Exchange Processes in Disordered Systems Studied by Solid-State 2D NMR

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1D and 2D ^{2}H NMR spectra of binary liquids were measured above and below the glass transition. We show that the molecular axes of the smaller molecules in these systems reorientate isotropically and that this dynamics is described by a broad distribution of correlation times. Further it is demonstrated that exchange processes within this distribution, i.e., exchange between fast and slow reorientational behavior of the molecules, are directly probed by measuring 2D NMR spectra. Exchange and reorientation occur on the same time scale.

1. Introduction

In disordered systems such as supercooled liquids or glasses, molecular dynamics is characterized by nonexponential correlation functions.[1,2] In the past, two possible explanations for that feature have been controversally discussed: homogeneous and heterogeneous dynamics. In the first case, an intrinsically nonexponential loss of correlation is assumed, whereas in the latter case, a spatially heterogeneous distribution of correlation times $G(\ln \tau)$ is supposed.[1] Several experimental techniques have been used in order to solve this problem for the dynamics close to the glass-transition temperature T_g, in particular, multidimensional NMR,[1,3−5] optical spectroscopy,[6] and dielectric nonresonant hole burning.[7] In all of the cited experiments, it was possible to select a subensemble of molecules with respect to the orientational correlation time. Thus, there are heterogeneous contributions on the time scale of the experiment. On the other hand, it has been demonstrated that the selected subensemble reequilibrates toward the dynamical behavior of the whole system. In the cited NMR,[1,3−5] and dielectric measurements,[7] changes of the correlation time have been observed that are on the time scale of the correlation time itself. Hence, the dynamics in the glass-transition regime are highly cooperative. In contrast to this, significantly longer lifetimes of the correlation time have been reported in the optical experiment,[6] where the dynamics of guest molecules in supercooled liquids were studied.

In the case of NMR measurements, a so-called reduced four-dimensional experiment was carried out to detect exchange processes within a distribution of correlation times. Here we want to demonstrate that even two-dimensional (2D) NMR directly proves the occurrence of exchange processes provided that the distribution of correlation times is sufficiently broad. More precisely, 2D NMR can be used to investigate dynamical exchange on the condition that a solid-state line shape and a motionally narrowed line (reflecting subensembles of molecules with sufficiently long and short correlation times, respectively) are simultaneously present in the 1D NMR spectrum. This precondition is not fulfilled in neat glass formers but in viscous binary liquids, as we want to demonstrate.

We have studied molecular dynamics in binary liquids consisting of small and large molecules close to T_g. The dynamics of the large molecules in binary liquids is essentially unchanged by the addition of the small molecules; i.e., they show the typical behavior of neat glass formers in a first approximation.[8] Some minor deviations will be discussed in another publication more comprehensively.[9] On the other hand, the dynamics of the small molecules is significantly different with respect to those of neat glass formers. They exhibit heterogeneous dynamical behavior with an extremely broad distribution of correlation times $G(\ln \tau)$ not too far above and even below T_g. As will be shown, binary liquids are model systems for an investigation of the nature of motional inhomogeneties.

2. Samples

The molecular dynamics of the deuterated components benzene (BE) or hexamethylbenzene (HMB) in an oligomer of styrene (OS) were investigated by ^{2}H NMR. We used OS that was produced by Polymer Standards Service. It was not deuterium-labeled and consisted of a narrow distribution of different chain lengths. The distribution was characterized by a weight average $M_w = 990$ g/mol and a ratio $M_w/M_n = 1.09$ (M_n: number average). The components were mixed in the NMR tube, degassed, and sealed. The concentration by weight of the samples was 26% BE in OS and 3.6% HMB in OS.

T_g was determined by means of differential scanning calorimetry. We define T_g by the first decrease of heat capacity while cooling because the step of heat capacity of mixed systems is significantly broadened compared to that of neat glass formers. The whole step extends over about 29 K for 26% BE in OS and about 17 K for 3.6% HMB in OS, but the first decrease could be determined with a precision of ±2 K. We found $T_g = 240$ K for the system BE/OS and $T_g = 294$ K for HMB/OS.

Over the whole chosen temperature range, anisotropic reorientations around the 6-fold axes of benzene and HMB and in addition methyl group reorientations in HMB are present, which are fast with respect to the value of the ^{2}H quadrupolar coupling constant. This leads to a motionally averaged spectrum and to short spin−lattice relaxation times ($T_1 < 1$ s). The latter fact is most important in order to obtain 2D NMR spectra within a reasonable time. A further investigation of these anisotropic motions is not the aim of this contribution. Instead, we focus on the reorientations of the 6-fold axes of benzene and HMB, which occur on a longer time scale as will be shown below. We note that only small deviations from an exponential behavior of the spin−lattice relaxation were found close to T_g.

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3. 2D NMR Spectra

In solid-state ^{2}H NMR, the NMR frequency ω (in the rotating frame) depends on the orientation of the external magnetic field with respect to the principal axes system of the electric-field gradient tensor. In the case of benzene and HMB, this tensor is averaged by the above-discussed fast anisotropic reorientations. The resulting tensor is symmetric and its principal *z*-axis points along the 6-fold axis of benzene or HMB. Thus, ω depends on the orientation of the molecule and is given by

$$\omega(\vartheta) = \pm(\delta/2)[3\cos^2(\vartheta) - 1] \tag{1}$$

where δ is the motionally averaged anisotropy parameter of benzene or HMB and ϑ the angle between the magnetic field and 6-fold symmetry axis. The two signs in eq 1 correspond to the two NMR transitions in the case of an $I = 1$ spin system.

