

● *Contributed Paper*

MICRODYNAMICS AND PHASE EQUILIBRIA IN ORGANIC NANOCRYSTALS

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The effects of confinement on various organic molecules have been studied by nuclear magnetic resonance (NMR) relaxation techniques (T_2 and $T_{1\rho}$) between room temperature and 77 K. Cyclohexane, pentadecane, squalane, and squalene have been constrained within 60 Å porous silica, and the behaviour of the resulting nanocrystals has been compared to that of the bulk material. In all cases the molecular dynamics of the confined material were found to be significantly different from the bulk, and there is evidence to suggest that the behaviour is largely dependent on the size and shape of the molecules and the resultant structural disorder present when constrained within the pores. © 1998 Elsevier Science Inc.

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INTRODUCTION

There is an increasing interest in the behaviour of liquids and solids within porous structures, especially where long chain molecules and polymers are involved. A nuclear magnetic resonance (NMR) relaxation study has been carried out for organic molecules of various shapes and sizes between room temperature and 77 K. Cyclohexane is a globular molecule approximately 4 Å in diameter and is interesting to study since it is well characterised and forms a plastic crystal phase in the bulk down to 186 K.^{1–7} Pentadecane ($C_{15}H_{32}$) is a flexible straight chain alkane, maximum 18 Å long, and can exist in many conformations. Squalane ($C_{30}H_{62}$) is also a long chain alkane, 24 carbons long, with six methyl groups attached at carbon sites 2, 6, 10, 15, 19, and 23. This molecule is flexible, but behaviour is also affected by the side methyl groups. Finally, squalene was chosen because it is the alkene equivalent of squalane. The presence of six double bonds along the chain (at each methyl side group) causes the structure to be more rigid, and fewer molecular conformations are possible. In each case the behaviour of the organic molecules when restricted within a 60 Å porous silica structure has been compared to the behaviour in the bulk material.

EXPERIMENTS

The organic liquids used in this work were 99.5% anhydrous cyclohexane, 99% squalane, 97% squalene, and 99% pentadecane. Silica samples were prepared using Unilever Sorbsil silica of nominal average pore size 60 Å. The pore-size distribution obtained for this silica using the NMR cryoporometry technique⁸ revealed a bimodal distribution, with the majority of the pores at 60 Å but with a significant number around 40 Å.

The glass tubes and silica were dried before preparing the samples. The volume of liquid required to fill the pores was calculated and carefully added to the silica. This was done under anhydrous conditions in a nitrogen atmosphere. The sample tubes were then sealed under vacuum to remove any dissolved oxygen and prevent evaporation and contamination. The silica samples were subsequently shaken to encourage the distribution of the liquid and absorption into the pores.

Proton NMR measurements were carried out on a home-built 21.5 MHz spectrometer, capable of cooling down to 77 K using a liquid nitrogen injection system. Temperature control was stable to within 1°. All measurements were taken while warming the sample from a low temperature to prevent supercooling or hysteresis effects.

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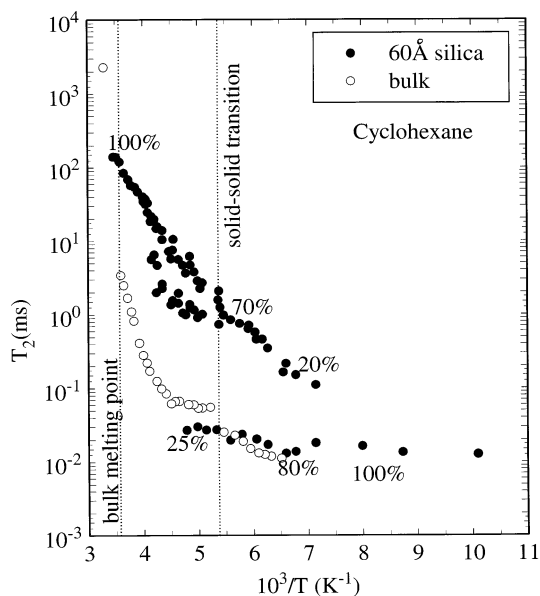


Fig. 1. T_2 results for bulk and confined cyclohexane in 60 Å silica.

Transverse relaxation time (T_2) was measured on all samples. The free-induction decay (FID) was used to measure short values of T_2 , then the single spin-echo (SSE) and Carr–Purcell–Meiboom–Gill (CPMG) sequences were used in order to eliminate effects due to magnetic-field inhomogeneities when recording longer values. The τ delay between 90° pulses in the Carr–Purcell–Meiboom–Gill sequence were in the range $0.05 \leq \tau \leq 0.5$ ms. The spin-lattice relaxation time in the rotating frame ($T_{1\rho}$) was measured for squalane to provide further information on the change in molecular motion. This used the standard method of applying a spin-locking pulse and then recording the height of the remaining decaying signal. The B_1 field was measured to be 1.34 mT for cyclohexane and 0.89 mT for squalane. Relaxation times were deduced by fitting up to three exponentials to the relaxation decays obtained (or a Gaussian to the FID).

