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Influence of Chemical Pressure and Reaction-Induced Stress in Solid-State Reaction : Lattice Instability During The Thermally Enhanced Reaction of MSE

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A p-dimethylaminobenzenesulfonate (MSE) polycrystalline powder is converted to the zwitterion p-trimethylammoniumbenzenesulfonate (ZWT) by chemical thermally induced reaction at T = 55,5°C. This reaction is associated to a first order ferroelastic phase transition in partially reacted MSE crystals. A ^{13}C-NMR study made during the in situ transformation MSE → ZWT shows that the reaction is of first order. A strong change appears in the low frequency Raman and Brillouin spectra of MSE monocrystals when passing the transition, but only a continuous evolution in the intensity of the high frequency modes is observed. Birefringence observations permit to specify the evolution of the optical axes position during the chemical reaction. The importance of stress induced by the reaction is discussed in relation to the phase transition.

Keywords: organic crystals; elasticity; phase transitions; solid-state reaction

INTRODUCTION

The effect of chemical pressure[1] and phonon assistance[2, 3] have been included recently in a general and unifying theory of solid state chemical

reactions[4]. Local stress influences the kinetics of a reaction but then the elastic compliance is also modified as the reaction proceeds. This is due to the fact that the variable σ describing the local change of a chemical nature is coupled to the local strain tensor ε. Such a chemical pressure is encountered in the case of thermal polymerization of diacetylene crystals : the activation energy depends in that case on the elastic properties of the mixed monomer-polymer crystal[5] and the elastic constant C_{22} undergoes a continuous change when going from pure monomer crystal to pure polymer crystal[6]. The variable σ may also be coupled to other dynamical variable Q. In the case of the photo-induced polymerization of 2,5-distyrylpyrazine (DSP)[7], the optical modes which are assisting the reaction are at the same time the ones which are mostly shifted during the polymerization. As the response functions for dynamical variables are affected by chemical pressure, the possibility arises of lattice instabilities[1]. For example, in the case of the thermal polymerization of 1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne (DNP), a phase transition occurs at the end of the polymerization[8], but its origin remains obscure. In this work, experimental results obtained by differential scanning calorimetry, ^{13}C solide-state NMR, Raman and Brillouin scattering and optical birefringence, indicate that reaction-induced stress gives rise to a lattice instability during the thermally enhanced solid state reaction of methyl p-dimethylaminobenzenesulfonate (MSE) which is converted in p-trimethylammoniumbenzenesulfonate (ZWT)[9-15].

Synthesis and Crystal Growth

MSE was synthesized according to ref. 9, using for the first run sulfanilic acid rather than monohydrate. The second and the third runs are the same than in ref. 9. The crude product was recrystallized from methanol, characterized by NMR and stored at - 70° C. The polycrystalline powder used in ^{13}C-NMR experiments was obtained by grinding the recrystallized compound. The monocrystalline samples used in the calorimetric, Raman and Brillouin scattering measurements were grown after filtration by slow evaporation of an acetone solution at a temperature near 0° C. For birefringence observations,

single crystals grown from methanol were used also. Single crystals of MSE are obtained in thin plates containing (bc) crystallographic plane.

Calorimetric Results : Reaction Kinetics

MSE converts to the p-trimethylaminoniumbenzenesulfonate zwitterion (ZWT) on standing at room temperature (≈ 500 h), or more rapidly at higher temperature (around T = 50°C : ≈ 50 h), or also on increasing slowly the temperature[10]. The calorimetric study of the thermal conversion of MSE to ZWT showed unusual behaviour[10]. Two main features were observed on the thermal recording : a broad maximum followed by a sharper peak. If one plots the fractional enthalpy $\Delta H/ \Delta H_T$ versus time, a double step kinetics appears[10]. This curve disagrees with the variation of the ZWT α fractional composition as determined by the authors by UV spectrophotometry with calibration curves constructed from absorbances of known concentrations of MSE and ZWT in acetonitrile-water solutions. The authors of ref. 10 concluded that there should be an excess of enthalpy in the second calorimetric peak : this peak could be due at the same time to a chemical process and to a physical process like a phase transition. The double step kinetics obtained by calorimetry should then better fit the double step kinetics obtained by UV spectrophotometry by removing the contribution due to the transition. It should also be pointed that α does converge to 0,85 and not to 1,0.

