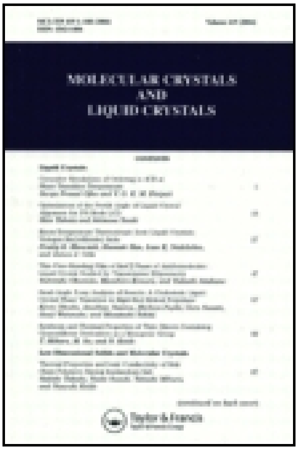


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Dielectric Relaxation in Liquid Crystalline Side Chain Polymers

Horst Kresse [a] , Heiko Stettin [b] , Eberhard Tennstedt [c] & Sergei Kostromin [d]

[a] Martin-Luther-Universität Halle, Sektion Chemie, Halle/S, GDR
[b] Pädagogische Hochschule "N. K. Krupskaja", Halle/S, GDR
[c] Ingenieurschule für Elektrotechnik, u. Maschinenbau, Eisleben, GDR
[d] Moscow State University, Chem. Pac, Moscow, USSR

To cite this article: Horst Kresse , Heiko Stettin , Eberhard Tennstedt & Sergei Kostromin (1990): Dielectric Relaxation in Liquid Crystalline Side Chain Polymers, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 191:1, 135-152

To link to this article: http://dx.doi.org/10.1080/00268949008038586

Mol. Cryst. Liq. Cryst. 1990, Vol. 191, pp. 135–152
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

DIELECTRIC RELAXATION IN LIQUID CRYSTALLINE SIDE CHAIN POLYMERS

HORST KRESSE
Martin-Luther-Universität Halle, Sektion Chemie, Halle/S, GDR

HEIKO STETTIN
Pädagogische Hochschule "N.K.Krupskaja" Halle/S, GDR

EBERHARD TENNSTEDT
Ingenieurschule für Elektrotechnik u. Maschinenbau, Eisleben, GDR

SERGEI KOSTROMIN
Moscow, USSR, Moscow State University, Chem. Fac.

Abstract The dielectric relaxation processes in liquid crystalline side chain polymers are discussed by chemical and physical variation of the respective substances. Furthermore, the dielectric data are related to possible technical applications.

INTRODUCTION

The increasing interest of many scientists on polymer liquid crystals originates in the relations between the new synthetic possibilities and the respective physical properties.[1]

Especially the combination of our knowledge about low molecular liquid crystals and polymers gives ideas which are also important for new technical applications. Here one has to differentiate between "static" processes, for example anisotropic glasses, and dynamical ones in which a smaller or bigger part of the polymer has to be modified by external fields (electrooptical switching, storage effects). All of these dynamical processes are connected with the mobility of different molecular units which need a different free volume for the respective change of the molecular arrangement. A survey about these processes and the approximated dielectric reorientation times τ are presented in Table I.

TABLE I Classification of the reorientation processes.

Process	Molecular unit	τ (s)	Glassy behaviour
1a rotation around a bond	atom, small group of atoms	$< 10^{-7}$	-
b cis-trans isomerization	bigger group of atoms		-
2a segmental motions	segment	$> 10^{-5}$	+
b rotation of the side chain around LMA	side chain	$> 10^{-7}$	+
c reorientation of the side chain around SMA	side chain	$> 10^{-5}$	+
3 rotation of the volume phase	polymer chains	> 1	+

LMA: long molecular axis, SMA: short molecular axis

A sketch of the different dielectric relaxation processes of side chain polymers according to the measurements by Kresse et al.[2,3] Haase and coworkers [4,5] as well as by Parneix et al.[6] is given in Fig. 1.

