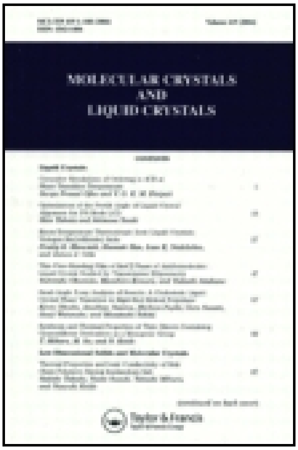


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Dielectric Measurements on Polymers with Crossing Mesogens

H. Kresse [a] , S. Ernst [a] , U. Rötz [a] , S. Lindau [a] & F. Kuschel [a]

[a] Martin-Lutner-Unlvarsität, Halle-Wittenberg, Sektion Chsmie, 4020, Halle/S., GDR

Version of record first published: 22 Sep 2006.

To cite this article: H. Kresse , S. Ernst , U. Rötz , S. Lindau & F. Kuschel (1990): Dielectric Measurements on Polymers with Crossing Mesogens, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 211-216

To link to this article: http://dx.doi.org/10.1080/00268949008031828

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 211–216
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

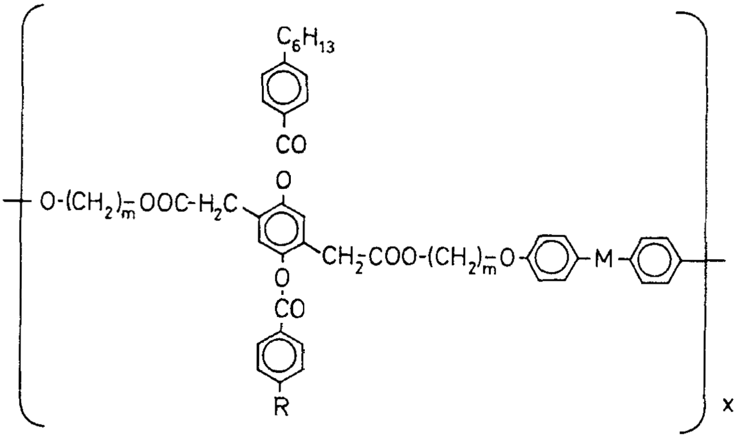
DIELECTRIC MEASUREMENTS ON POLYMERS WITH CROSSING MESOGENS

HORST KRESSE, SABINE ERNST, UWE RÖTZ, JÜRGEN LINDAU, FRANK KUSCHEL
Martin-Luther-Universität, Halle-Wittenberg,
Sektion Chemie, 4020 Halle/S., GDR

Abstract Comparative dielectric investigations on polymers with crossing mesogenes have been carried out in the frequency range from 1 Hz to 100 kHz. The spacer length and the mesogenic parts of the main chain as well as the dipole of the crossing units have been altered.

INTRODUCTION

Recently Rötz et al.[1] reported on dimesogenic liquid crystalline polymers consisting of bilaterally and biterminally linked mesogenic units of the following general structure:



m = 2 - 6, 11
M = —, —N=N—
R = $-CN$, $-C_6H_{13}$

Dielectric measurements have already been performed in the frequency range from 1 Hz to 100 kHz on the above given derivatives of biphenyle PCBm.[2] Here we will report about substances with the same general structure: M = -N = N- (PCAm). The phase transition temperatures, polymorphism and the half width of the DSC peaks ΔT at the clearing point are given in Table I.

TABLE I Phase transition temperatures (K) of PCAm polymers

m	P_g		P_s		P_n		P_{is}	ΔT/K
2	•	341	–	–	•	452	•	4.0
3	•	332	–	–	•	395	•	3.2
5	•	322	–	–	•	390	•	3.1
6	•	323	P_{sA}	374	•	410	•	5.0
11	•	309	P_{sC}	320	•	364	•	2.1

P_g - glassy, P_s - smectic, P_n - nematic, P_{is} - isotropic.[3]

By comparison with the homologous PCBm polymers the PCAm series shows an about 20 K higher clearing temperature, an effect which arises from the stabilization of the liquid crystalline phases due to the azobenzene unit.

RESULTS

The calibration of the measuring capacitor was not possible before investigating the substances due to their high viscosity. Therefore, from the measured capacity C' and resistivity R the dielectric loss

$$C'' = (2\pi f R)^{-1}, \qquad (f - \text{frequency})$$

has been calculated as reported previously.[4] The curves of the dielectric loss of PCA3 and PCA11 measured with decreasing temperature are given in Figures 1 and 2 respectively.

