

Are There Two Temperature Regions with Different Structure of N-Alkane Melts?

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Summary

From the comparison of measurements of viscosity, Brillouin scattering and depolarized Rayleigh scattering it appears that two types of structure exist in the n-alkane melts. The regions where these structures are dominant are separated by a relatively well defined temperature T_u . The difference in the activation energies of viscous flow in these two regions is $\Delta E = 2.8$ kJ/mol. From the molecular weight dependence of T_u we conclude that polyethylene always retains the low temperature structure which should not be much different from that of n-alkanes with $n \approx 28$.

The n-alkane melts and their structure are of current interest because of their model character for polymer melts. There seems to be no doubt about the existence of short range order (FISCHER et. al. 1979, LONGMAN et. al. 1979) but the kind and extent of this order or orientation correlation is still a matter of controversy. Moreover, recent results from measurements of magnetic susceptibility (BALTA-CALLEJA et.al. 1976) and of the velocity of sound (KRÜGER 1979) have been interpreted as indicating the existence of a transition between two differently ordered structures of the $C_{24}H_{50}$ melt. In this communication we shall demonstrate that viscosity data also point to the existence of two temperature regions with different structures within the n-alkane melts.

There are numerous measurements of viscosities (e.g. DOOLITTLE 1951 a,b) and also critical discussions of the equations used for the interpretation of the data (IBAR 1979). However it appears that the temperature intervals between the measured values are usually too large to allow the behaviour reported here to be clearly observed. Additionally the temperature regions of the measurement were very often not extended enough. Consequently we have remeasured the kinematic viscosities of several n-alkanes.

For the measurements we used an UBBELOHDE viscosimeter (ASTM D 2515, DIN 51562) with electronic flow time measurement. (Capillary 0C for $n < 20$, 1 for $n \geq 20$). The temperature intervals were 3K and were only increased to 10K if an uniform behaviour at the higher temperatures was to be expected. The n-alkanes, from HUMPHREY (North Haven, Connecticut) had been purified by filtration of the melts through a 0,5 μm filter. The measurements were performed with rising temperature but for the $n = 20$ and $n = 28$ samples the measurements were repeated with decreasing temperature. The results with increasing and decreasing temperature were essentially identical except near the melting point. The data were plotted using a direct Arrhenius representation, i.e. describing the viscosity by

$$\eta = \eta_0 \exp(-E/kT)$$

and plotting $\ln \eta$ versus $1/T$. For the present purpose we see no special need to use an inverse Arrhenius plot as proposed by IBAR. The plots obtained (see fig.1) were all very similar: There are always two straight lines with a relatively sharp intersection. If we use regression lines for these, we calculate a regression coefficient of $r^2 > 0.999$ for the temperatures above that of the intersection which we shall call T_u . As an example we have shown in fig.2 the deviations of the measured values from the regression line of the high temperature region for $\text{C}_{28}\text{H}_{58}$. It is easily recognized that the high temperature region is described well by a straight line whereas in the temperature region

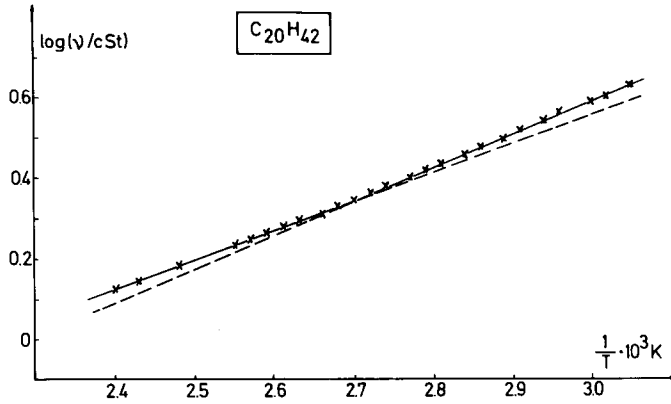


Fig. 1: The direct Arrhenius plot of the viscosity of $C_{20}H_{42}$ (measured with increasing temperature).

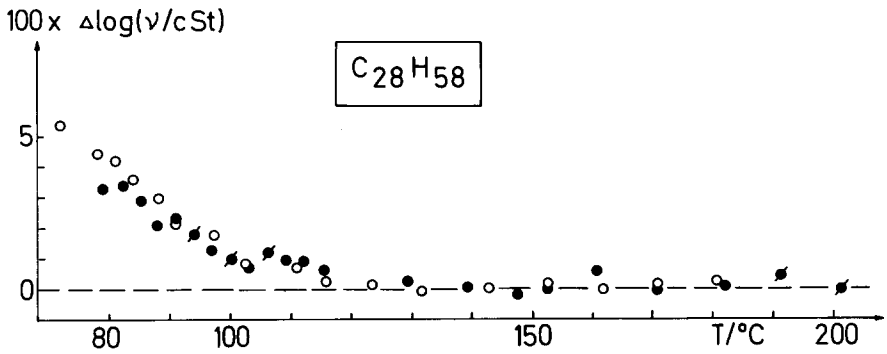


Fig. 2: Deviations of the data points from the regression line of the high temperature region versus temperature for the $C_{28}H_{58}$

- : increasing temperature
- : decreasing temperature
- ⦿ : ● and ○ identical

below T_u the points follow a slight curve but are still well approximated by a straight line ($r^2 > 0.998$).