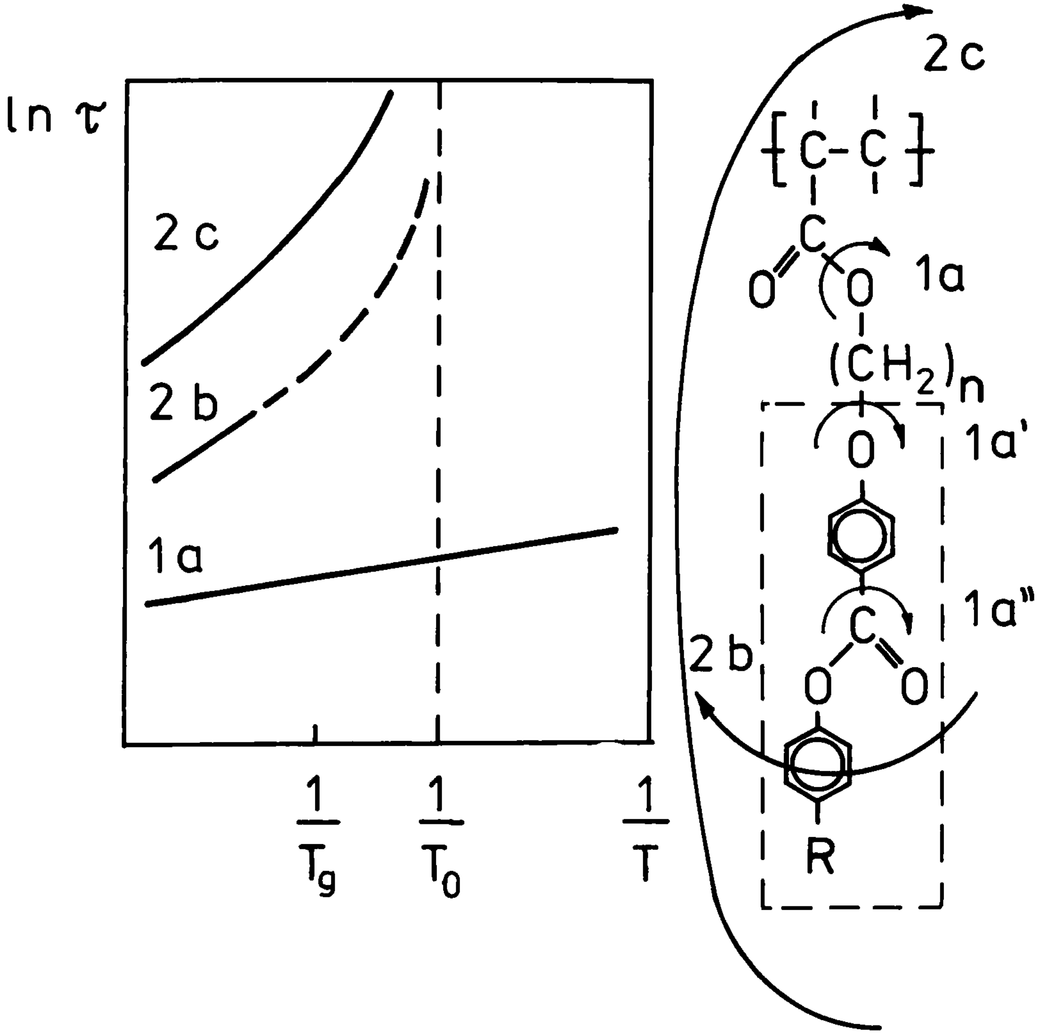


FIGURE 1 Dielectric relaxation processes in side chain polymers T_g-glassy temperature, T_0-Vogel-Fulcher temperature.

There are dielectric active processes on a level of one or few atoms (γ,β) and on bigger molecular units (α) which produce at first a dielectric anisotropy in the volume phase and after that the reorientation of the bulk (process 3) can take place. If we compare the relaxation time of the process 2c and the switching time at $U = 5U_0$ (process 3) of an oligomere 5 K below the phase transition into the isotropic phase ($\tau \sim 10^{-4}$s [3] , $\tau(5U_0) \sim 10$s [7]) we obtain a factor of about fife decades. In order to improve the electro-optical switching behaviour one has at first to decrease the time which is necessary to produce the dielectric anisotropy. Therefore, we will study now the influence of the chemical variation on the relaxation time τ(2c).

CHEMICAL VARIATION OF THE POLYMERS

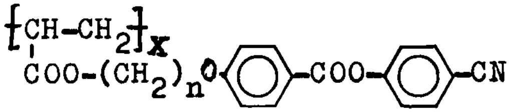
If we separatly regard the main and the side chain one can observe two glassy temperatures, one of the main chain polymer T_g(P) and a second one of the pure liquid crystal T_g(LC). The glassy temperature of the liquid crystalline part is more than 100 K lower [8] but it can be increased by chemical variation of the substance. Recently dielectric measurements on an oriented low molecular liquid crystal gave strong hints for the existence of a common Vogel-Fulcher temperature for both relaxation processes, 2b and 2c respectively [9] . Therefore, we should assume similar behaviour in the Arrhenius plot and a common freezing in process (dashed line in Fig. 1).
Because of the corresponding behaviour of all polymers

with respect to the freezing in process [10] one can never obtain both, a high mobility and a high glassy temperature. Due to the coupling of the main and the side chain via the spacer one should expect at least one common glassy temperature T_g between T_g(LC) and T_g(P).

The influence of the spacer

Increasing spacer length gives decreasing T_g-values and a shorter relaxation time as demonstrated in the case of substituted polyacrylates with nearly the same mean degree of polymerization x.

