Polymer Bulletin 9, 245–251 (1983)

Polymer Bulletin

About the Transition of n-Alkanes Above the Melting Point

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Summary

The thermal behavior of a series of n-alkanes has been studied by means of a Mettler TA 2000 B heat flow differential scanning calorimeter. Between 450-480 K all n alkanes studied show an exothermic effect bound only to the first run and with hermetically sealed crucibles. The exothermic effect decreases with the mass of sample. If the crucible is sealed in an argon filled glove box, no effect occurs. On the contrary, if the experiment is carried out under oxygen a large exothermic effect is observed. We have concluded that the effect observed with sealed sample pans is not a phase transition but a slight oxydation of n alkanes.

Introduction

Several authors have recently presented results about a transition observed above the melting point of n-alkanes. Pietralla and Krüger (1) using both Brillouin scattering and bulk viscosity showed evidence for a transition designated Tu > Tm in the n-alkanes. Denny and Boyer (2) by means of DSC measurements interpreted the effect observed as the destruction of persistent structures in the liquid. Höhne (3) measured the specific heat capacity of a series of alkanes. Up to 430 K no transition could be found. But he observed between 450 and 480 K that the n-alkanes showed an exothermic effect bound to the first run only with hermetically sealed sample pans. He concluded that this effect is a pressure induced epitactic phenomenon correlative to the surface of the sample pan. It seems surprising that this effect should be interpreted as an increasing of the order in the liquid. Therefore we have decided to study the same n-alkanes under different conditions of manipulation : mass of the sample, type of pan and gas above the sample.

Experimental

Samples of very pure n-alkanes (purity > 99 %) have been used. DSC measurements have been carried out by means of a Mettler TA 2000 B heat flow D.S.C. apparatus. The mass of the sample ranged from 0,5 to 15 mg. Heating rate was 3.5 Kmn^{-1}. Gas flow in the apparatus was argon chosen on the grounds of its density and its low thermal conductivity. Calibrations for temperature and enthalpy were made using the melting temperature and the enthalpy of melting of elements or compounds (4). Enthalpies are considered to have a probable error of about 3 per cent. The temperature was obtained with a precision of ± 0.2 K. Some operations were carried out in an argon filled glowe box equipped with a recirculating system to remove oxygen and moisture traces using

MnO and molecular sieves (5).

Results

The n-alkanes studied show after the melting point no transition of first, second ord third order transition up to 450 K. In accordance with Hőhne's (3) findings all n alkanes show an exothermic effect for the case of first runs in closed crucible. When opened sample pans were used no effect is observed. Whe have reported in figure 1 the DSC curves obtained. It is surprising to obtain the same effect in the same range of temperature with the same enthalpy : - 130 ± 20 10^{-3} J. (the mass of sample was in the range 1.3 - 1.7 mg.

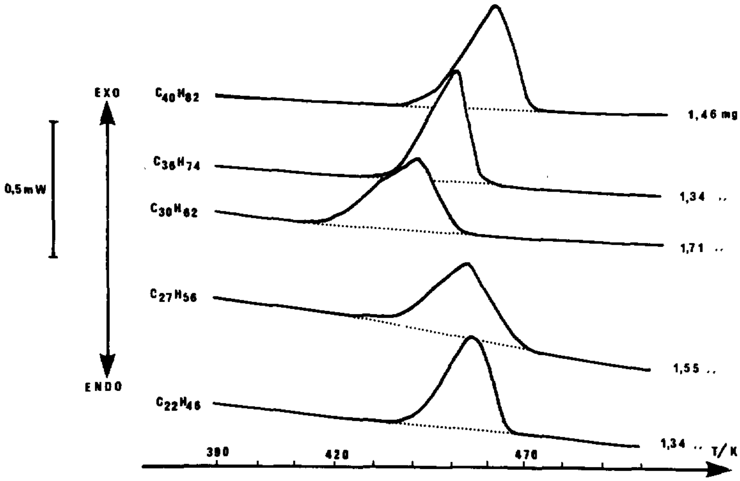

Fig. 1 - DSC curves (1 run) of n alkanes in sealed pans (1.3 mg < mass of sample < 1.7)

Next, we have studied the influence of the mass of the sample. We have reported in figure 2 the DSC curves obtained with a mass of $C_{22}H_{46}$ (docosane) in the range 0.5 to 15 mg.

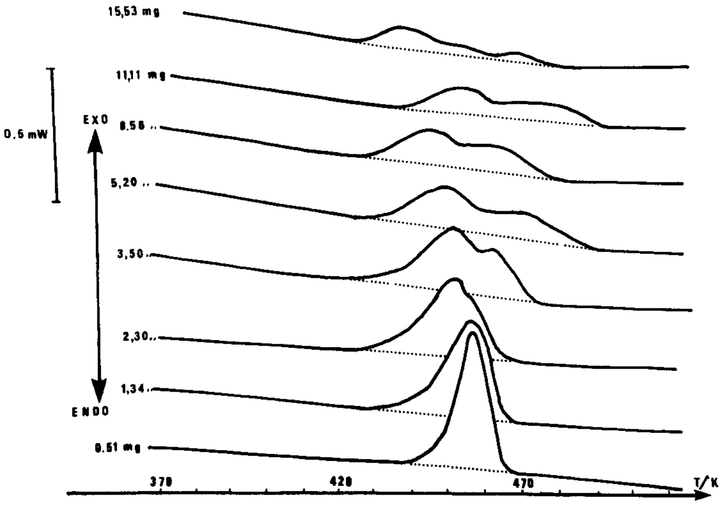

Fig. 2 - Variation of DSC curves versus mass of sample of $C_{22}H_{46}$ (Docosane)

When the mass of sample increases, the thermal effect becomes less and less prononced and occurs within a larger range of temperatures. If mass of 15 to 20 mg are used, the exothermic effect is so weak that the enthalpy cannot be determined. We have reported in figure 3 the variation of the enthalpy in $J.g^{-1}$ versus mass of sample and a decrease is observed.

