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DSC study of 2-bromothiophene: a compound with three melting points

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Abstract

By means of a DSC study, 2-bromothiophene was shown to possess three different phases which melt at atmospheric pressure. These phases, the existence of which was subsequently checked by Raman spectroscopy, were obtained reproducibly through simple thermal treatments, and melt at 196.2 K, 200.3 K and 203.9 K respectively. Their relative stabilities were established, and a nomenclature is proposed. A high pressure–temperature phase diagram pattern is suggested. Finally, premelting phenomena seem to depend on the observed phases.

INTRODUCTION

A number of solid five-membered heterocyclic molecules (unsubstituted or monosubstituted) exhibit intricate phase behaviour (see for instance refs. 1–3). This could be related to the shapes of these rigid planar molecules, which favour the existence of in-plane large-amplitude molecular motions in crystalline phases. This in turn should lead to solid–solid phase transitions [4] or to the emergence of glassy crystalline states [5] for symmetry reasons.

2-Bromothiophene was studied as a member of this group of molecules to disclose eventually new glassy crystalline phases. The results were quite unexpected.

EXPERIMENTAL

2-Bromothiophene was purchased from Janssen Chimica (stated initial purity 98%) and purified by bulb-to-bulb distillation. The final purity was 99.5% according to gas chromatography.

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A few milligrams of product (typically 5 or 6 mg) were sealed in aluminium capsules under a nitrogen atmosphere inside a glove box.

Scanning calorimetry measurements were performed in the 100–300 K temperature range by means of a Perkin–Elmer DSC-2C apparatus equipped with a TADS-3600 thermal analysis data station and a home-made cooling attachment [6]. The temperature and enthalpy scales were calibrated with respect to the II–I phase transition and the melting point of cyclohexane [7,8] using the same heating rate as in the ensuing measurements. The accuracy and reproducibility of the temperature are better than 1 K and the relative accuracy of enthalpy determinations is 3%.

RESULTS

In what follows, all the thermograms obtained on heating correspond to a 10 K min^{-1} heating rate (the same measurements have also been performed using a 40 K min^{-1} rate: the results were essentially the same).

Cooling the liquid to T > *140 K*

When the samples have been first cooled to $T > 140$ K using cooling rates ranging from 80 to 10 K min^{-1}, the thermograms obtained on heating only exhibit an endothermic peak at about 196 K (Fig. 1, curve a). This peak corresponds to melting, because no other thermal event occurs up to 300 K, where 2-bromothiophene is liquid.

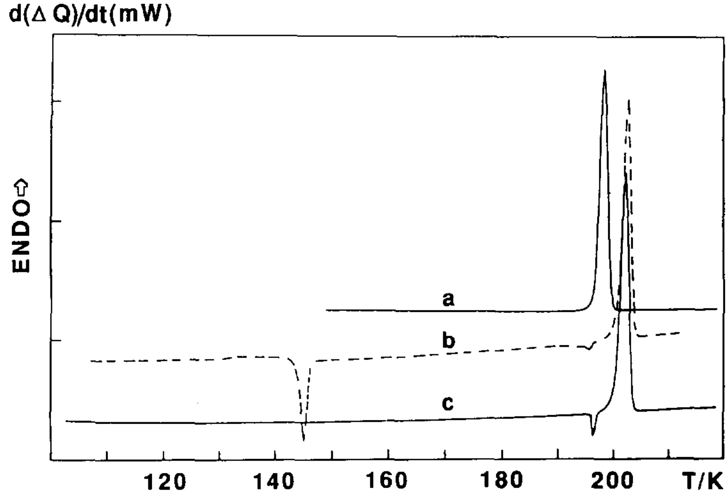

Fig. 1. DSC study of 2-bromothiophene (heating rate, 10 K min^{-1}): curve a, after cooling a liquid sample to $T > 140$ K; curve b, after quenching a liquid sample in liquid nitrogen; curve c, after annealing a quenched sample at 150 K and cooling to 100 K. The energy scale division corresponds to 310 J mol^{-1}.

