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# Biaxiality Phenomenon in Molecular Properties of Comb Lc Polymer with Lateral Structure: First Evidence

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# BIAXIALITY PHENOMENON IN MOLECULAR PROPERTIES OF COMB LC POLYMER WITH LATERAL STRUCTURE: FIRST EVIDENCE

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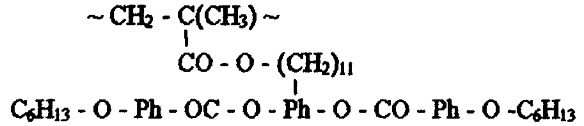
**Abstract** Dynamooptical and electrooptical properties have been investigated in dilute solutions for comb-like LC polymer with mesogenic groups laterally attached by middle point to the macromolecule backbone via flexible spacer. For polymer solution in chloroform, the *T*-range was found where the Kerr constant *K* is increasing (in absolute value) with increasing *T* while the shear optical coefficient $[n]/[\eta]$ remains invariable. This reflects the intramolecular parking of the mesogen dipole axes with keeping the same order in mesogen optical axes. Dipole axis of the mesogenic group in the chain of this polymer is known to form a large angle with the optical one. Hence, the result can be explained by change in the mesogen short axes parking with the invariable long axes one. By other words, as evidence for present biaxiality phenomenon in molecular properties of the polymer.

## INTRODUCTION

Biaxial nematic phase behaviour is promising but rare experimental phenomenon.[1,2] For a comb-like polymer, this was surely observed only in the melt of the polymer PMA with the structure shown below:

PMA



$$\begin{array}{l} \sim CH_2 - C(CH_3) \sim \\ \qquad\quad | \\ \qquad CO - O - (CH_2)_{11} \\ \qquad\qquad\qquad | \\ C_6H_{13} - O - Ph - OC - O - Ph - O - CO - Ph - O - C_6H_{13} \end{array}$$

Here the three-ring mesogenic group in every monomer unit is laterally attached by the middle point to the main chain of the macromolecule via flexible spacer.

Note that the similar polymer with a shorter spacer[3] as well as the polymers with a siloxane main chain[4] do not possess this property. There seems to be an optimal length of the spacer in PMA providing the phenomenon under investigation.

Besides conoscopic proofs for present nematic phase biaxiality[1], a very surprising dynamic behavior of the PMA LC phase was observed in the Kerr effect investigations.[5]

The real work relates to investigations of the molecular nature of the phenomena by the dynamo-optical and electro-optical methods. The value and a sign of the Maxwell and the Kerr effects observed in dilute polumer solution are known to be determined by structure (optical anisotropy) and space orientation of the anisotropic groups in the macromolecule.

## EXPERIMENTAL

Flow birefringence (FB) and the Kerr effect (KE) were investigated for the PMA sample with $M_w = 6.8 \times 10^6$ in chloroform with techniques described previously[6,7].

## RESULTS AND DISCUSSION

### Flow birefringence

Dependence of the FB $\Delta n$ on the shear rate $g$ was well approximated by a linear function with the slope giving the shear optical coefficient $[n] / [\eta]$

$$[n] / [\eta] = \lim (c \to 0) \lim (g \to 0) \Delta n / \Delta\tau \ , \quad \Delta\tau = g(\eta - \eta_0)$$

where $\eta$ ($\eta_0$) is the solution (solvent) viscosity. Lower curve in Figure 1 shows the $\Delta n/\Delta\tau$ value at different temperatures $T$ for PMA sample in chloroform. Over the all $T$-range investigated, the $[n] / [\eta]$ values are negative in sign as for other comb-shaped polymers having both aliphatic and mesogenic aromatic groups in the side chains[7]. Further, this value is practically temperature-independent.

A sign of shear optical coefficient in the PMA solution is determined by orientation of the optically anisotropic mesogenic side groups.[6] Negative sign of $[n]/[\eta]$ implies that the polarizability of the molecule and its segment in the direction of greatest geometric length is lower than in that normal to segment axis, i.e., the mesogenic groups in the side chain are preferably oriented in the normal (to molecule axis) direction. Further, invariable values of both $[n]/[\eta]$ and the Kuhn segment length[8] correspond to the same orientational order of the mesogen long axes over the all $T$-range investigated.

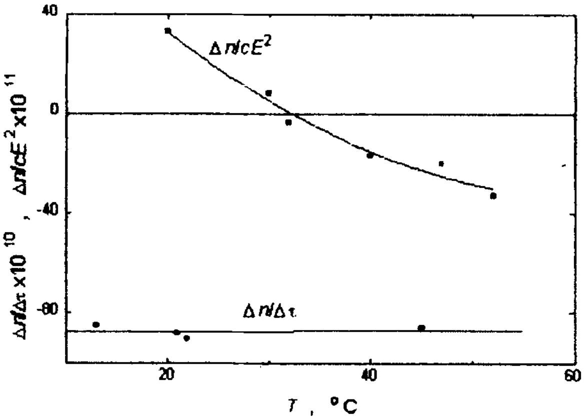


FIGURE 1 Temperature dependence of the Kerr constant $\Delta n/cE^2$ and the Maxwell constant $\Delta n/\Delta\tau$ (in CGSE units) for PMA in dilute solution in chloroform during a cool-down process.

