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A calorimetric study of pTS (bis-p-toluenesulphonate of 2,4-hexadiyne 1,6-diol) and its phase transitions as a function of polymerization (*)

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Résumé. — On a mesuré la chaleur spécifique de pTS entre 135 et 225 K, pour des taux de polymère $0 \leq \mathcal{F} \leq 1$. Pour $\mathcal{F} \leq 0,01$, deux endothermes entre 156 et 192 K limitent la phase incommensurable. Pour $0,01 \leq \mathcal{F}$ deux autres transitions s'y ajoutent vers 161 et 182 K. Les enthalpies correspondantes diminuent de 25 à moins de 1 cal./mole et les transitions cessent d'être observables à $\mathcal{F} > 0,04$ (182 et 192 K) ou $0,12$ (150 et 161 K). Une transition est à nouveau observable vers 189 K pour $\mathcal{F} \geq 0,95$, avec $\Delta H \sim 10$ cal./mole.

Abstract. — The specific heat C_p of pTS was measured from 135 to 225 K, for polymer contents $0 \leq \mathcal{F} \leq 1$. For $\mathcal{F} \leq 0,01$, two endotherms near 156 and 192 K limit the incommensurable phase. For $\mathcal{F} \geq 0,01$, two other transitions occur near 161 and 182 K. The corresponding enthalpies decrease from about 25 to less than 1 cal./mol, and the transitions are no longer detected for $\mathcal{F} \geq 0,04$ (182 and 192 K) and for $\mathcal{F} \geq 0,12$ (150 and 161 K). For $\mathcal{F} > 0,95$ a transition is again observed near 189 K with $\Delta H \sim 10$ cal./mol.

1. Introduction. — The bis-paratoluenesulphonate of 2,4-hexadiyne 1,6-diol, or pTS (also sometimes named TS or TSHD), polymerizes in the solid state, with conservation of crystallinity, up to the pure polymer single crystal stage [1]. Interest first focussed on the polymerization reaction kinetics, which shows an « induction » period up to a polymer content $\mathcal{F} \sim 0,1$, then an « autocatalytic » range up to $\mathcal{F} \sim 0,9$ in which the rate is enhanced by about 3 orders of magnitude [2]. Another interesting property of pTS is the modulated incommensurable phase recently discovered in the monomer crystal by Robin *et al.* [3] between a high T phase above $T_i \simeq 200$ K, and a low T phase below $T_i \simeq 155$ K. In the polymer, only high and low T phases are present, with a transition around 190 K [5]. In partially polymerized crystals, the modulated phase exists only for $\mathcal{F} \leq 0,15$ [6].

A calorimetric study of pTS may then be of interest for several reasons. A phase diagram as a function of $\mathcal{F}$ can be determined. It can also help understand

the order and nature (displacive or order-disorder) of the transitions at T_i and T_1 : up to now structural work [4], Raman studies [7] and neutron inelastic scattering [8] have failed to give a clear understanding of the processes. Finally, the dependence of C_p on $\mathcal{F}$ at a given temperature may give information about the role and behaviour of polymer chains in the matrix, hence on the polymerization process. We have therefore undertaken a DSC study of microcrystalline pTS powders (prepared by us) and this note reports our first results with a brief discussion.

2. Experimental. — pTS was prepared according to [9] and purified by several recrystallizations in CH_2Cl_2 , CH_3OH mixtures [10]. The microcrystalline powder thus obtained was placed in a thermostat at 60 °C, and sampling at different times yielded the 25 samples studied. $\mathcal{F}$ was measured using two methods which were found in good agreement. For $\mathcal{F} \leq 0,1$, the melting point was measured by DSC [11]: sample weight ~ 3 mg, heating rate 10 K/min. For $\mathcal{F} \geq 0,1$, and for cross-checking for several samples in which $0 \leq \mathcal{F} \leq 0,1$, the heat evolved during total polymerization of the sample, which is proportional to $1-\mathcal{F}$, was measured by DSC [12]: sample weights were 10

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Fig. 1. — Specific heat of partially polymerized microcrystalline pTS samples. Polymer contents : $a(f \sim 0)$; $b(f \sim 0.002)$; $c(0.03)$; $d(0.06)$; $e(0.45)$; $f(f > 0.99)$.

to 20 mg, the heating rate increasing with f from 0.31 to 2.5 K/min.

In pure pTS monomer, a new, metastable phase was found. Most of it transforms into the stable phase by annealing at 60 °C for 30 min. The new phase is under study.

All measurements were performed on a Perkin-Elmer DSC 2 microcalorimeter, with a Tektronix 31 attachment. Between 125 and 225 K, the measurement head was cooled with liquid N_2 and purged with helium gas. Calibrations in T (± 0.2 K) and in energy ($\pm 0.3\%$) were made using the phase transitions of cyclohexane [13] and checked by measuring C_p of sapphire from 135 to 225 K [14]. pTS samples weighing 15 to 25 mg were put in aluminium capsules : the heating rate was 10 K/min.