TABLE II Glassy temperature of polyacrylates.[11]



Polymer	n	x	T_g/K	$T_{N/I}$/K
1	2	50	348	388
2	6	54	306	406

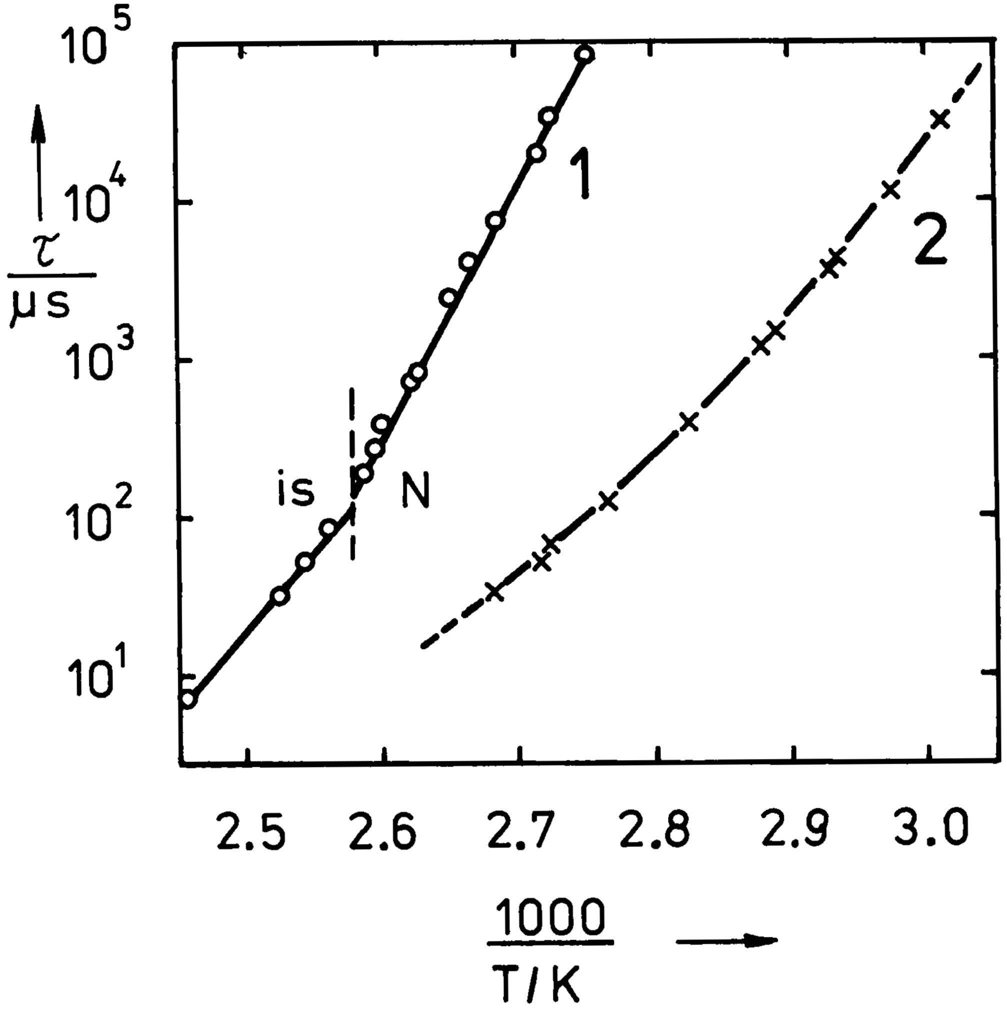


FIGURE 2 Arrhenius plot of the relaxation time τ (2c) of the polymers in Table II.

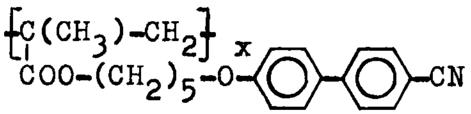
An increasing spacer length allows a faster reorientation of the CN dipole which is coupled with the stiff part of the side chain. On the other hand the absorption intensity can be only explained if a complete reorientation of the side chain takes place.[3] Therefore, the reorientation mechanism should be a common complex motion of the spacer (by conformational changes) and of the stiff liquid crystal part. An elongation of the spacer decouples the main and side chain from each other due to the dynamics of the spacer.

The influence of the degree of polymerization

The reorientation of the side chain must depend on the flexibility of the main chain because both parts are coupled. If the main chain is relatively enlarged and the mean degree of polymerzation times the length of one monomer unit is higher than the correlation length in the main chain one should expect no influence of the degree of polymerization on the relaxation time τ (2c).