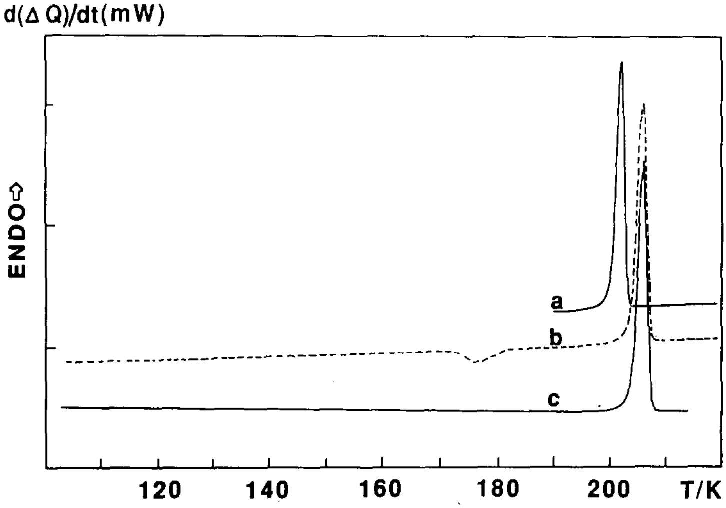

Fig. 2. DSC study of 2-bromothiophene (heating rate, 10 K min^{-1}): curve a, after the 196 K recrystallization is complete and cooling to $T > 170$ K; curve b, after the 196 K recrystallization is complete and cooling to 100 K; curve c, after the recrystallization shown by curve b is complete and cooling to 100 K. The energy scale division corresponds to 310 J mol^{-1}.

Cooling the liquid to T *< 140 K*

If the sample-containing capsule has been dipped into liquid nitrogen, the heating thermogram exhibits a step increase characteristic of a glass transition near 130 K, then an exothermic peak near 140–150 K (Fig. 1, curve b).

If the heating procedure is stopped after the latter peak is complete and the sample is cooled back to a temperature below 130 K, the former step increases and the exothermic peak no longer exists on heating (Fig. 1, curve c).

In either case, if the heating process is continued, another exothermic peak occurs at about 195 K, followed by an endothermic one at 200 K, which also corresponds to a melting process (Fig. 1, curves b and c).

When the previous heating process is stopped after the exothermic peak at 195 K is complete and the sample is cooled to a temperature not less than 170 K, the thermogram obtained on heating exhibits only the same melting endothermic peak at 200 K (Fig. 2, curve a).

If the previous cooling process, starting when the exothermic peak at 195 K is complete, is stopped at a temperature less than 170 K, the ensuing heating thermogram exhibits a new exothermic peak around 175 K and a new melting endothermic peak at 204 K (Fig. 2, curve b).

Last, if the heating process is stopped after the exothermic peak at 175 K is complete and the sample is cooled to some lower temperature, say 100

K, the ensuing heating thermogram exhibits only the melting peak at 204 K (Fig. 2, curve c).

DISCUSSION

Phase assignment

These results show that 2-bromothiophene has three crystalline phases that can melt at atmospheric pressure. The vapour pressures at $T \approx 200$ K are neglected.

Compounds with plural melting points are thought to be numerous. Kuhnert-Brandstatter [9] gives series of such compounds. However, Byrn [10] points out that these results have been obtained using a Kofler stage, have not been confirmed by crystallographic studies and should be considered as tentative. For instance, barbital is reported by Kuhnert-Brandstatter as having six melting temperatures, but a recent thermal analysis study by Fournival [11] reveals only two of them.

First, we consider the naming of these phases. (i) To conform with the usual numbering, they all have I as the principal denomination because they are all phases which are in equilibrium with the liquid. (ii) A left-hand superscript characterizes the relative stabilities of these phases; 0 designates the most stable one and may be omitted, 1 the next most stable, etc. (*Note*: A right-hand subscript is used to number the crystalline phases in a metastable phase sequence [3]).

