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A Comparative Study of the Conformational Mobility of Octamethyltetrasiloxane and Cyclododecane in the Solid State

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Abstract

A crystalline mesophase state in which molecules show conformational mobility is discussed for cyclododecane and octamethyltetrasiloxane. ^{13}C and ^{29}Si solid state NMR spectra show changes of the resonance signals which can be explained by changes of the conformation. The transition temperatures in the NMR spectra are correlated with the thermal transitions detected by DSC. Comparisons with the solution spectra give evidence that in case of octamethyltetrasiloxane, the conformational mobility is determined mainly by the molecular packing in the crystal, while packing effects are neglegibly small for cyclododecane. The data are discussed with concern to the corresponding linear chain molecules, i. e. poly(ethylene) and poly(dimethylsiloxane).

Introduction

Molecular mobility in the crystalline state is a rather common phenomenon for macromolecules. A most striking example is the growth of the lamellae of chain folded to chain extended crystals which has been described for several polymers including poly(ethylene), poly(tetrafluorethylene), poly(vinylidenfluoride), and Nylon 6. In addition, conformational mobility is well established for the pseudohexagonal phases of e. g. n-alkanes, poly(ethylene), 1,4-trans-poly(butadiene), and cis-1,4-poly-(2-methylbutadiene). For a review see ref. 1. Therein B. Wunderlich points out that conformational mobility has to be considered as a specific mesophase characteristic. In order to make a distinction from plastic crystals, which - in their usual definition - show orientational disorder but positional order, Wunderlich coined the term 'condis crystal' for the variation of the crystalline state, in which flexible molecules change conformations without loosing positional and orientational order. 'Condis crystal' is a contraction of 'conformational disordered crystal'.

With this paper we attempt to elucidate the interrelation between conformational transitions and crystalline ordering with the aim finally to get more information, whether it is necessary to introduce the 'condis' concept in addition to that of the plastic crystal.

A fairly new method which can give further insight into these problems is high resolution solid state NMR-spectroscopy. Spectra obtained by means of the cross-polarization and the magic angle sample spinning technique$^{2-4)}$ give isotropic chemical shifts similar to solution spectra, differing from solution spectra in that they also reflect the molecular packing in the bulk. Hence, they provide detailed information concerning the structure and dynamics in the solid state with respect to individual atoms. The restricted mobility of conformations, in association and complexation equilibria can yield distinctive chemical shifts for the different sites.

In a paper recently published$^{5)}$, we described the temperature dependence of CP-MAS ^{13}C-NMR spectra of a series of cycloalkanes, $(CH_2)_{12}$, $(CH_2)_{24}$, and $(CH_2)_{36}$ in comparison to their thermal behaviour as detected by DSC. For the two smaller ring molecules we described a high temperature solid state phase for which the CP-MAS ^{13}C-NMR spectra demonstrate fast conformational interconversion. Although in case of cyclododecane the DSC trace indicates only a small change of enthalpy for the transition to the fully ordered crystal, our data clearly show the 'condis' crystalline mesophase for small molecules. In the present paper, we attempt to compare the cyclododecane data with similar experimental results which we obtained for octamethyltetrasiloxane (OMTS). While cyclododecane is a fairly unpolar molecule, this is not the case for OMTS with its polar Si-O bonds. As we shall show this is of particular influence in the conformational characteristics and the 'condis' phase behaviour. Our data should be helpful for the understanding of the crystalline state of the corresponding polymers, i. e. poly(ethylene) and poly(dimethylsiloxane) .

Results and Discussion

Fig. 1 shows the ^{13}C-NMR spectra of cyclododecane at various temperatures: On the left side the solution spectra in propane-d_1, on the right side the solid state spectra. In solution as well as in the solid, the same changes can be seen. Above 200 K, the methylene carbons give only one single signal, below 180 K two signals with an intensity ratio of 1:2 were recorded. Chemical shifts against TMS for the solid and the solution phases differ by about 1-2 ppm. Similar differences in chemical shifts between solution and solid state spectra were reported by Lippmaa et al.$^{6)}$. Slow exchange solution spectra of cyclododecane were obtained by Anet et al. first in 1972[7)]. The splitting of the ^{13}C-NMR signal can be explained by the ring conformation. At high temperatures the carbon atoms exchange rapidly between the different diastereotopic sites within the molecules. At low temperatures the exchange rate is slow with respect to the time scale of the NMR experiment, resulting in a splitting of the resonance signal. For a detailed discussion of the spectra and the assignment see ref. 4.