An example for this is given in Table III and Fig. 3

TABLE III Characteristic data of the used polymethacrylates.[12]



Polymer	$\overline{x}$	T_g/K	$T_{S_A/I}$ /K
1	600	313	393
2	250	313	392
3	120	313	390

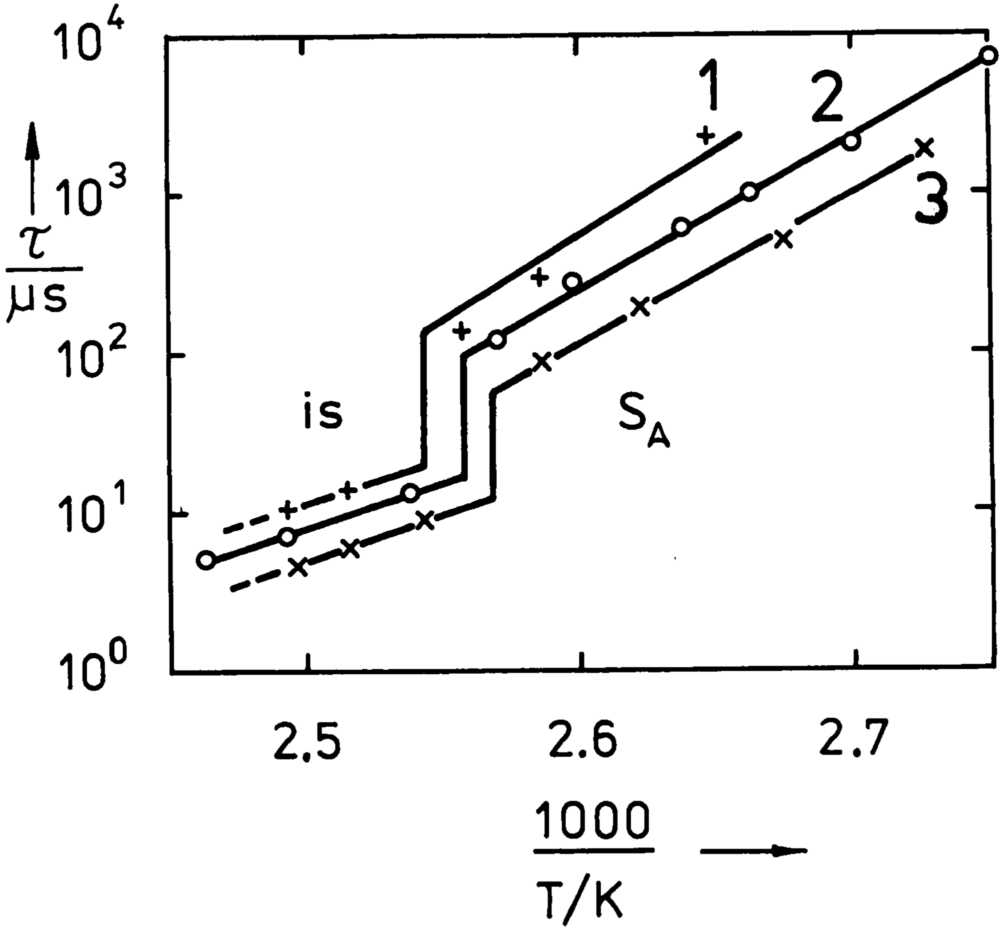
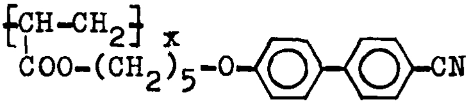


FIGURE 3 Dielectric relaxation times of the substances given in Tab. III.

Similar results have also been obtained for polyacrylates.

TABLE IV Relaxation times of polyacrylates.[13]



Polymer	$\bar{x}$	T_{Cl}/K	τ(2c)/ms (333K)
1	1000	391	10
2	200	391	3,2
3	20	360	2,7

T_{Cl}-phase transition temperature into the isotropic phase

From the data can be concluded:

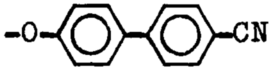
i Generally there is a slight decrease of the mobility of the side chain with increasing mean degree of polymerization.

ii In all cases given in Tables III and IV the correlation length in the main chain is smaller than the lowest $\bar{x}$ value. Even for $\bar{x}$ = 20 in Table IV, in which a drastical change of the clearing temperature has been found, the relaxation time decreases only slightly.

The influence of the main chain

The variation of the relaxation time for the reorientation of the liquid crystalline unit by changing of the main chain and nearly constant chemical structure of the side chain is given in Table V.

TABLE V Relaxation time by variation of the main chain.