The chain conformation in solution for the investigated PMA sample is a random coil.[6] In molecular solution of these chains, the shear optical coefficient does not depend on $M$ and is determined by the optical anisotropy of the Kuhn segment $\Delta\alpha_s$:

$$[n] / [\eta] = B\Delta\alpha_S \tag{1}$$

where $B$ is the optical constant, $B \equiv (4\pi/45k_BT)\,[(n^2+2)^2/n]$, $n$ is the refractive index of the solvent, and $k_B$ is the Boltzmann constant.

The experimental $[n] / [\eta]$ value is provided by the proper segment anisotropy, $\Delta\alpha$, and the form effects connected with the difference in refractive indexes of PMA substance and solvent. Whole macromolecule and each segment, being asymmetrical in geometric form, are oriented in the shear field preferably along the flow direction. As a result, the positive in sign contributions of the macroform effect $([n] / [\eta])_f$ and microform effect $([n] / [\eta])_{fs}$ are added to the proper $([n] / [\eta])_e$ value:

$$([n] / [\eta]) = ([n] / [\eta])_e + ([n] / [\eta])_f + ([n] / [\eta])_{fs} \tag{2}$$

These contributions of the macroform (index "$f$") and microform (index "$fs$") effects were evaluated by[7]:

$$([n]/[\eta])_f = \{[(n^2+2)^2(n^2_k - n^2)^2 \mathrm{x}0.058\,\Phi] / (\pi\rho^2 n^3 N_A RT)\}\ \{M/[\eta]\} \tag{3}$$

$$([n]/[\eta])_{fs} = B\,(dn/dc)^2\,(M_0 s / \pi\,\mathrm{N_A}\ \bar{v})\,\varepsilon_s \tag{4}$$

with the refractive index $n_k$ and density $\rho$ of the polymer, the Flory coefficient $\Phi$, Avogadro's number $N_A$, the gas constant $R$, the refractive index increment $dn/dc$, the monomer (repeat) unit mass $M_0$, number of the monomer units in the segment $s$, partial specific volume $\bar{v}$, and the segment form factor $\varepsilon_s$. Using eqs 3 and 4, the proper monomer unit anisotropy $\Delta a$ was evaluated at different $T$ from :

$$\Delta a = \Delta\alpha / s = ([n]/[\eta])_c / B\, s \qquad (5)$$

The mesogenic core of the PMA side chain is separated from the main chain by a flexible spacer - $(CH_2)_{11}$ - . This weakenes the correlation between orientations of the main chain and the mesogenic part of the side chain. Additional space mobility of the mesogenic groups in the PMA chain is provided by the type of their attachment. Hence, the contribution of the mesogenic groups to the optical anisotropy of the PMA molecule segment may be considered to be independent of each other. As in previous paper,[6] we may thus represent $\Delta a$ by the following sum:

$$\Delta a = \Delta a_{mes} S_{opt} + \Delta a_{main} \qquad (6)$$

with the orientational order parameter $S_{opt}$ for the optical axes of the mesogenic groups :

$$S_{opt} = (3\,\overline{\cos^2 \vartheta} - 1)/2 \qquad (7)$$

The first term in eq 6 takes into account the optical anisotropy of the mesogenic group $\Delta a_{mes}$ and the angle θ formed by the optical axis of the group and the segment; $\overline{\cos^2 \theta}$ is the value averaged over all mesogens. The second term in eq 6 is the optical anisotropy of the rest of the PMA monomer unit (methacryloyl and - $C_{11}H_{22}$ - groups). In a previous paper,[6] $\Delta a_{mes}$ was determined to be $\Delta a_{mes} = 230\times10^{-25}$ cm$^3$ while $\Delta a_{main}$ may be evaluated to be[7] $\Delta a_{main} = -7.5\times10^{-25}$ cm$^3$.

The temperature dependence of the form effects for PMA in chloroform is not significant, as it follows from eqs 3 and 4. Hydrodynamic data show, additionally, that the Kuhn segment has the same length (the same $s$ value) for the PMA molecules in chloroform at different temperatures[8]. Hence, insensitivity of the experimental $[n]/[\eta]$ value to changing $T$ reflects the same ordering in the long mesogenic group exes (coinsided with the optical ones) in the PMA macromolecule at different $T$.

## Electro-optical properties

Birefringence $\Delta n$ induced in PMA solution by electric field increased proportionally to the square field strength $E^2$ with the slope giving the Kerr constant. Specific Kerr constant for PMA was obtained by $K = (K_c - K_0)/c$ , where $K_c$ is the $\Delta n/E^2$ value for a solution with concentration $c$, and $K_0$ is that for a solvent. The $K$ value did not depend on concentration but was very sensitive to change in $T$. With solution cooling from 52 to 20

$^0$C, the $K$ value increases monotonically and reversably from $-3.3\times10^{-10}$ to $+3.3\times10^{-10}$ $cm^5g^{-1}(300V)^{-2}$ (Figure 1). The change in sign of $K$ was observed at temperature close to 32 $^0$C which coinsides with the low $K$ value obtained earlier for PMA in carbon tetrachloride at room temperature.[6]

At low temperature, $T \leq 32\,^0$C, the Kerr constant $K$ and the shear optical coefficient $[n]/[\eta]$ have opposite signs. This effect may be attributed to intramolecular aggregation of the mesogenic cores observed earlier for a comb-shaped *end*-on polymers[7]: change in thermodynamic quality of the solvent (due to changing $T$) may be followed by change in orientational ordering of the side chains due to changing polymer-solvent interactions which compete with interactions between the side chains into the polymer molecule.