Here, the phase that melts at 196 K spontaneously transforms to the phase that melts at 200 K which, in turn, spontaneously transforms to the crystal that melts at 204 K. Therefore, the last named phase is the most stable one and will be named ^{0}I or I. The phases which melt at 196 K and 200 K will consequently be named ^{2}I and ^{1}I respectively.

It is now possible to describe the different transformations which occur in 2-bromothiophene. Figure 3 shows a possible thermal treatment that would allow one to observe all the phases we described.

It is to be noted that ^{1}I nuclei form from phase ^{2}I or from the undercooled liquid only at temperatures less than 140 K. It seems that some stresses are necessary to form them because, in one run in which an initially liquid sample had been cooled to 100 K with a 0.3 K min^{-1} cooling rate, only the melting of phase ^{2}I was observed on heating.

Table 1 shows the thermodynamic data which correspond to all crystalline phase transformations. The melting enthalpies increase as the stabilities of the phases increase. Moreover, the enthalpy increments at recrystallization are almost equal to the differences between the melting enthalpies of the phases involved: this is another indication that our phase assignment is correct.

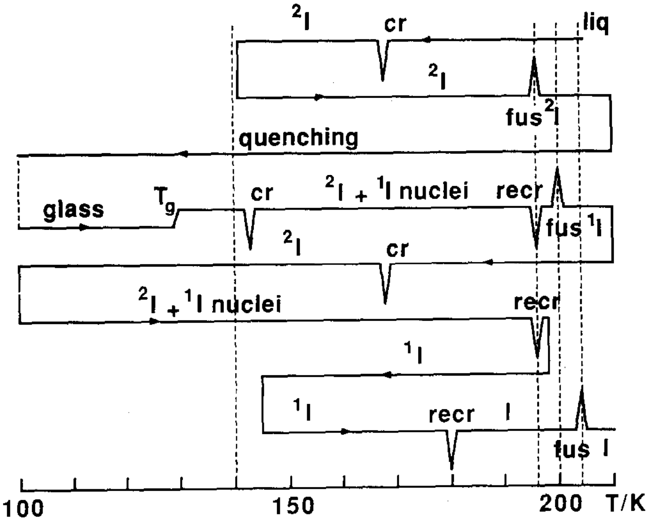

Fig. 3. A possible thermal treatment which would enable one to observe all known phases of 2-bromothiophene. The up direction corresponds to endothermic transformations ("recr" stands for recrystallization).

The glassy phase

Let us now consider the ability of liquid 2-bromothiophene to form a glass on cooling. We have seen that a glass transition is observed at 130 K for samples which have been immersed rapidly in liquid nitrogen. If the quenching plunge into liquid nitrogen is less sudden, glass formation is less efficient. If a sample is cooled with the fastest rate that the DSC-2C can achieve, that is 80 K min^{-1} around 130 K, neither a glass transition nor subsequent crystallization is observed.

Figure 4 shows the DSC curves corresponding to sudden quenching (curve b) and to a "less sudden" one (curve a). Table 2 shows the

TABLE 1

DSC-determined thermodynamic data for phase transformations of solid 2-bromothiophene

Phase	^{2}I		^{1}I		I
Recrystallization		^{2}I $\to$ ^{1}I		^{1}I $\to$ I	
T_{fus} (K)	196.2 ± 0.2 [a]		200.3 ± 0.2 [b]		203.9 ± 0.2 [c]
T_{recr} (K)		172–187		193–197	
$\Delta_{fus}H_m$ (J mol^{-1})	6290 ± 40 [a]		6500 ± 80 [b]		7580 ± 80 [c]
$\Delta_{recr}H_m$ (J mol^{-1})		−260 ± 30		−1090 ± 110	
$\Delta_{fus}S_m$ (J K^{-1} mol^{-1})	32.1 ± 0.2		32.5 ± 0.5		37.2 ± 0.5

[a] Uncertainty is the standard deviation for 11 determinations.

[b] Uncertainty is the standard deviation for 14 determinations.

