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On the cooperative nature of the β-process in neat and binary glasses: A dielectric and nuclear magnetic resonance spectroscopy study

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By means of dielectric as well as ^{2}H and ^{31}P nuclear magnetic resonance spectroscopy (NMR) the component dynamics of the binary glass tripropyl phosphate (TPP)/polystyrene (PS/PS-d_3) is selectively investigated for concentrations distributed over the full range. We study the secondary (β-) relaxation below T_g, which is found in all investigated samples containing TPP, but not in neat polystyrene. The dielectric spectrum of the β-process is described by an asymmetric distribution of activation energies, essentially not changing in the entire concentration regime; its most probable value is $E/k \cong 24\ T_g$. Persistence of the β-process is confirmed by ^{31}P NMR Hahn-echo and spin-lattice relaxation experiments on TPP, which identify the nature of the β-process as being highly spatially hindered as found for other (neat) glasses studied previously, or re-investigated within this work. The corresponding ^{2}H NMR experiments on PS-d_3 confirm the absence of a β-process in neat PS-d_3, but reveal a clear signature of a β-process in the mixture, i.e., polystyrene monomers perform essentially the same type of secondary relaxation as the TPP molecules. Yet, there are indications that some fractions of PS-d_3 as well as TPP molecules become immobilized in the mixture in contrast to the case of neat glasses. We conclude that in a binary glass the β-process introduced by one component induces a highly similar motion in the second component, and this may be taken as an indication of its cooperative nature. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4816374]

I. INTRODUCTION

Since the works of Johari and Goldstein (JG)[1] a second (or β-) relaxation peak is a well documented relaxation feature observed in many liquids at frequencies higher than those of the primary α–relaxation upon (super-) cooling.[2–7] In some cases, for type-A glass formers[8] (in contrast to type-B systems with a well resolved secondary process), such a β-peak is missing and only an "excess wing" appears on the high-frequency flank of the α-peak. Even two resolved secondary relaxation peaks may be found.[9,10] Photon correlation spectroscopy (PCS) studies of type-B glass formers have identified only an excess wing, which is masked by a strong β-peak in the dielectric spectrum.[10–12] Why PCS does not probe the β-process while it is clearly detected in dielectric and mechanical relaxation as well as in nuclear magnetic resonance (NMR) experiments remains a challenge to be understood. Thus, the situation is quite puzzling since there exists no final conclusion concerning the nature of these processes and their relevance with regard to the glass transition phenomenon.

As a β-process is also observed for molecules without internal degrees of freedom, it is assumed to be generic to the glassy state. In contrast to the α-process the β-process is often loosely called a "local" process. This classification may suggest that the extent of cooperativity of the dynamics typical of the α-process is not found for secondary relaxations. Actually, however, all correlation lengths discussed for the α-process are, if at all present, on the order of a few nanometers which still is rather local. A prominent feature which might point to a local character of the dynamics is the fact that below T_g the most probable relaxation time τ_β of the β-process follows an Arrhenius temperature dependence, the peak width increases with reciprocal temperature as expected for a temperature independent distribution of activation energies, and the relaxation strength changes only weakly.[8,13] Yet, the mean activation energies are quite high, usually in the range $E/k \cong 11$–$26\ T_g$.[5,7] Its generic nature is also signaled by the fact that the relaxation strength strongly increases above T_g, i.e., the β-process probes the "softening" of the glass above T_g. Important to note is that a β-process is also observed in super-cooled plastic crystals (glassy crystals) with activation energies almost not altered with respect to that of the corresponding structural glass.[13,14]

Systematic ^{2}H NMR solid-echo studies on structural glass formers such as toluene, decalin, and polybutadiene[15–18] as well as on glassy crystals like ethanol[19] or cyano cyclohexane[20,21] have been carried out in the past. Due to its high sensitivity on small-angle reorientations, the solid-echo technique yields a clear picture of the nature of the β-process in terms of its single-particle dynamics.[22,23] Spatially highly restricted reorientation of essentially all molecules prevails in the glassy state of neat systems. As suggested by random walk simulations,[22,24] the β-process is a multi-step process (like the α-process), so that the overall loss of correlation is not achieved before a number of elementary steps with a jump time $\tau_J \ll \tau_\beta$ are performed. The wobbling-on-a-cone model allows to reproduce the salient features of the NMR spectra as well as to quantify the extent of spatial

restriction with a full opening cone angle $\chi < 10^{o}$.[22,23] The NMR manifestation of the β-process in plastic crystals is essentially indistinguishable from that in canonical glasses.[19–21] Investigating the β-process in binary glass formers has shown that in a certain concentration range both components exhibit the same highly hindered (slow) wobbling of their molecular axis independent of size and shape of the molecules.[17] These experimental findings may allow to speculate that the β-process displays some extent of cooperativity, too.

In the present study the binary glass tripropyl phosphate (TPP)/(deuterated) polystyrene (PS/PS-d_3, $M_w \approx 2 \times 10^3$ g/mol) is investigated well below T_g by means of dielectric spectroscopy, ^{2}H and ^{31}P NMR. Nine concentrations spread over the complete range are chosen. The system is characterized by a large T_g contrast of the pure components ($\Delta T_g \cong 200$ K). Caused by the choice of this system the application of ^{31}P and ^{2}H NMR allows to probe selectively the dynamics of TPP and PS-d_3, respectively. Beyond that, dielectric spectroscopy (DS) provides information on the evolution of the distribution of activation energies when changing concentration. For comparison we included unpublished ^{2}H NMR results on ethanol for which a β-process is well identified by DS[14] (cf. also Ref. 17). As the molecular dipole moment of TPP is significantly higher than that of PS, the DS experiment of the mixture probes, in reasonable approximation, solely the TPP dynamics. For the first time we probe the characteristics of the β-process also by a ^{31}P NMR Hahn-echo sequence. As will be demonstrated, in binary glasses the type-B component causes the other component to participate in a common β-process. Yet, a fraction of both components becomes immobilized, i.e., in binary glasses – in contrast to neat systems – islands of rigidity appear, as already reported previously.[25] Our results clearly favor the interpretation that the β-process is a cooperative process – as is the α-process.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

A. Systems

A polystyrene sample with the molecular mass $M_w = 2250$ g/mol (PS) and another polystyrene sample, partially deuterated at the backbone, with very similar mass $M_w = 2440$ g/mol (PS-d_3) were purchased from Polymer Standards Service (Mainz, Germany) and used without further treatment. Since the chains consist of more than 20 monomer units, we assume that any specific end group of the polymer chains will not have a considerable effect on the investigation of the segmental dynamics. For the dielectric experiments PS was used for the preparation of the mixtures, while PS-d_3 was used for the NMR measurements. Tripropyl phosphate (TPP, 99%) was bought from Sigma Aldrich and used as received, too (cf. also Ref. 26). A list of mass concentrations $c = m_{TPP}/(m_{TPP} + m_{PS/PS\text{-}d3})$ of the mixtures measured by DS and/or NMR is given by Table I. Ethanol-d_2 (deuterated at the methylene group) was purchased from Aldrich. We do not find any indication that phase separation or crystallization occurs in the binary glasses. Among other tests, light scattering experiments show a homogeneous sample.

TABLE I. Mass concentrations of systems measured by DS and/or NMR.

c	0	0.1	0.2	0.3	0.45	0.5	0.6	0.8	0.9	0.95	1
DS	x	x	x	x	x	…	x	x	x	x	x
^{2}H NMR	x	x	x	…	…	x	…	x	x	…	…
^{31}P NMR	…	x	x	…	…	x	…	…	…	…	x

B. Dielectric spectroscopy

Dielectric measurements were carried out with the Alpha-A analyzer by Novocontrol while temperature was kept constant within ±0.2 K by using the Quatro-H temperature controller by Novocontrol. The absolute accuracy is assumed to be better than ±1 K. The sample cell has the design published by Wagner and Richert and assures a constant sample volume.[27] All β-relaxation peaks have an asymmetric shape and can be interpolated with the $G_\beta(\ln \tau)$ distribution introduced in Ref. 28. Actually, the time constant is the only parameter discussed in this article, which can also be obtained in good approximation via $\tau_\beta = 1/(2\pi \nu_{max})$ by determining the maximum positions ν_{max}. In order to obtain the time constants of the α-relaxation of neat PS a Kohlrausch function is used for the data interpolation. In the case of neat TPP a Cole-Davidson model is preferred. Time constants of the α-process in the mixtures, where the primary relaxation peak is significantly broadened in relation to neat TPP, were defined by the peak positions like $\tau_\alpha = 1/(2\pi \nu_{max})$. A more detailed analysis of the structural relaxation peaks of all investigated mixtures will be presented in a forthcoming publication.

