

LETTERS

Type A versus Type B Glass Formers: NMR Relaxation in Bulk and Confining Geometry

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We report ²H NMR spin–lattice relaxation times T_1 and spectra of two fragile molecular glass forming liquids, deuterated *o*-terphenyl-*d*₁₄ (OTP) and toluene-*d*₅, confined in a nanoporous SBA-15 type matrix with a pore diameter of 7.1-nm size. We compare these results with bulk data of several glass formers. The temperature dependence of T_1 allows us to differentiate type A (without secondary β process) from type B glass formers (with β process). We find that the α process of both OTP (type A) and toluene (type B) in confinement is governed by a broad heterogeneous distribution of correlation times, not seen in the bulk. Additionally, there is evidence that the β process in toluene changes under confinement conditions, where it exhibits a distribution of spin–lattice relaxation times that is substantially broadened toward faster times. In contrast, the excess wing for OTP is not altered in confinement.

Introduction

Supercooled liquids exhibit a main relaxation (α process), which determines the long-time behavior of any correlation function. While cooling the liquid toward the glass transition temperature T_g , secondary relaxation processes emerge, which characterize the dynamic response at intermediate times, that is, between fast dynamics (ps) and the α process. Two phenomena are distinguished, namely, the Johari–Goldstein (JG) β process and the excess wing.^{1–3} The JG process is identified as a secondary relaxation peak, whereas the excess wing is observed as a distinct power law on the high-frequency side of the α peak. Not all glass formers show a β process but rather only an excess wing, which degenerates to a nearly constant-loss (NCL) behavior at $T < T_g$.³ For these systems,

Kudlik et al. introduced the term type A glass formers to differentiate them from type B glass formers that exhibit a discernible β peak.³

The nature of secondary processes is currently widely discussed.² NMR⁴ and solvation⁵ techniques demonstrated that essentially all molecules participate in a spatially highly restricted motion. Recently, the distinction between type A and type B glass formers was challenged, and the excess wing was regarded as a peculiar JG β process.^{2,6} Because the mean time constant of the β process follows an Arrhenius law ($T < T_g$), the β process is considered to be rather “local” as compared to the α process.² The latter is governed by some cooperativity, but correlation lengths of not more than of a few nanometers are discussed.^{7,8} To address this question, we investigated supercooled liquids in confining geometries;^{9–11} yet, no quantitative estimation of a correlation length emerges from these experiments because, in addition to finite size effects, surface effects play an important role.¹⁰ Moreover, confinement induces a significant broadening of the relaxation spectrum, as compared

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to the bulk, rendering it somewhat ambiguous to define a characteristic time constant.

Most studies on supercooled liquids in confining geometries focused on the α process, whereas not much attention was given to secondary relaxation processes. The main purpose of the present work is to demonstrate that changes in the secondary relaxations occur when the supercooled liquid is confined to nanometer-sized pores. These changes can be monitored by measuring NMR relaxation, and hence, one may hope that the controversy about the nature of excess wing and JG β process can be settled by such experiments. In addition, our NMR studies allow us to draw important conclusions concerning the α process under confinement conditions.

As a first approach, we investigate the type B glass former toluene and the type A glass former *o*-terphenyl (OTP) confined in nanostructured porous silicates of SBA-15 type. These materials offer a unique possibility to study the confined phases in highly regular geometries with a pore diameter of 7.1 nm and different surface interactions. The dynamics are monitored by measuring ^2H NMR spin–lattice relaxation and line shape. We further compare the relaxation behavior of both types of glass formers in the bulk. Although in early experiments¹ a β process had been observed in OTP, this was not confirmed in more recent work. Wagner and Richert¹² showed that a secondary process in OTP occurs only when the liquid is quenched into the glass, whereas the secondary relaxation peak disappears when the system is annealed and it is not observed when the systems is slowly cooled. This is confirmed by our NMR measurements (cf. below). In the case of toluene, dielectric and NMR studies demonstrated the presence of a strong JG β process.^{3,4}