From these plots the activation energies within the two temperature regions as well as the temperatures T_u as a function of chain length (fig. 3) were determined. The activation energies above and below T_u are best described by $E = E_0 + bn^{1/2}$. The difference between the two activation energies has a mean value of $\Delta E = 2.8$ kJ/mol with a tendency to increase slightly with n . This value is near to that of LEMAIRE and BOTHEREL (1979) who concluded from a computer simulation study

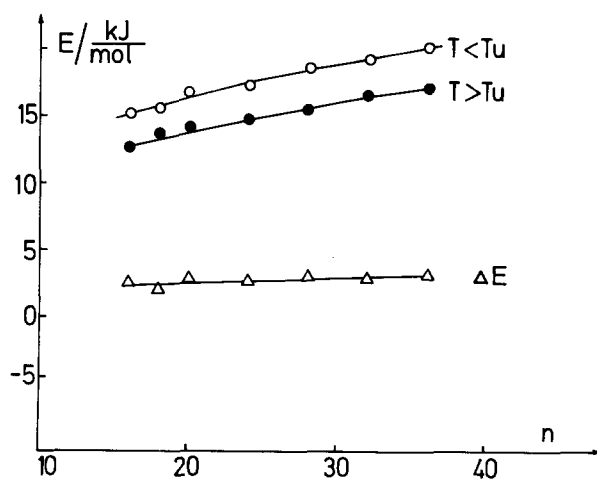


Fig. 3: Activation energies of viscous flow: ○ below T_u and ● above T_u . Difference in activation energy. The n-alkanes measured are: $n = 16, 18, 20, 24, 28, 32, 36$.

that two differently structured stable states of the melt of $C_{17}H_{36}$ with a difference in free energy of about 3 kJ/mol might exist. The viscous flow possibly takes place only in one of the two states which means that the activation energy E_1 in first (low temperature) state is higher than $E_{11} + \Delta E$, where E_{11} denotes the activation energy in second (high temperature) state. So the second state becomes established when the viscous flow starts.

In plotting $T_u(n)$ (fig. 4), we have also incorporated data from other experiments. The data from Brillouin scattering (KRÜGER et. al. 1980) are denoted by full circles. Brillouin scattering results in the determination of the hypersonic velocity (~ 5 GHz). The temperature dependence of this velocity in the melt also shows a kink at a definite temperature T_u . The temperatures derived from depolarized Rayleigh scattering data of CARLSON (1976) are denoted by the open circles. From these measurements a constant polarizability anisotropy γ^2 is determined for each molecule at high temperatures. This anisotropy increases relatively sharply with decreasing temperature below a definite temperature (DETENMAIER et. al. 1977, CARLSON 1976). We have determined this temperature from the data of CARLSON (1976). Despite the very different methods used, the temperatures determined are in good agreement. The dependence on chain length is pronounced for $n \lesssim 28$ and is much weaker for longer chains. A very similar dependence exists for the temperature independent part of the segmental anisotropy γ_0^2/n and of the Cotton-Mouton constant. Both were calculated from measurements below T_u . (FISCHER et.al.1979). From this dependence it appears that the short range order of n-alkane melts with $n > 28$ already resembles that of melts of much longer chains. From their measurements of the radial distribution function of n-alkanes and of linear polyethylene (PE) in the melt LONGMAN et.al.(1979) also concluded that this similarity existed. From our extrapolation of the T_u temperature to high molecular weights we conclude that PE always retains the structure of the low temperature region because T_u exceeds the temperature of decomposition of the molecule.

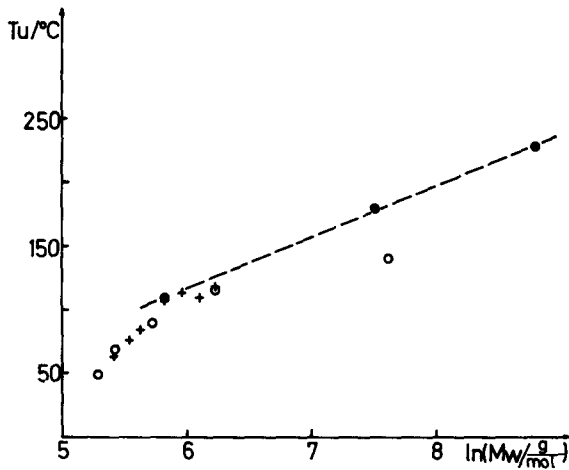


Fig. 4: T_u -temperatures of n-alkane melts

+ : from viscosity measurement (this work)

● : from Brillouin scattering data (KRÜGER et.al.1980)

○ : from Rayleigh scattering data (CARLSON 1976)

From our Brillouin experiments (KRÜGER et.al.1980) we conclude that below T_u the melt transforms from an isotropic into a locally mesomorphic structure. This is confirmed by the hypersonic behaviour of MBBA (4-butyl-N(p-methoxy-benzylidene)aniline) at the transition from the isotropic to the nematic phase also measured in our laboratories. For the determination of the possible structures however other methods must be used. The temperature range of such investigations should be extended enough on both sides of T_u in order to get a clear picture of the two regions. Our determination of the T_u -temperatures opens the possibility of experiments in this direction.

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