[c] Uncertainty is the standard deviation for 5 determinations.

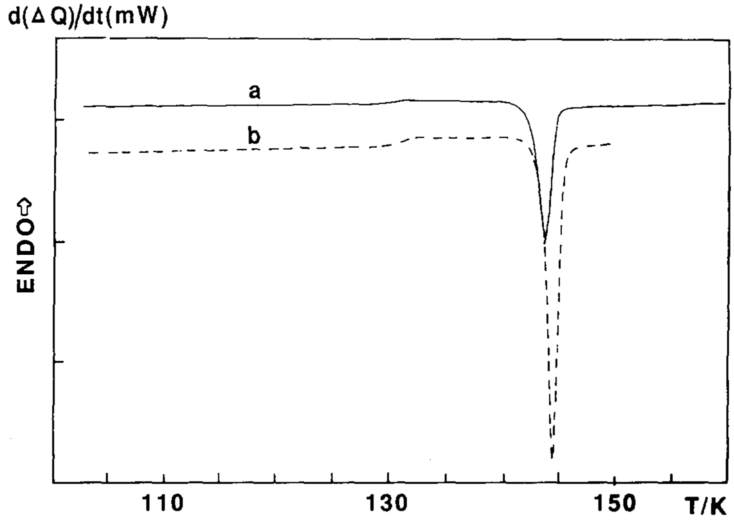

Fig. 4. DSC curves for 2-bromothiophene quenched in liquid nitrogen (heating rate, 10 K $\min^{-1}$): curve a, after moderate quenching; curve b, after sudden quenching. The energy scale division corresponds to 190 J mol^{-1}.

corresponding thermodynamic data. Obviously the crystallization intensities are related to the heat capacity increments at T_g.

The heat capacity increment at T_g that we determined for run 2 (Table 2) was the highest we ever measured, and it was thought to correspond to the total vitrification of the liquid sample. We shall presently substantiate this assumption.

On cooling at 10 K $\min^{-1}$, the liquid phase crystallizes to phase ^{2}I at 168 K (generally) or at 192 K (sometimes) with crystallization enthalpies equal to -4890 J mol^{-1} or -6110 J mol^{-1} respectively.

Thermodynamic cycles including melting of phase ^{2}I and the above crystallizations allow us to determine mean values for the difference between the heat capacity of the liquid and that of phase ^{2}I. We obtain $C_p^{\mathrm{liq}} - C_p^{2\mathrm{I}} = 50$ J K^{-1} mol^{-1} between 168 and 196 K by considering melting and crystallization at 168 K, and $C_p^{\mathrm{liq}} - C_p^{2\mathrm{I}} = 51$ J K^{-1} mol^{-1} between 168 and 192 K by taking both crystallizations into account.

TABLE 2

DSC-determined thermodynamic data for the glass transition and the ensuing crystallization after quenching liquid 2-bromothiophene (see text)

Run no.	T_g (K)	$\Delta_{T_g}C_{p,\mathrm{m}}$ (J K^{-1} mol^{-1})	T_{cr} (K)	$\Delta_{\mathrm{cr}}H_{\mathrm{m}}$ (J mol^{-1})
1	129.2	34	140.4	−1760
2	129.0	73	142.4	−3450

As it was assumed that run 2 corresponds to the freezing of all the liquid into a glass, $\Delta_{T_g}C_{p,m} = 73$ K^{-1} mol^{-1} is a good (low) approximation for $(C_p^{\text{liq}} - C_p^{2\text{I}})$ at 129 K. Assuming that $(C_p^{\text{liq}} - C_p^{2\text{I}})$ varies linearly with temperature, it amounts to 67 J K^{-1} mol^{-1} at 143 K and 44 J K^{-1} mol^{-1} at 196 K.