A significant surface effect is induced by the large surface-to-volume ratio of porous systems. Its influence on the dynamical properties of the confined fluid depends strongly on the nature of the fluid–wall interaction.^{13,14} As a consequence, the pore size dependence of the calorimetric glass transition temperature T_g becomes nontrivial and depends on the interplay of finite size effects and surface effects (and possibly on density changes in confinement when compared to the bulk¹⁰). Slower dynamics and higher values of T_g than in the bulk are observed for small pore diameters d , small being referred to the size σ of the molecules, that is, for d smaller than roughly 10σ . However, in this case, a postsynthesis surface treatment, like silanization, can play a major role. It can suppress large interactions with polar molecules and, hence, lead to a lower rather than a higher value of T_g , or it may introduce an amplified corrugation. In contrast, faster dynamics and lower values of T_g are systematically observed for larger pore size, that is, for d larger than and decreasing to roughly 10σ , depending on the surface treatment and the shape of the pore. This latter behavior was interpreted as resulting from the topological limit imposed by confinement on the development of spatially heterogeneous dynamics in the viscous liquid. These complex situations were noticed for both toluene¹⁰ and OTP.¹⁵

The SBA-15 samples were synthesized according to the procedure reported in ref 16. They are formed of parallel cylindrical pores arranged in a honeycomb-type lattice with a narrow pore size distribution. The length to diameter ratio is greater than 1000. Their structure was confirmed by small- and wide-angle neutron scattering experiments,¹³ and the porosity was checked by adsorption isotherms of nitrogen at liquid nitrogen temperature. The pore volume and specific surface area of the materials were calculated using the standard BET method, and pore sizes, by applying the BJH method. The pore diameters

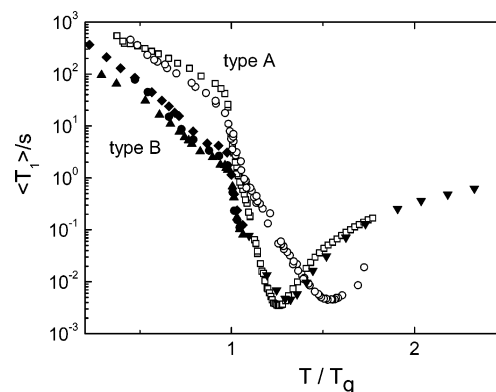


Figure 1. Temperature behavior of the ^2H NMR spin–lattice relaxation time $\langle T_1 \rangle$ in type A and type B glass formers. Type A systems: *o*-terphenyl- d_{14} ($\omega_L/2\pi = 55$ MHz,¹⁷ \square) and glycerol- d_5 ($\omega_L/2\pi = 55$ MHz,¹⁸ \circ). Type B systems: toluene- d_5 ($\omega_L/2\pi = 46$ MHz, \blacktriangle , this work, and $\omega_L/2\pi = 55$ MHz,¹⁹ \blacktriangledown), 45% chlorobenzene- d_5 /decalin ($\omega_L/2\pi = 46$ MHz, \bullet , this work), and 45% chlorobenzene/decalin- d_{18} ($\omega_L/2\pi = 46$ MHz, \blacklozenge , this work).

of the present matrixes are 7.1 and 8.0 nm, respectively. Postsynthesis silanization of the surface of the 8.0-nm sample was carried out, leading to a pore diameter of 7.1 nm as checked again by N_2 adsorption isotherms.

Considering all of these aspects in a simple way, we have chosen as a start to perform experiments on toluene- d_5 ($\sigma \approx 5$ Å) confined in silanized SBA-15 materials, that is, we are in the limit $d/\sigma > 10$ (here, 14), so that finite size effects are expected to dominate the overall dynamics of the liquid. Consistently, $T_{g,\text{confined}} \approx 112$ K is found, which is somewhat lower than the bulk value $T_g = 117$ K. Furthermore, we study OTP- d_{14} ($\sigma \approx 8$ Å) confined in a unsilanized SBA-15 matrix with some silanol groups at the surface. In this case, we are in the limit $d/\sigma < 10$, (here, 8), where the surface plays a dominant role. For this sample, we observe $T_{g,\text{confined}} \approx 265$ K, higher than the bulk value of 248 K as measured by DSC.