At $T > 32\,^0$C for PMA in chloroform, the sign of the Kerr constant coincides with that of the shear optical coefficient. They are both negative as well as those of other LC side chains polymers elsewhere investigated.[7] This coincidence may be attributed to the existence of the longitudinal component $\mu_\parallel$ of the dipole moment of the macromolecule. It is the sum of the longitudinal components of the monomer dipole moment $\mu_{0\parallel}$ which was evaluated by[7]

$$\mu_{0\parallel}{}^2 = 54\, k_B T M_0 K \,/\, \{([n]/[\eta])\, s N_A (\varepsilon+2)^2\} \qquad (8)$$

with $\varepsilon = 2.28$ being the dieletric permeability of the solvent.

For PMA, the value and sign of the Kerr constant and, hence, the $\mu_{0\parallel}$ value are determined by the mesogenic groups.[6] Therefore, in the manner above, we may represent $\mu_{0\parallel}$ by the following expression

$$\mu_{0\parallel} = \mu_0\, S_{dip} = \mu_0 (3\,\overline{\cos^2\varphi}\; - 1)/2 \qquad (9)$$

with $\mu_0$ being the dipole moment of the mesogenic group, and $\varphi$ the angle formed by the dipole direction and the optical axes of the segment; $\overline{\cos^2\varphi}$ is the value averaged over all mesogens.

The orientational order parameter $S_{dip}$ for the mesogen group dipole axes was evaluated by eq 9 with $\mu_0 = 3$ D.[6] The $S_{dip}$ value thus determined increases gradually from 0.16 to 0.40 with increasing temperature (in accordance with the $K(T)$ dependence) while parameter $S_{opt}$ remains temperature-independent and close to -0.16.

## CONCLUSIONS

The optical axis (direction of maximal polarizability) of the mesogenic group in the PMA molecule coincides with the long geometric one. This means that parameter $S_{opt}$ is the direct quantity for degree of the mesogen long axes ordering. On the other hand, for the mesogenic group under investigation, the angle between the dipole direction and the optical axis is large enough, from 68 to 69 deg rad.[9,10] This is as close to normal direction, as the direction of the short mesogen axis is. Hence, orientational ordering of the dipole axes reflects orientational ordering of the mesogens in normal direction, and parameter $S_{dip}$ may be accepted as the quantity for degree of the mesogen short axes ordering.

From this point of view, increasing $S_{dip}$ with increasing $T$ at invariable $S_{opt}$, observed for PMA in chloroform at $T > 32\,^0\mathrm{C}$, may be interpretted as change in the mesogen short axes parking with the invariable long ones. By other words, as evidence for present biaxiality phenomenon in molecular properties of the PMA.

Finally, parameter $S_{dip}$ reflects polar ordering of the mesogen dipoles, and the axial ordering of the mesogen boards along their normals may be expected to be even higher.

## REFERENCES

1. F.Hessel, R.-P.Herr and H.Finkelmann, Makromol. Chem., 188, 1597 (1987).
2. M.Ebert, O.Herrmann-Schoenherr, J.H.Wendorff, H.Ringsdorf and P.Tschirner, Makromol. Chem., Rapid Commun., 9, 445 (1988).
3. Q.F.Zhou, H.M.Li and K.D.Feng, Macromolecules, 20, 233 (1987).
4. F.Hardouin, Macromol. Symp., 98, 329 (1995).
5. B.-J.Jungnickel and J.H.Wendorff, The Kerr Effect as Applied to the Investigation of Polymers. In: Chemistry and Physics of Macromolecules. E.W.Fischer, e.a., eds. (VCH Verlag, Weinheim, 1991), pp.349-375.
6. P.N.Lavrenko, I.P.Kolomietz and H.Finkelmann, Macromolecules, 26, 6800 (1993).
7. V.N.Tsvetkov, Rigid-Chain Polymers (Plenum Publishing Corp., New York, 1989).
8. P.N.Lavrenko, O.V.Okatova, E.V.Korneeva and H.Finkelmann, Vysokomolek. Soedin., A 38, in press (1996).
9. E.I.Ryumtsev, T.A.Rotinyan, A.P.Kovshik and M.A.Agafonov, Opt. Spektrosk., 51, 131 (1985).
10. H.Hirschmann, Elektro-optische Eigenschaften fluessig-kristalliner Polymerer: Seitenkettenpolymere mit longitudinaler und lateraler Ankopplung der Mesogenen (Masters Thesis, TH Darmstadt, 1988).