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The Thermal Behaviour of n-Tetracosane and Low Molecular Weight Polyethylene Studied by NMR and a Refined Brillouin Scattering Technique

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SUMMARY

A new type of Brillouin spectrometer has been used to show that transition-like phenomena exist in the melt of low molecular weight Polyethylene (M_n=2230). Because of the enhanced accuracy of the new spectrometer it could be shown that the sound velocity gradient is a constant above and below T_u=436 K in a wide temperature range, but is discontinuous at T_u. The same hypersonic behaviour has been found for MBBA at the nematic-isotropic-transition. NMR investigations have confirmed the existence of T_u previously reported for n-Tetracosane ($C_{24}H_{50}$).

INTRODUCTION

The controversial structure of polymers and n-alkanes has been the subject of many recent investigations. According to FLORY 1) there is no order in n-alkane melts exeeding that of other low molecular weight liquids. According to BALTA-CALLEYA 2), KRÜGER 3), KRÜGER 4), PIETRALLA 5), KRÜGER 6) and DENNY 7) in n-alkanes and some crystallisable polymers there exists a kind of transition temperature T_u which probably separates differently ordered regions in the melt. Such transitions have been already reported for n-alkanes by MOORE 8) in 1953. Two different liquid states in n-alkane melts have also been discussed by LEMAIRE 9) on the base of Monte Carlo calculations. BENDLER 10) and FISCHER 11) conclude from their investigations that n-alkane melts contain some local order, due to a hypothetical transition to a mesomorphic state which should occur far below the melting point. FISCHER's objection against the interpretation of Brillouin data 3) has been that the hypersonic velocity data could as well be described without any discontinuity in the sound velocity gradient. It appeared therefore desirable to confirm our conclusions by further experimental techniques and improved Brillouin measurements. In this work we present NMR investigations on $C_{24}H_{50}$ which corroborate the previously found transition temperature and we present a new type of Brillouin spectrometer with a strongly enhanced accuracy with which we were able to prove the existence of a discontinuous change of the sound velocity gradient in a Polyethylene melt.

EXPERIMENTAL

For our Brillouin investigations a new type of Brillouin spectrometer 12)13) was used. This spectrometer consists of two Fabry-Pérots (fig. 1) for tandem application but only FP1 (triple pass

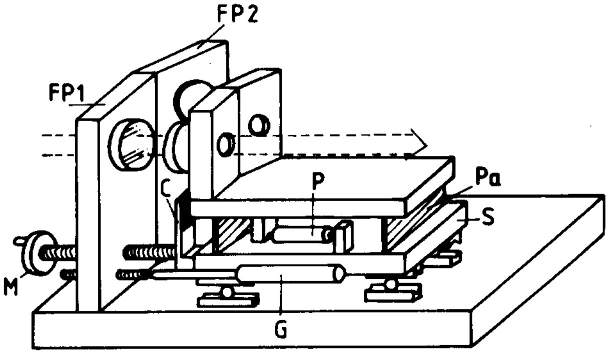

Fig. 1 Schematic view of a Tandem Fabry-Pérot; FP1, FP2 Fabry-Pérots; Pa deformable parallelogram; P piezoelectric transducer; S translation stage; M micrometer screw; G electronic gauge clock.

configuration) was used for this application.

Classical piezoelectric scanned Fabry-Pérots can operate quite successfully but there are several aspects where considerable improvement is to be desired: 1) Since piezoelectric transducers are somewhat non-linear, the scan produced is not linearly proportional to the scan voltage. 2) Piezoelectric transducers do not have identical characteristics. As a result the three stacks do not produce identical displacements and so the mirror tilts during the scan. 3) When the mirror spacing must be changed the scanning mirror assembly must be slid as a whole along the three rods. As a result mirror alignment is lost and the handling produces local temperature changes.