It seems remarkable that the coalescence temperature lies within the same range between 170 and 195 K for the dissolved molecules and the solid. The comparison with the results from DSC measurements in Fig. 2 suggests that the solid state phase transition at 184.4 K has to be correlated with the coalescence in the CP-MAS NMR spectra. This means, the molecular changes which happen to occur at the solid state phase transition can be observed with a similar temperature dependence for the dissolved molecules.

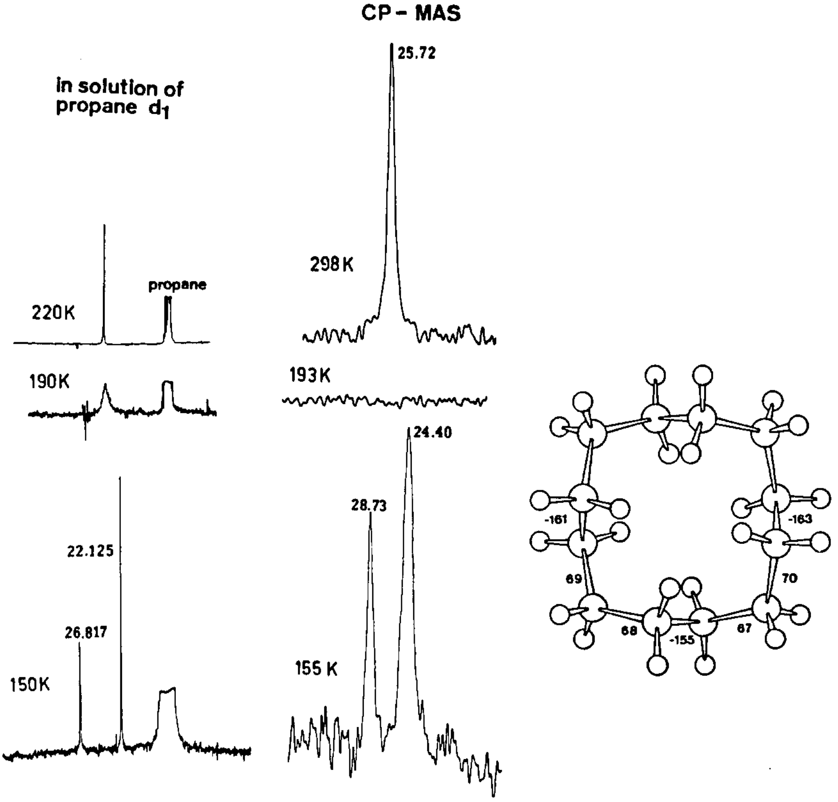

Fig. 1: Temperature dependence of solution and CP-MAS solid state ^{13}C-NMR spectra of cyclododecane. On the right side a molecular model of the crystal conformation from X-ray diffraction (ref.8). Spectra were recorded at 75.47 MHz, TMS=0 ppm (see also ref. 4).