Results and Discussion

In Figure 1, we compare the temperature dependence of the ^2H spin–lattice relaxation time of type A (OTP- d_{14} ¹⁷ and glycerol- d_5 ¹⁸) and type B glass formers in the bulk (toluene- d_5 , this work and ref 19, 45% chlorobenzene- d_5 in decalin, and 45% chlorobenzene in decalin- d_{18} , this work). Below T_g , the relaxation is nonexponential, and the time constant $\langle T_1 \rangle$ as given by the integral over the normalized spin–lattice relaxation function (cf. eq 2) is plotted as a function of the reduced temperature T/T_g for the purpose of comparison. At $T > T_g$, a minimum associated with the α process is observed at similar temperatures (except for glycerol). For glycerol, because of its low degree of fragility, the minimum occurs at higher temperatures. An important difference can be found on the low-temperature side of the minimum, that is, close to and below T_g . Here, $\langle T_1 \rangle$ of type A glass formers is longer than that of type B glass formers by a factor of 10 and exhibits a different temperature dependence. These differences result from the enhancement of the spectral density in type B systems due to the presence of the β process. We also find that the relaxation times among type A and type B systems, respectively, are quite similar. For type B glass formers, this is a direct consequence of the fact that the activation energy E of the β process is given by $E \approx 24 T_g$. Furthermore, its amplitude $(1 - S)$ and even the shape of the spectral density $J_\beta(\omega)$ are similar.^{3,4} Here, S is the fraction of correlation relaxed by the α process. At $T < T_g$, the structural relaxation no longer contributes to the spin–lattice

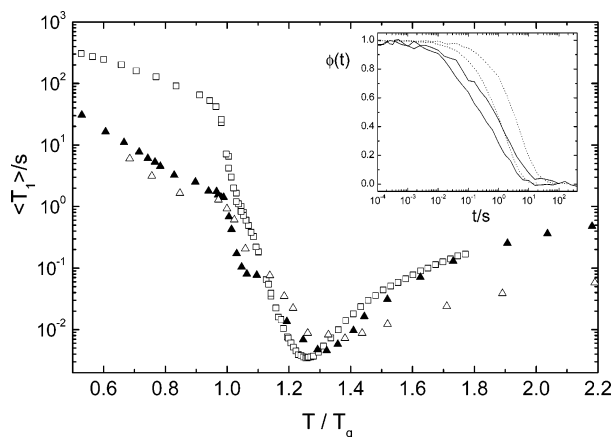


Figure 2. ^2H NMR spin–lattice relaxation time $\langle T_1 \rangle$ of bulk toluene- d_5 (\blacktriangle), toluene- d_5 confined in silanized SBA15 (\triangle), and for comparison, $\langle T_1 \rangle$ of bulk OTP- d_{14} (\square); error bars are smaller than symbol size. (Inset): Corresponding relaxation curves below T_g . Solid line, toluene in SBA-15 at $T = 85$ and 109 K; and dashed line, bulk toluene at $T = 87$ and 109 K.

relaxation, and one can write in fair approximation

$$\frac{1}{\langle T_1 \rangle} \propto \left\langle \frac{1}{T_1} \right\rangle \propto (1 - S)J_\beta(2\omega_L) \quad (1)$$

with ω_L being the Larmor frequency.²⁰ For the mixture of chlorobenzene/decalin, this means that despite their different size and mass, both components participate in the same way in the β process. Similar results were reported by a solid echo study analyzing the corresponding line shape changes.²¹ Regarding the behavior $\langle T_1 \rangle(T)$ of type A glass formers close to and below T_g , Blochowicz et al.²⁰ demonstrated that the excess wing determines the relaxation. We conclude that type A and type B glass formers can be distinguished via their behavior in the spin–lattice relaxation.

