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Synthesis and Molecular Properties of New Side-Chain Liquid Crystalline Polymers Based on the Baylis-Hillman Reaction

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A new methodology has been employed in synthesis of two side-chain liquid-crystalline polymers with cyanobiphenylene mesogenic groups and variation of -CN, -COCH₃ and -OH groups displacement in the backbone surrounding. Hydrodynamic and electrooptical (the Kerr effect) methods were used to study their molecular properties in solution in benzene and chloroform. Electrooptical properties of polymers are compared with the same ones of homologous series of alkoxy cyanobiphenylenes as the model compounds of the polymer mesogenic groups. Different mobility of the side-chain mesogenic groups in polymers under investigation was observed and related to the chemical and dipole structure.

Keywords: LC polymers; electro-optics; mesogens mobility; stereotacticity

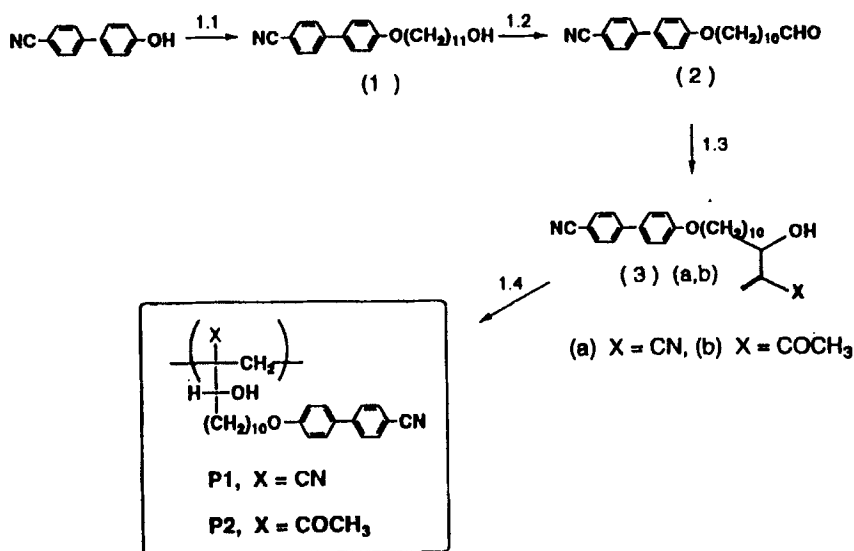
INTRODUCTION

The simultaneous insertion of optically and electrically anisotropic groups (such as -C≡N and -C=O) into the main and side chains of the comb-like polymer may lead to a model convenient for the detection of mobility of the main or side chain elements of the polymer. Additionally, these functional groups are capable of

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forming the inter- and intra-molecular hydrogen bonds important in formation of the different types of mesophases.

In the present work, hydrodynamic and electrooptical properties in solution have been carried out on two new side-chain liquid crystalline polymers, P1 and P2, with structures shown below. Hydrodynamic data were used to characterize dimensions and form of the isolated macromolecules, and electrooptical ones, in turn, were applied for evaluation of mobility of cyanobiphenylene mesogenic side chains. These polymers are known to form well-defined SmA liquid crystal phases^[1]. They were prepared by a new synthetic methodology^[1] based on the Baylis-Hillman reaction by which functional groups can be incorporated along the polymer backbone, and through specific interactions between these groups, control the tacticity of the polymer. The main theme of this methodology is outlined in Fig. 1.