In a 2D NMR experiment, ω—and consequently the orientation of the molecules—is measured at two times that are separated by a time interval called mixing time t_m. For the mixing time, the expression $T_2 \ll t_m \leq T_1$ should be valid. A detailed description of 2D NMR experiments is found in ref 1. If the molecular axis reorientates in the slow motion limit, i.e., for the corresponding correlation time τ applies $\tau \gg 1/\delta$, the 2D spectrum will map the joint probability density $P_{2|0}(\omega_1,\omega_2;t_m)$ to find the frequency ω_1 before the mixing time t_m and the frequency ω_2 afterward.[1] $P_{2|0}(\omega_1,\omega_2;t_m)$ can be written as product of the a priori probability density $P_{1|0}(\omega_1)$ and the conditional probability density $P_{1|1}(\omega_2;t_m|\omega_1)$:

$$P_{2|0}(\omega_1,\omega_2;t_m) = P_{1|0}(\omega_1)\cdot \mathrm{P}_{1|1}(\omega_2;t_m|\omega_1) \tag{2}$$

For simplicity, only one of the two NMR transitions of the $I = 1$ spin system is considered below. The complete 2D spectrum can be obtained by adding the contributions of both transitions. In glasses, $P_{1|0}(\omega_1)$ is given by a normalized 1D powder (Pake) spectrum $P_{\mathrm{powder}}(\omega_1)$ corresponding to a single transition.

If no reorientations of the molecular axis (6-fold axis of a benzene or HMB molecule) occur during t_m, i.e., $\tau \gg t_m$, ω_1 will equal ω_2 and the spectral intensity of the corresponding 2D NMR spectrum $S^{\mathrm{dia}}(\omega_1,\omega_2)$ is given by

$$S^{\mathrm{dia}}(\omega_1,\omega_2) \propto P_{2|0}(\omega_1,\omega_2) = P_{\mathrm{powder}}(\omega_1)\cdot\delta(\omega_2 - \omega_1) \qquad \tau \gg t_m \gg 1/\delta \tag{3}$$

Here $\delta(\omega_2 - \omega_1)$ denotes a delta function. A 1D powder spectrum is obtained along the diagonal of the complete 2D spectrum (cf. Figure 1a). Now, we consider reorientations of the molecular axis that lead after a time $t \gg \tau$ to a complete loss of orientational correlation. This motional behavior will be called isotropic reorientation in the following. In the case of such isotropic reorientations with $1/\delta \ll \tau \ll t_m$, the NMR frequency ω_2 after the mixing time becomes statistically independent of ω_1 and the spectral intensity $S^{\mathrm{reo}}(\omega_1,\omega_2)$ for this kind of motion can be written as

$$S^{\mathrm{reo}}(\omega_1,\omega_2) \propto P_{2|0}(\omega_1,\omega_2) = P_{\mathrm{powder}}(\omega_1)\cdot P_{\mathrm{powder}}(\omega_2) \qquad t_m \gg \tau \gg 1/\delta \tag{4}$$

As displayed in Figure 1b a box-like pattern results (cf. also ref 1).

If a broad distribution of correlation times (for example caused by different local enviroments of the molecules) determines the isotropic reorientation, the 2D spectra will be dominated by the above-discussed slow-motion line shapes and by a narrow central line $S^{\mathrm{ce}}(\omega_1,\omega_2)$ caused by molecules with $\tau \ll 1/\delta$. No discernible contributions from molecules with $\tau \approx 1/\delta$ are observed.[10,11] In addition, exchange between molecules with $\tau \ll 1/\delta$ and $\tau \gg 1/\delta$ may take place. Assuming that for all molecules exactly one exchange process between these two limiting cases occurs during t_m, the resulting 2D spectrum $\mathrm{S}^{\mathrm{ex}}(\omega_1,\omega_2)$ is determined by