Our isothermal and scanning DSC results on reaction kinetics are comparable to the one of ref. 10 for MSE powders or low-quality MSE crystals grown in solution. But we took great care to choose by optical method (birefringence) high quality MSE monocrystals for DSC reaction kinetics. In such cases much more precise results are obtained. For example figure 1 shows the reaction kinetics of a MSE monocrystal obtained by increasing temperature with a scanning rate of 0.1K/mn. The second calorimetric peak is about 30 times higher than the first one. The maximum of this second peak is reached in only 30 seconds. All these results show that this peak can not be attributed to the chemical process but only to a physical process (sudden structural change). This is consistent with the fact that the second peak broadens whereas the first

one is almost unaffected when studying polycristalline powders or crystals containing defects (Fig. 4 in ref. 10).

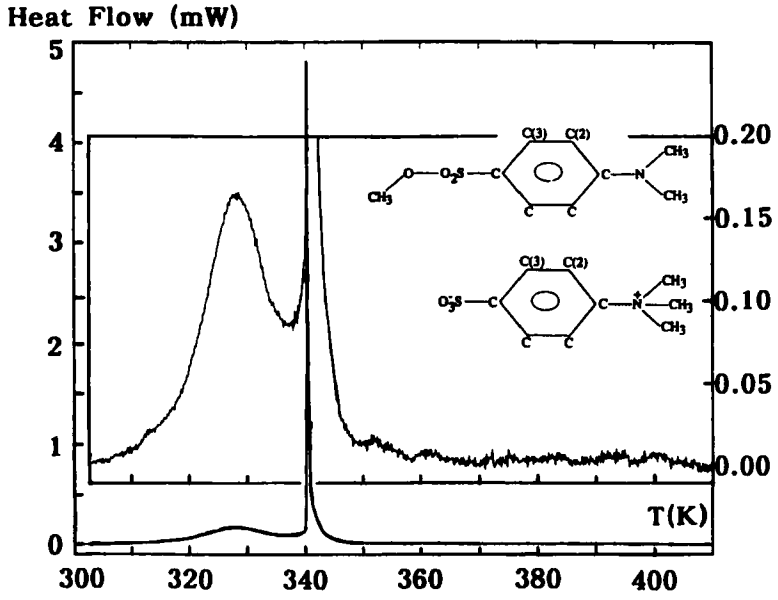

FIGURE 1 Reaction kinetics of a MSE monocrystal (m=9.715mg) by DSC measurement at a scanning rate of 0.1K/mn in the [300K - 410K] temperature range. A scheme of MSE and ZWT molecules, is shown in the inset representing an enlargement of the kinetics (same temperature scale, different heat flow scale on the right side).

In our case total enthalpy of the exotherm in the [300K-400K] temperature range is ΔH=-66 kJ mole^{-1}, in agreement with results of ref. 10. The enthalpies of the two contributions are respectively -37 kJ mole^{-1} for the chemical reaction and -29 kJ mole^{-1} for the structural change.

Calorimetric Results : ZWT Specific Heat

The crystalline structure of MSE is monoclinic $P2_1/c$ at 193 K and 255 K (Z = 4)[9, 11]. In the case of ZWT, the situation appears more complex according to ref. 12. The low temperature (at 193 K) phase III is orthorhombic

Pnc2 (Z = 8) and the high temperature (at 385 K) phase I is tetragonal P4/nmm (Z = 2). There is an intermediary orthorhombic Pbma (Z = 4) phase II. The transition between phase I and phase II is first order and located at T = 383 K ; the authors of ref. 12 obtained no indication on the phase change between phase II and phase III between 193 and 335 K.

To try to clarify this problem, we made DSC studies on monocrystals or powders of ZWT. A sharp endotherm between phase I and phase II is detected at about T_1 = 110° C in the ZWT crystal of the previous study (figure 1) in good agreement with ref. 12. The same feature is observed when using a sample of polycrystalline powder of ZWT obtained from ^{13}C NMR experiments with broader and less pronouced anomalies. The new result is that a phase transition is detected at about T_2 = 25-30°C in all the cases. This explains why the authors of ref. 12 have met with some difficulties in determining the structure of ZWT at room temperature very near T_2. The conclusion is that when the thermally enhanced reaction of MSE is made completely at around T = 50° C, the initial crystallographic structure is monoclinic $P2_1/c$ (Z = 4) and the final is orthorhombic Pbma (Z = 4).

^{13}C NMR Results

We decided to use solid state high resolution ^{13}C NMR for studying the transformation MSE → ZWT because this experimental technique is very sensitive to the nature of the bonds between carbon atoms and neighbouring atoms in a molecule[15] and then to the chemical reaction. It has also some advantages over the spectrophotometric method used by the authors of ref. 10 : first it is a direct characterization of the chemical species ; second, the thermal annealing can be performed in-situ ; third, there is no need of calibration curves. The isothermal kinetics at T = 55,5 ± 1,0° C (fig. 2) was constructed by calculating the fraction of methyl transfert α from the areas of MSE and ZWT CH_3 peaks for partially reacted MSE. The curve is the result of a fit by a simple first order kinetic law $\alpha = 100(1 - e^{-kt})$ with k = 0,143 h^{-1}. A double step reaction mechanism does not seem to be required to explain the evolution of the experimental data.