A thermodynamic cycle including crystallization of the supercooled liquid to phase ^{2}I at 143 K and melting of this phase leads to

$$\int_{143\text{ K}}^{196\text{ K}} \left(C_p^{2\text{I}} - C_p^{\text{liq}}\right) \mathrm{d}T + \Delta_{\text{cryst}}^{\to 2\text{I}} H + \Delta_{\text{fus}}^{2\text{I}} H = 0$$

or

$$(-2940 - 3450 + 6290) \text{ J mol}^{-1} = -100 \text{ J mol}^{-1}.$$

This residue amounts to only 3% of the crystallization enthalpy and is clearly less than the inaccuracy in this value. Therefore the assumption according to which run 2 represents complete freezing of the liquid sample corresponds to a good approximation.

A possible PT *phase diagram*

A possible explanation for the existence of phases ^{1}I and ^{2}I is that they are phases which are stable at high pressure (say in the kilobar range).

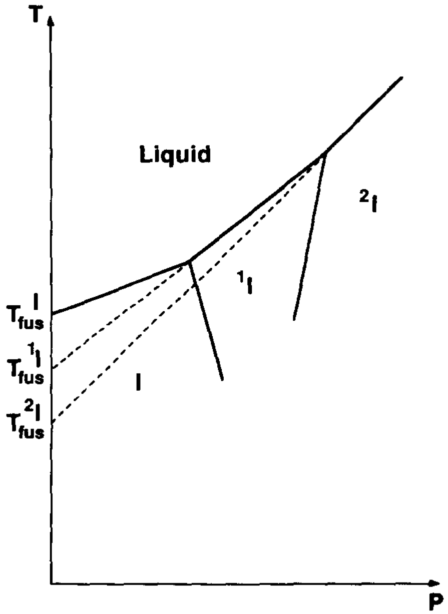

Fig. 5. A possible phase diagram for 2-bromothiophene. The broken lines are taken to represent the melting curves of metastable ^{1}I and ^{2}I.

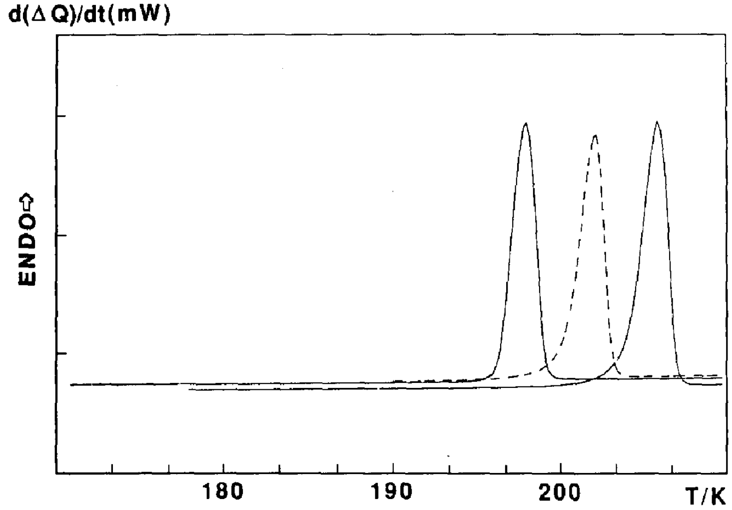

Fig. 6. Temperature scale expanded melting DSC curves of 2-bromothiophene (heating rate 10 K min^{-1}). The energy scale division corresponds to 310 J mol^{-1}.

Thus $T_{\text{fus}}^{1\text{I}}$ and $T_{\text{fus}}^{2\text{I}}$ would be the metastable extrapolations at atmospheric pressure of the high pressure melting lines of stable ^{1}I and ^{2}I.

At the I^{1}Il triple point, we obtain as usual

$$\Delta_{\text{fus}}^{\text{I}}S - \Delta_{\text{fus}}^{1\text{I}}S + \Delta_{\text{trs}}^{1\text{I}\to\text{I}}S = 0$$

Because $\Delta_{\text{fus}}^{\text{I}}S$ is much larger than $\Delta_{\text{fus}}^{1\text{I}}S$ at atmospheric pressure (Table 1), it may be assumed that the same inequality holds at the above triple point, so that $\Delta_{\text{trs}}^{1\text{I}\to\text{I}}S < 0$. This is possible only if the slope of the I–^{1}I transition line $(\mathrm{d}T/\mathrm{d}P)_{\text{I}-^1\text{I}}$ is negative. Figure 5 shows a scheme for the proposed P–T phase diagram.

