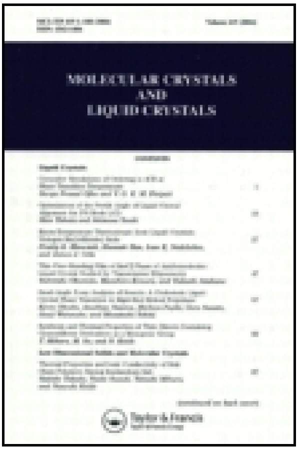


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Ultrasound Studies of the Polymer Liquid Crystal P_{41}

L. Benguigui [a] & P. Ron [a]
[a] Solid State Institute and Physics Department, Technion-Israel Institute of Technology, Haifa, 32000, Israel
Version of record first published: 13 Dec 2006.

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 241-247
Photocopying permitted by license only

Printed in the United States of America

ULTRASOUND STUDIES OF THE POLYMER LIQUID CRYSTAL P_{41}

L. BENGUIGUI and P. RON
Solid State Institute and Physics Department, Technion - Israel Institute of Technology, Haifa 32000, Israel

Abstract

We measured the velocity of the longitudinal round waves of the side chain polymer liquid crystal P_{41}, in the range 2-10 Mhz. This compound exhibits an isotropic, nematic and Sm A phases. In this frequency range, we found that in the nematic phase we are already in the $\omega\tau > 1$ situation and $\omega\tau \sim 1$ in the Sm A phase. We have also investigated the variation of the velocity with the angle between the director and the wavevector.

INTRODUCTION

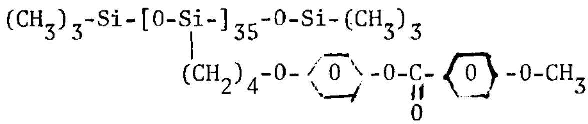
The acoustic properties of liquid crystals are characterized by properties which are absent in isotropic liquids as well as in crystals. In the nematic phase the sound velocity is isotropic at low frequency, but becomes anisotropic at high frequency, whereas the sound absorption is always anisotropic. In the smectic A and C phases, the velocity and the absorption are anisotropic at all frequencies. Moreover in the smectic phases there is a breakdown of conventional hydrodynamic and the damping has now a divergent contribution since some viscosities behave like 1/f (f is the frequency of the sound wave). (For a very good survey of the acoustic properties of liquid crystals, we refer the reader to ref. 1 and for more recent results concerning the break-down of the conventional hydrodynamic see ref. 2).

In this paper, we present the first investigation of the acoustic properties of a side chain liquid crystal polymer.

It is clear that properties related to the symmetry of the structure will be as observed in regular liquid crystals. However, we expect quantitative differences and this is effectively observed.

EXPERIMENTAL

The material used in the present investigation is a polymethylsiloxane (P_{41}) with the following formula



Details on the preparation of this material and other analogous compounds can be found in ref. 3. The transition temperatures of the compound P_{41} (as determined by microscopic observation) are

SmA-72°C-N-101°C-I

There is also a glass transition around 7°C.

The acoustic measurements were performed at 2.1-2.5-3.5-7.5 and 9.3 Mhz in a conventional set-up with two PZT ceramics as piezoelectric transducers. In the pulse mode, we can measure absolute velocity by the standard echo technique (precision 4%) and in the CW mode the relative velocity from the phase difference between the applied signal and the received signal on the second piezoelectric element (precision 0.1%). The phase measurement was made by a Hewlett-Packard Vector Voltmeter. In this paper only data on the velocity are reported and the results on the absorption will be presented in another publication. The sample was slowly cooled at a rate of 10 min/°C above 90°C and 2 min/°C below 90°C. We also cooled the sample with much more slower rates and we did not observe difference in the results. The alignment of the molecules was made by a magnetic field of 10 kG.

RESULTS

In Fig. 1, we show the variation of the velocity with the temperature T at 7.5 Mhz, in the two main configurations: when the wave vector is parallel to the director and when it is prependicular to it. The results of 3.5 and 9.3 Mhz are almost identical to those at 7.5 Mhz. The Isotropic-Nematic transition is marked by the apparition of the velocity anisotropy (around 100°C) and the Nematic-Smectic A transition by a slight change in the slope (around 74°C).