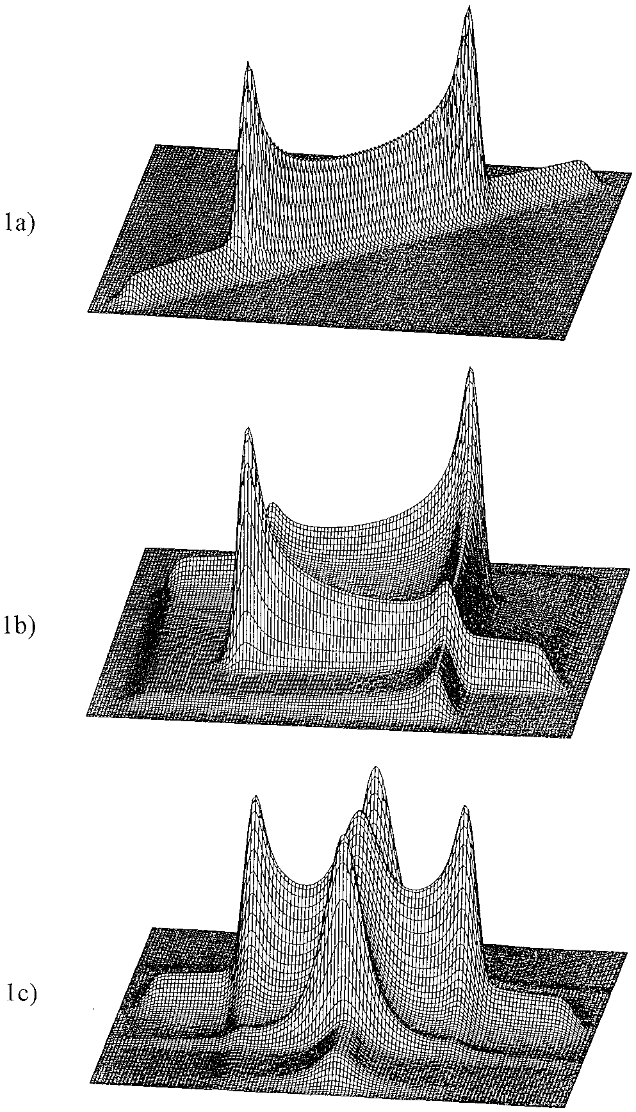

Figure 1. Simulated 2D spectra for (a) $t_m \ll \tau$ (no motion); (b) complete isotropic reorientation with $t_m \gg \tau \gg 1/\delta$; (c) one exchange process between fast ($\tau \leq 1$ μs) and slow reorientational behavior ($\tau \geq 1$ μs) of all molecules during mixing time.

$$S^{\mathrm{ex}}(\omega_1,\omega_2) \propto P_{2|0}(\omega_1,\omega_2) = P_{\mathrm{powder}}(\omega_1)\cdot P_{\mathrm{ce}}(\omega_2) + P_{\mathrm{ce}}(\omega_1)\cdot P_{\mathrm{powder}}(\omega_2) \tag{5}$$

where P_{ce} is given by the appropriately normalized 1D line shape of the central line—here a Lorentzian line. The simulated spectrum exhibiting a crosslike pattern is shown in Figure 1c. As will be demonstrated, all these spectral patterns S^i ($i \in \{\mathrm{dia,reo,ce,ex}\}$) can be found in 2D spectra of viscous binary liquids.

4. Experimental Details

All NMR experiments were carried out on a Bruker DSX 400 spectrometer with a magnetic field strength of 9.4 T corresponding to a ^{2}H Larmor frequency of 61.4 MHz. The

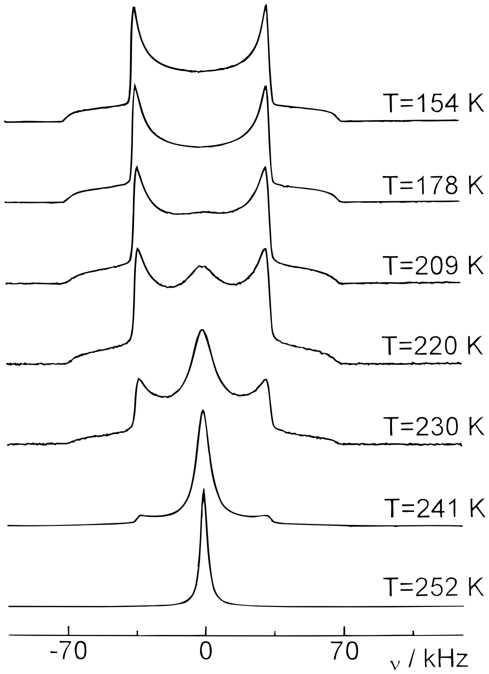

Figure 2. ^{2}H NMR spectra of 26% benzene in oligomeric styrene (T_g = 240K).

duration of the 90° pulses was between 2.7 and 2.9 μs. A flow of nitrogen gas controlled by a Bruker VT 2000 heating unit was used to adjust the sample temperature; no significant temperature gradients were present. The absolute values of temperature were corrected according to a calibration with an additional thermocouple because deviations between set and real temperatures appeared. They are correct within ±1 K. The variation of temperature with time is assumed to be less than 1 K. A solid-echo pulse sequence with a delay of 20 μs between both pulses was used to measure the 1D NMR spectra.[1] The 2D NMR experiments were carried out by applying a five-pulse sequence with an appropriate phase cycle as described in ref 12 (the minimal phase cycle consists of eight scans). The delay Δ between the first and the second as well as between the fourth and the fifth pulse was set to 20 μs. Cosine and sine time signals were separately measured. In each time dimension, 256 real data points were recorded with a dwell time of 2 and 4 μs for benzene and HMB, respectively and then zero-filled up to 512 points. After a Fourier transformation, both data sets were added by applying a proper weight factor, which was chosen in such a way that unwanted signal contributions along the minor diagonal were canceled in a first approximation.[1] The experimental spectra were symmetrized with respect to the diagonal in order to improve the signal-to-noise ratio. This was done only after ascertaining that no significant asymmetry was suppressed. About 160 scans with a recycle delay of 700 ms were accumulated for the system BE in OS and about 96 scans with a recycle delay of 2 s for HMB in OS. A complete 2D spectrum took about 24 h.

