends as a result of the presence of chain connectivity [18,19], which actually enhances the self-concentration. Here we demonstrate that, though to a less extent, self-concentration is also important for quasiathermal mixtures of low-molecular-weight glass formers. Thus, we highlight that the difference between the case of polymer blends, where the self-concentration is markedly enhanced by chain connectivity, and mixtures of low-molecular-weight glass formers, where the localized nature of the glass transition is the only source providing an effective concentration larger than the macroscopic one.

We also highlight the strong analogy between the dynamical response of DEP/PDE mixtures with that of PI/PVE miscible blends [4,8]. However, in the case of DEP/PDE blends due to the absence of chain connectivity, the clear separation between the two relaxational processes in the former case is achievable with a larger dynamical contrast in comparison to PI/PVE. In particular, the $T_g$ difference between DEP and PDE is 107 K, whereas in PI/PVE the same separation between the dynamics of the two components is achieved with a $T_g$ difference of 60 K between PI and PVE. Thus, the difference of almost 50 K between the dynamical contrasts of the two miscible systems quantifies the effect of chain connectivity. This effect allows the separation between the dynamics associated with the two components of the mixture even for relatively small dynamical heterogeneities as in the case of PI/PVE blend.

In comparison to the homogenous van der Waals mixture toluene/PCB54 recently investigated by us [21], it is noteworthy that DEP/PDE dynamics display non-Arrhenius temperature dependence for both components dynamics, whereas in the former case a crossover from super-Arrhenius to Arrhenius temperature dependence can be observed with decreasing temperature. This is the result of the nonequilibrium effects—driven by the freezing in of the PCB54 related dynamics—inducing restricted motion of toluene moieties, as also observed in miscible polymer blends with large dynamical asymmetry [38–41]. On the other hand, in DEP/PDE mixture the dynamics related to one component only mildly decouples from that of the other and such a crossover is not observed in complete analogy to PI/PVE blends.

An important implication of the employment of the AG-SC model is that—apart from the knowledge of the dynamics and thermodynamics of the pure components of the mixture—it requires the knowledge of glass-former specific parameter $\alpha$ connecting the characteristic length scale for the glass transition to the configurational entropy. In this work, we demonstrate that once the $\alpha$ parameter is independently obtained—e.g., applying the AG-SC model to concentrated solutions of the glass formers for which this parameter is required with another glass former with relatively different dynamics [24]—the AG-SC model turns out to be fully predictive. In other words, once the $\alpha$ parameter is known for both glass formers of the mixture under examination, one can predict the dynamics of both the components in the mixtures without possessing any experimental data on the dynamics of the mixture. Such a predicting power has been exploited in this work to predict the dynamics related to DEP at relatively low concentration of this component in DEP/PDE mixtures (10 and 20 wt %). In such mixture, DEP related dynamics is actually hidden by that related to PDE, which dominates the overall dielectric response.

Finally, we would like to comment shortly on the characteristic length scale for the glass transition obtained for DEP and PDE both in the mixture and alone. Apart from the slight differences in the absolute values of such a length scale, it is worth remarking that the obtained length scales (between 12 and 20 Å) are of the order of twice the typical intermolecular distance as obtained by conventional scattering experiments from the static structure factor [22]. This means that the cooperative relaxation postulated by the AG theory [29] typically extends to the first neighbors of the structural unit under examination. We speculate that such a conclusion may provide a link between theories based on cooperative dynamics and the mode coupling theory (MCT) [42].
VI. CONCLUSIONS

The dynamics of homogeneous DEP/PDE mixtures were investigated by means of broadband dielectric spectroscopy. The most peculiar feature of the dielectric response of the mixture is the presence of two dynamics with non-Arrhenius temperature dependence. These were attributed to the concentration that relies on the limited size of the volume involved in the $\alpha$ relaxation. The incorporation of this concept in the AG theory of the glass transition allowed a satisfactory description of the component dynamics of both DEP and PDE in the blends. As an output of the fitting of experimental data, the characteristic length scale for the glass transition was determined for the dynamics of each component of the mixture. This was found on the order of 1–2 nm in agreement with previous determination on other glass formers.

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temperature of both the effective concentration and the $\alpha$ parameter, we plot in the insets of Fig. 4 the average values of these two magnitudes.