Figure 2 presents the ^2H spin–lattice relaxation time of toluene- d_5 that was confined as explained above as a function of the reduced temperature. The data are compared with the relaxation times that were obtained for bulk toluene- d_5 and bulk OTP- d_{14} . Three temperature ranges deserve attention: around the minimum of $\langle T_1 \rangle(T)$, around T_g , and well above the temperature of the minimum. In the confinement, the relaxation time is longer by a factor of 2 near the minimum of $\langle T_1 \rangle(T)$, whereas it is considerably shorter at the highest temperatures, as compared to the bulk data. As demonstrated many times,^{17–19,22} the $\langle T_1 \rangle(T)$ curves around the minimum can be well described by assuming a Cole–Davidson spectral density in the Bloembergen–Pound–Purcell expression for the relaxation rate, in other words, by introducing a distribution of correlation times $G(\ln \tau_\alpha)$. At $\omega\tau_\alpha \cong 1$, that is, at the minimum of $\langle T_1 \rangle(T)$, one can write $\langle T_1 \rangle_{\min} \propto \beta_{\text{CD}}^{-1}$, with β_{CD} being the Cole–Davidson width parameter. Because, in the case of confined toluene- d_5 , the minimum is higher than that in the bulk by a factor of ~ 2 , one can estimate that the distribution of the α correlation time, $G(\ln \tau_\alpha)$, is broader than that in bulk toluene- d_5 by a factor of 2, which is consistent with previous work using inelastic neutron scattering.^{15,23} The heterogeneous character of the distribution in confinement is confirmed by line-shape analysis. This will be demonstrated below for the case of OTP, which shows similar spectra to toluene.

The low-temperature behavior ($T < T_g$) of the $\langle T_1 \rangle(T)$ curves for bulk and confined toluene are different, too. Here, the relaxation behavior is determined by the β process. Thus, we can conclude—and this is a major contribution of the present

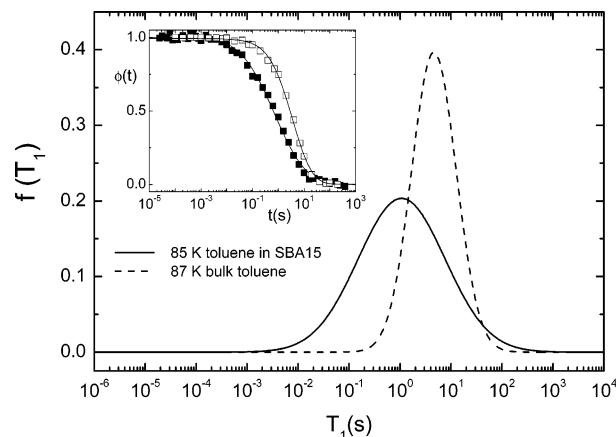


Figure 3. Distribution of relaxation times $f(\ln T_1)$ (log Gaussian) reflecting in first approximation the distribution $G(\log \tau_\beta)$ of the β process in toluene: bulk (---) versus confined (—). (Inset): Relaxation curves fitted by a log Gaussian. Solid symbols, toluene confined in SBA-15 at $T = 85$ K; and open symbols, bulk toluene at $T = 87$ K.