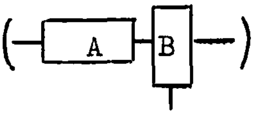
R =


Polymer	main chain	side chain	x	τ/ms(345K)
1	$-O-Si(CH_3)-$	$-(CH_2)_4CO-R$	36	0.013[14]
2	$-O-Si(CH_3)-$	$-(CH_2)_{10}CO-R$	36	0.008[14]
3	$-CH-CH_2-$	$-COO(CH_2)_5R$	240	0.2 [3]
4	$-C(CH_3)-CH_2-$	$-COO(CH_2)_5R$	200	160[15]

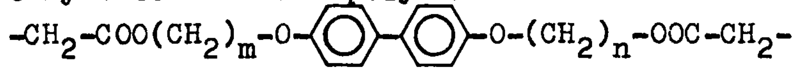
From Table V the increasing mobility by elongation of the spacer from polymer 1 to 2 can be seen again. But the difference in the mobility seems to be smaller in the case of the very flexible siloxane main chain in comparison with the polyacrylates in Table II. Generally the reorientation time τ(2c) of the side chain increases if the siloxane main chain is replaced by acrylate. The methacrylate main chain effects a further increase of the relaxation time. Furthermore the chemical structure of the liquid crystalline part, its length-to-width ratio [16] and the structure of the liquid crystalline phase [17] should play a similar role as observed on low molecular liquid crystals.

The influence of combined structures

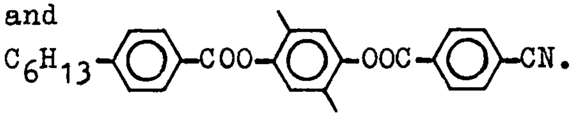
In main chain polymers we can observe only the mechanism 2b if there are dipole components perpendicular to the main chain. [18] Combined polymers of the geometry



should show a relatively free mobility of the longitudinal dipole of B. Recently Rötz et al.[19] have synthesized such polymers in which

A:


and

B:


For m>1 a strong decrease of the absorption intensity due to the formation of cybotactic groups has been found.[20] The phase transition temperature from the nematic into the isotropic phase $T_{N/I}$ and the reorientation time of the CN-dipole are given in Table VI:

TABLE VI Relaxation time by variation of the spacer length m

m	2	3	4	5	6	11
$T_{N/I}$/K	430	368	420	368	396	356
τ(357K)/ms	48	1.8	13	0.32	9.5	0.09

The alternation of the clearing temperatures and of the relaxation times is in the same direction as it has been observed already for low molecular liquid crystals.[21] In comparison with the relaxation times in Table V measured at a 12 K lower temperature the mobility of the group B is too low.

PHYSICAL VARIATION OF THE POLYMERS

The influence of plasticizers

The influence of plasticizers has been investigated by Tennstedt et al.[22] The substance 1 in Table II was given for 240 h in $CHCl_3$. After this chloroform was evaporated ($2 \cdot 10^3$ Pa, 333K). The substance has had the same transition point into the isotropic phase as before but it contains about 0.5 mass % $CHCl_3$. Relaxation measurements in a sandwich cell which allows a slow evaporation of $CHCl_3$ gives at first a strong decrease of $\tau(2c)$ and after this a slow increase with time (Fig. 4)

From these data can be concluded that the dynamical behaviour of side chain polymers can only be compared if the sample was dryed before at high temperatures in a good vacuum.

The influence of low molecular liquid crystals

Mixtures of low and high molecular liquid crystals have been investigated in order to study the plasticizer effect and the influence of the polymer matrix on the mobility of the low molecular compound.[23,24] The general behaviour should be demonstrated for the absorption curves of two different mixtures. Instead of ε'' the imaginary part of the capacity, $C'' = (2\pi f R)^{-1}$ is presented here.