The desired improvements have been realized in the new spectrometer illustrated schematically in fig. 1: The scanning mirror sits on a compound translation stage comprising a deformable parallelogram (Pa) (for small displacements) attached to a rolling ball translation stage (S)(for large displacements). The latter can be driven by a micrometer screw (M) for obtaining the gross setting of the mirror spacing. The mirror translation stage must satisfy two conditions. Firstly, over the scan which would normally be a movement of less than 5 μm, the parallel alignment of the mirrors must not be detectably altered. Secondly, after a gross change of the mirror spacing over a range of several mm the mirror alignment should have changed so little that strong spectral features are still discernible in the scanned spectrum. In this case a fine mirror adjustment using the piezoelectric alignment transducers will bring the mirrors back into full alignment. The first condition requires that during a scan of 5 μm all parts of the mirror move by the same distance to within a few Å. The second condition requires that during a gross movement of a few mm all parts of the mirror move by the same distance to within about .5 μm. The high accuracy scan movement is achieved using a deformable parallelogram, which is capable of producing movements of 100 μm without detectable tilt. The scan is actuated by a piezoelectric crystal (P) acting between the upper plate of the rolling stage and the upper plate of the deformable parallelogram stage. The deformable parallelogram stage sits on a rolling ball translation stage. A high precision translation stage using precision ground steel flats as runners is in itself sufficient for achieving the required tilt free movement over distances of several cm. The mirror spacing is measured by an electronic digital gauge (G) LY-111 (Sony) with 1 µm resolution and a range of 50 mm.

A novel feature of the interferometer construction is the use of a capacitive displacement transducer (C) for measuring the mirror spacing. The output of the transducer is made accurately proportional to the spacing between the capacitor plates. The scan is achieved by comparing the scan voltage with the transducer output voltage and thus obtaining a correction voltage for driving the piezoelectric scanning transducer. This feedback scanning system achieves two goals. Firstly, the linearity of the scan is now determined by the linearity of the displacement transducer and is independent of non-linearities in the scanning transducer. Secondly, high stability is achieved against thermal expansion - as seen in fig. 1, the only paths which are thermally important are the short distances between the mirror holders and the capacitor (including of course the micrometer screw used for setting a given spacing).

The linearity of the spectrometer was checked with a 1024 channel analyzer over a scan of 10 orders performing a Brillouin measurement on benzene at room temperature. Fig. 2 shows the successive interorder spacing, FSR, of related peaks, including the Brillouin lines, versus increasing number, N, of interference peaks. The data set has been fitted to the linear function FSR=a+bN with b=0.00064 indicating an extremely small deviation from linearity. The scatter of the data around the straight line reflects the overall accuracy of the spectrometer including e.g. the finite resolution of the multichannel analyzer.

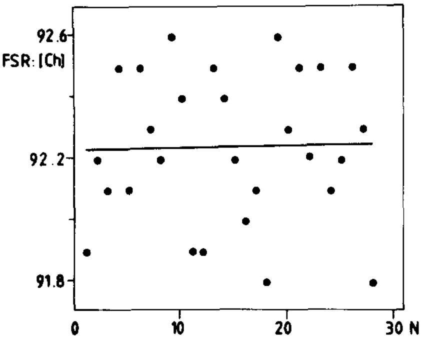

Fig. 2 Spectral orders, FSR, measured in channels, Ch, versus the order number, N, (s. text).

The Brillouin experiments were performed in the 90A scattering geometry [14] for which the related phonon wave length remains constant. The temperatures of the sample were measured with a thermocouple close to the scattering volume within ± 0.1 K.

The polyethylene sample (PE 2475) was of low molecular weight (M_n=2230) with a rather narrow molecular weight distribution (M_w/M_n=1.11). The melting temperature of the sample was T_m=117°C.

The longitudinal proton relaxation time T_1 of $C_{24}H_{50}$ has been measured by the aid of a Bruker p 40 spectrometer using the 90°- τ -90°-pulse sequence. The Lamor frequency was 40 MHz. The absolute temperature accuracy was ± 0.5 K.

RESULTS AND DISCUSSION

$C_{24}H_{50}$: From the magnetic $C_{24}H_{50}$ susceptibility measurements of BALTA-CALLEYA [2] and our own Brillouin investigations on $C_{24}H_{50}$ [3]

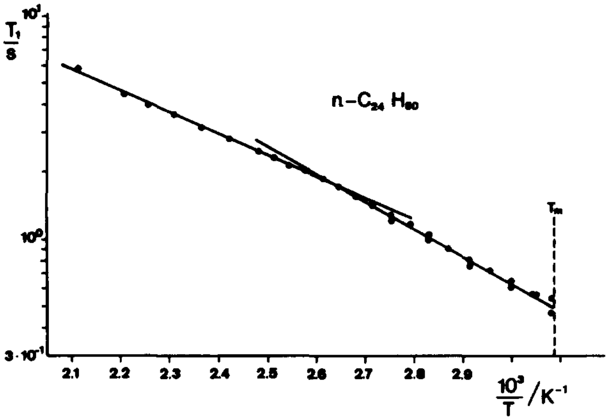

Fig. 3 Semilogarithmic plot of the longitudinal proton relaxation time of $C_{24}H_{50}$ versus the inverse temperature