C. NMR

The ^{31}P NMR experiments were carried out using a Bruker Avance III console and a Spectrospin 400 MHz cryomagnet. The field strength of 9.4 T corresponds to a Larmor frequency $\nu_L = 161.98$ MHz for ^{31}P. The length of the $\pi/2$-pulse was 2.2 μs. A home-built (in cooperation with Bruker Biospin GmbH) double resonance probe was cooled by liquid nitrogen using an Oxford CF1200 cryostat, controlled by an Oxford ITC-503. Temperature accuracy was ±2 K, stability was better than ±0.2 K. The ^{2}H NMR experiments were carried out on a Bruker Avance DSX spectrometer and an Oxford 300 MHz cryomagnet. The field strength of 7 Tesla corresponds to a ^{2}H Larmor frequency of $\nu_L = 46.067$ MHz; the length of the $\pi/2$-pulse was 2.8 μs. A home-built probe was cooled by liquid nitrogen using a CryoVac Konti cryostat and an Oxford ITC-503 temperature controller. Temperature accuracy was better than ±1 K, stability was better than ±0.2 K.

At temperatures below its minimum the spin-lattice relaxation time $T_1(T)$ was measured via a saturation recovery sequence. Above the T_1 minimum temperature the inversion recovery sequence was applied. In the case of ^{31}P the spin-lattice relaxation was found to be in non-exponential, as in this ^{2}H NMR the relaxation below T_g is non-exponential as in this case spin-diffusion can be neglected at least at short relaxation times. Therefore the mean value $\langle T_1 \rangle$ is given, which is obtained by interpolating the relaxation function by

a Kohlrausch decay (stretched exponential). This decay function is also used to interpolate the decay of the solid-echo (cf. below and Eq. (3)).

The NMR frequency depends on the angle θ between the principal interaction tensor axis and the magnetic field direction:

$$\nu_{local}(\theta) = (\pm)(3\cos^2\theta - 1)\cdot\delta_{CSA/Q}/2, \qquad (1)$$

where ν_{local} is the shift of the resonance frequency with respect to the Larmor frequency ν_L. The parameter $\delta_{CSA/Q}$ (in kHz) specifies the anisotropy of the interaction tensor, which is given by the interaction of the nuclear quadrupolar moment (Q) with the electrical field gradient in the case of ^{2}H NMR. In the case of PS-d$_3$, the orientation of the ^{2}H-C bonds at the chain backbone is probed. Due to the spin $I = 1$ two transitions occur and positive as well as negative signs are valid. In the case of ^{31}P NMR (spin $I = 1/2$) the rigid lattice spectrum is determined by the chemical shift anisotropy (CSA), and in Eq. (1) δ_{CSA} is used and only the negative sign is found. Both interaction tensors CSA and Q are axially symmetric in the present case. In the case of an isotropic distribution of tensor orientations (e.g., in glasses) characteristic powder spectra are observed, a (symmetric) Pake spectrum in the case of ^{2}H NMR whereas the CSA spectrum is asymmetric.

The solid-state spectra were collected by applying a Hahn-echo (^{31}P NMR) or a solid-echo sequence (^{2}H NMR) preceded by a saturation sequence of five $\pi/2$ pulses; the buildup time was chosen to be 2.5 T_1 or 1 s at least. In the case of ^{31}P NMR ^{1}H decoupling was applied during the echo sequence. Appropriate 8-fold (^{2}H) and 16-fold (^{31}P) phase cycling was applied.[29] Fits to the solid-echo Pake spectra were corrected for finite pulse excitation.[30,31] Simulations have shown that in the case of small angle reorientations as typically found for the β-process the largest effect in the solid-echo spectrum is found for the condition $\tau_\beta\delta_{local} \cong 1$.[32]

III. RESULTS

A. Neat components—Dielectric spectra

The susceptibility spectra of PS ($T_g = 335$ K) are shown in Fig. 1(a). Above T_g a pronounced peak is visible, which is identified as the structural or α-relaxation. The low amplitude reflects the rather non-polar nature of the PS monomer. Close to T_g, the high-frequency side of the α-peak is made up of a crossover from one power-law behavior to another one usually called excess wing. This spectral shape is typical for a type-A glass former, where no explicit secondary relaxation peak is resolvable. While temperature is increased the main relaxation peak shifts to higher frequencies. When the sample is cooled below T_g the α-peak moves out of the frequency window and the signal, now consisting only of the excess wing contribution, drops close to the resolution limit of the spectrometer. No indications for a secondary (β-) relaxation peak are observed.

The dielectric spectra of neat TPP ($T_g = 134$ K) are displayed in Fig. 1(b). As in the case of PS above T_g an α-relaxation peak can be identified, the amplitude of which exceeds the one of PS by a factor of about 1000, i.e., the TPP molecule carries a strong dipole moment. At frequencies several decades above the maximum position of the α-peak a secondary relaxation is well resolved (type-B glass former). This secondary peak survives at temperatures below T_g when the α-peak has already left the frequency window. Its spectrum broadens significantly when temperature is lowered. When temperature is increased above, say, $T = 150$ K, both peaks approach each other until above $T = 156$ K the measurement of the super-cooled liquid cannot be continued due to the crystallization of the sample.

The time constants of both α- and β-process are shown in Fig. 2. In the case of neat PS we added the results of Ediger and co-workers,[33] and for TPP we included the ^{31}P NMR results obtained by applying the stimulated echo technique as well as the data from an analysis of the spin-lattice and spin-spin relaxation.[26] Good agreement is found between the NMR and DS results. While the τ_α show the typical super-Arrhenius temperature dependence, the β-process in TPP exhibits an Arrhenius behavior. The mean activation energy is found to be $E/k = 3240\ \text{K} = 24\ T_g$.

B. Neat components—^{31}P and ^{2}H NMR results

As seen in Fig. 3(a), below T_g the spin-lattice relaxation time $T_1(T)$ of PS-d$_3$ displays a rather weak temperature

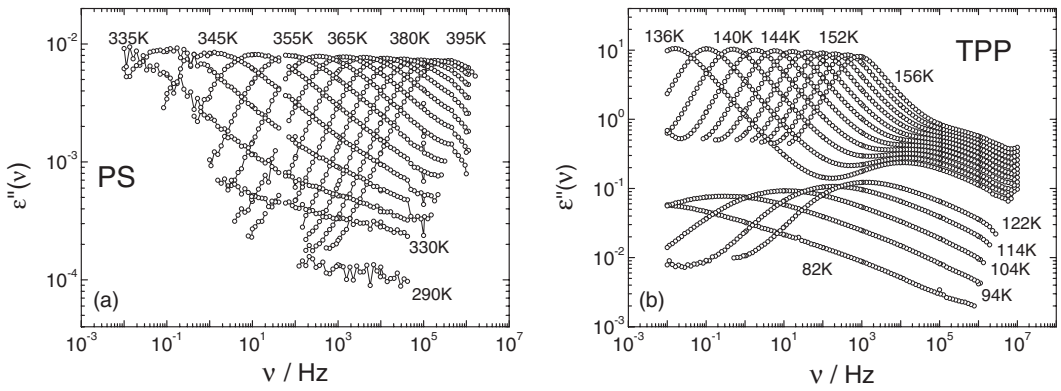

FIG. 1. (a) Dielectric spectra of neat PS; $T = 290$K and $T = 330$ – 395 K in 5 K steps (some temperatures indicated). (b) Susceptibility spectra of neat TPP revealing a well resolved β-process (some temperatures indicated; data above T_g partially taken from Ref. 26).

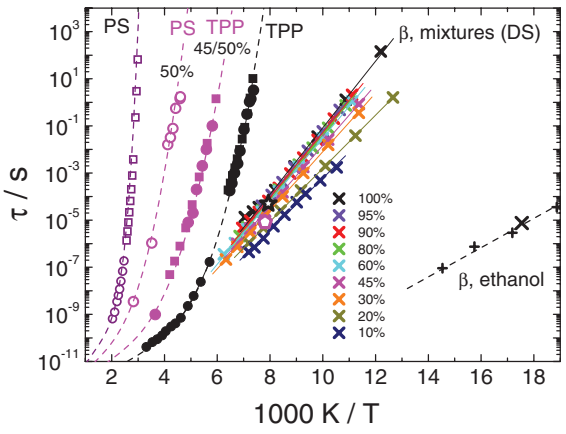

FIG. 2. Structural relaxation times τ_α in neat PS (DS: open squares, NMR: open circles[33]), and neat TPP (DS: full squares, NMR: full circles[26]) and in the mixtures $c = 45\%$ (DS probing TPP, full squares) and $c = 50\%$ (^{31}P NMR probing TPP, full circles; and ^{2}H NMR probing PS dynamics, open circles); time constant τ_β of the β-process in neat TPP and in the mixtures as revealed by DS (crosses, color code for the concentrations given in legend), τ_β of TPP yielded by ^{31}P Hahn-echo (open star) and of PS in the mixture by ^{2}H solid-echo (open pentagon). For comparison, time constants of the β-process of ethanol as given by DS (plus signs)[14] and NMR (cross). Solid lines: Arrhenius-fits (see Fig. 7), dashed lines: guides for the eye.

dependence typical of an excess wing determining the relaxation in the glass as indicated by the dielectric spectra (cf. Fig. 1(a)). Approximately an exponential temperature dependence $\langle T_1 \rangle \propto e^{-T/To} \propto 1/J(\omega = const.)$ with $T_o = 96$ K is observed (dashed line), as also found for the spectral density $J(\omega)$ of many type-A glasses by dielectric spectroscopy.[7,8,34,35] We note that dynamic mechanical analysis appears to show a β-process in high molecular mass polystyrene,[36] yet, we do not see any indication of this in our NMR as well as dielectric experiments on our sample. Despite of the low molecular dipole moments of polystyrene samples dielectric spectroscopy is principally able to detect a β-relaxation in polystyrene.[37] Above T_g the α-process dominates and T_1 decreases, yet a relaxation minimum is not observed as it occurs at even higher temperatures.