1.1 Br(CH₂)₁₁OH, K₂CO₃, butanone

1.2 DMSO, oxalyl chloride

1.3 acrylonitrile or methyl vinyl ketone, 3-quinuclidinol

1.4 Irgacure 184, DCM, UV

FIGURE 1 Scheme of the Baylis-Hillman methodology

Polymerization

Preparation and properties of corresponding monomers were described previously^[1,2]. A solution of monomer 3a or 3b (4.4 mmol) and Irgacure 184 photoinitiator (Ciba-Geigy) (0.09 mmol) in dry dichloromethane (3 cm³) was spread over a glass plate (18×25 cm) and the solvent evaporated to leave a thin film of monomer and photoinitiator. The film was irradiated with UV radiation from a UVA sunlamp (Philips) for 6 h. The resultant polymer was purified by the precipitation of the polymer from dry dichloromethane by the addition of methanol. The polymer was separated by centrifugation (5000 rpm for 30 mins). The purification procedure was repeated until the monomer precursor had been completely removed (t.l.c., silica gel, dichloromethane). The polymer was then dissolved in dry dichloromethane (5 cm³) and the resultant solution added dropwise to petroleum fraction (bp 40–60 °C) with vigorous stirring. The resultant white precipitate was recovered by filtration and washed with two further quantities of petroleum fraction (bp 40–60 °C) (2×50 cm³), then redissolved in dry dichloromethane (5 cm³). The solution was then passed through a 0.5 mm membrane filter and the solvent removed to leave the polymer as a glass. The polymer was then dried at 50 °C in vacuo for 6 h.

Structures of the intermediates, monomers and polymers were confirmed by one or more of the following techniques; ¹H and ¹³C NMR (JEOL JNM-GX 270 MHz spectrometer), infrared spectroscopy (Perkin-Elmer 783 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020G / MS spectrometer). Transition temperatures were measured using a Mettler FP 52 hot-stage and FP 5 control unit in conjunction with an Olympus BH2 polarising microscope, and these results were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7C, with data station and cooling accessory). The instrumental accuracy of the DSC was calibrated against an indium standard. The glass transition temperatures of the SCLC polymers were measured using a DDSC-7C calorimeter. The purity of the intermediates and monomers were checked by NMR spectroscopy (Jeol JNM-GX 270 MHz spectrometer), tlc (single spot purity) and reverse phase chromatography (5 μm ODS Microsorb, 25×0.46 cm Dynamax column, eluting with acetonitrile or methanol). The degree of polymerization index and degree of polymerization of the polymers were determined by gel permeation chromatography using a PLgel column (5 mm, 30×0.75 cm, mixed C column) as the stationary phase and THF as the mobile phase. The column was calibrated using polystyrene standards (M_p = 1000–430500). The identification of the mesophases was carried out using optical microscopy.

Solution measurements

Polymer P1 is insoluble in CCl_4 but readily soluble in chloroform and THF. Polymer P2 is soluble, additionally, in benzene. 4'-n-alkoxy-4- cyanobiphenyls (nOCB) $\text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$ with $n=7, 10$ and 12 were the Merk products. The electrooptical and hydrodynamic properties were studied by the methods described previously^[2] at 26°C in benzene and in chloroform.

Hydrodynamic properties

The intrinsic viscosity $[\eta]$ and diffusion coefficient D values are given in Tab. I. The P1 polymer density is close to $1.14 \text{ g}\cdot\text{mL}^{-1}$ as estimated from picnometry data. Experimental data were used in evaluation of molecular weight, M , by the equation

$$M_{D\eta} = 100 \cdot (A_0 T / D \eta_0)^3 / [\eta]$$

where T is the Kelvin temperature and A_0 is a hydrodynamic invariant^[3]. The value $A_0 = 3.4 \times 10^{-10} \text{ erg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1/3}$ was used. The polymers under investigation form real solutions in benzene and chloroform as well as in THF.

TABLE I Hydrodynamic and electrooptical properties of the polymers in solution

Polymer	Solvent	$[\eta]$ ($\text{mL}\cdot\text{g}^{-1}$)	$10^7 \times D$ ($\text{cm}^2\cdot\text{s}^{-1}$)	dn/dc ($\text{mL}\cdot\text{g}^{-1}$)	$M_{D\eta}$ ($\text{g}\cdot\text{mol}^{-1}$)	$10^{10} \times K$ ($\text{g}^{-1}\cdot\text{cm}^3 \cdot (300\text{V})^{-2}$)
P1	Chloroform	7.8	27.5	0.16	4200	5.2
P2	Benzene	5.6	31	0.06	3000	4.4
	Chloroform	—	—	—	—	4.4

The degree of polymerization, DP, is equal to 10 and 7 for P1 and P2, respectively. Hence, the length of the molecule does not exceed here one statistical segment. The form asymmetry of the macromolecule and the degree of its solvation in solution was estimated from viscometric and diffusion data using the hard models. The P1 molecule in solution in chloroform, if in globular state, may be modeled by sphere with density equal $1/\bar{\nu}$ ($\bar{\nu}$ as partial specific volume) and radius $r_{\text{gl}} = 11.35 \text{ \AA}$ ($\bar{\nu} = 0.8776 \text{ mL}\cdot\text{g}^{-1}$ and $M = 4200$ were used). According to Einstein and Stockes, for solution of these spherical particles we have

$$[\eta]_{\text{gl}} = 2.5 \bar{\nu} = 2.2 \text{ mL}\cdot\text{g}^{-1} \text{ and } D_{\text{gl}} = kT/6\pi\eta_0 r_{\text{gl}} = 32.69 \times 10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$$