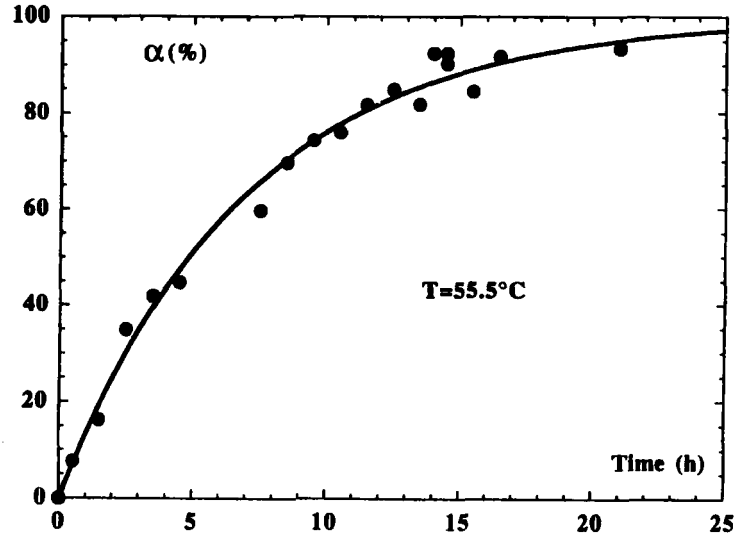

FIGURE 2 Variation of the fraction of methyl transfer α as a function of time t during an in situ isothermal transformation of a MSE polycrystalline powder at T = 55,5° C.

Raman Scattering

The low frequency Raman spectra of a MSE monocrystal (grown from acetone solution) were recorded in the [15-300 cm^{-1}] frequency range when heating at a constant temperature T=65,5°C. We can conclude from the spectra recorded at several times from 0 to 350mn that the lattice modes are strongly dependent of the structural transition which takes place at t=135mn ; the spectra observed at times lower than 135mn are characteristic of the monoclinic phase and those observed at times higher than 135 mn are characteristic of a structural phase similar than of the orthorhombic ZWT phase as checked by cell parameters obtained by X-ray diffraction. On the other hand we observed a continuous evolution in the intensity of the high frequency modes which are a superposition of pure MSE and pure ZWT internal modes. They are characteristic of the chemical reaction for the evolution of their relative intensity as a function of time varies in good agreement with the first order kinetics at the same temperature.

Birefringence Observations

Optical indicatrix orientation with regard to the crystallographic axes of MSE crystal[9,11] was determined by conoscopic studies of as-grown (bc) plates. In pure MSE crystal the relation between the three principal refractive indices is as follows : $n_3 \gg n_2 > n_1$ with $n_3/n_2=1,17$; birefringence (n_2-n_1) amounts to only 0.005 and the optic axial angle is $(+)2V=21.1°\pm0.7°$. The binary axis is parallel to the n_1 direction ; the n_3 direction (practically parallel to the long molecular axis) is at the angle of about 40° to the plate normal (figure 3).

During the isothermal chemical reaction at various temperatures in the monoclinic monocrystalline plates (before the transition), we have observed that the n_3 direction is practically the same, but we have noted progressive exchange between the relative values of n_1 and n_2 indices (via optically pseudouniaxial "state") and initially $b // n_1$ becomes $b // n_2$. During the structural change we have observed the appearance by nucleation of small regions of irregular shape (about 5-10 μm in size) yielding polycrystalline ZWT samples of orthorhombic structure. Often in the case of very thin plates rather rarely in the case of thick samples, when starting from good optical quality monocrystals of MSE, we could observe the presence of monocrystalline orthorhombic ZWT regions. We have verified by X-ray diffraction that an average orthorhombic structure exists in the whole ZWT samples which are polycristalline.

In the above mentioned monocrystalline regions the n_3 direction is roughly the same as in the initial monoclinic structure of MSE crystals. By optical examination of monocrystalline (ab) ZWT plates grown directly from water solution we have determined the indicatrix orientation within orthorhombic lattice[12] : $a // n_2$, $b // n_1$, $c // n_3$; similarly to the monoclinic MSE structure, $n_3 \gg n_2 > n_1$, and $(+)2V=25.7°\pm 0.9°$. It is to be noted that the long molecular axis is parallel to the c-axis[12]. We can also conclude by conoscopic image analysis of monocrystalline ZWT regions obtained from transformation of MSE crystals that the b monoclinic axis of MSE becomes the a orthorhombic axis of ZWT. Orientation of the samples by X-ray methods is in good agreement with this conclusion.