In the case of ^{31}P NMR on TPP, a well resolved T_1-minimum is found and attributed to the α-process. The corresponding time constant $\tau_\alpha(T) = 1/(2\pi\nu_L)$ agrees with the results from a full T_1/T_2 analysis.[26] Below T_g the temperature dependence of T_1 becomes weaker, yet, it is much stronger than in the case of PS-d$_3$ due to the β-process controlling the relaxation. As the ^{31}P relaxation is controlled by the chemical shift anisotropy (CSA; cf. Sec. II C) the relation $1/T_1 \propto \varepsilon''(\omega_L)$[26,38,39] is expected to hold and one can check this relationship by inserting the intensity of the dielectric spectra of the respective temperatures (cf. Fig. 1(b)) extrapolated to the Larmor frequency ($\nu_L = 161.98$ MHz) of the ^{31}P NMR experiment. As indicated by the dashed line in Fig. 3(a), indeed, the temperature dependence of $T_1(T)$ is well reproduced by that of ε''. A different situation is found for the comparison of the ^{2}H and ^{31}P T_1 data of the mixtures (Fig. 3(b)), which will be discussed in detail in Sec. III D.

The β-process can also be accessed by analyzing the NMR spectra via the application of a two-pulse echo sequence, namely the Hahn-echo (^{31}P) or the solid-echo (^{2}H) sequence. The majority of former NMR studies on the β-process in molecular glasses are based on ^{2}H solid-echo experiments.[15–22] There, subtle spectral changes characteristic of a highly hindered molecular reorientation have been identified by varying the inter-pulse delay t_p. In Fig. 4(a) this is first documented for the structural glass of neat ethanol-d$_2$ for which DS has identified a comparatively fast β-process with $E/k = 15\ T_g$ (cf. also Fig. 2).[14] While at low as well as high temperatures (yet below $T_g = 92$ K) rather weak spectral changes are recognized and the spectra display more or less the typical solid-state ^{2}H NMR powder (Pake) shape, at intermediate temperatures (T_g – 30 K) a strong decrease of the spectral intensity around zero frequency is observed for long delay time t_p, yet the singularities prevail. We conclude that well in the glassy state of ethanol the β-process passes through the NMR time window.

Fig. 4(b) shows the results of an analogue experiment on TPP. Due to the different spin dynamics for the $I = 1/2$ nucleus ^{31}P, in contrast to the $I = 1$ spin systems in the case

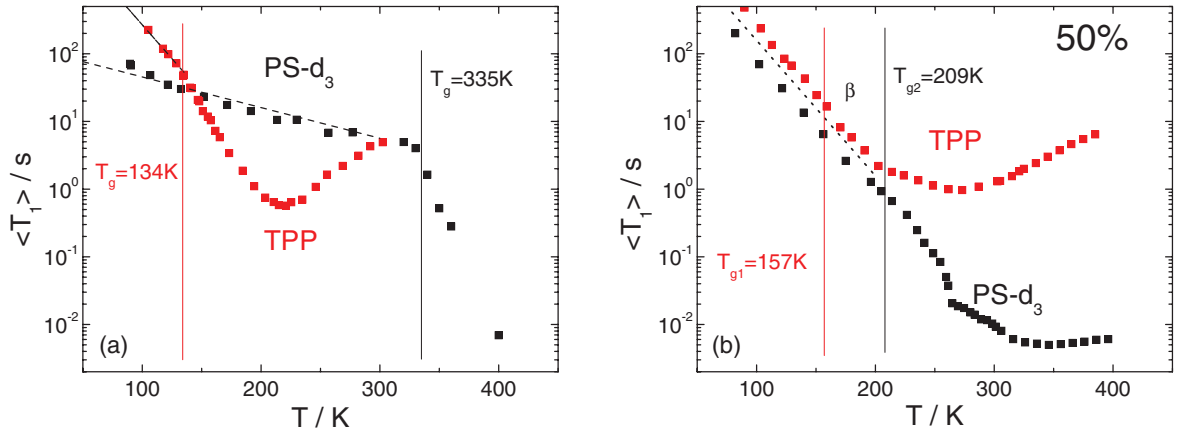

FIG. 3. (a) Spin-lattice relaxation times of neat TPP (^{31}P NMR) and neat PS-d$_3$ (^{2}H NMR). ^{2}H relaxation is non-exponential below T_g and therefore the mean relaxation time $\langle T_1 \rangle$ is given. Glass transition temperatures T_g are indicated by vertical lines; dashed line: interpolation by an exponential relaxation law for PS-d$_3$; dashed line below T_g of TPP: estimate of T_1 of TPP from the dielectric spectral density. (b) Spin lattice relaxation times of 50% TPP/PS-d$_3$ (^{31}P NMR and ^{2}H NMR; dashed line: estimate from the dielectric spectral density; vertical solid lines indicate T_g (for a detailed assessment cf. Sec. III D).

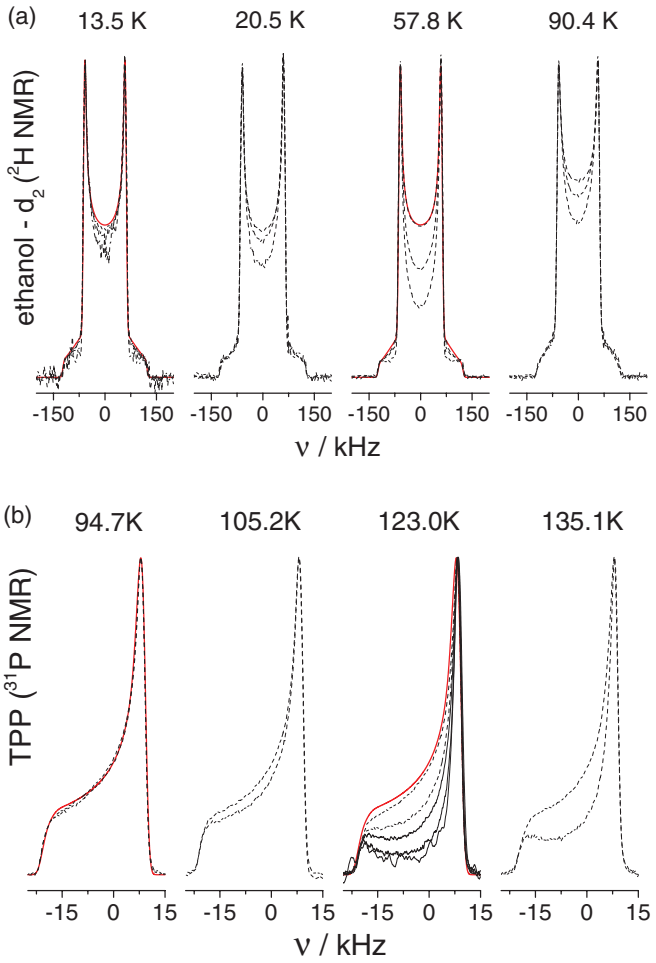

FIG. 4. (a) Solid-echo spectra of ethanol-d_2 at indicated temperatures, each set representing inter-pulse delays of 20 μs, 100 μs, and 200 μs; for shortest inter-pulse delay t_p a fit with a Pake model is shown as solid line ($\delta_Q = 123$ kHz); (b) Hahn-echo spectra of neat TPP, each set with inter-pulse delays of 20 μs and 200 μs, at 123 K additionally 400 μs, 800 μs, and 1600 μs (solid lines). A fit to the powder spectrum is included for shortest t_p as solid line ($\delta_{CSA} = 20.5$ kHz). All datasets are normalized to their maximum values.

of ^{2}H, a Hahn-echo sequence was applied. Like in Fig. 4(a), all spectra are normalized to their maximum values. As mentioned the relevant spin interaction in TPP is given by the CSA, which leads to an intrinsically asymmetric solid-state powder spectrum. The heteronuclear ^{1}H-^{31}P coupling was removed by ^{1}H decoupling, and the homonuclear ^{31}P-^{31}P coupling can be ignored safely due to the large distance between the nuclei in different molecules. Again, spectral intensity is lost mainly at the center of the spectra. In contrast to ethanol the effect is most prominent close to $T_g = 134$ K. Qualitatively, this is understood as the β-process in TPP is much slower than the one in ethanol (cf. Fig. 2). At $T = 123$ K extremely large inter-pulse delays (spectra marked by solid line) were applied. Here the intensity around $\nu = -5$ kHz almost vanishes, indicating that essentially all molecules participate in the β-process.