work—that not only the α process but also the β process is affected by the confinement. By comparing the relaxation curves at these temperatures (cf. inset of Figure 2), we see that the relaxation is more stretched in the confinement; thus, not only the average $\langle T_1 \rangle$ but also the width of the distribution $f(T_1)$ is altered. Because we are in the glass ($T < T_g$), no dynamical exchange is expected, and the nonexponential spin–lattice relaxation reflects the heterogeneous dynamics of the β process. Therefore, the normalized spin–lattice relaxation function provides the average²²

$$\Phi(t) = \frac{M_\infty - M(t)}{M_\infty} = \int f(T_1) e^{-t/T_1} dT_1 = \langle e^{-t/T_1} \rangle \quad (2)$$

where $M(t)$ is the magnetization and M_∞ its equilibrium value. As previously noted, the distribution $f(T_1)$ reflects the heterogeneous dynamics of the β process. Convoluting an exponential decay with a log Gaussian distribution $f(T_1)$ provides an estimate of $\Phi(t)$. As illustrated in Figure 3, the distribution in confinement is significantly broadened toward faster times. However, a clear-cut conclusion concerning the change of the distribution $G(\ln \tau_\beta)$ is not straightforward. In a strict sense, eq 1 holds only for one site in the glass because the relaxation strength $(1 - S)$ may depend on the site in the glass, for example, on the activation energy E of the β process. Because the β process is slow with respect to the NMR time scale, that is, $\omega\tau_\beta \gg 1$ and, hence, for a given site $1/T_{1,i} = (1 - S_i)C/\tau_{\beta,i}$, where C is a coupling constant, we can rewrite eq 2

$$\langle e^{-t/T_1} \rangle = \sum_i e^{-t/T_{1,i}} = \sum_i e^{-t(1-S_i)C/\tau_{\beta,i}} \quad (3)$$

where the sum is over all sites. Thus, regarding the difference observed between the relaxation functions in confinement and in bulk, one cannot decide whether the distribution $G(\ln \tau_\beta)$, or the distribution of $(1 - S)$, or both have changed. Only in the case, where $(1 - S_i)$ and $\tau_{\beta,i}$ are independent of each other and the distribution of $(1 - S)$ is unaltered in the confinement, can the change in the distribution $f(T_1)$ be directly traced back to a change in the distribution $G(\ln \tau_\beta)$. Because the different $(1 - S_i)$ are not expected to change by an order of magnitude, one may argue that the large changes observed in $f(T_1)$ on a logarithmic scale are mainly caused by changes in $G(\ln \tau_\beta)$ (cf. Figure 3).

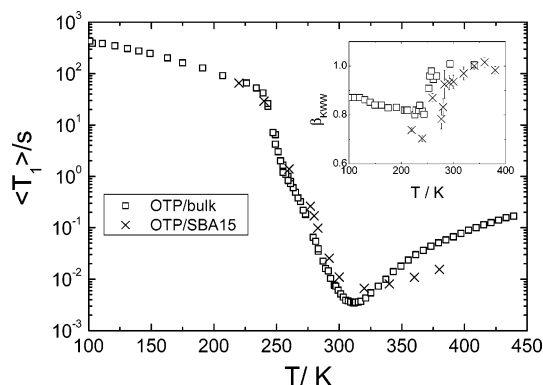


Figure 4. ^2H NMR spin–lattice relaxation time $\langle T_1 \rangle$ of *o*-terphenyl- d_{14} (OTP) in the bulk (\square) and confined in SBA-15 (\times). (Inset): Exponent of the stretched exponential spin–lattice relaxation function (same symbols as in main figure) β_{KWW} ; data for bulk OTP taken from ref 18.

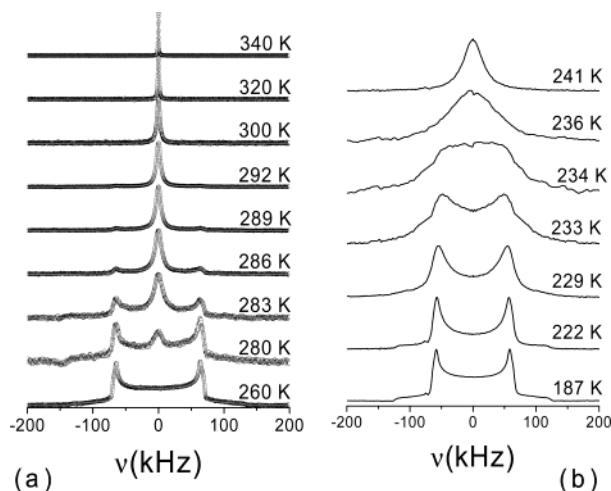


Figure 5. (a) ^2H NMR spectra of *o*-terphenyl- d_{14} confined in SBA-15. Solid lines, fit of the two-phase spectra by a sum of a Lorentzian and a Pake spectrum. (b) For comparison, spectra of glycerol- d_5 in the bulk.