we have concluded that in the melt of $C_{24}H_{50}$ at $T_u \cong 110^{\circ}C$ a transition like phenomenon takes place. The obvious coupling of the unknown order parameter to the magnetic properties of $C_{24}H_{50}$ stimulated us to check up whether the longitudinal proton relaxation time T_1 also reflects the transition behaviour. As shown in fig. 3 the semilogarithmic plot of T_1 versus the reciprocal temperature can be represented by two straight lines with a kink at $108^{\circ}C$ in agreement with T_u from Brillouin- and diamagnetic susceptibility investigations.

The rotational diffusion of n-alkane molecules in the melt is certainly anisotropic, so that in general several correlation times are needed for a description of the motions $^{15)}$. At 40 MHz and in the temperature range of this investigation we expect that the so called "extreme narrowing case" $^{16)}$ concerning all components of the molecular motions is relevant. It is then possible to define an effective correlation time τ_c so that the longitudinal relaxation time T_1 is inversely proportional to τ_c. Assuming an Arrhenius law $\tau_c = \tau_c^{\infty} \exp(E/RT)$ leads to "apparent activation energies": E_I $(T > T_u)$=18.3 kJ/mole and $E_{II}(T < T_u)$=23.6 kJ/mole. These values are higher than those obtained from viscosity data $^{4)}$: E_I=13.7 kJ/mole, E_{II}=16.6 kJ/mole. The differences $E_{II}-E_I$ are 5.3 kJ/mole from the NMR and 2.9 kJ/mole from the viscosity measurements. The discrepancy could result from the fact that the effective correlation time τ_c determining T_1 is composed of two or more components. Such a multicomponent behaviour has been discussed in context with polymer melts $^{17)}$. Viscosity on the other hand is expected to depend mainly on translational components.

PE 2475: As mentioned above our Brillouin experiments on the low molecular weight Polyethylene followed up two goals: 1.) to corroborate our recent results by an improved measurement technique, 2.) to extend our recent investigations on n-alkanes and Polyethylene to a different molecular weight.

Fig. 4 shows the hypersonic velocity of PE 2475 versus temperature. To decide whether a description of our sound velocity data by two straight lines, inclined at a temperature T_u is recommended, we fitted several types of functions by the method of least squares to the data:

(1) $v(T)=a-bT+c\ abs(T-T_u)$

(2) $v(T)=a\ exp(-bT)$

(3) $v(T)=a-bT-cT^2$

(4) $v(T)=a-bT+c/(T-T^*)^x$

Fig. 5a to fig. 5c show plots of the deviations between the measured and the estimated (residual) sound velocities versus temperature for eq. 1 to eq. 3. In eq. 4 we have formally introduced a critical exponent x and a hypothetical transition temperature $T^* < T_m$. The application of the method of least squares fits to eq. 4 led to no stable solutions for the five parameters.

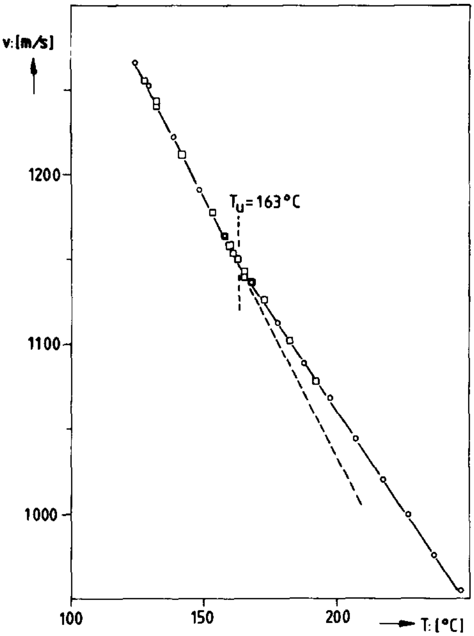

Fig. 4 Hypersonic velocity of PE 2475 versus temperature

From fig. 5a to fig. 5c it is obvious that both the sum of squares as well as the distribution of the residuals are most satisfactory for eq. 1. Hence our sound velocity data are best described by eq. 1 including a transition temperature T_u=163°C and without any critical contribution to the elastic stiffness. At T_u the gradient of the sound velocity changes discontinuously. In so far the elastic behaviour of PE 2475 is similar to the elastic behaviour of liquid crystals at the nematic-isotropic transition at high ultrasonic frequencies [18], and hypersonic frequencies (fig. 6a). The data set has been fitted to eq. 1 and fig. 6b shows the corresponding residuals. It should be noticed that we have increased the accuracy of our sound velocity measurements by nearly one order (∼0.1%) compared with previous measurements [14].