The spectral changes observed for neat ethanol ($T < T_g$) as well as TPP are very similar to those reported previously for pure toluene, decalin or polybutadiene or a decalin/chlorobenzene mixture;[17,23] even for the glassy crystalline phases of ethanol[19] or cyano cyclohexane.[20] The NMR spectrum looses intensity in the center of the spectrum, as said, a characteristic of a highly hindered motion. Assuming a wobbling-on-a-cone model, one finds for all examples that the angular displacement does not exceed 10°, which is therefore a rather generic feature of the β-process.[21,22] The second Legendre polynomial, determining the NMR frequency shift in the solid state, exhibits the highest sensitivity on a small angle reorientation at $\theta = 45°$ or $\nu = \delta_{CSA/Q}/4$, respectively, because here the derivative $|d\nu_{local}/d\theta|$ is maximal. This is seen directly in the case of ^{31}P NMR. Since in ^{2}H NMR the contributions of both signs in Eq. (1) are combined (two NMR transitions are involved), due to reasons of symmetry the highest sensitivity is found at $\nu = 0$.

The spectral effect can be quantified by measuring the intensity at the center of the spectrum with respect to that at the singularity,[18] explicitly a quantity R is defined by

$$\begin{aligned} R &= I(\nu = 0)/I(\nu = \delta_Q/2) && {}^2\text{H NMR}, \\ R &= I(\nu = -\delta_{CSA}/4)/I(\nu = \delta_{CSA}/2) && {}^{31}\text{P NMR}. \end{aligned} \tag{2}$$

In Fig. 5(a) the R values for long t_p (200 μs) (solid symbols) measured in ethanol (^{2}H NMR) and TPP (^{31}P NMR) are displayed as a function of the reduced temperature T/T_g. As expected a minimum is observed for ethanol at which the condition $\tau_\beta \delta_Q \cong 1$ applies with δ_Q specifying the quadrupolar interaction (cf. Sec. II C).[20] We note that in the case of short t_p values (e.g. $t_p = 20$ μs) no such minima are found in $R(T)$ as essentially no dephasing of the NMR frequencies (due to molecular reorientation involved in the β-process) is monitored; i.e., the spectrum has the undistorted powder shape (cf. Fig. 4). An analysis of the undisturbed low-temperature Pake spectrum (cf. Fig. 4) yields $\delta_Q = 123$ kHz for ethanol-d_2. From this an estimate of the time constant of the β-process can be given. The resulting τ_β is included in Fig. 2 and fits well into the DS findings.

In Fig. 5(a) we also included the ^{2}H NMR results on the glassy crystalline phase of cyano cyclohexane.[20] Again a minimum is observed in $R(T)$, however, at higher reduced temperature, which correlates well with the fact that $E/k = 19\ T_g$ is larger than in ethanol (15 T_g). In the case of TPP, with its much slower β-process, i.e., with higher activation energy $E/k = 24\ T_g$, a minimum can only be anticipated at highest temperatures, as above T_g the α-process interferes. Still, the time constant extracted via $\tau_\beta \delta_{CSA} \cong 1$ with $\delta_{CSA} = 20.5$ kHz is compatible with those from DS (cf. Fig. 2). The results for TPP are very similar to those of toluene (cf. again Fig. 5(a)), the paradigmatic glass former without internal (DS active) degrees of freedom, the β-process of which has been systematically investigated by ^{2}H NMR.[15–17] It turns out that the mean activation energy is the same as for TPP.[5] Finally, the result for PS-d_3 is included in Fig. 5(a). Here, essentially no temperature dependence is observed in agreement with the results from DS where no β-process is resolvable. In conclusion, the NMR spectra clearly reflect the β-process in the different glasses. Depending on the value of the mean activation energy E the quantity R reveals a minimum more or less below T_g.

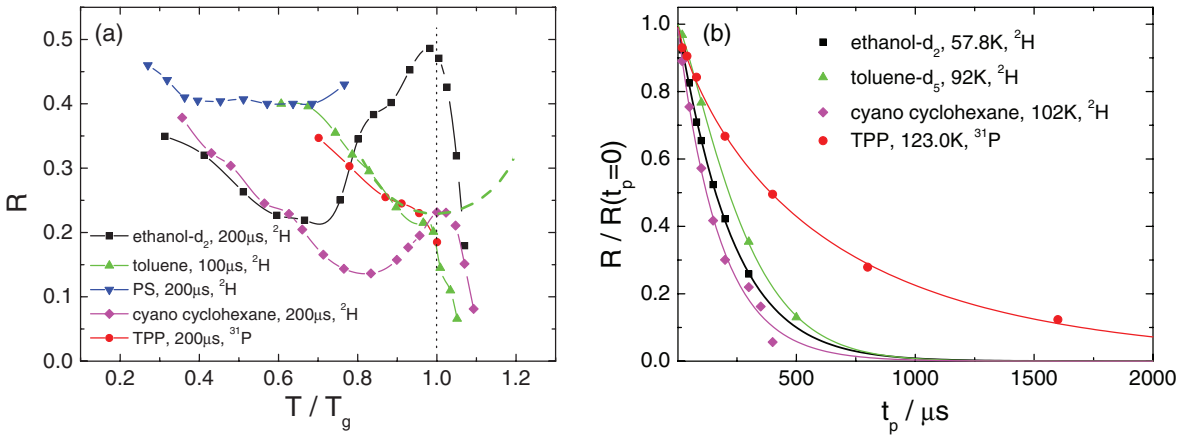

FIG. 5. (a) The parameter $R(T)$ at (high) $t_p = 200\ \mu s$ quantifying the spectral changes occurring in the solid-state NMR spectra for glassy ethanol, PS and plastically crystalline cyano cyclohexane (CNC),[20] TPP, as well as toluene-d_5[15] at $t_p = 100\ \mu s$. Lines are guides for the eye. For toluene (as well as TPP) a minimum above T_g, as would be expected without the influence of the α-process, is anticipated (dashed line). (b) Parameter R normalized to $R(t_p = 0)$ characterizing the spectral changes of the NMR spectra of ethanol, toluene, CNC, and TPP as a function of the inter-pulse delay t_p for temperatures as indicated; lines: Kohlrausch fits.

Figure 5(b) displays the dependence $R(t_p)$, normalized by $R(t_p = 0)$, for the temperatures of the minima found in Fig. 5(a). For ethanol, toluene[15] and cyano cyclohexane[20] $R(t_p)$ reaches almost zero at longest time t_p, which signals that essentially all molecules participate in the β-process. Again, $R(t_p)$ completely decays to zero. In the case of TPP, $R(t_p)$ shows a very similar behavior, yet, on somewhat longer inter-pulse times which are not accessible by ^{2}H NMR due to its faster spin-spin relaxation. We can conclude that essentially all TPP molecules participate in the β-process of neat TPP glass.

C. Characterizing the β-process in the TPP/PS mixtures by dielectric spectroscopy

In order to gain information about the β-relaxation in the mixture, PS molecules are now added stepwise to the TPP. By producing mixtures with $c = 0\%$, 10%, 20%, 30%, 45%, 60%, 80%, 90%, 95%, 100% mass fraction of TPP (cf. Table I), the entire concentration range is covered by DS experiments (as well as by NMR, cf. below). As the dielectric signal of PS is significantly smaller than that of TPP, we can safely assume that in the mixtures only the TPP dipoles are probed by DS.