5. Results

In Figure 2 the 1D spectra of benzene in oligomeric styrene are shown. Whereas at lowest temperatures ($T < 178$ K) the typical ^{2}H NMR powder spectrum is found, at the highest temperature ($T = 252$ K) a narrow central line is observed. In the temperature range between, the spectra can be approximately described by a superposition of these both line shapes with a temperature-dependent weighting factor $W(T)$ representing the fraction of the central line. The spectra can be explained in the heterogeneous picture assuming a broad distribution of correlation times $G(\ln \tau)$ for an isotropic reorientation of the 6-fold axes of the benzene molecules. Molecules with long correlation times $\tau \gg 1/\delta$ contribute to the Pake spectrum, those with $\tau \ll 1/\delta$ to the central line. Molecules with $\tau \approx 1/\delta$ can be neglected, because a broad distribution is present.[10] For benzene and HMB at the chosen temperatures, δ is of the order of 100 kHz. Since the center of $G(\ln \tau)$ shifts to longer correlation times while cooling, the corresponding fraction of fast moving molecules $W(T)$ decreases continuously. Qualitatively the same behavior is found for the 1D spectra of HMB in OS. We note that in the case of an extremly broad distribution of correlation times that contains only a small fraction of molecules with $\tau \approx 1/\delta$ the weighting factor W can be approximately interpreted as the a priori probability to find a molecule with a correlation time $\tau \ll 1/\delta$, whereas $1 - W$ represents the a priori probability to observe $\tau \gg 1/\delta$. This fact will be exploited below analyzing the 2D NMR spectra.

Looking at the 2D spectra, the existence of a broad distribution $G(\ln \tau)$ for an *isotropic* reorientation of the 6-fold axes can be clearly seen. For that purpose, 2D spectra of BE/OS for mixing times $t_m \approx 100$ ms but various temperatures are displayed in Figure 3 and 2D spectra of HMB/OS for different t_m at $T = 299$ K are shown in Figure 4. Observing the different spectra of HMB/OS and that of BE/OS at $T = 209$ K, it is obvious that, besides some diagonal intensity, off-diagonal intensity appears as the boxlike pattern S^{reo}. As explained, this pattern is typical of slow isotropic molecular reorientations (cf. also Figure 1b). At higher temperatures a central line is present in the 2D spectra of BE/OS as well. This indicates a fraction of fast isotropically reorientating molecules with $\tau \ll 1/\delta$. We conclude that benzene as well as HMB molecules in OS perform an isotropic reorientation on various time scales.

The presence of a *continuous* distribution becomes clear by inspecting the mixing-time dependence of the 2D spectra of HMB/OS in Figure 4. An increase of the off−diagonal intensity with increasing mixing time t_m can be seen. On the other hand, the diagonal intensity S^{dia} (cf. Figure 1a) caused by molecules that do not reorientate during t_m decreases. Thus, more and more molecules reorientate during t_m with an extension of this time parameter as is expected by a continuous distribution of correlation times. The statement of a continuous distribution is further confirmed by the simultaneous presence of diagonal intensity, boxlike pattern and central line in the spectrum of, for example BE/OS at $T = 230$ K (cf. Figure 3). It is possible to estimate the minimal width of $G(\ln \tau)$ from this spectrum. The appearance of the central line reveals the existence of molecules with $\tau \leq 1$ μs. On the other hand, there is strong diagonal intensity caused by molecules, which have not reorientated during $t_m = 150$ ms. Therefore, the distribution of correlation times extends over at least 5 decades. Such broad distributions $G(\ln \tau)$ are not found in neat glass formers.[1]

So far, a scenario of completely heterogeneous dynamics was sufficient to explain the observed spectral patterns. Now we demonstrate that exchange processes within the broad distribution $G(\ln \tau)$ lead to additional features in the measured 2D spectra. Looking at the 2D spectra of BE/OS at $T = 230$ K and $T = 240$ K more closely (cf. Figure 3), it becomes obvious that the off-diagonal patterns are completely different from that expected for slow isotropic reorientations. Strong intensity along the frequency axes is now observed. This crosslike pattern can be recognized best in the contour plots (cf. Figure 5, left). A cut along $\omega_1 = 0$ or along $\omega_2 = 0$ yields in each case a Pake

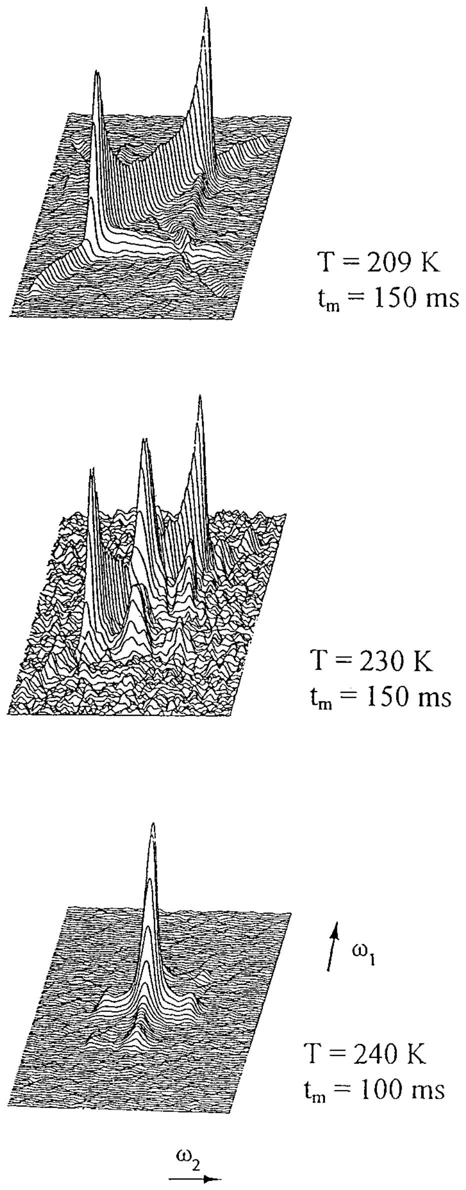

Figure 3. 2D spectra of 26% benzene in oligomeric styrene at different temperatures with t_m of the order of 100 ms. Displayed spectral range in each dimension −80 to 80 kHz.