Figure 4 presents the temperature dependence of $\langle T_1 \rangle$ for OTP- d_{14} confined in standard nonsilanized SBA-15 and in the bulk.¹⁷ From low temperatures up to T_g , essentially the same long $\langle T_1 \rangle$ values with a small temperature dependence are observed. Above the bulk $T_g \cong 248$ K, the relaxation times strongly drop over several orders of magnitude reaching a minimum at the same temperature $T \cong 310$ K. Here again, as for toluene, the relaxation time in the confinement is longer at the minimum by a factor of 2 but stays considerably shorter at the highest temperatures, as compared to the bulk data. Thus, $G(\ln \tau_\alpha)$ is broader by a factor of ~ 2 than that in bulk OTP- d_{14} . Furthermore, the temperature dependences of bulk and confined data are similar below the minimum, indicating that the excess wing and its crossover to the NCL behavior ($T < T_g$) are not modified under confinement.

Figure 5 displays the ^2H NMR spectra of OTP- d_{14} in SBA-15 that were obtained by applying the solid-echo technique.²¹ The spectra show a crossover from a motionally averaged spectrum typical of a liquid at the highest temperatures (central Lorentzian line) to a broad Pake spectrum at the lowest temperatures, characteristic of slow motion. The spectra at intermediate temperatures can be reproduced by a weighted superposition of a Lorentzian line and a Pake spectrum (cf. fits in Figure 5a). We emphasize that the fraction of the corresponding subspectra continuously changes with temperature.

Such “two-phase” spectra are the fingerprint of a heterogeneous distribution of correlation times $G(\ln \tau_\alpha)$. Fast ($\tau_\alpha \ll 10 \mu\text{s}$) and slow molecules ($\tau_\alpha \gg 10 \mu\text{s}$) exist simultaneously,²² thus confirming our relaxation results. Two-phase spectra are neither observed in bulk OTP nor in any other glass former (cf. Figure 5b for the case of glycerol). Here, the spectra continuously broaden upon cooling. Usually, it is argued that the width of $G(\ln \tau_\alpha)$ in bulk glass formers is too small to provide two-phase spectra.²² Clearly, this is no longer the case for OTP- d_{14} under confining conditions. Similar two-phase spectra were measured for toluene in SBA-15 (not shown). Also, for benzene in SBA-15²⁴ and ethylene glycol in a zeolite,²⁵ such spectra were reported. In the latter case, although not comparable with SBA regarding pore size and fluid–wall interaction, 2D NMR experiments showed that no exchange between fast and slow molecules occurs on the millisecond time scale, confirming the presence of a heterogeneous distribution, $G(\ln \tau_\alpha)$.