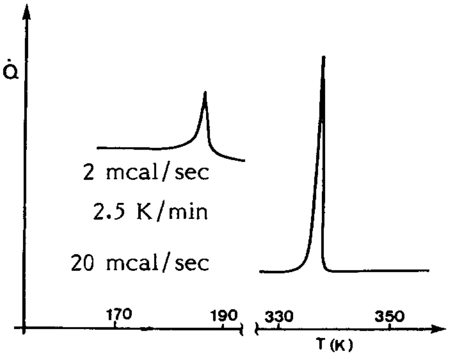

Fig. 2: DSC trace of cyclododecane

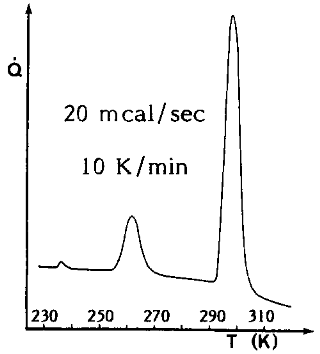

Fig. 3: DSC trace of OMTS

Different behaviour was observed with octamethyltetrasiloxane. The CP-MAS spectra in Fig. 4 show a fast exchange - slow exchange transition for the crystalline state. As indicated by the DSC trace in Fig. 3, this transition occurs at the same temperature as the solid state phase transition at $T_u = 265$ K. Similar to cyclododecane, the solid state phase transition is correlated with a change of the rate of conformational interconversion. Different, however, is that in solution no slow exchange - fast exchange transition could be observed in either the ^{13}C- or the ^{29}Si-NMR spectra. Moreover, the transitions in the NMR spectra occur within a narrow temperature range. At 265 K, the signals of both the the 'condis' and the fully ordered crystalline phase were recorded in the same spectrum. Hence, the observed changes of conformational mobility are bound to the crystalline state. Decreasing the temperature further results in an additional change of the solid state ^{13}C-NMR spectra. Directly below T_u, the maximum splitting to four signals with an intensity ratio of 1:1:1:1 could be observed. At lower temperatures, the signals move together again. At 130 K, the two downfield signals coincide and a splitting pattern of 2:1:1 results indicating a higher molecular symmetry than at 250 K e. g..

With the aid of a conformational model, it can be easily seen that the carbon atoms as well as the silicon atoms have to occupy diastereotopic positions within the molecule. Therefore, it seems reasonable to explain the NMR signal splitting at first approach by the conformation. Fig. 5 shows a conformational model which we propose as explanation of the NMR spectra. On the left side, a tilted crown conformation is shown. The four diastereotopic carbons and the two diastereotopic silicons are distinguishable. On the right side, the same conformation is shown without the tilt of the outer methylgroups. In this case, they are in a position symmetric with respect to the plane of the ring molecule. The structure on the right is in agreement with X-ray diffraction data [10,11], but only