For the concentration $c = 45\%$ dielectric spectra are compiled in Fig. 6. At temperatures above $T = 160$ K a peak is observed, which shifts to higher frequencies when temperature is increased. This peak is caused by the α-relaxation of TPP in the mixture. The corresponding time constants lie between those of the two neat systems as is seen in Fig. 2. Adding PS to TPP always ends up in a slowing down of the structural relaxation of the TPP ensemble due to the anti-plasticizer effect. The α-peak is strongly broadened; especially the low-frequency power-law exponent is reduced to values much smaller than 1, which is not found in the neat systems. In Fig. 2 we included the results of ^{2}H and ^{31}P NMR obtained from analyzing stimulated echo decays, for $c = 50\%$, which probe the structural relaxations of PS and TPP, respectively. Clearly, the time constant τ_α of PS is significantly longer than that of TPP, i.e., the dynamics of the two components are decoupled and two T_g can be defined, T_{g1} (PS) and T_{g2} (TPP). As stated before, a detailed assessment of the structural relaxations of the TPP/PS mixtures is given in a forthcoming publication; here we focus on the β-relaxation.

Below 160 K, when the α-peak has left the low-frequency limit of the spectrometer (Fig. 6), a β-relaxation is found like in the case of neat TPP. In particular, no essential change of the time constant is observed. This rather weak concentration dependence of the β-process is reflected in the Arrhenius plot of the time constants extracted from the maximum positions of the β-relaxation (Fig. 2). As in neat TPP the time constants τ_β follow Arrhenius laws for any concentration. For all TPP concentrations higher than $c \cong 60\%$ the $\tau_\beta(T)$ curves are essentially the same, yielding a mean activation energy $E/k = 24\ T_g$. At lower concentrations a slight reduction of E is observed, and the attempt frequency ν_0 is reduced, too. This is best seen in Fig. 7 where ν_0 and E are plotted as a function of concentration. Below $c = 60\%$ both E and ν_0 show a weak linear decrease. The slight extent of the concentration dependence of E is rather surprising, and one could argue that it points to the interpretation of the β-relaxation to be an intramolecular process due to some particularity of the TPP

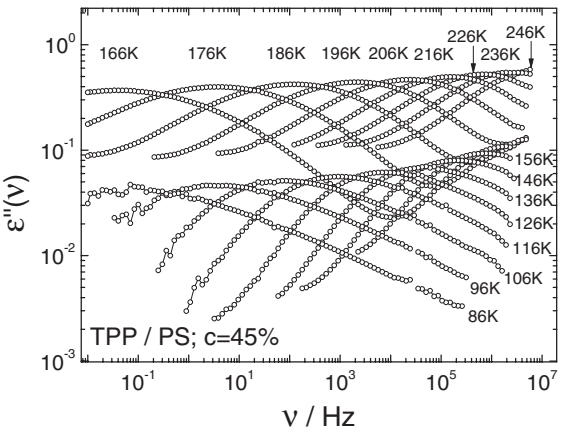

FIG. 6. Dielectric spectra of 45% TPP in PS at indicated temperatures.

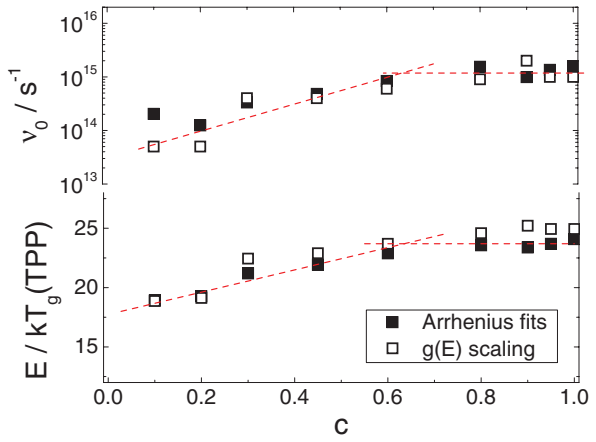

FIG. 7. Attempt rates ν_0 (upper panel) and activation energies (lower panel) for the whole concentration range of TPP. Full symbols: yielded by Arrhenius fits of $\tau_\beta(T)$ data in Fig. 2. Open symbols: yielded by $g(E)$ scaling (cf. text).

molecule. As we will demonstrate, however, this interpretation is misleading. Comparing the time constants of the β- and α-process in the mixtures one recognizes that their separation grows when PS is added (cf. Fig. 2). In other words, as the β-process essentially does not change but T_g of the mixture grows with the amount of PS, no structural relaxation of any considered mixture interferes with the analysis of the secondary relaxation carried out here.

The concentration dependence of the τ_β shown in Fig. 2 is also seen directly from the peak positions: comparing the β-peak of different mixtures, its spectral position shifts only weakly when PS molecules are added (cf. Fig. 8(a)). The only obvious change is a decrease of its amplitude. Next we consider the spectral shape of the β-peaks. As a first attempt, in Fig. 8(a) a symmetric log-Gaussian function, as usually found for β-processes,[5] is fitted to the data set for $c = 45\%$. However, the fit is not fully successful; the spectra do not appear symmetric. The asymmetric shape becomes even more obvious in Fig. 8(b), where data of the $c = 45\%$ sample at different temperatures are scaled onto their maximum height and position. Here, a temperature dependent broadening of the peak is observed, which is typical of a thermally activated process.

If a relaxation process is governed by a temperature independent distribution of activation energies $g(E)$ (which is actually a characteristic of a thermally activated process) the resulting distribution of correlation times $G(\ln\tau/\tau_o)$ can be calculated via the Arrhenius law $\ln\tau/\tau_o = E/kT$, leading to $G(\ln\tau/\tau_o) = kT\, g(kT \ln\tau/\tau_o)$. Here, a constant attempt time τ_o is assumed. In the case of a broad function $g(E)$, the shape of the resulting distribution $G(\ln\tau/\tau_o)$ is reproduced by the corresponding susceptibility in good approximation, $G(\ln\nu_o/\nu) \cong \chi''(\ln\nu_o/\nu)$. As a consequence, the susceptibility peak must increase with temperature, while it shifts to higher frequencies and decreases its width, exactly as it is observed experimentally in the case of most β-processes.[7] Thus, a re-scaling of the susceptibility spectra can be applied to yield a master curve representing the distribution $g(E)$.[35,40,41] Plotting $\varepsilon''/T\Delta\varepsilon_\beta$ as a function of $T\ln\nu_0/\nu$ is expected to yield master curves, provided that the $g(E)$ is indeed temperature independent. The only free parameter of this scaling is the attempt rate ν_0 of the relaxation, which is assumed to be constant for all spectra, i.e., temperature independent.

The results of the scaling procedure applied to the data of the TPP/PS mixtures are shown in Fig. 9. In all samples a broad but asymmetric $g(E)$ is revealed, justifying to identify the β-relaxation in all mixtures as thermally activated. This is in accord with the time constants τ_β following Arrhenius laws (Fig. 2). While $g(E)$ in Fig. 9 are very similar for all concentrations, the peak position (most probable energy barrier) is only constant for concentrations $c > 60\%$. For $c \leq 60\%$ a trend to lower activation energies becomes obvious. This corresponds to the above findings, where activation energies of the Arrhenius laws (Fig. 2) and peak positions at a fixed temperature (Fig. 8(a)) became concentration dependent below $c = 60\%$. This is once again demonstrated in Fig. 7, where activation energies and attempt rates ν_o gained from the $g(E)$ scaling (Fig. 9) as well as from the Arrhenius fits (Fig. 2) are compared. Both analyses yield comparable results and the same concentration dependences. Summarizing, we can state that the β-relaxation of all investigated mixtures is

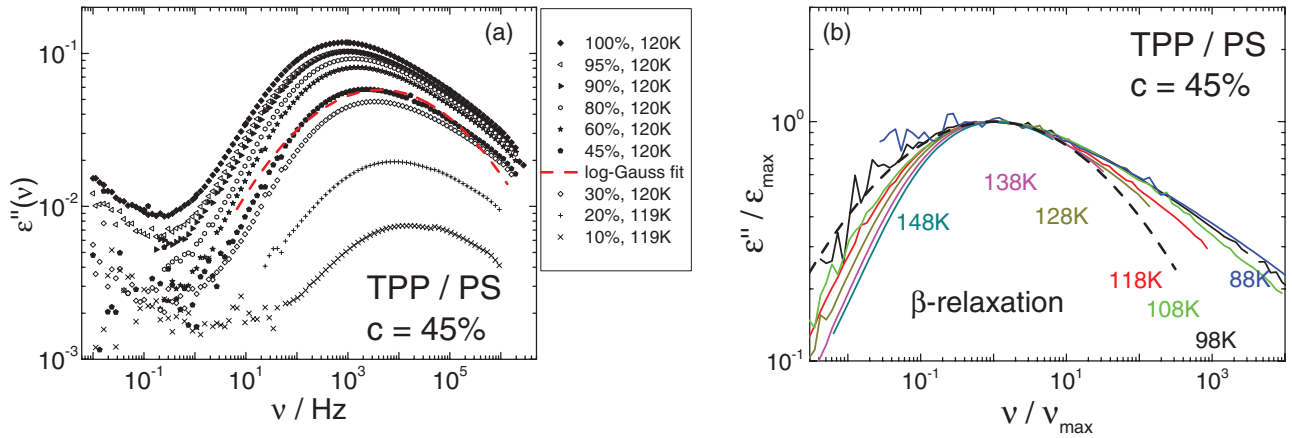

FIG. 8. (a) Susceptibility data of several mixtures of TPP in PS at similar temperature (119–120 K; mass fractions and temperatures indicated). Dashed line: Symmetric model function (log-Gauss) fit to the $c = 45\%$ data. (b) Data of the 45% sample at indicated temperatures, scaled to match maximum height and position. Dashed line: Fit from Fig. 5(a) scaled to maximum.