Melting and premelting

Figure 6 shows a temperature scale expanded representation of I, ^{1}I and ^{2}I melting curves. From these curves, it is obvious that premelting is almost non-existent for ^{2}I, but becomes important for ^{1}I and even more so for I.

The same curves have been obtained repeatedly in any order during five months for several samples, so no change of the overall impurity content is involved.

Different solubilities of some impurity in the different phases could be invoked to explain the above observations. In any event, such melting and premelting phenomena deserve further investigation.

CONFIRMATION THROUGH RAMAN SPECTROSCOPY

To prove the existence of the three phases, Raman spectroscopy measurements were performed.

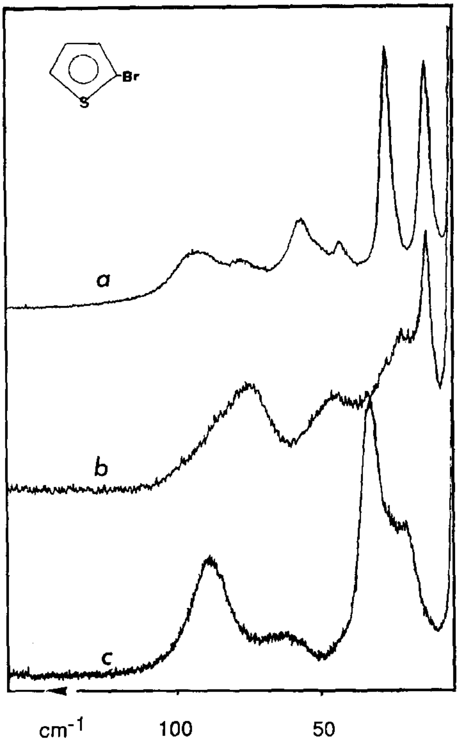

Fig. 7. Low frequency Raman spectra of three crystalline phases of 2-bromothiophene: curve a, phase I at 171 K; curve b, phase ^{1}I at 171 K; curve c, phase ^{2}I at 164 K.

None of the purified 2-bromothiophene sample used in the experiments above described was left, but subsequent DSC measurements on 2-bromothiophene (purified or unpurified) from different commercial sources led to essentially the same results, which shows that impurities have little influence in the case. Therefore the following Raman study was performed on the commercial Aldrich product (stated purity 98%).

Raman spectra were obtained using a computerized Dilor RTI 30 triple monochromator equipped with a Spectra Physics argon ion laser (Model 2020); 514.5 nm radiation was used for excitation with 200 mW power. The compound, placed in an open glass cell 3 mm in diameter, was introduced into a helium convection Meric cryostat. The resolution was about 1 cm^{-1} and the reproducibility was about 0.2 cm^{-1}.

Various thermal treatments were performed, but the results were not as reproducible as the DSC measurements, possibly because the laser beam impact causes a local thermal gradient. The low frequency spectra of three different crystalline phases were recorded. Figure 7 shows the three spectra near 170 K.

It was possible to keep all three phases in equilibrium with the liquid phase, which proves that they indeed melt at atmospheric pressure.

CONCLUSION

A DSC study of 2-bromothiophene has disclosed the existence of three crystalline phases which melt at atmospheric pressure.

Numerous compounds with plural melting points have been described, but we failed to find in the literature another compound for which simple heat treatments allow one to obtain reproducibly three different crystalline modifications that melt. Moreover, the stability relationships between these three phases are unambiguously established owing to clearly defined recrystallizations and accurate enthalpic data. This makes 2-bromothiophene a textbook case for plural melting studies.

Another interesting point arises from the dependence of the intensity of the premelting phenomenon on the nature of the phase which melts. This is sufficient reason to continue studying 2-bromothiophene.

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