Heterogeneous dynamics may also show up in a nonexponential spin–lattice relaxation, as already discussed for the β process of toluene. Concerning the structural relaxation, above T_g , the situation is different because in the supercooled liquid dynamical exchange may take place on the time scale of T_1 so that a monoexponential spin–lattice relaxation may result. By inspecting the exponent β_{KWW} of the stretched exponential describing the relaxation function $\Phi(t)$ of OTP- d_{14} in SBA-15 (cf. inset of Figure 4), we see that its value drops below 1 at about 340 K and finally reaches $\beta_{\text{KWW}} \cong 0.7$ at 220 K, which is somewhat below the bulk T_g of OTP. Compared to bulk OTP- d_{14} , the deviation from exponential relaxation starts at significantly higher temperatures for OTP- d_{14} in SBA-15. At temperatures where the spectra are given by a central line (cf. Figure 5a), the correlation times of the molecules are on the order of nanoseconds or faster. The observation of a nonexponential spin–lattice relaxation at these temperatures leads to the conclusion that exchange processes among fast and slow molecules do not occur on the time scale $t \cong \langle T_1 \rangle \cong 10$ ms. In the SBA-15 confinement, the various subensembles of OTP molecules with different dynamical behaviors are isolated on that time scale. In contrast, this is not the case for bulk OTP, where the exchange rate is always on the order of the time constant τ_α , resulting in an exponential relaxation function at $T > T_g$, as demonstrated by several experiments²² (cf. also inset of Figure 4). This unexpected result demonstrates that molecules in a given environment do not change their dynamic state and that the two-phase spectra displayed in Figure 5a are thus a fingerprint of this heterogeneous distribution. Of course, exchange on a time scale longer than T , may occur.

Conclusion

Presenting NMR results on type A and type B glass formers in confining geometry we found that the α relaxation is considerably heterogeneously broadened and that the meantime constant $\langle T_1 \rangle$ exhibits a different temperature dependence in the confinement as compared to the bulk. We emphasize that we did not see indications of immobilized molecules at $T > T_g$ in the spectra or in the spin–lattice relaxation, but rather a continuous broad distribution $G(\ln \tau_\alpha)$ was observed. Thus, it may be possible that the dynamics gradually slows down, being faster in center of the pore and slower at surface, a situation encountered by solvation-dynamics experiments on confined methylpentane²⁶ and neutron spin-echo measurements on confined OTP²³ and also by recent MD simulation of a Lennard-Jones binary liquid.^{11,14} Then, however, exchange among the different subensembles is slow with respect to the time scale of the reorientational dynamics.

Regarding the JG β process, its distribution $f(T_1)$ is also significantly broadened in confinement. In the presence of a heterogeneous distribution of correlation times, it is not straightforward to conclude from a single averaged time constant whether the molecules become faster in the confinement. The full information can only be obtained by the corresponding distribution functions. For toluene, NMR allowed us to determine the distribution $f(T_1)$, which extends to shorter time constants in the confinement. The finding that the distributions are similar at the long time side may be an artifact because here spin diffusion (magnetization exchange without mass transport) may average the relaxation. Thus, although the β process is believed to be a local process, it is strongly changed in a 7-nm confinement. However, from the present experiments, we cannot strictly decide whether the geometry (in terms of the angular amplitude of the spatially restricted motion) and/or the dynamics are modified. To disentangle both contributions is not an easy task. It is possible that line shape experiments can settle this point. The claim that the β process is local may also be challenged on the basis of the relaxation behavior of the components in the chlorobenzene/decalin mixture (cf. Figure 1) where the spectral density of the β process depends on neither the mass nor the size of the participating molecules.

We are inclined to attribute the changes in the confinement to finite size effects because previous experiments have demonstrated that, in the case of toluene in SBA-15 close to the glass transition temperature, finite size effects dominate the dynamics for pore diameter $d > 5$ nm. Concerning the excess wing in OTP, the NMR results indicate no change in the confinement. However, in the latter experimental situation, the presence of an attractive surface plays a major role in addition to a possible decrease of the confined density when compared to the bulk. Under such conditions, a change of the excess wing should not be expected and further experiments with larger pore sizes are planned.