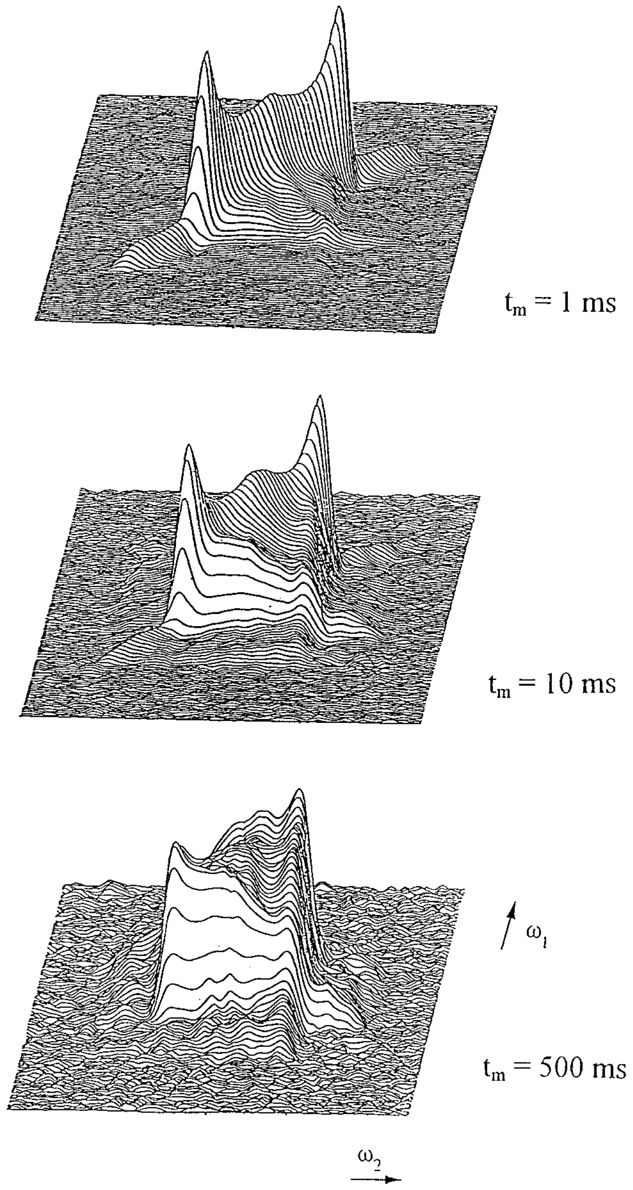

Figure 4. 2D spectra of 3.6% HMB in oligomeric polystyrene at $T = 299$ K for different mixing times t_m ($T_g = 294$ K). Displayed spectral range in each dimension: −25 to 25 kHz.

spectrum, and the 2D spectra resemble that of S^{ex} in Figure 1c. From these findings we conclude that some of the molecules have interchanged their correlation times: fast isotropically reorientating molecules at $t = 0$, which contribute to the central line ($\omega_1 \approx 0$), have become sufficiently slow during t_m, and ω_2 is determined by their orientation with respect to the external magnetic field; i.e., the distribution of the additional spectral intensity along $\omega_1 = 0$ is represented by a Pake spectrum. Vice versa, slow molecules, which have become fast during t_m, are observed along $\omega_2 = 0$. Of course, not all molecules have exchanged their correlation times during t_m. Molecules that have reorientated but not exchanged and those that have neither reorientated nor exchanged during t_m, contribute to the 2D spectra at $T = 230$ K and $T = 240$ K (cf. Figure 3), too. As will be demonstrated below, the spectra can be approximately described by a weighted superposition of the spectral patterns S^i discussed in section 3. Because of the dependence of the line shape on the correlation time, it can be concluded that the observed exchange takes place between $\tau \le 1\ \mu$s and $\tau \ge 1$ ms. We note that also in the case of HMB in OS a small exchange pattern on top of the pattern typical of isotropic reorientation can be recognized (cf. Figure 4).

To get information about the time scale of this exchange, the spectra of BE/OS at $T = 230$ K for different t_m are displayed in Figure 5. The crosslike intensity grows with t_m increasing from 1 to 150 ms (see also the spectrum of BE/OS at $T = 230$ K with $t_m = 150$ ms in Figure 3). This fact can be closer examined in a first approximation by integrating over the intensity along the frequency axes without the origin and over the other off-diagonal intensity separately. To correct for spin−lattice relaxation, the resulting intensities should be divided by the intensity of the whole 2D spectrum. However, a separation of intensity caused by molecular reorientation on one hand and by exchange on the other hand is not possible with this method because the mixing-time dependence of the boxlike pattern contributes to the values of the intensities along the axes as well and because exchange processes can cause intensity in the other off-diagonal area. The latter fact will be discussed below, whereas the first is avoided using another kind of evaluation. As shown in Figure 6, the 2D spectra $S(\omega_1,\omega_2;t_m)$ of the benzene