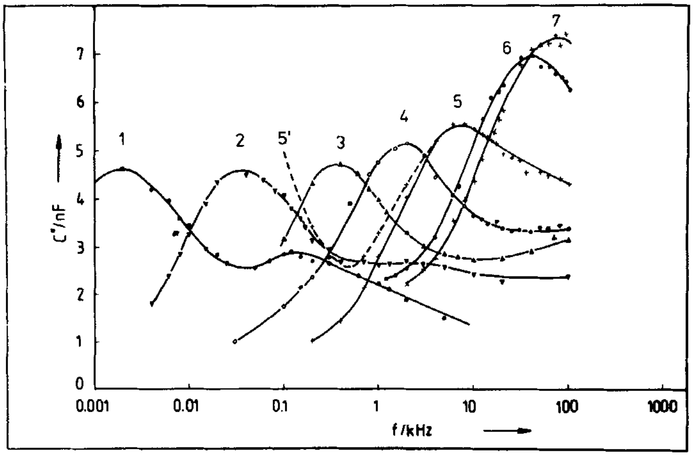


FIGURE 1 Dielectric loss C" of PCA3 versus frequency f at different temperatures
1: 353.4 K, 2: 364.2 K, 3: 369.8 K,
4: 378.7 K, 5: 385.6 K, 6: 392.5 K,
7: 396.2 K.

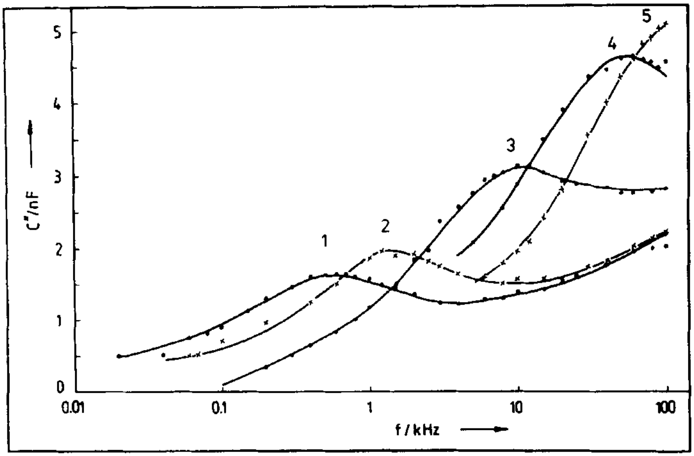


FIGURE 2 Dielectric loss C" of PCA11 versus frequency f at different temperatures
1: 346.9 K, 2: 351.9 K, 3: 361.2 K,
4: 364.2 K, 5: 372.1 K.

For PCA3 we could detect a nearly constant absorption intensity in the nematic phase and an increase of C" in the isotropic state. Due to our incomplete knowledge about the orientation in the nematic phase we can only say that there are no strong dipole-dipole interactions in this state. Furthermore a second absorption mechanism at frequencies about two decades higher has been found. By comparison with the former measurements[2] it can be concluded that the intensive absorption is connected with the reorientation of the crossing mesogens whereas the broadened absorption arises from a complex reorientation of the

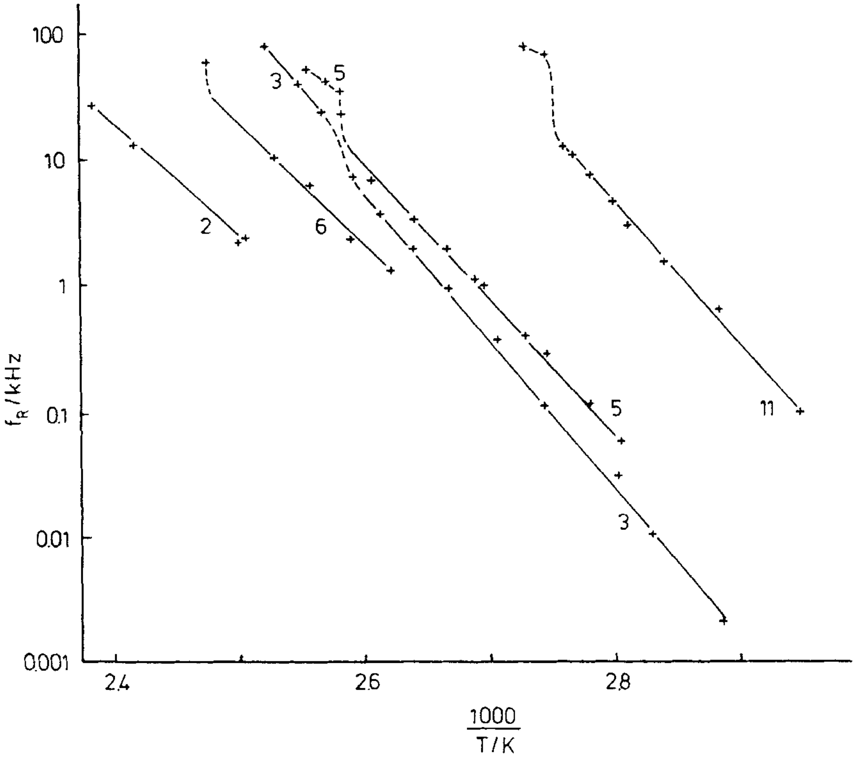


FIGURE 3 Activation diagram of the PCAm polymers
2: PCA2, 3: PCA3, 5: PCA5,
6: PCA6, 11: PCA11.