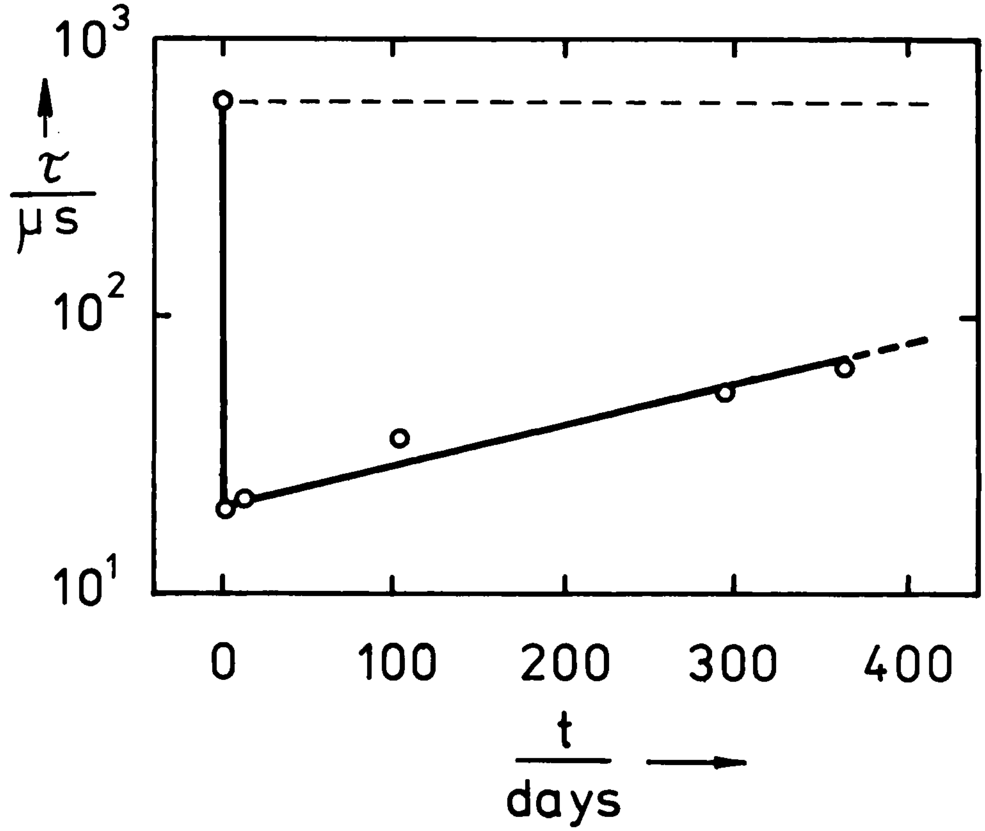


FIGURE 4 The change of the relaxation time τ(2c) during the evaporation of $CHCl_3$

Similar to low molecular liquid crystals the relative position of the relaxation frequencies of L and P depends on the molecular shape. The relaxation time of the low molecular compound increases with its increasing length-to-width ratio.[16] The relaxation time of the pure low molecular compound is much lower as in the mixture - an evidence for a molecular disperse solution in the polymer. The decrease of the relaxation time of the polymer in Fig. 6 (process 2c) for T = 333 K is given in Table VII

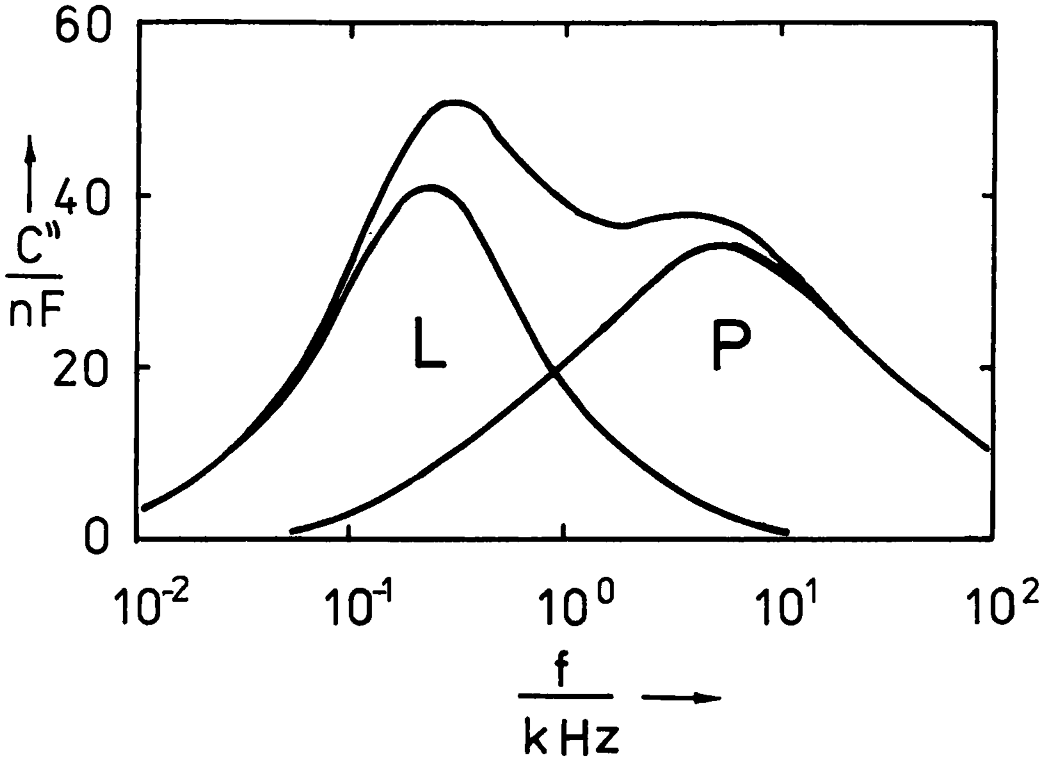
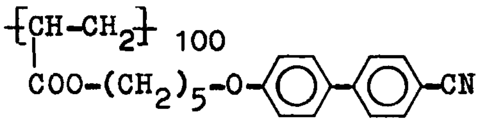
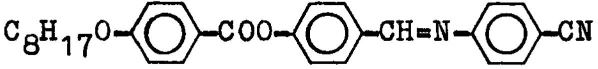


FIGURE 5 Dielectric absorption curves of a mixture of 70 mole %



(P) and

30 mole %



(L) at 340 K.