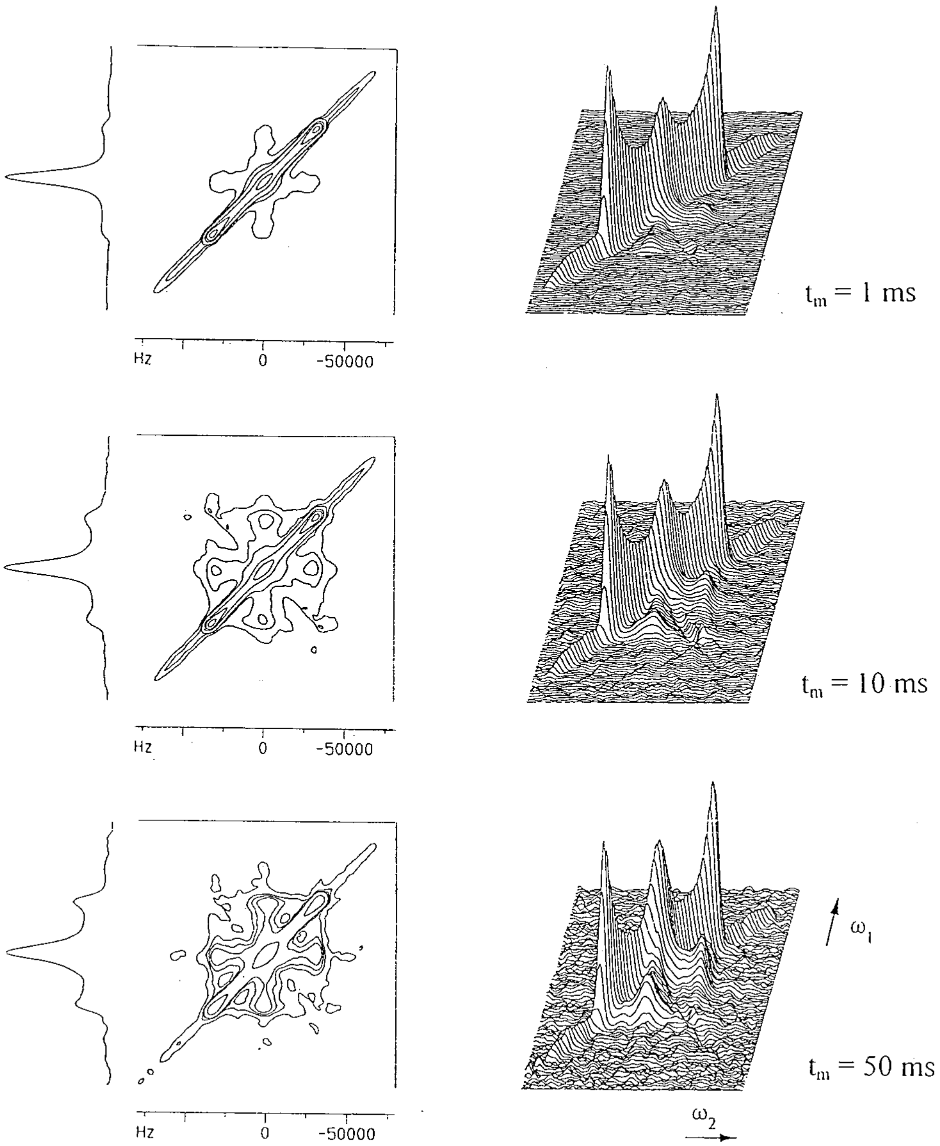

Figure 5. 2D spectra of 26% benzene in oligomeric styrene at $T = 230$ K for various t_m. A cut along $\omega_2 = 0$ is displayed in the contour plots.

molecules in the binary liquid BE/OS can be described by a weighted superposition of all of the above-discussed line shapes $S^i(\omega_1,\omega_2)$

$$S(\omega_1,\omega_2;t_m) \propto p_{\mathrm{dia},t_m} S^{\mathrm{dia}}(\omega_1,\omega_2) + p_{\mathrm{reo},t_m} S^{\mathrm{reo}}(\omega_1,\omega_2) + p_{\mathrm{ce},t_m} S^{\mathrm{ce}}(\omega_1,\omega_2) + p_{\mathrm{ex},t_m} S^{\mathrm{ex}}(\omega_1,\omega_2) \quad (6)$$

For simplicity, the spectral patterns S^i are here scaled in such a way that they have equal integral spectral intensity $I = \int\int \mathrm{d}\omega_1\, \mathrm{d}\omega_2\, S^i(\omega_1,\omega_2)$ and the weighting factors p_{i,t_m} are normalized according to $p_{\mathrm{dia},t_m} + p_{\mathrm{reo},t_m} + p_{\mathrm{ce},t_m} + \mathrm{p}_{\mathrm{ex},t_m} = 1$. In this case, the values p_{i,t_m} directly represent the fraction that is contributed by the different spectral patterns S^i to the whole 2D spectrum $S(\omega_1,\omega_2;t_m)$. The weighting factors depend parametricly on the mixing time t_m.

One reason for the good agreement of experimental results and spectra obtained by this simple model is again the extremely broad distribution of correlation times. As in the case of 1D NMR spectra, the effect of correlation times $\tau \approx 1/\delta$ can be neglected.[10,11] Deviations from a description of the experimental spectra with our model due to the influence of molecules with $\tau \approx t_m$ depend on the kind of the motion. For an isotropic rotational diffusion or any small angle reorientation on the whole, differences are expected to be larger than for a random-jump model. Whereas in the case of rotational diffusion only correlation times $t_m \gg \tau \gg 1/\delta$ lead to a 2D spectrum as described by S^{reo}, the 2D spectra resulting from a random-jump with correlation times $\tau \gg 1/\delta$ are a weighted superposition of only S^{dia} and S^{reo} as was demonstrated in ref 1. Therefore, the good agreement of experimental data and spectra calculated according to the superposition of eq 6 might be an indication that the random-jump model applies rather than small angle reorientations. Other NMR measurements support this supposition.[9]