-COO- and probably also of the -COC- dipoles. In PCA11 we could clearly see only the first mechanism. The decreasing absorption intensity with decreasing temperature should be connected with pretransitional effects of the nematic-smectic C transition which arises from the dipole-dipole interactions of higher ordered aggregates.[5] The relaxation frequencies f_R of the reorientation of the crossing mesogenic groups with the CN-dipole are plotted in Figure 3 versus the reciprocal temperature.

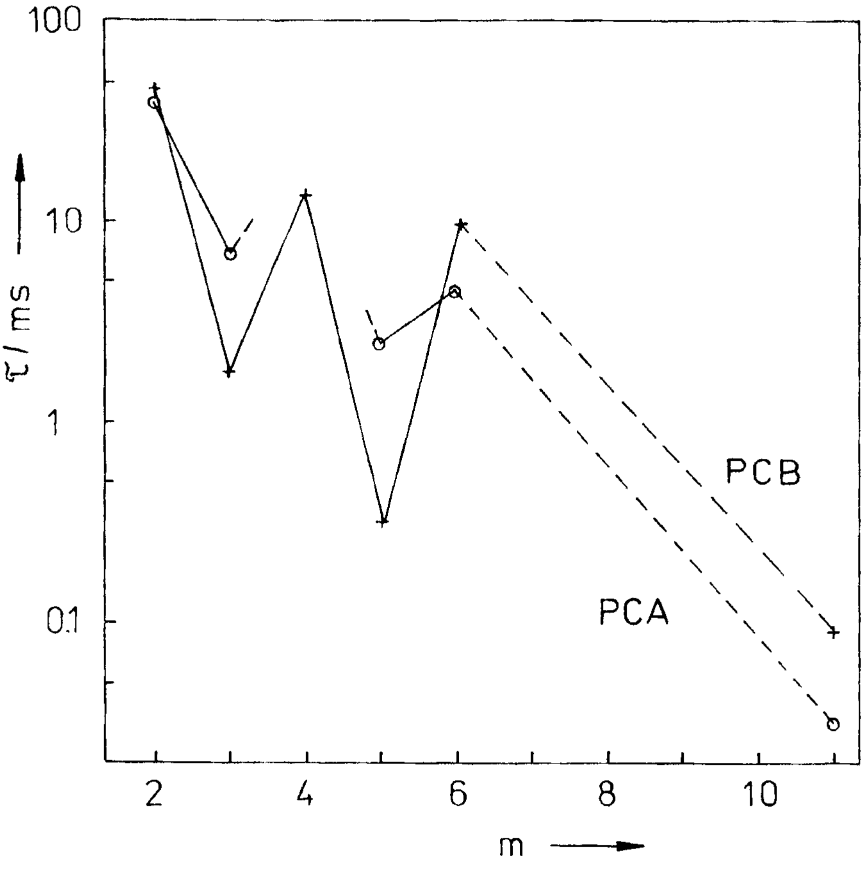


FIGURE 4 Relaxation times τ of the PCBm and PCAm polymers depending on the spacer length m at 390.5 K

Generally the relaxation frequencies of the substances with m = 2 and 6 are lower what has already been observed for the PCBm series.[2] The change in the order at the nematic-isotropic transition can clearly be seen at the step in f_R. A plot of the relaxation times τ versus m for the first mechanism of both homologous series at T = 390.5 K (Figure 4) shows the general agreement in the dynamical behaviour of the PCBm and PCAm polymers. It indicates also that the crossing part of the molecule reorients nearly independently on the liquid crystalline part of the main chain. Dielectric investigations in the smectic phases were not possible because of the stronger influence of the conductivity at lower temperatures (the activation energy of the dielectric relaxation is higher than that of the conductivity) and the extremely low relaxation frequencies.

The activation energies of the nematic phases according to the Arrhenius equation are between 150 kJ mol^{-1} (PCA2) and 250 kJ mol^{-1} (PCA3). They are in the same order of magnitude as observed for the PCB series.

REFERENCES

1. U. Rötz, J. Lindau, W. Weißflog, G. Reinhold, W. Unseld and F. Kuschel, Mol. Cryst. Liq. Cryst. 170, 185 (1989).
2. H . Kresse, U. Rötz, J. Lindau and F. Kuschel, Makromol. Chem., in press.
3. S. Diele, M. Naumann, F. Kuschel, B. Reck and H. Ringsdorf, Liquid Crystals, in press.
4. H. Kresse and R. Talroze, Makromol. Chem., Rapid. Commun., 2, 369 (1981)
5. W. H. de Jeu and P. Bordewijk, J. Chem. Phys., 68, 109 (1978).