(with the solvent viscosity $\eta_0 = 0.59 \times 10^{-2}$). These $[\eta]_{\text{gl}}$ and D_{gl} differ noticeably from the experimental values $[\eta]$ and D (Tab. I) $[\eta] = 7.8 > [\eta]_{\text{gl}}$ and

$D = 27.5 \times 10^{-7} < D_{gi}$. There are two clear causes of the result: aspherical form of the molecule and its solvation. For a spheroid and straight spherocylinder particles we have^[4]

$$2\pi N_A M^2 / 45 M_L^3 [\eta] = F_\eta(L/d)$$

where L and d are the length and the diameter of the particle, $F_\eta(L/d)$ is a function of form asymmetry given in paper^[3]. Using $[\eta]$, M and $M_L = 166.4 \times 10^8$ Dalton cm^{-1} we obtain $F_\eta = 0.4126$ and the ratio $L/d = 2.5 \pm 0.4$ as averaged for two models discussed. The solute part in the volume occupied by the particle is close to 37%.

The low DP values of the samples can be responsible for the Maxwell effect observed in chloroform solution of polymer P2. The same zero flow birefringence was observed in this solution as well as in pure solvent.

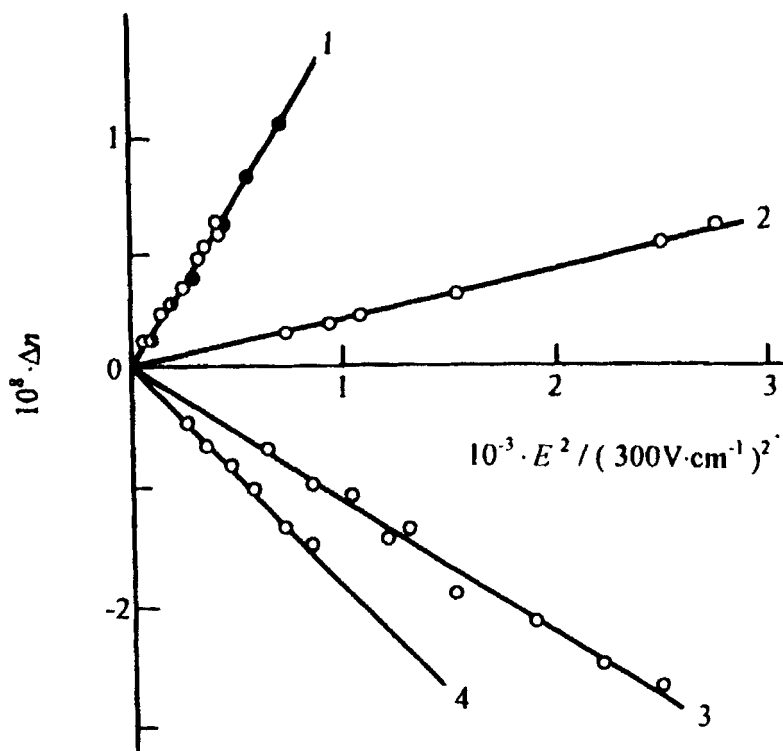


FIGURE 2 Δn versus E^2 for P2 in (1) benzene and (3) chloroform solutions in pulsed (open circles) and sinusoidal (filled circles) electric field at 20°C. Solute concentration c is: (1) 2.84 and (3) 1.61 $\text{g} \cdot \text{dL}^{-1}$. Points 2 and 4 present the Kerr effect observed in pure solvents: (2) benzene and (4) chloroform, respectively.