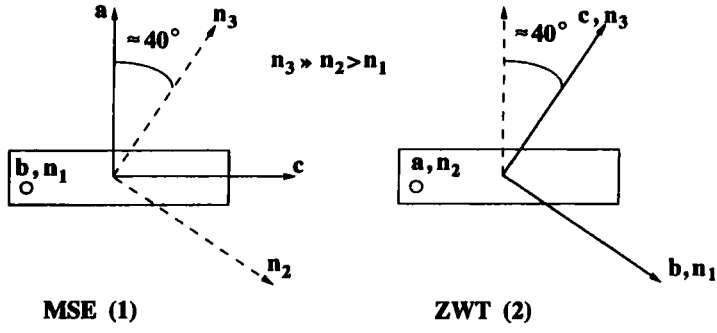

FIGURE 3 Projection of MSE monocrystalline (b,c) plates (monoclinic structure from ref. 9,11) in the (a,c) plane (1) and of ZWT monocrystalline regions (2) (orthorhombic structure from ref. 12) obtained from the transformation of the MSE plate (1). The crystallographic axes and directions of principal indices [9,11,12] are drawn for the two representations (1) and (2).

Moreover, orthoscopic observations confirmed the existence of the first-order transition from orthorhombic to tetragonal ZWT phases at T_C=113°C (see Calorimetric Results of ZWT Specific Heat and ref. 12).

Brillouin Scattering

The low-frequency Brillouin spectra of a MSE monocrystals grown from acetone solution were recorded in the [0-20 GHz] frequency range when heating at a constant temperatures T=42.5°C and T=65.5°C. We observed on the spectra recorded at several times before and after the transition a strong decrease of the frequencies of the longitudinal and the transversal modes when passing the transition. It can be related to a stress relaxation in the crystal at the transition .

Discussion and Conclusion

The results indicate that the thermal conversion of MSE to ZWT is associated with a change from the $P2_1/c$ (Z = 4) monoclinic structure of MSE to the Pbma (Z = 4) orthorhombic structure of ZWT when the MSE crystals are annealed in

the [25°C-65°C] temperature range. From the point of view of group theory, this structural transformation is then mainly characterized by a change of point group from 2/m (MSE) to mmm (ZWT). It corresponds to one of the 94 cases of full ferroelastics[18]. The original feature of the (MSE - ZWT) mixed system is that the driving force for the structural transformation is not the temperature but the chemical reaction. One may expect a gradual 2/m → mmm structural transformation but the recent theory for solid state chemical reactions[1, 4] predicts that the possibility arises of lattice instabilities. In the particular case of MSE → ZWT transformation the NMR results of section 4 indicate that the second peak obtained by calorimetry[10] is associated to a well defined ferroelastic phase transition. The comparison with temperature induced structural ferroelastic phase transitions[18] does not fully work : first, the transition occurs in mixed crystals of MSE-ZWT during the reaction ; second, in the case of classical ferroelastic compounds[18] the transition from the low symmetry phase to the high symmetry phase is endothermic whereas it is exothermic for the transition induced by thermally enhanced reaction in mixed crystals of MSE-ZWT. The last difference illustrates the fact that at the beginning of the reaction pure MSE crystal is in a metastable state both from the electronic and the structural points of view as compared to the stable state of pure ZWT at the end of the reaction[1].

Birefringence indicates that there is a relation between the average crystallographic structures before (monoclinic) and after (orthorhombic) passing the structural transition. On the contrary it is claimed in ref. 9 and 22 the product of this solid state reaction (ZWT) has a crystalline structure that does not resembles that of the reactant (MSE). The binary axis that exists in the monoclinic structure and the molecular orientation (**c** axis in the orthorhombic structure) are preserved. Defects which exist in the initial MSE monocrystals often prevent to obtain monocrystalline regions of large size. A general point of view[19] is to associate to a chemical solid state reaction either single-crystal to single-crystal transformation, or a preferential crystallization of product in localized regions leading to disruption of the parent crystal. In the case of MSE,

the two aspects are present but rather than to say "a preferential crystallization" we prefer to talk about lattice instability. Indeed the average crystalline structures before and after the structural change are related. According to another description[1,4] we can say that the average lattice strain ε_{xz} is associated to the evolution of the chemical reaction. After the structural instability occured, two cases are observed : if monocrystalline ZWT is obtained, the use of the average lattice strain ε_{xz} is still well defined ; if completely disordered polycrystalline ZWT is obtained, it means that the fluctuations of ε_{xz} induced by the structural change are much greater than the average lattice strain ε_{xz}. ZWT samples obtained after reaction and structural change are in all the possible situations between these two borderline cases.

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