3. Results and discussion. — The heat capacity C_p of pTS monomer and of 25 samples in which f varied from 0.002 to more than 0.995 were measured

Fig. 2. — Variation with polymer content f of the temperature of the maxima of thermal phenomena observed on specific heat $C_p(T)$ curves of microcrystalline pTS samples. One scale is linear in heating time (hours) at 60 °C. For f there is a scale change $\times 100$ at $t = 25$ h ($f \sim 1$ at $t > 25$ h).

from 136 to 220 K. Figure 2 shows six characteristic $C_p(T)$ curves, exhibiting thermal phenomena whose changes depend on f . For $f < 0.01$ (Figs. 2a, 2b) two transitions are observed, with maxima around 156 and 192 K (± 1 K) and enthalpies of about 20 and 10 cal./mol respectively. They correspond to the limits T_i and T_f of the incommensurate phase already observed with X-rays [3] and neutrons [4].

For $0.01 < f < 0.12$, these transitions are split, and the corresponding enthalpies ΔH decrease when f increases (Fig. 2e); they are no longer detected when $\Delta H < 1$ cal./mol which occurs near $f \sim 0.04$ at 182 and 190 K, and near $f \sim 0.12$ at 150 and 161 K (Fig. 2d). The lowest transition temperature is the only one varying substantially with f , from 156 to 150 K (Fig. 3). These values of f correspond to the polymerization induction period [2]. No thermal phenomenon distinct from the overall increase of C_p with T is observed in the autocatalytic range

$$0.12 < f < 0.95 \quad (\text{Fig. 2e}).$$

A single broad transition reappears between 170 and 200 K near $f = 0.95$, and quickly localizes near $T = 189$ K with an enthalpy of 10 cal./mol (Figs. 2f and 3). This corresponds to the already known pure polymer transition [5].

For $0.01 \leq f \leq 0.20$, the temperatures of the maxima of the thermal phenomena corresponding to T_i and T_f are not identical to the transition temperatures found in X-ray [6] or neutron [4] measurements. The maxima measured in a dynamic DSC experiment as here do not necessarily correspond to the exact transition temperature. In addition, the influence of the grain size of the powder studied cannot be excluded. Experiments on single crystals are in progress.

One can only speculate at present about the origin of endotherms near 161 and 182 K. There may be a succession of modulated phases, commensurate or not; however δ is always small [3, 4] : $\delta \sim 0.06$ at T_i .

Fig. 3. — Dependence on polymer content f of the specific heat C_p of microcrystalline pTS samples at different temperatures between 140 and 220 K. One scale is linear in heating time (hours) at 60 °C. For f there is a scale change $\times 100$ at $t = 25$ h ($f \sim 1$ at $t > 25$ h).

Alternatively, there may be a macroscopic heterogeneity, as suggested by some neutron data for $\mathcal{F} \gtrsim 0.2$ average value [15].

Comparing the enthalpies ΔH found here to those in other materials showing similar transitions — chloranil [16], Rb_2ZnCl_4 [17], terphenyl [18] or biphenyl [19] for instance — shows that ΔH and ΔS associated with the transitions in pure monomer or polymer pTS are larger than any of them; on the other hand, for $\mathcal{F} \sim 0.1$, the ΔH at 150 K is smaller than the small value found for the displacive transition at 38 K in biphenyl [19]. Preliminary neutron data also show [4] a change in the behaviour of the system near T_1 when $\mathcal{F}$ increases from 0.002 to 0.03. However no soft mode has been detected up to now in perdeuterated pTS with an estimated $\mathcal{F} \lesssim 0.01$ [8]. pTS might be a system in which the character of the transitions changes continuously with $\mathcal{F}$.

From $C_p(T)$ curves like those displayed in figure 2, the change of C_p with $\mathcal{F}$ at constant T (in cal./gK) can be extracted (Fig. 3). The polymer value of C_p is always smaller than the monomer value by 5-10%. This may be related to the large variation of thermal

expansion coefficient along the b axis, which at these temperatures decreases from 10^{-4} K^{-1} in the monomer [4] to practically zero in the polymer [20], or to the large increase of sound velocity in that direction [15]. The larger part of the decrease occurs in the autocatalytic range, whose boundaries are marked by maxima of C_p .

In this note, we limited ourselves to presenting our first calorimetric data, and to sketching avenues for discussion. A further study is in progress. Since completion of this work, measurements of $C_p(T)$ from 3 to 300 K for pure monomer and polymer pTS single crystals have appeared [21]. These data are in good agreement with ours for the corresponding microcrystalline samples.

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