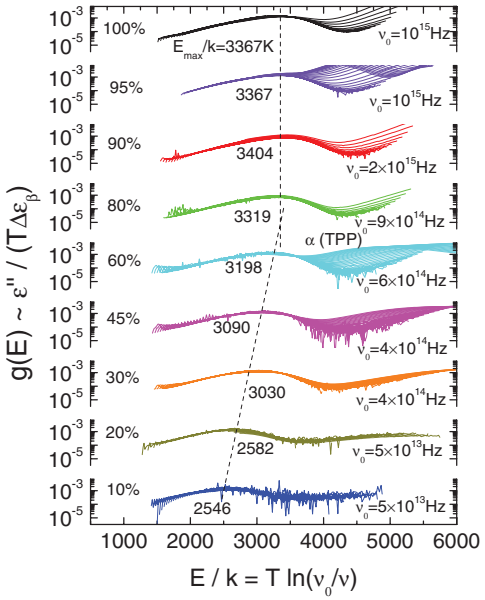

FIG. 9. Distribution of activation energies $g(E)$ obtained from scaling the susceptibility (cf. text) of the sub-T_g measurements of all investigated mixtures (concentrations, attempt rates, and most probable activation energies indicated). Dashed lines: Guides to the eye. Note: At high E/k deviations are observed due to the α-process of TPP.

governed by asymmetric but temperature independent distributions of activation energies $g(E)$. As a consequence, all time constants τ_β follow Arrhenius laws. All susceptibility data can be collapsed in order to reveal $g(E)$, making a detailed discussion of shape parameters, as obtainable by data fitting, needless in the context of this work.

D. Characterizing the β-process in the TPP/PS-d$_3$ mixtures by NMR experiments

As documented by the dielectric spectra, the β-process in the TPP/PS mixtures is well separated from the α-process. This is an important prerequisite for probing it by NMR, in particular, by applying a Hahn-echo (^{31}P) or a solid-echo (^{2}H) two-pulse sequence. The concentration selection of TPP/PS-d$_3$ mixtures investigated with these techniques can be inferred from Table I. Figure 10(a) shows the Hahn-echo spectra of TPP of the $c = 20\%$ mixture. A series of spectra, again normalized to their maximum values, is collected at three selected temperatures with a pulse delay $t_p = 40\ \mu$s, 80 μs, and 200 μs. While at high as well as low temperature no spectral changes are recognized, a weak but well discernible decrease of intensity around $\nu = -\delta_{CSA}/4$ is recognized at the intermediate temperature $T = 121.0$ K. Again, the characteristic spectral changes associated with a β-process are well identified. In the case of the $c = 50\%$ sample a similar evolution of the ^{31}P spectra is observed (cf. Fig. 10(b)), here, even longer t_p values have been applied at $T = 120.3$ K (solid lines) and the intensity around $\nu = -\delta_{CSA}/4$ almost vanishes at longest time t_p as in the case of neat TPP (cf. Figs. 4(b) and 5(b)).

As before for the neat components the spectral effect can be quantified by measuring the intensity close to the center of the spectrum with respect to the singularity, i.e., the quantity $R(t_p)$ (cf. Eq. (2)). In Fig. 11(a) the R values for long t_p (200 μs) (solid symbols) measured for three TPP concentrations ($c = 10\%$, 20%, 50%, and for comparison 100%) are plotted versus temperature. Except for $c = 100\%$ (as discussed before) a distinct minimum, essentially not shifting, is displayed. This signals immediately that the time constant of the process does not significantly change in the mixtures, a result already known from our DS study (cf. Fig. 2). In contrast to the $c = 100\%$ sample the minimum in $R(t_p)$ is well resolved due to the larger separation of α- and β-process in the mixtures. Also the depth of the minimum is very similar, at lowest concentration $c = 10\%$ it is somewhat less deep.

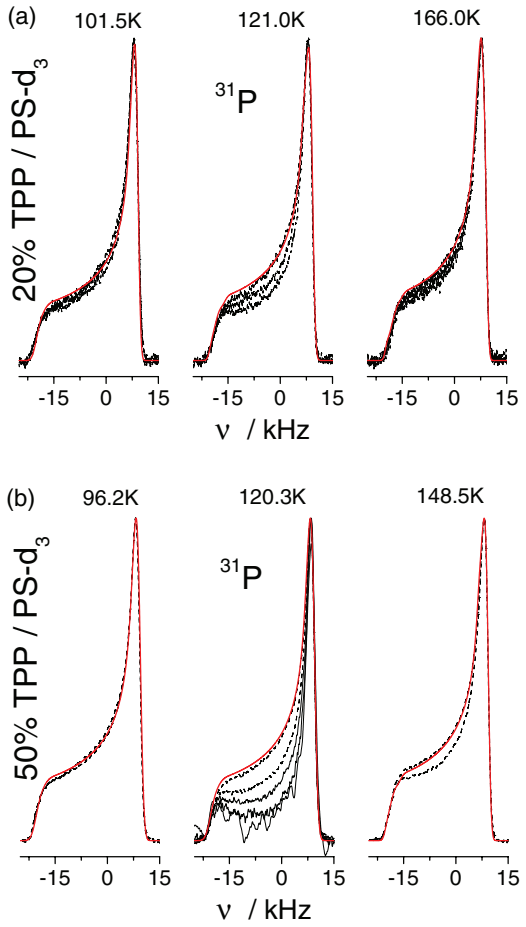

FIG. 10. ^{31}P Hahn-echo spectra of TPP/PS-d$_3$ glass at indicated temperatures, (a) $c = 20\%$, each set with $t_p = 40\ \mu$s, 80 μs, and 200 μs (b) $c = 50\%$, 20 μs and 200 μs each, at $T = 120.3$ K very long interpulse delays were applied additionally (solid lines, $t_p = 400\ \mu$s, 800 μs, and 1600 μs) and the intensity at $\nu = -\delta_{CSA}/4$ almost vanishes. For shortest t_p a fit by a CSA powder spectrum is included (solid line).

The decays of $R(t_p)$ for the different TPP concentrations at very similar temperatures are displayed in Fig. 11(c) and compared to the data of neat TPP. While for the $c = 50\%$ sample the decay of $R(t_p)$ is similar to that of $c = 100\%$, the situation for $c = 20\%$ is different. The $R(t_p)$ appears not to relax completely down to zero, indicating that at low TPP concentrations only a fraction of TPP molecules participates in the β-process, i.e., some molecules have become immobilized. Yet, in all cases the decay is described by a Kohlrausch function (cf. Eq. (3), below) with $\beta = 0.95$, and the apparent

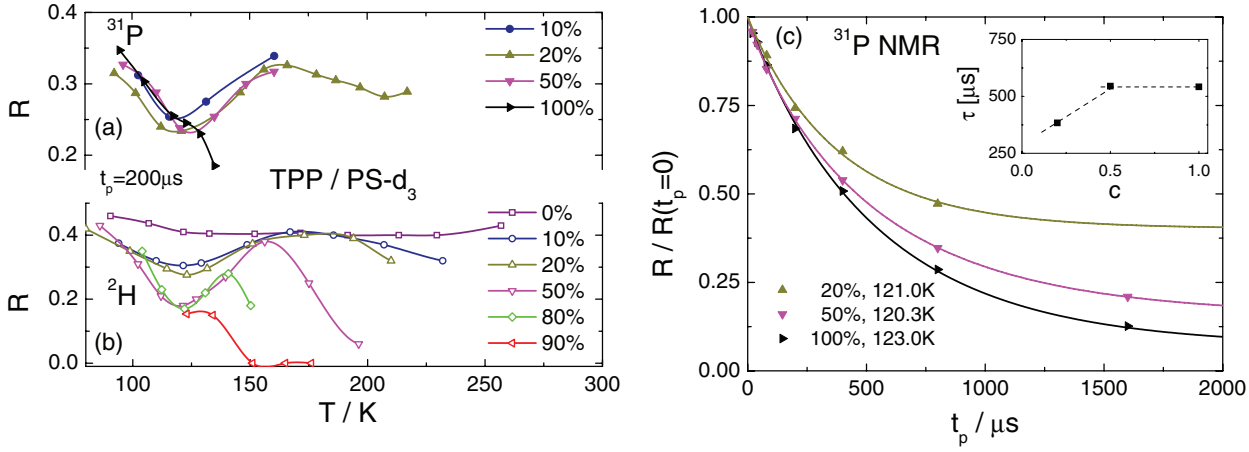

FIG. 11. Temperature dependence of line-shape parameter R at $t_p = 200$ μs for (a) TPP and (b) PS-d$_3$; mass fractions as indicated. Lines serve as guides for the eye. (c) Dependence of $R(t_p)$, normalized to short t_p values, on the inter-pulse delay t_p as revealed by ^{31}P Hahn-echo; mass fractions, and temperatures as indicated; inset: time constant as a function of concentration, dashed lines: a possible interpretation.

time constant (Fig. 11(b), inset) becomes somewhat shorter as also observed in the dielectric spectra (cf. Fig. 2).