Electrooptical properties

The Kerr effect observed in the solvents (Fig. 2, curves 2 and 4) was close to published data. A linear growth in electric birefringence Δn with the square electric field strength E^2 was observed (Fig 2) in accord with the Kerr law: $\Delta n = KE^2c$ where K is the specific Kerr constant. The Kerr effect in dilute solution is small in value (comparable with that in the solvent) and positive (in sign) in both the solvents. In chloroform solution of P2, at low concentration only, the negative effect was observed (curve 3 in Fig. 2). The polymer effect is here too small to exceed the solvent one. For a polymer in solution, the contribution of a solvent to the birefringence observed in the solution was first subtracted out. No concentration dependence of the specific Kerr constant was observed. The molar Kerr constant ${}_mK$ was evaluated by

$${}_mK = 6n[(n^2 + 2)(\epsilon_o + 2)]^{-2}(M/\rho_o)(\Delta n_{12} - \Delta n)/(WE^2)$$

where n , ρ_o and ϵ_o are refractive index, density and dielectric constant of the solvent, respectively, W the solute weight fraction, M molecular weight of the compound (with comparative purposes, molecular weight of the monomer unit was taken for the polymers).

Oxyalkylcyanobiphenylenes

The Kerr effect observed in solution of the polar substance has usually an orientational nature and depends on the value and direction of the permanent dipole moment of the dissolved particles. We may suppose that in the P1 and P2 macromolecules, the polar structure is connected mainly with the side chain mesogenic moieties. Therefore, polar and electrooptical properties of the low molecular weight compounds, nOCB, $C_nH_{2n+1}O-C_6H_4-C_6H_4-CN$ with $n = 7, 10$ and 12 were first investigated because these compounds may be considered as the models suitable for the P1 and P2 macromolecules side chains. The dipole moment μ of the nOCB molecule in benzene solution was determined from the data of dipole polarization of its dilute solution as described earlier^[2,5]. Results are listed in Tab. II together with the literature data.

One can see that in this homologous series, the Kerr constant is decreasing from 10.3×10^{-10} to $6.3 \times 10^{-10} \text{ cm}^5 \cdot \text{g}^{-1} \cdot (300\text{V})^{-2}$ with n increasing from 1 to 12. The similar tendency for nOCB was observed in the isotropic melt^[8]. However, the molar constant ${}_mK$ for nOCB in solution is practically independent of n and equal $({}_mK)_{av} = (64 \pm 3) \times 10^{-10}$ CGSE units. Simultaneously, the μ value is also practically independent of n . The latter effect is supported by the results of a computer simulations of the OCB dipole moments given in Tab.III: for nOCB with n from 1 to 4, the μ value does not depend on n and is determined mainly by

dipole moment of the polar CN- group (compounds from 2CN to 5CN). This means that it is really the mesogenic moiety what is responsible for the polar structure and electrooptical properties of the nOCB in solution and provides the mK and μ values.

TABLE II Electrooptical and dielectric properties of alkoxy cyanobiphenylenes in benzene solution

Sample	<i>n</i>	$K \times 10^{10}$ ($\text{cm}^5 \cdot \text{g}^{-1} \cdot (300\text{V})^{-2}$)	$mK \times 10^{10}$ ($\text{cm}^5 \cdot \text{g}^{-1} \cdot (300\text{V})^{-2}$)	μ (D)	Ref.
1OCB	1	10.3	60.0	—	[6]
5OCB	5	9.4	68.8	—	[6]
6OCB	6	—	—	5.23	This work
7OCB	7	7.9	62.7	5.28	This work
8OCB	8	7.2 ^a	62.7	5.20	[7]
10OCB	10	6.7 ^b	60.8 ^b	5.26	This work
12OCB	12	6.3	62.0	5.23	This work

a. The value is calculated using $\Delta K/W$ and Eq (4) given in paper [7].

b. The values $K = 7.3 \times 10^{-10}$ and $mK = 68.6 \times 10^{-10}$ are available from paper [6].

TABLE III Dipole moments of some cyano-derivatives as calculated using CHARGE-2/COSMIC in Nemesis, version 2

Substance	Structure	μ , (D)
1OCB	$\text{CH}_3\text{-O-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CN}$	4.64
2OCB	$\text{C}_2\text{H}_5\text{-O-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CN}$	4.79
4OCB	$\text{C}_4\text{H}_9\text{-O-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CN}$	4.79
2CN	$\text{C}_2\text{H}_5\text{-CN}$	3.66
3CN	$\text{C}_3\text{H}_7\text{-CN}$	3.68
4CN	$\text{C}_4\text{H}_9\text{-CN}$	3.67
5CN	$\text{C}_5\text{H}_{11}\text{-CN}$	3.68