TABLE VII Relaxation time of the polymer with increasing concentration of the low molecular compound

x/mole %	100	90	80
τ/ms	10	1.3	0.21

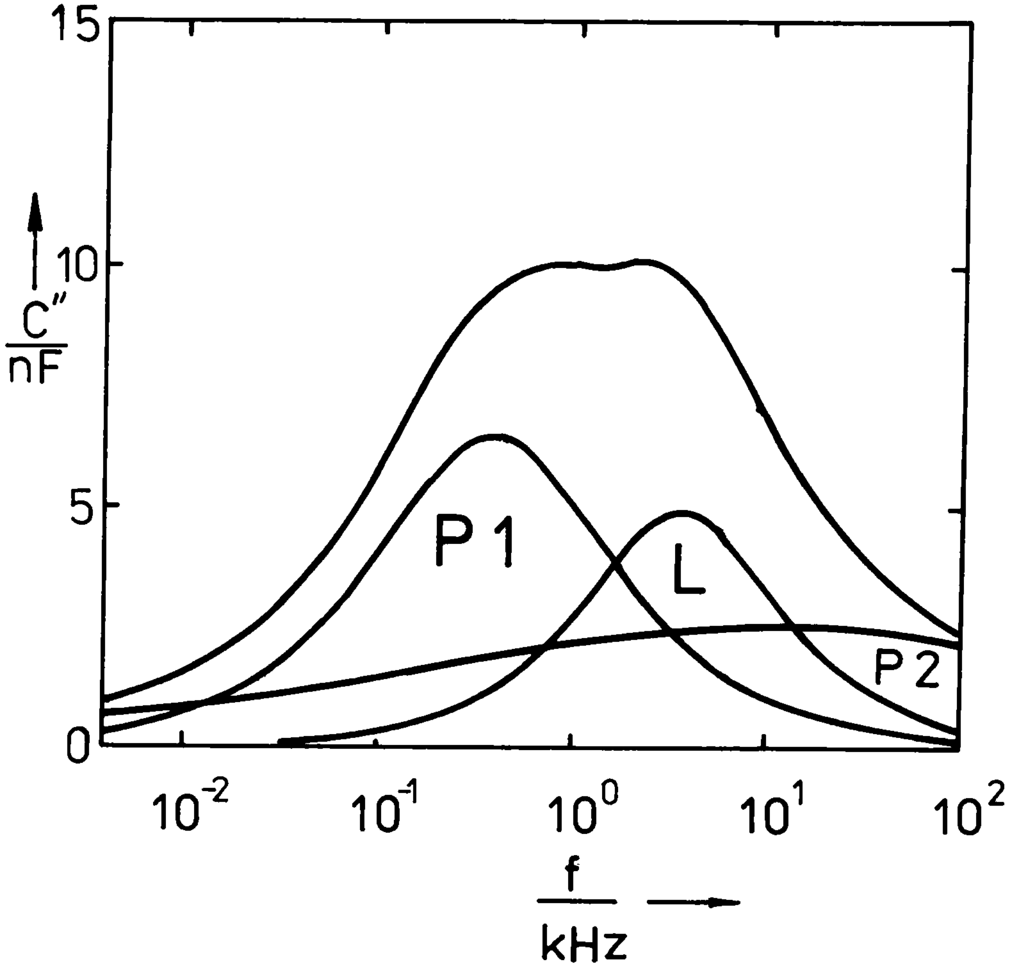
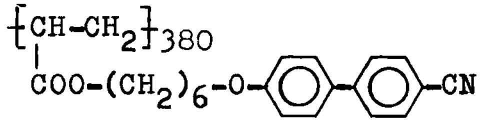
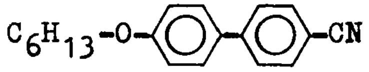


FIGURE 6 Dielectric absorption curves of a mixture of 80 mole %



(P) and

20 mole %



(L) at 329.8 K

In the same direction in which we increase the molecular mobility of the polymer by addition of a low molecular compound we will lose the advantages of the polymers in relation to the low molecular liquid crystals.