Neat PS is a type-A glass former not showing any spectrally resolved β-process in the DS spectra. This is also confirmed by ^{2}H spin-lattice relaxation measurements, which display only a weak temperature dependence in the glassy state as discussed before (cf. Fig. 3). Here, the question arises whether polystyrene in the mixture exhibits a β-process. Due to the selectivity of ^{2}H NMR probing solely the dynamics of the PS-d$_3$ molecules ^{2}H solid-echo spectra can give a clear-cut answer. Figure 12 shows a series of solid-echo spectra of TPP/PS-d$_3$ with $c = 50\%$ taken at different t_p values for three temperatures. A pronounced spectral change is observed at intermediate temperature $T = 121.5$ K. Similar results are observed for the $c = 20\%$ sample, in particular, the largest spectral change is again observed at 123.0 K. Moreover, the effect is found at similar temperatures as in the case of TPP studied by ^{31}P NMR. It seems that PS in the mixture shows some secondary relaxation, too, which passes through the solid-echo time window well below T_g at similar temperatures as in the case of TPP. The corresponding $R(T)$ values (at long inter-pulse delay $t_p = 200$ μs) are included in Fig. 11(b). While no distinct temperature dependence is observed in neat PS-d$_3$ ($c = 0\%$), a minimum emerges when TPP molecules are added. Up to $c = 50\%$ the minimum depth increases monotonously. Remarkably, the minima do not shift with concentration and they are positioned roughly at the same temperature as the minima resulting from the ^{31}P Hahn-echo experiment on TPP (Fig. 11(a)). Actually, the minimum of $R(T)$ is slightly shifted to higher temperatures in the case of the ^{2}H spectra of PS-d$_3$, which is expected due to the higher coupling constant δ_Q. Taking $\delta_Q = 122.4$ kHz from an analysis of the low-temperature ^{2}H solid-state spectra of PS-d$_3$, the extracted time constant τ_β agrees well with those determined by DS as well as by ^{31}P Hahn-echo experiment (cf. Fig. 2). These findings strongly suggest that in the mixtures polystyrene monomers participate in the highly hindered reorientation of the β-process introduced by the TPP molecules. In other words, the β-process is not solely an intramolecular process. It appears that the TPP molecules cause the monomer units of polystyrene to wobble in a rather similar way and on the same time scale as the TPP molecules do.

In order to further investigate the t_p dependence of the ^{2}H solid-echo spectra, Fig. 13(a) shows the solid-echo spectra at very similar temperatures for the different investigated

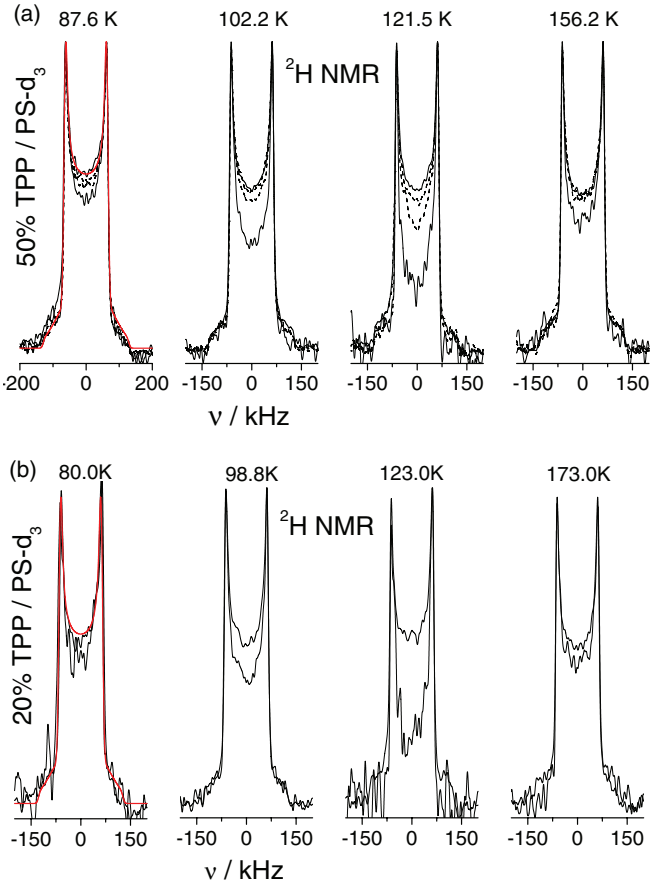

FIG. 12. ^{2}H NMR spectra of TPP/PS-d$_3$, normalized to maxima, at indicated temperatures. (a) c = 50%; each set with $t_p = 20$ μs, 200 μs (solid lines), 40 μs and 80 μs (dashed lines), (b) $c = 20\%$, $t_p = 20$ μs and 200 μs. For lowest temperatures fits with Pake spectral shape are included (solid red line, $\delta_Q = 122.4$ kHz).

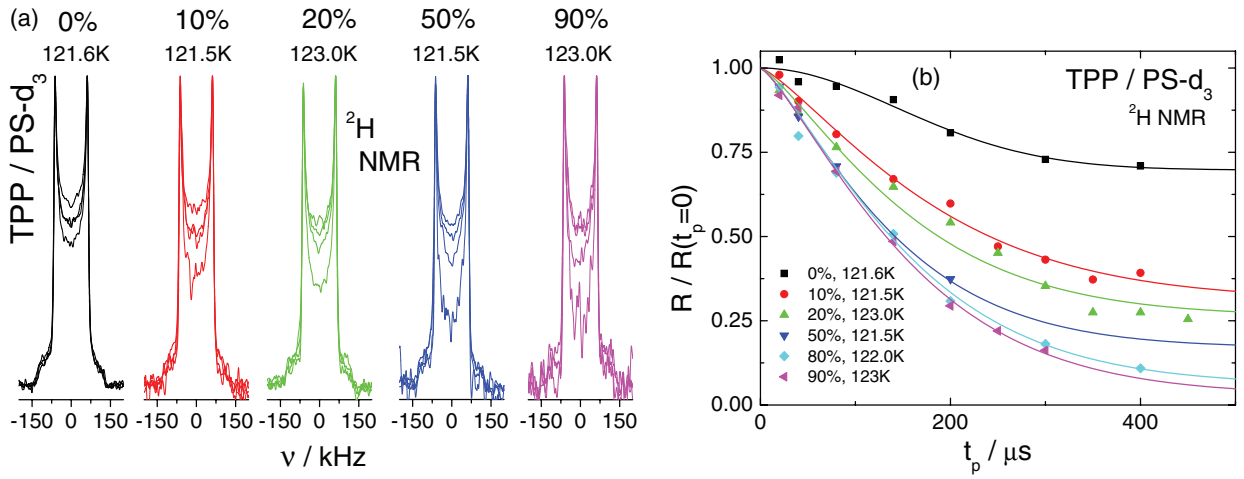

FIG. 13. (a) ^{2}H NMR spectra of TPP/PS-d$_3$ for various concentrations of TPP at indicated temperatures; each set with $t_p = 20\ \mu$s, 40 μs, 80 μs, and 200 μs. (b) R values as a function of inter-pulse delay, normalized to short t_p value. Lines are fits according to Eq. (3).

concentrations. For neat PS-d$_3$ one recognizes only weak spectral changes, which is actually due to some other relaxation mechanism, while the spectral changes induced by large t_p values significantly grow with increasing TPP concentration. Explicitly, at $t_p = 200\ \mu$s the spectral intensity at zero frequency is the lower, the higher c is. It seems as if the fraction of PS molecules participating in the β-process grows with the fraction of TPP molecules present in the mixture. Figure 13(b) displays the corresponding evolution of $R(t_p)$. For all concentrations c > 0 $R(t_p)$ decays on similar t_p time scale ($\tau = (170 \pm 20)$ ms and $\beta = 1.28$), while for $c = 0$ (neat PS-d$_3$) a qualitatively different, slower decay is observed. The latter finding is in accordance with the fact that actually neat PS does not exhibit a β-process and another relaxation process may be active. For $c = 90\%$ and $c = 80\%$ $R(t_p)$ decays down to very low values at long delay times, while for $c \leq 50\%$ $R(t_p)$ appears to level off at different plateaus at longest t_p. In particular, a systematic trend of the final plateau to increase with decreasing concentration is recognized.