Table 1

	mass of sample mg	Q $J.10^{-3}$	ΔH $J.g^{-1}$
n $C_{22}H_{46}$	1.34	114	85
n $C_{27}H_{56}$	1.55	118	76
n $C_{30}H_{62}$	1.71	131	76.5
n $C_{36}H_{74}$	1.43	127	89
n $C_{40}H_{82}$	1.46	127	87,4

Table 2

Mass of sample n $C_{22}H_{46}$	Q exp. $J.10^{-3}$	ΔH $J.g^{-1}$
0.51	122	240
1.11	140	135
1.34	114	85
2.30	125	54
3.66	149	41
5.20	119	21
7.00	125	17
8.56	103	12
11.14	68	6
15.93	41	2,5

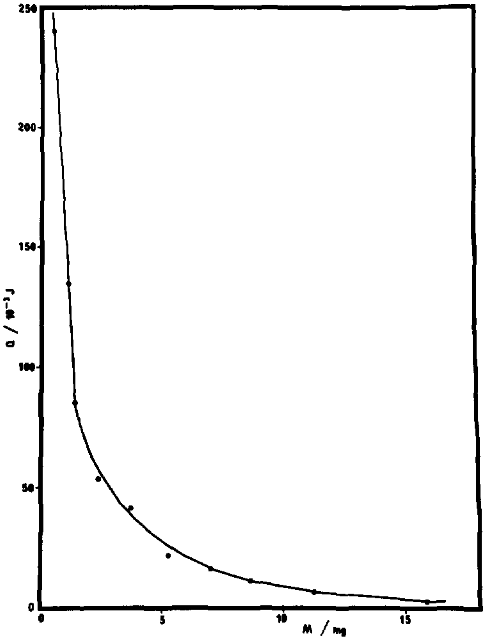

Fig. 3 - Variation of the enthalpy versus mass of sample

In most cases crucibles of 40 µl in aluminium were used. We have used gold crucibles having the same volume and we have noted no change. Then aluminium crucibles of 120 µl have been used. In this case the enthalpy of the thermal effect is greater than previously for the same mass of sample. We have used heptacosane n $C_{27}H_{56}$ (purity > 99.8 % GC controled). If the final temperature is lower than 430 K 2 phase transitions and the melting can be observed (figure 4 (2)).
It is well known that the shape of the peak at the onset of melting is directly influenced by the purity of the sample and a quantitative examination can be made.
If the exothermic peak is observed, during the next run, phase transitions and melting are modified (figure 4 (1)) as impurities are present in the sample.

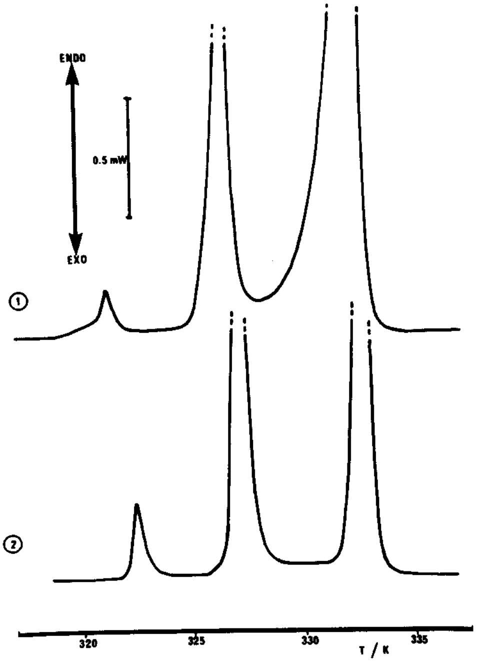

Fig.4 - DSC curves of $C_{27}H_{56}$ (heptacosane) before (2) and after (1) the exothermic effect

Finally crucible with a little hole in the top have been used. No effect appears if the calorimeter is flushed with argon. On the contrary if oxygen is used, a large exothermic peak is observed in the range 430-480 K.
These facts suggest that the effect observed corresponds to the oxydation of the n alkane by a very little quantity of oxygen trapped inside the crucible. To confirm this hypothesis, we have sealed the crucible in an argon filled glove box and no effect can be found during the first run.

Conclusion

A transition in the liquide phase of n alkanes discussed by some authors could not be found in our heat flow DSC measurements. The exothermic effect observed by Höhne (3) can not be attributed to a pressure induced epitactic ordering phenomenon. All our experiments show that the effect is due to a slight oxydation of the n alkane.

References

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Received November 11, accepted November 22, 1982

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