CONCLUSIONS

If we discuss the technical applications in the light of the possibilities to decrease the time necessary for the production of the dielectric anisotropy we have to point out: from the dynamical point of view low molecular substances are quite faster for switching processes in the bulk. Under extrem conditions (high temperatures and voltages) polymers can be switched with times lower than 1 s.[25] The decreased mobility with respect to the low molecular liquid crystals can also be found for the switching process in ferroelectric polymers.[26]
These limitations are also important for writing in and erasing processes of optical memories.[27] If one want to store an information in a quite shorter time one has to take mechanisms of the first group in Table 1. First investigations in this direction has been done by Eich et al.[28]
At the end should be pointed out that liquid crystalline side chain polymers are substances with such interesting properties that they will find a proportiomate place in the technique.

REFERENCES

1. H. Ringsdorf, B. Schlarb and J. Venzmer, Angew. Chem. 100, 117 (1988).
2. H. Kresse and V.P.Shibaev, Z. phys. Chem.(Leipzig) 264, 161 (1983).
3. H. Kresse and R.V. Talroze, Makromol. Chem., Rapid Commun. 2, 369 (1981).
4. W. Haase, H. Pramoto and F.J. Bormuth, Ber. Bunsenges. Phys. Chem. 89, 1229 (1985).
5. F.J.Bormuth and W. Haase, Liquid Crystals 3, 881 (1988).
6. J.P. Parneix, J.P.Njeumo, C. Legrand, P. Le Barny and J.C. Dubois, Liquid Crystals 2, 167 (1987).
7. R.V. Talroze, S.G.Kostromin, H. Kresse, C. Sauer, V.P. Shibaev, D. Demus and H.A. Plate, Makromol. Chem., Rapid Commun. 2, 305 (1981).
8. H.P. Zeller, Phys. Rev. Lett. 48, 334 (1982).
9. W. Wedler, D. Demus, W. Weißflog, W. Schäfer, H. Kresse, Proceedings of the 8. Liquid Crystal Conference of Socialist Countries, Cracow. Aug. 28. - Sept. 1., Proceedings, Poster B 27
10. E.J. Donth, Glasübergang, WTB, Akademieverlag, Berlin, 1981.
11. H. Kresse, E. Tennstedt and R. Zentel, Makromol. Chem. Rapid Commun. 6, 261 (1985).
12. E. Tennstedt, Thesis, Halle 1986.
13. H. Kresse, S. Kostromin and V.P. Shibaev Acta Polymerica, in press
14. H. Kresse, A. Wiegeleben and B. Krücke, Acta Polymerica 39, 583 (1988).
15. H. Kresse, S. Kostromin and V.P. Shibaev, Makromol. Chem., Rapid Commun. 3, 509 (1982).

16. H. Kresse, H. Stettin, F. Gouda and G. Andersson, phys. stat. sol. (a) 111, 265 (1989).

17. H. Kresse, Ch. Selbmann, D. Demus, A. Buka and L. Bata, Cryst. Res. Technol. 16, 1439 (1981).

18. M.H. Alhaj-Mohammed, G.R. Davies, S. A. Jawad and I.M. Ward, Journ. Polym. Sci., B. Polym. Phys. 26 1751 (1988).

19. U. Rötz, J. Lindau, W. Weissflog, G. Reinhold, W. Unseld and F. Kuschel, Mol. Cryst. Liq. Cryst. 170, 185 (1989)

20. H. Kresse, U. Rötz, J. Lindau and F. Kuschel, Makromol. Chem., in press.

21. H. Kresse, J. Pietscher, S. König. W. Weissflog and H.J. Deutscher, Z. phys. Chem. (Leipzig) 259, 779 (1978).

22. E. Tennstedt, H. Kresse and R. Zentel, Acta Polymerica 37, 685 (1986).

23. H. Kresse, S.G. Kostromin and V.P. Shibaev, Liquid Crystals, in press.

24. H. Kresse, H. Stettin, S.G. Kostromin and V.P. Shibaev, Mol. Cryst. Liq. Cryst., in press.

25. R. Kiefer and G. Baur, 12 Internat. Liquid Crystal Conf. Freiburg/Br, Abstracts PO 09.

26. V.P. Shibaev. M.V. Kozlovsky, L.A. Beresnev, L.M. Blinov and N.A. Plate, Polymer Bulletin 12, 299 (1984).

27. V.P. Shibaev. S.G. Kostromin, N.A. Plate, S.A. Ivanov, V. Yu Vetrov and I.A. Yakovlev, Polymer Commun. 24,364 (1983).

28. M. Eich, J.H. Wendorff, B. Reck and H. Ringsdorf, Proceedings of the 16. Freiburger Arbeitstagung Flüssigkristalle, 19-21.3 1986, Lecture Nr. 6.