To access quantitatively the decay $R(t_p)$ and in particular the plateau at longest times t_p we describe the normalized decay by the following expression[25]

$$R_n(t_p, c) = f_\beta(c) \cdot \exp\left(-\left(\frac{t_p}{\tau}\right)^\beta\right) + (1 - f_\beta(c)), \qquad (3)$$

where $f_\beta(c)$ is interpreted as a fraction of molecules which contributes to the β-process, and τ and β are parameters describing the effective time evolution of the echo spectra. We note that the latter time constant is not identical with τ_β as determined from the DS spectra. In the case of TPP, a free fit by Eq. (3) to $R(t_p)$ (cf. Fig. 11) provides similar relaxation times τ (and similar $\beta = 0.95 \pm 0.05$) with a small trend to become somewhat shorter at low $c = 20\%$. Since a correlation between τ and τ_β is expectable, this is in accordance with the DS result where a weak trend to shorter τ_β is revealed for $c < 60\%$ (cf. Fig. 3). The long-time value $1 - f_\beta$ is not any longer zero but increases with decreasing TPP concentration. The corresponding value $f_\beta(c)$ reflecting the fraction of TPP molecules participating in the β-process is found in Fig. 14. The higher is the TPP concentration, the higher is the fraction of TPP molecules participating in the β-process. We note that in the case of ethanol, cyano cyclohexane, and toluene (Fig. 5(a)) we find a plateau value $1 - f_\beta = 0.0 \pm 0.04$ while in the case of neat TPP we find $f_\beta = 0.93$, i.e., $1 - f_\beta = 0.07 \pm 0.04$ putting our above given statement on a quantitative basis: in neat glasses essentially all molecules take part in the β-process while this is no longer the case in a binary system.

In the case of PS-d$_3$ a corresponding analysis of $R(t_p)$ along Eq. (3) (solid lines in Fig. 13(b)) provides essentially the same time constants, but, nevertheless, varying fractions of PS molecules participating in the β-process. The result is included in Fig. 14. With increasing TPP concentration also the fraction of PS molecules participating in the β-process grows quickly. It even appears that the fraction f_β of PS is higher than that of TPP. This excess fraction becomes most conspicuous at $c = 0$, where a plateu value of $f_\beta(c = 0) = 0.25$ is found. This is somewhat unreasonable, since, due to the absence of TPP molecules, no contribution to the β-relaxation is expected at all. One can argue that, due to some further

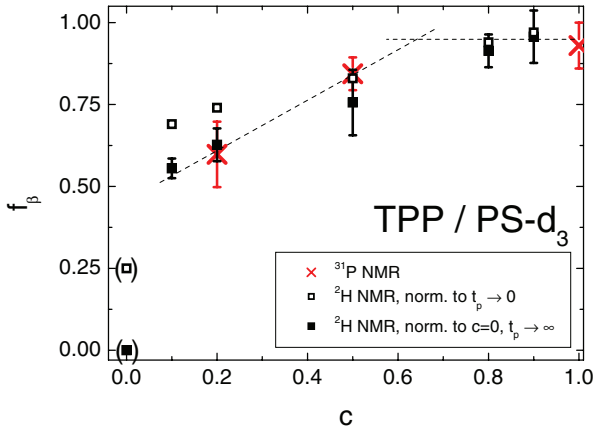

FIG. 14. Fraction of molecules of TPP (crosses) and PS-d$_3$ (full squares: normalized to behavior of neat PS-d$_3$; open squares: normalized to short t_p value) participating in the β-process as estimated by the Hahn-echo and solid-echo experiments. Dashed straight lines: A possible interpretation.

relaxation process in neat PS, $R(t_p)$ decays to some plateau which has to be taken into account also in the mixture. Thus renormalizing $1 - f_\beta$ by $1 - f_\beta(neat\ PS)$, the fraction f_β decreases and becomes similar to that of TPP. Thus the fractions of TPP and PS molecules participating in the β-process coincide for each concentration.

As discussed above, the dynamics of neat PS-d_3 and TPP have also been characterized by the spin-lattice relaxation monitored as a function of temperature (cf. Fig. 3(a)). No indication of a β-process shows up for PS-d_3 while below T_g in TPP the ^{31}P relaxation is clearly controlled by the β-process. The findings for the TPP/PS mixture with $c = 50\%$ are shown in Fig. 3(b). With respect to the neat components, the results are now quite different. Below T_g the temperature dependences $T_1(T)$ of TPP and PS-d_3 run parallel, i.e., the same strong temperature dependence is observed in both methods. Above T_g a minimum is found for TPP which reflects the isotropic reorientation of the TPP molecules in the mixture. A similar minimum occurring yet at higher temperatures is found for PS-d_3. This difference directly reflects the decoupling of the primary (isotropic) dynamics of the components: in the mixture PS reorients much slower than TPP, a fact well known from results on asymmetric binary glass formers.[42,43] There is a further feature the detailed discussion of which is postponed to a forthcoming publication: At temperatures for which the T_1 minimum of TPP occurs, particularities are also observed in the ^{2}H relaxation of PS-d_3. This shows that the fast isotropic dynamics of TPP affects the polystyrene monomers leading to a highly hindered (i.e., non-isotropic) dynamics, however, occurring at similar time scale as the TPP molecules. These findings demonstrate that a plasticizer molecule does not only change the T_g but also induces additional dynamics on the polymer.

As in the case of neat TPP the temperature dependence of the spin-lattice relaxation can be understood on a quantitative level by taking the dielectric results into account. These provide the dynamic susceptibility determined by a temperature independent distribution of activation energies, which actually does not change significantly in the mixture. Analogously to the case of ^{31}P dielectric susceptibility data can be compared to $T_1(T)$ of ^{2}H NMR after extrapolating it to higher frequencies. As can be seen in Fig. 3(b) (dashed line) the slope of $T_1(T)$ of TPP as well as PS-d_3 is reproduced.

IV. DISCUSSION AND CONCLUSION

We have studied the secondary (β-) relaxation process in the binary glass mixture TPP/PS by dielectric spectroscopy as well as TPP/PS-d_3 by ^{31}P and ^{2}H NMR. While neat TPP exhibits a β-process (type-B glass former) and neat polystyrene shows none (type-A), in the mixture also PS-d_3 molecules clearly participate in the β-relaxation. Here, for both TPP and PS-d_3, NMR spectra reveal a spatially highly restricted motion as identified by NMR in other type-B systems, like toluene[16,22] or ethanol.[17,23] Up to our knowledge a Hahn-echo sequence (here for ^{31}P) has been applied for the first time to monitor the subtle spectral changes deep in the glass characteristic of the β-process. The dielectric spectra reflect a distribution of activation energies which is temperature independent; yet, its asymmetric shape is rather unusual for β-processes and does not change with concentration, a phenomenon observed also in other binary glass formers.[25,43,44] Even at a TPP concentration of $c = 10\%$ the mean activation energy is still similar to that of neat TPP. The β-process introduced by the type-B component survives in the mixture and induces the type-A molecule to participate in the relaxation process. Yet, in contrast to neat systems not all molecules participate in the β-process; islands of rigidity or immobility appear. The higher the concentration of the type-B component the higher is the fraction of both components which participate. We emphasize, as we do not find any indication for the mixed glasses to decompose, the immobilized molecules are not part of crystalline regions. Instead the mixtures become glasses with inhomogeneously distributed dynamics. In a recent ^{2}H NMR study of another binary system (toluene/aroclor) an indication of a threshold concentration has been found below which immobile type-B molecules appear.[25] Although not sufficient NMR data at various concentrations has been collected in the present study a similar behavior can be anticipated also for TPP/PS-d_3. Only below, say, $c = 60\%$ some relevant fraction of TPP or PS-d_3 appear to become immobilized. This corresponds with the (slight) change of the mean activation energy below 60% (cf. Figs. 7 and 9).

All together the presented experimental findings point into the direction that also the β-process exhibits some cooperative nature. When mixed with type-B molecules, type-A molecules do react to the highly hindered motion introduced by the β-process, actually a behavior expected in (dense) condensed matter. A similar phenomenon is observed for the decoupled isotropic reorientation of the TPP molecules in the vitrified matrix of polystyrene. Whether the extent of spatial hindrance is the same for the two molecules is yet to be investigated. In any case both components show dynamics on the same time scale.

ACKNOWLEDGMENTS

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