Carrying out an evaluation of the 2D spectra of BE/OS at $T = 230$ K for different mixing times t_m with our model, the evolution of the different fractions p_i as a function of t_m will result ($p_i(t_m)$). In Figure 7, $p_{\mathrm{dia}}(t_m)$, $p_{\mathrm{reo}}(t_m)$ and $p_{\mathrm{ex}}(t_m)$ are shown. It is obvious that both p_{reo} and p_{ex} grow with increasing t_m. The mixing time dependence of p_{ex} can be explained qualitatively: If short mixing times ($t_m \leq 10$ ms) are applied so that in a first approximation at most one exchange process between slow ($\tau \geq 1$ ms) and fast ($t \leq 1$ μs) reorientational behavior takes place, each exchange slow−fast or fast−slow will lead to intensity along the frequency axes. Hence, the contribution of S^{ex} to the spectral intensity of the complete 2D

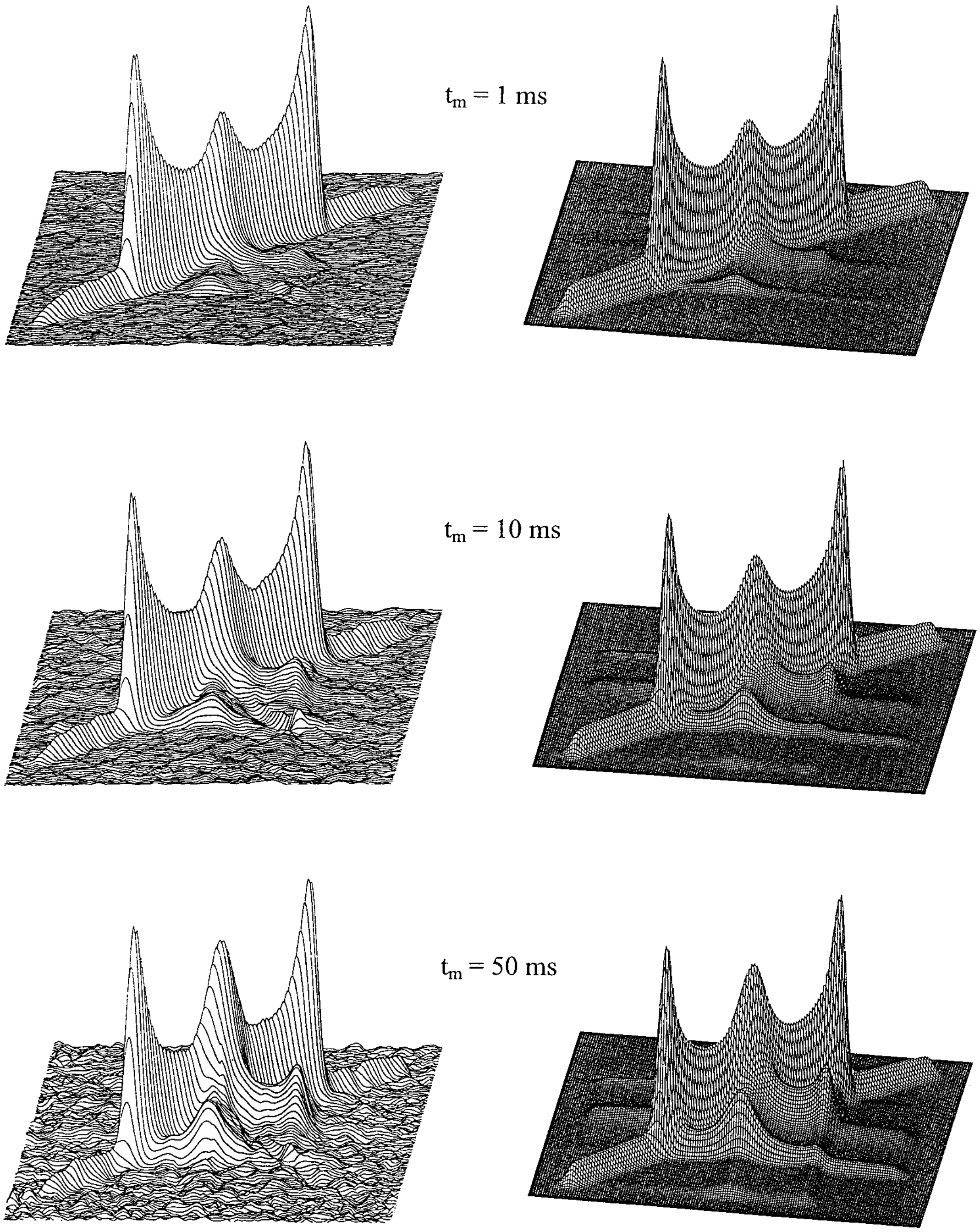

Figure 6. Measured (left) and according to eq 6 simulated (right) 2D NMR spectra of 26% benzene in oligomeric styrene at $T = 230$ K for $t_m =$ 1 ms, $t_m = 10$ ms and $t_m = 50$ ms.