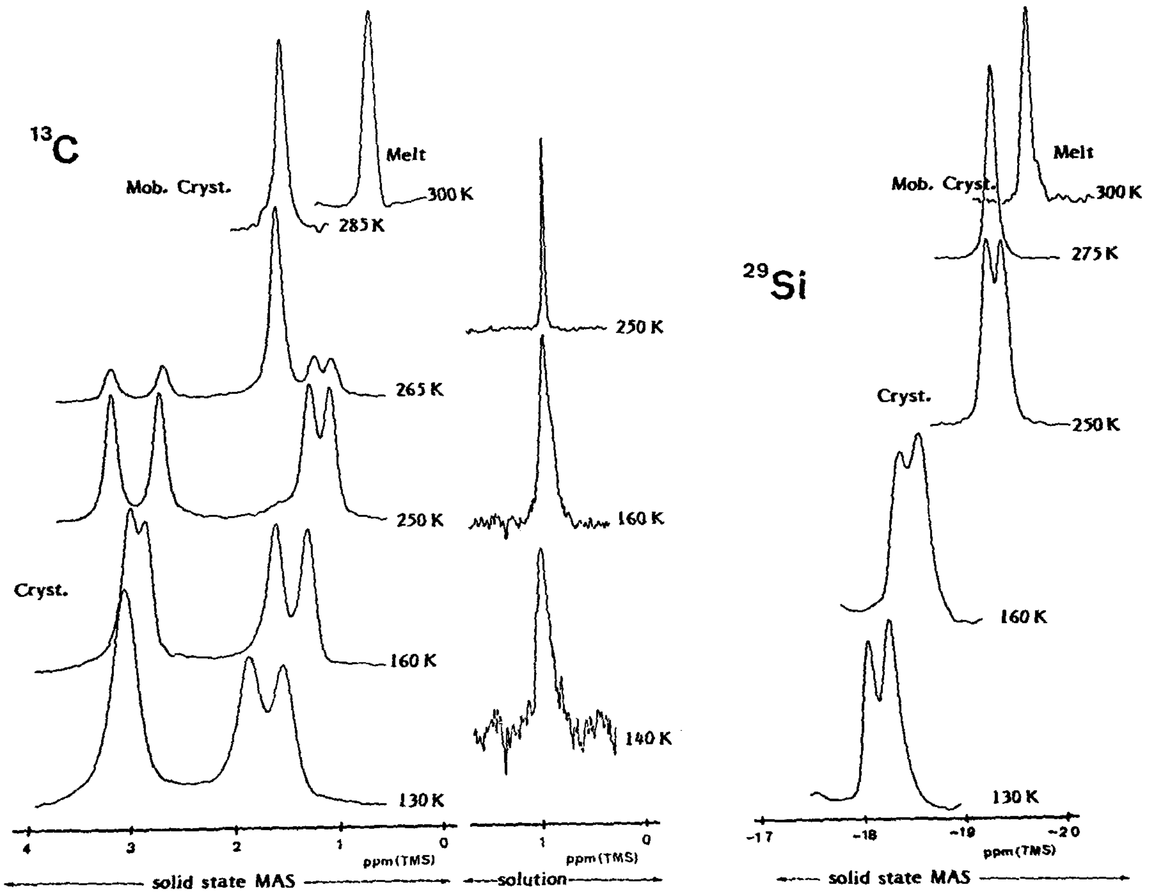

Fig. 4: Temperature dependence of solution and CP-MAS solid state ^{13}C and ^{29}Si spectra of OMTS, recorded at 75.47 and 59.63 MHz with a Bruker CXP 300 spectrometer, TMS = 0 ppm.

suffices to explain the slow exchange spectrum showing three carbon signals with an intensity ratio of 2:1:1 as it was observed at 130 K. At higher temperatures, the solid state carbon spectra gave four signals. This pattern can be explained by the tilted crown conformation, in which the outer methyl carbons become inequivalent. As expected for this conformational variation no change of the silicon spectra could be observed. In general it appears that the ^{29}Si signals exhibit very little change with temperature. Because of their location 'inside' the molecule, they are much less influenced by conformational and packing effects as are the carbons atoms.

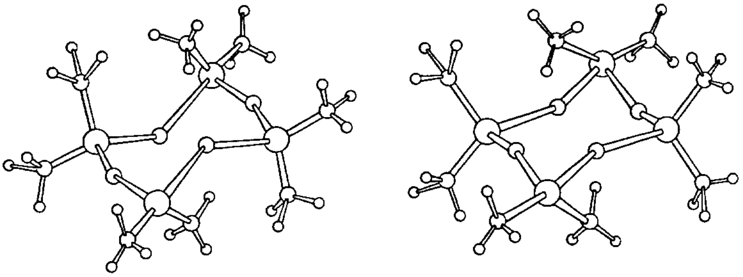

Fig. 5: Conformational model for octamethyltetrasiloxane

Tilted crown Untilted crown

We propose to interprete our data in the following manner: The untilted crown conformation at low temperatures is caused by competing influences of conformational and polar intermolecular interactions. The 'free' conformation is observed before the transition from the fully ordered into the mobile crystal, at 265 K. A tilted crown conformation is expected in solution also, where fast interconversion of the conformers impedes conformational analysis. On decreasing the temperature below 265 K this conformation is changed gradually to the untilted crown conformation because of the increasing influence of intermolecular interactions. This can be seen in the carbon spectra, where the downfield signals coincide when lowering the temperature. The low energy barriers between the conformers facilitate the distortion of the rotational angles. Hence, the polarity of the bonds in OMTS influences the arrangement of the molecules within the crystal lattice strongly. The conformational changes at T_u are much more cooperative as in the case of cyclododecane. For cyclododecane the solid state phase transition is determined quite exclusively by the temperature dependence of the conformational interconversion due to the intramolecular barriers. The change in mobility is little influenced by the fact that the molecules are incorporated in a crystal. In case of OMTS, the change in the exchange rate between the diastereotopic positions is dominated by the variation of molecular packing. In agreement with this interpretation, first X-ray diffraction experiments gave different patterns below and above T_u9).

Finally we want to discuss the significance of the shown data with respect to the conformational mobility in poly(ethylene) and poly(dimethylsiloxane). The high mobility of cyclododecane below the melting transition is similar to the behaviour observed for n-alkanes and poly(ethylene) in the pseudohexagonal phase. Hence, it may be concluded that for the linear chain molecules the conformational mobility in the crystal is mainly controlled by the intramolecular rotational barriers and that the mobility changes in a rather broad range of temperature with minor cooperativity. MAS-CP NMR spectra of poly(dimethylsiloxane) 12) show similar variations with temperature as observed in the low temperature range of the OMTS spectra. Because of the low rotational barriers and the flat potential minima rather large deviations may be allowed for the minimum conformations of the Si-O bonds. Hence, the conformation of PDMS in the semicrystalline state is the temperature dependent consequence of competing influences from rotational isomerism for the single molecule and the interchain interactions due to the polar groups of adjacent molecules. The low storage modulus of semicrystalline PDMS also may be caused by the highly deformable bonds in the crystalline state.

Separation of conformational and packing effects as well as verification of the proposed model should be possible by X-ray diffraction studies being under work.

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