RESULTS

An extensive study was carried out for cyclohexane. The T_2 relaxation times obtained for cyclohexane in the bulk and in 60 Å silica are shown in Fig. 1. The results for the bulk agree closely with previously published data.^{5,6} Because cyclohexane has a well-documented phase diagram, only a brief summary of the results will be given here. The melting point is seen as a discontinuous change in T_2 from several seconds to 4 ms at 280 K. Below this temperature, a plastic crystal is formed which

allows molecular diffusion through the lattice. This motion gradually decreases with temperature, until around 220 K the molecules are restricted to their lattice sites and isotropic reorientation occurs with a T_2 of 50 μ s. At 186 K a discontinuous drop in T_2 to 25 μ s is observed. This is associated with a structural phase transition from the face-centred cubic plastic crystal to a monoclinic structure. Below 186 K, anisotropic reorientation is taking place, which gradually reduces until the temperature independent T_2 value of 15 μ s is observed, consistent with the rigid lattice.

The results obtained for cyclohexane in 60 Å silica are very different from the bulk. At room temperature, $T_2 \approx 150$ ms, a value which decreases uniformly with temperature down to 30 ms at 250 K. The relaxation time then becomes two components, the slightly shorter component due to an amorphous solid forming in the larger pores, and the longer component due to the remaining liquid in the smaller pores. This two-component region coincides with the expected melting-point depressions for cyclohexane in this size pore.⁹ The two components recombine at 180 K indicating that the cyclohexane is in a mobile solid or glassy state. The translational mobility continues to decrease uniformly down to 140 K, below which it can no longer be observed. A very short component with $T_2 = 30$ μ s appears below 210 K. This component shows a slight decrease in relaxation time (and increase in intensity) down to 140 K, below which this is the only component observed. This T_2 value is consistent with the region of anisotropic reorientational motion in the bulk and gradually slows to the typical rigid-lattice value of 15 μ s at 100 K. For cyclohexane, therefore, it seems that the liquid gradually freezes to a disordered or glassy solid, well below the bulk melting point, and then below 210 K we observe the nucleation of a more ordered nanocrystal forming in the pores. This is most likely to be at the centre of the pores, away from the disorder at the surfaces.

The T_2 results obtained for pentadecane, both in the bulk and in porous silica, are shown in Fig. 2. The melting point in the bulk material is seen as a discontinuous change in T_2 at 283 K, where the value drops from 500 ms in the liquid to 30 μ s in the rotator-phase solid. A further discontinuity is observed at 267 K, where T_2 drops further to ~ 12 μ s, consistent with dense, tightly packed chains with a specific chain-chain interaction. For pentadecane in the 60 Å pores, T_2 values in the liquid state are lower than in the bulk. This is due to exchange between the molecules at the centre of the pores with those at the surface, which undergo enhanced relaxation due to surface effects. This is a well-documented phenomenon.¹⁰ There is a discontinuous change from 35 ms to 0.5 ms at 274 K, corresponding to a depressed melting point. Below this temperature two T_2 components are

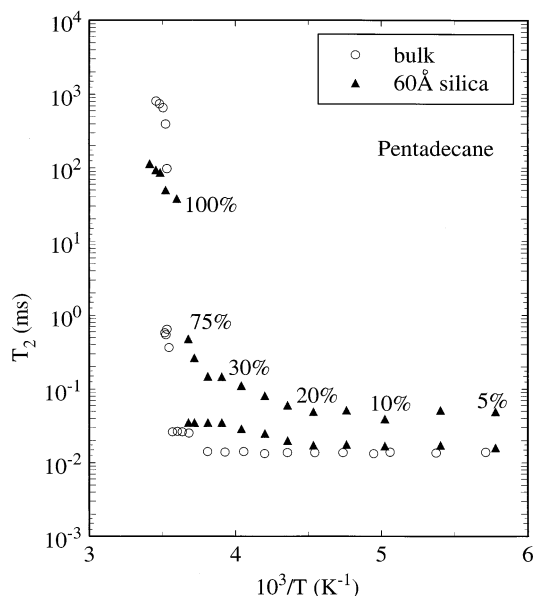


Fig. 2. T_2 results for bulk and confined pentadecane in 60 Å silica.

observed. The longer component has a value of 0.5 ms just below the melting point, much higher than in the bulk material. This would indicate that the solid formed contains considerable disorder. The chains will be more loosely packed with little or no specific chain-chain interaction to hinder rotation of the chain. This is supported by the continual decrease in T_2 to lower temperatures (with an associated decrease in signal intensity), finally becoming constant below 220 K at around 40 μ s, indicating residual disorder in this region of the solid. The shorter component drops slowly from 25 μ s at 274 K to 12 μ s at 170 K. There is an associated increase in signal intensity, indicating the growth of an ordered solid. Again this is likely to be the formation of a crystal at the centre of the disordered region in the pores.