Polymers

The mK value obtained for polymer P1 in solution (59×10^{-10} CGSE units) is very close to corresponding value of the low molecular weight compound, OCB (64×10^{-10} CGSE units). This conclusion is confirmed by a short time effect which was observed in the pulsed electric field: it was comparable with the response time of the photo-recording system. On one hand, the same Kerr effects observed here in solutions of polymer and mesogenic groups is the result typical of flexible chain polymers^[3] where the space orientation of the polar groups is

not correlated with the main chain. The geometric structure of the chain repeat unit promotes the orientational freedom of the side mesogens. On the other hand, this experimental result shows that the main chain contributes nothing to the electric birefringence effect, in spite of the fact that the rest part of the repeat P1 unit has an cyano-substituent with high dipole moment. This may be clear if we analyze the chain structure and possible interactions between the main chain and nearest neighbor groups.

In the repeat P1 chain unit, there is the $\text{-C}\equiv\text{N}$ group which is fixed strongly to the polymer backbone. Its dipole axis is oriented in a direction normal to the chain contour. The statistical distribution of these substituents along the macro-chain would lead, therefore, to a mutual compensation of their dipole moments. Significant chain isotacticity only could lead here to the formation of a significant total dipole moment linked strongly with the main chain. Experimentally, as mentioned above, practically the same Kerr effect was observed in solutions of P1 and nOCB. Hence, the electrooptical properties of P1 in a dilute solution in chloroform do not show high *isotacticity* of the polymer chain.

The ${}_mK$ obtained for polymer P2 in solution is ${}_mK = 52 \times 10^{-10}$ CGSE units in both benzene and chloroform, independently of the different nature of the solvents. On one hand, this value does not strongly differ from ${}_mK$ obtained above for P1 because polymers P1 and P2 have the same mesogenic groups and the same spacers in the side chains. They are clear the mesogenic groups which mainly provide the Kerr effect observed in polymer solution.

On the other hand, the ${}_mK$ value obtained for polymer P2 is somewhat lower (14%) than that of P1. Taking into account the low inhomogeneity of the P1 and P2 samples ($M_w/M_n \leq 1.7$) and their close microtacticity^[1] we have to relate this difference to the different chemical structure of the P1 and P2 monomer units. In fact, P1 differs from P2 in that P1 has a cyano-substituent and P2 a methylcarboxy-substituent along the respective backbones.

In the P2 repeat unit, an angle formed by the dipole axis of the $\text{C}=\text{O}$ bond in the methylcarboxy-substituent with the chain contour is smaller than 90° . In this way, the lower ${}_mK$ value obtained for P2 may reflect an accumulation of the longitudinal (with respect to the principal axis) components of dipole moments of the $\text{C}=\text{O}$ bonds in polymer P2 which are not compensated. This effect may be provided by *any* type of the chain microtacticity if the last is noticeable. As a result, partial orientation of the macromolecule backbone in an internal electric field (due to result dipole moment of the main chain) may somewhat disturb the orientational ordering of the mesogenic groups in this field (or lead to an increase in optical anisotropy in a direction normal to the field direction). Thus, difference between the ${}_mK$ values obtained for P1 and P2 may be explained by a polymer chain microtacticity effect which is detectable for P2 due to the special structure

of the side-substituent. The effect may be predicted to be more pronounced for the polymer with higher molecular weight.

For a sample with $DP < 10$, as in the present work, this polymer effect might be undetectable in the polymer melt^[9]. We may note, nevertheless, that the SmA phase exists in the P1 melt over the wider temperature range than that in the P2 one: P1 (°C): T_g 41.0 SmA 84.0 Iso and P2: T_g 38.5 SmA 54.5 Iso

The results may be resumed as follows. Electrooptical properties of the CN-containing polymer are very close to properties of the low molecular weight compounds nOCB which are model molecules analogous to the macromolecule side chain. The insertion of the polar -COCH₃ group close to the main chain of the macromolecule was shown to effect the electrooptical and mesomorphic properties of the polymer more significantly than the CN-one (decrease in the isotropization temperature and the Kerr effect as observed in solution). The molar Kerr constant was found for polymer P2 to be smaller (52×10^{-10} CGSE units) than that of polymer P1 (59×10^{-10} CGSE units). This may reflect some *stereotacticity* of the polymer chain detectable (in the case of P2) with the presence of the -C=O bonds close to the main chain.

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