References and Notes

- (1) Johari, G.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.
- (2) Ngai, K. L.; Paluch, M. *J. Chem. Phys.* **2004**, *120*, 857.
- (3) Kudlik, A.; Benkhof, S.; Tschirwitz, T.; Blochowicz, T.; Rössler, E. *J. Mol. Struct.* **1999**, *479*, 201.
- (4) Vogel, M.; Rössler, E. *J. Chem. Phys.* **2001**, *114*, 5802. Vogel, M.; Rössler, E. *J. Chem. Phys.* **2001**, *115*, 10883.
- (5) Wagner, H.; Richert, R. *J. Non-Cryst. Solids* **1998**, *242*, 19.
- (6) Schneider, U.; Brand, R.; Lunkenheimer, P.; Loidl, A. *Phys. Rev. Lett.* **2000**, *84*, 5560.
- (7) Donth, E.; *The Glass Transition*; Springer: Berlin, 2001.
- (8) Tracht, U.; Wilhelm, M.; Heuer, A.; Feng, H.; Schmidt-Rohr, K.; Spiess, H. W. *Phys. Rev. Lett.* **1998**, *81*, 2727.
- (9) cf. contributions in *Eur. Phys. J. E* **2003**, *12*, .
- (10) Morineau, D.; Xia, Y.; Alba-Simionesco, C. *J. Chem. Phys.* **2002**, *117*, 8966.
- (11) Teboul, V.; Alba-Simionesco, C. *J. Phys.: Condens. Matter.* **2002**, *14*, 5699.
- (12) Wagner, H.; Richert, R. *J. Phys. Chem. B* **1999**, *103*, 4071.
- (13) Alm  ras, Y.; Barrat, J.-L.; Bocquet, L. *J. Phys. IV* **2000**, *10*, Pr7-27.
- (14) Scheidler, P.; Kob, W.; Binder, K. *Europhys. Lett.* **2000**, *52*, 277.
- (15) Alba-Simionesco, C.; Dosseh, G.; Dumont, E.; Frick, B.; Geil, B.; Morineau, D.; Teboul, V.; Xia, Y. *Eur. Phys. J. E* **2003**, *12*, 19. Patkowski, A.; Ruths, T.; Fischer, E. W. *Phys. Rev. E* **2003**, *67*, 021501. LeQuellec, C.; Brodie-Linder, N.; Xia, Y.; Alba-Simionesco, C., to be submitted for publication.
- (16) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. Triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀) was used as a surfactant, and tetraethoxysilane (TEOS) was used as a silica source. After it was reacted at 35 °C for 20 h and then aged at given temperature for another 24 h, the mixture was collected by filtration without washing, dried, and calcined in air at 500 °C for 6 h. Different pore sizes were obtained by changing the aging temperature from 35 °C to 100 °C.
- (17) Dries, Th.; Fujara, F.; Kiebel, M.; R  ssler, E.; Sillescu, H. *J. Chem. Phys.* **1988**, *88*, 2139.
- (18) Schnauss, W.; Fujara, F.; Sillescu, H. *J. Chem. Phys.* **1992**, *97*, 1378.
- (19) R  ssler, E.; Sillescu, H. *Chem. Phys. Lett.* **1984**, *112*, 94.
- (20) Blochowicz, T.; Kudlik, A.; Benkhof, S.; Senker, J.; R  ssler, E. *J. Chem. Phys.* **1999**, *110*, 12011.
- (21) Vogel, M.; Tschirwitz, Ch.; Schneider, G.; Koplin, Ch.; Medick, P.; R  ssler, E. *J. Non-Cryst. Solids* **2002**, *307*, 326.
- (22) B  hmer, R.; Diezemann, G.; Hinze, G.; R  ssler, E. *Prog. Nucl. Magn. Reson. Spectrosc.* **2001**, *39*, 191.
- (23) Dosseh, G.; Ehlers, G.; Xia, Y.; Alba-Simionesco, C., to be submitted for publication.
- (24) Gedat, E.; Schreiber, A.; Albrecht, J.; Emmeler, Th.; Shenderovich, I.; Findenegg, G. H.; Limbach, H.-H.; Buntkowsky, G. *J. Phys. Chem. B* **2002**, *106*, 1977.
- (25) Medick, P.; Blochowicz, T.; Vogel, M.; R  ssler, E. *J. Non-Cryst. Solids* **2002**, *307-310*, 565.
- (26) Richert, R.; Yang, M. *J. Phys. Chem. B* **2003**, *107*, 895.