spectrum increases fast. Using mixing times $t_m > 10$ ms, the occurrence of manifold exchange processes during t_m becomes more probable. This leads to a saturation behavior of $p_{ex}(t_m)$. For example, 2-fold exchange during the mixing time does not cause intensity along the frequency axes: On one hand exchange fast−slow−fast contributes to S^{ce} because $\tau \ll 1/\delta$ applies before and after t_m; on the other hand exchange slow−fast−slow contributes to S^{reo} because ω_1 as well as ω_2 are determined by the well-defined orientations before t_m and afterward but all orientational correlation is lost during the state of fast reorientational behavior. Therefore, molecules that change their correlation time two times and also those that change τ another even number of times during t_m do not contribute to S^{ex}, and the slope of $p_{ex}(t_m)$ becomes smaller. For $t_m \rightarrow \infty$, saturation should be reached. Assuming that all molecules have exchanged their correlation time sufficiently often during a mixing time $t_m \rightarrow \infty$, the value $p_{ex}(t_m \rightarrow \infty)$ can be calculated from the weighting factor W of the 1D NMR spectrum. In this special case, the correlation time of the molecules after t_m becomes independent of that before and the probability to find fast ($\tau \ll 1/\delta$) and slow ($\tau \gg 1/\delta$) reorientational behavior is approximately determined by W and $1 - W$, respectively. Therefore, $p_{ex}(t_m \rightarrow \infty)$ is given by

$$p_{ex}(t_m \rightarrow \infty) = W(1 - W) + (1 - W)W = 2W(1 - W) \quad (7)$$

Some deviations can occur due to the existence of molecules with $\tau \approx 1/\delta$ and due to the applied echo techniques in order to obtain the 1D and 2D NMR spectra. In our case of BE/OS at 230 K, a weighting factor W of 0.36 leads to $p_{ex}(t_m \rightarrow \infty) =$ 0.46. The values of p_{ex} have been fitted with a Kohlrausch−Williams−Watts function $f(t_m) = p_{ex,\infty}[1 - \exp(-(t_m/\tau_{ex})^{\beta})]$

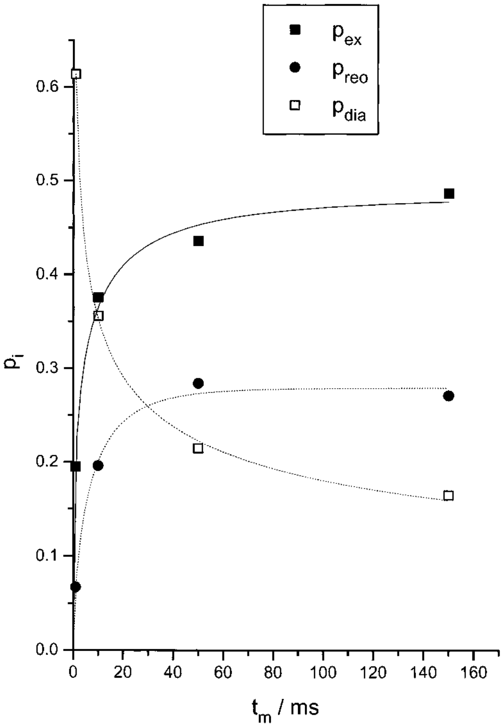

Figure 7. Fractions p_{dia}, p_{reo} and p_{ex} of the corresponding spectral patterns S^{dia}, S^{reo} and S^{ex} as function of the mixing time t_{m}. The solid line represents a fit of p_{ex} with a Kohlrausch−Williams−Watts function $f = 0.48[1 - \exp(-(t_{\text{m}}/4.5\ \text{ms})^{0.42})]$; the dashed lines are a guide for the eye.

yielding $p_{\text{ex},\infty} = 0.48$, $\tau_{\text{ex}} = 4.5$ ms, and $\beta = 0.42$ in good agreement with the prediction. The results are estimated to be correct within 10% of the absolute values.

As explained above, p_{reo} is influenced by exchange processes and does not only represent the reorientation of the molecules. However for short mixing times $t_{\text{m}} \leq 10$ ms, contributions of manifold exchange processes during t_{m} can be disregarded in a first approximation. Then, $p_{\text{reo}}(t_{\text{m}})$ represents the intensity caused by slow molecular reorientations, and the time scales of reorientation and exchange of the molecules can be compared. As is seen in Figure 7, $p_{\text{reo}}(t_{\text{m}})$ and $p_{\text{ex}}(t_{\text{m}})$ increase with very similar time constants. Thus, we conclude, that reorientation and exchange of benzene molecules in oligomeric styrene occur on the same time scale.

6. Conclusions

Our results clearly prove that the motional heterogeneities observed in the 1D spectrum of the small molecules in a binary liquid close to T_g are actually dynamical in nature. In our case of an extremly broad distribution of correlation times, this evidence can be provided without having to recourse to NMR experiments of higher dimension than 2D. The time scale of exchange processes between fast and slow reorientational behavior can be determined: the exchange takes place on the same time scale as the correlation time of the slowly reorientating molecules. Therefore, as in the case of neat glass formers, the dynamics of the small molecules in binary liquids is highly cooperative. Furthermore, we note that the cross-peaks indicating exchange processes are also found in the glassy state (cf., for example Figure 3, $T = 230$ K). Thus, the small molecules behave like a liquid in the glass, too. This dynamical behavior of the small molecules was also found in binary liquids containing high molecular weight polystyrene instead of OS[8] and in binary liquids consisting of benzene in tricresyl phosphate.[9] The latter fact shows that the dynamics of the small molecules is not caused by a polymer effect. However, it is still not clear whether the exchange takes place because translational diffusion occurs or whether the oligomer matrix exhibits small-angle reorientations and such kinds of matrix fluctuations enable a reorganization of the correlation times.[8,9] 1D and 2D NMR experiments on deuterated large molecules in binary liquids are in preparation to answer this question.

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