Both T_2 and $T_{1\rho}$ measurements were carried out for squalane in the bulk and in pores. The results are plotted in Fig. 3. There is not a definitive melting point for this material. From room temperature down to 180 K there is a continual decrease in T_2 from 200 ms down to 20 μ s. This indicates difficulty in molecular packing to form an ordered state, and is expected for a molecule of this size with six methyl side groups. The squalane in silica shows significant distribution in the values for T_2 , which is due to the combination of intra- and extra-granular squalane. However, the value for T_2 is shorter for the confined material than it is for the bulk at any particular temperature, indicating a loss of mobility when the molecule is constrained in the pores. The $T_{1\rho}$ results support this finding, with the $T_{1\rho}$ minimum at around 220 K, compared to 190 K for the bulk.

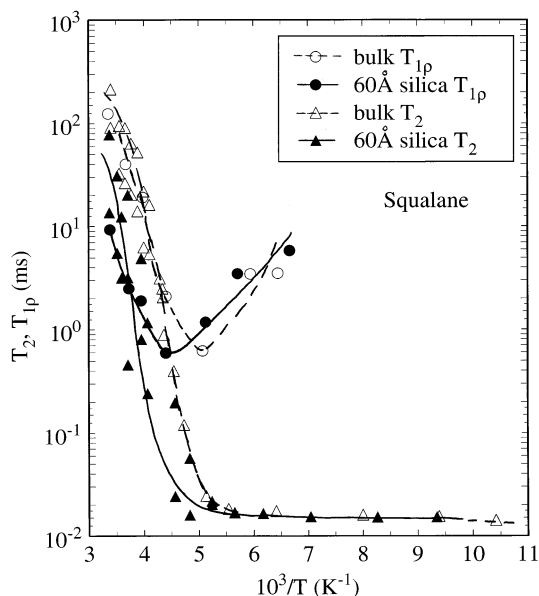


Fig. 3. T_2 and $T_{1\rho}$ results for bulk and confined squalane in 60 Å silica.

Finally the T_2 results for squalane are shown in Fig. 4. The melting point was seen as a discontinuous change from 35 ms down to 17 μ s at 265 K. This is in disagreement with the melting point of 198 K stated by Aldrich, who measured using differential thermal analysis. However, at this temperature an anomalous jump is observed in T_2 to 50 μ s. Although we are now in agreement over

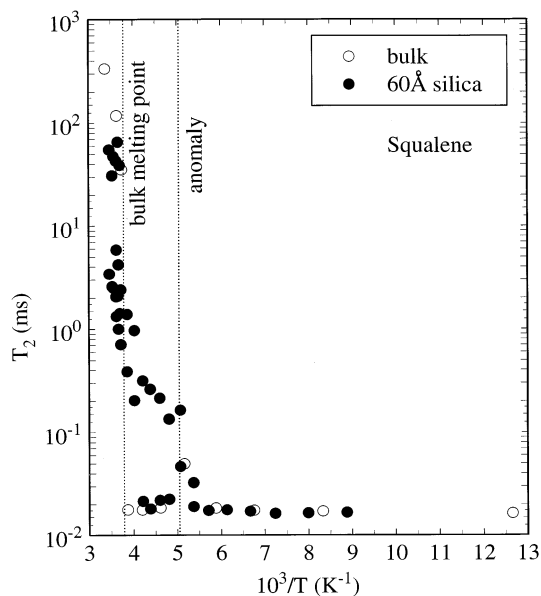


Fig. 4. T_2 results for bulk and confined squalane in 60 Å silica.

the melting point at 265 K, the nature of the anomaly at 198 K is unknown. The solid state T_2 value of 17 μs remains unchanged down to low temperatures and corresponds to a monoclinic crystal structure.¹¹ In its most stable conformation this molecule is flat, with the methyl groups in the same plane as the coiled chain. This is due to the specific coiling of the chain because of the double bonds. This allows the molecule to close-pack easily in the solid state. In the pores the low temperature value for T_2 is the same as in the bulk, indicating the formation of the same crystalline state. Above 180 K, two components are seen. The short component of 20 μs continues to 240 K, but the longer component increases continuously from 20 μs to 60 ms at room temperature. This indicates that the molecule is not necessarily in its most stable conformation, and therefore cannot easily close-pack in the lattice. Once again this material indicates a disordered solid state, with the formation of an ordered crystalline state at low temperatures.

CONCLUSION

The molecular dynamics of the organic materials confined in 60 Å porous silica were found to be largely dependent on the shape and size of the molecules. Cyclohexane, pentadecane, and squalene have highly ordered crystalline structures in the bulk at low temperatures. When they are constrained within the pores, there is evidence for considerable disorder below the bulk melting point, which exists down to low temperature. This suggests the inability of the molecules to form a dense, closely packed structure and a significant amount of residual rotational motion. However, there is evidence for the growth of an ordered nanocrystalline region at lower temperatures for these materials, which is likely to occur at the centre of the pore, away from the disorder at the surfaces. The different results obtained for squalene are explained by the fact that the side groups make packing very difficult, and this material forms a crystal-

line structure with difficulty even in the bulk. When it is constrained within the pores, the motion is restricted further, and this is reflected in the loss of molecular mobility observed in T_2 .

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