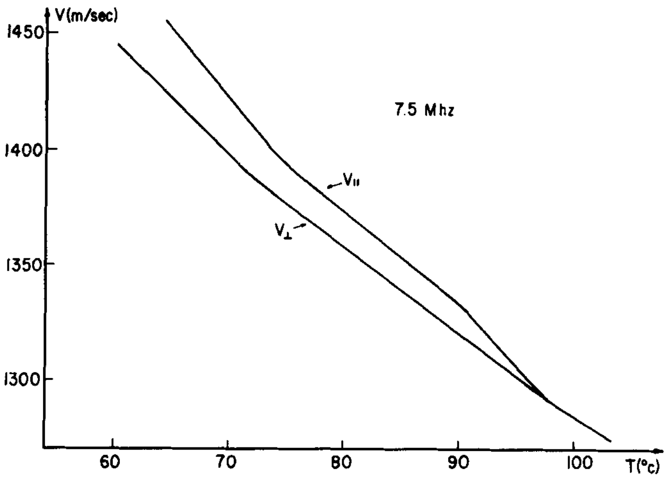


FIGURE 1. Sound velocity versus the temperature at 7.5 Mhz in the two main configurations

In Fig. 2 we present the velocity anisotropy $\Delta V = V_{\parallel} - V_{\perp}$ as a function of T, at the different frequencies. We note that in the nematic phase all the curves are near one another and, in particular, for f $\gtrsim$ 3.5 Mhz, the velocity anisotropy is independent of f. The behavior of V in the Smectic A phase is very different. ΔV increases strongly if T is

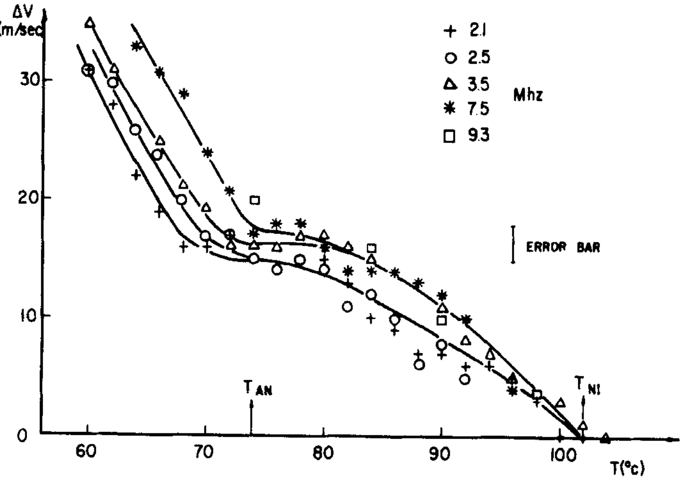


FIGURE 2. Velocity anisotropy ($V = V_{\parallel} - V_{\perp}$) versus T at different frequencies. Note the different behavior in the nematic and the SmA phases. The lines are quides for the eye.

In Fig. 3, we show the variation of V with the angle between the wavevector and the director for two temperatures in the nematic phase. The behavior is similar below 74°C, in the smectic A phase.

DISCUSSION

The fact that ΔV is strongly dependent on the frequency in the SmA phase is a clear indication of a relaxation mechanism in this range of frequency. One can say that for the range 3-7 Mhz we have $\omega\tau \sim 1$ and one gets $\tau \sim 2\text{-}5\times10^{-8}$ sec. It is difficult to discuss the results in this range and it should be very interesting to perform measurements at lower frequency ($\omega\tau \ll 1$) and higher frequency ($\omega\tau \gg 1$). This is now in planning. At the actual time, we note that ΔV is relatively large (30 m/sec of 60°C and 2.1Mhz, i.e. 2%.

In regular SmA phases the anisotropy is of the same order of magnitude. However, in the present case the anisotropy comes not only from the structure, but also from the dispersion (since $\omega\tau \sim 1$), whereas in the regular SmA phase, the measurement was made in the range $\omega\tau \ll 1$ and the anisotropy is structural.