DENNY has studied a similar polyethylene (M_n ∼2000) with DSC finding a T_u of 169°C at a heating rate of 0.5 K/min. Taking into account that the heating rate plays an important role for the value of T_u [7][19] it seems that Brillouin spectroscopy and DSC indicate the same transition. However, to reproduce the thermal anomaly DENNY [7] needed a certain time delay between successive DSC experiments. Such a time delay was not necessary in our Brillouin experiments. It seems therefore that the equilibrium value of the elastic stiffness of the low temperature melt phase is more rapidly reached than of the thermal properties. Recent DSC- and Brillouin-investigations on cyclotetracosane ($C_{24}H_{48}$) melt[20] have shown two transitions with a hypersonic behaviour similar to those in n-alkane- and PE-melts at T_u. No time delay between successive temperature cycles was needed for the reproduction of these transitions by both techniques indicating that the time effect on certain physical properties may be a secondary effect. After having established the existence of a transition like phenomenon in the melt of n-alkanes, cycloalkanes and some crystallizable polymers the question arises about the physical nature of these transitions. The hypersonic behaviour at these transitions is similar to that of liquid crystals at the nematic-isotropic transition. However no long range order seems to exist in alkane melts below T_u 1)11).

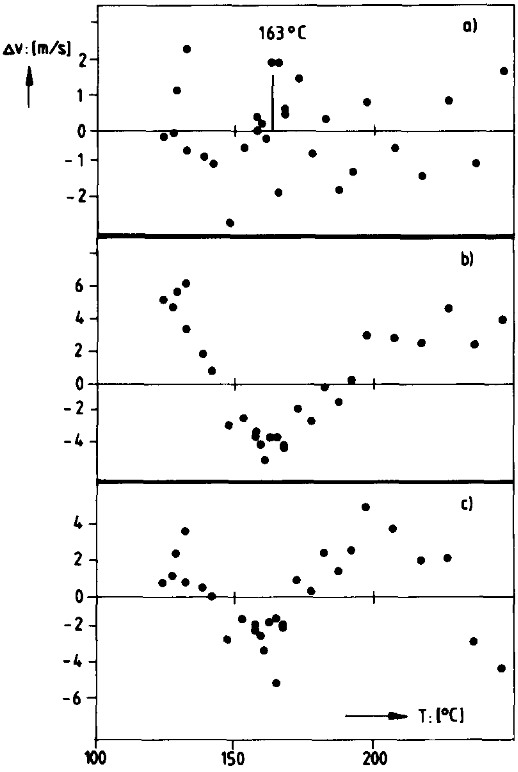

Fig. 5 Residuals of the hypersonic velocity versus temperature for: a) eq. 1; b) eq. 2; c) eq. 3.

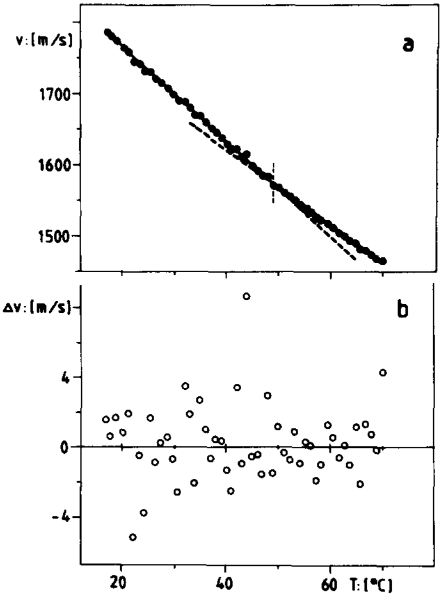

Fig. 6 Hypersonic velocity of N-(p-Methoxybenzylidene)-p-butylaniline (MBBA) versus temperature around the nematic-isotropic transition, b) corresponding residuals.

One may therefore speculate that at T_u an intramolecular transition takes place: For $T > T_u$ the molecules have a random coil conformation, between T_m and T_u the molecules exist partly in a very disturbed planar or helix like conformation, respectively, with a main axis preserved. Recent hypersonic investigations on $C_{36}H_{74}$ single crystals 21) in the rotator phase seem to support this idea. Further investigations of this model are underway.

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