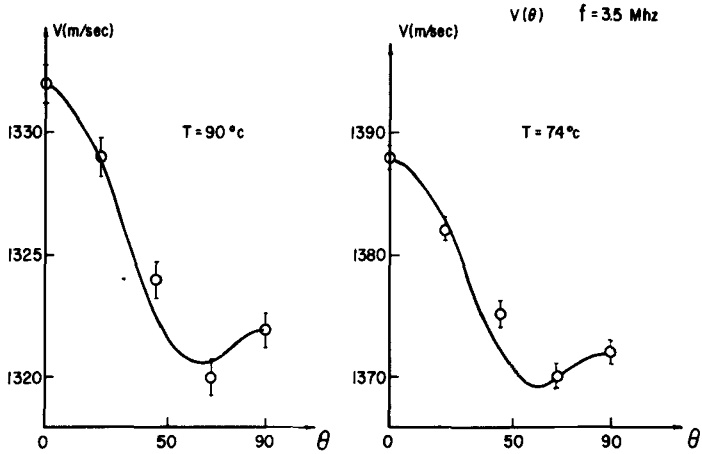


FIGURE 3. Velocity versus the angle between the wave vector and the director at two temperatures. The line is calculated (see text).

In the nematic phase we are clearly in the range of frequency above the relaxation frequency. ΔV is independent of f for $f \leqslant 3.5$ Mhz and we conclude that in this range $\omega\tau \gg 1$. This gives $\tau \gg 1/(2\pi x 3.5x10^6) = 4.5x10^{-8}$ sec, which means that τ is relatively large. We recall that in the regular nematics[4,5] it was found $\tau \sim 10^{-8}$ sec. We have also the same situation for ΔV. In our case, in the saturation region of ΔV, one has $\Delta V/V \sim 10^{-2}$ and in regular nematics[4,6] $\Delta V/V \sim 3.10^{-3}$.

The curves $V(\theta)$ are characterized by a minimum around $\theta \simeq 60°$. Here we have a new situation, which was not observed until now. In the regular nematic liquid crystals, and for the frequency range $\omega\tau >> 1$, the variation of V versus the angle θ was analyzed with the following expression[4,6]

$$V = A_1 + B_1 \cos^2\theta \qquad (1)$$

It is clear that in our case the expression (1) is not adequate, since this expression does not give a minimum. Thus we tried the expression

$$V^2 = A - 2C \cos^2\theta + B \cos^4 \qquad (2)$$

which is valid in the smectic phases, in the low frequency range. As shown in Fig. 3, our results can be correctly fitted with (2). Two authors have proposed the exp.(2) for the velocity anisotropy in the nematics when $\omega\tau >> 1$. Liu[7] has investigated the influence of the smectic order on the dispersion in the nematic phase and we expect that his results will be correct not too far from the nematic--Smectic A transition temperature. Jahnig[8] includes the frequency dependence of the elastic and dissipative parameters of the system. This is equivalent to consider the nematic phase as a visco-elastic medium. In such an approach, the coupling to the smectic A order parameter is not introduced (as Liu did) and the results are expected to be applicable in all the nematic phase. The two approaches are not exclusive. However, at the present time, it is difficult to delimit their use without a determination of the constants A, B and C as functions of the frequency and the temperature. We hope to be able in the near future to perform this task in extending the frequency range of our measurements.

REFERENCES

1. K. Miyano and J.B. Ketterson in "Physical Acoustics", W.P. Mason and R.N. Thurston Ed. (Academic, New York, 1979) Vol. 14.
2. D. Collin, J.L. Gallani and P. Martinoty, Phys. Rev. A34, 2255 (1986).
3. M. Mauzac, F. Hardouin, H. Richard, M.F. Achard, G. Sigaud and H. Gasparoux, Eur. Polymer. J. 22,137(1986).
4. M.E. Mullen, B. Luthi and M.J. Stephen, Phys. Rev. Lett. 28, 799 (1972).
5. D. Eden, C.W. Garland and R.C. Williamson, J. Chem. Phys., 58, 1861 (1973.
6. J.C. Bacri, J. Physique 35, 601 (1974).
7. M. Liu, Phys. Rev. A19, 2090 (1979).
8. F. Jahning, Z. Phys. 258, 199 (1973).