IR dichroism study of orientational ordering of liquid-crystalline acrylates

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Orientational ordering of four liquid-crystalline acrylates induced by the surface of KBr plates over a wide temperature range was studied by the IR dichroism technique. IR spectra of homogeneously aligned samples were used to calculate the angles between the direction of the transition moment for a series of vibrations of the mesogenic fragment and its long axis. A method for calculation of the homeotropic orientation parameter of molecules was proposed. The orientation parameters of homogeneously and homeotropically aligned samples in the nematic, smectic (*A*), and chiral smectic (*I* and *H*) phases were calculated. The *in situ* photopolymerization of acrylates in the smectic phases occurs with retention of the orientational ordering in the polymer films formed.

Key words: IR dichroism, smectic *A* phase, chiral smectic *I* and *H* phases, homogeneous and homeotropic orientation, acrylates.

Interest in liquid-crystalline (LC) compounds whose molecules contain a reactive double bond has recently increased. Photopolymerization of these compounds in the surface-aligned state makes it possible to form films of aligned polymers, used as new electrooptical materials.[1—3] Therefore, investigation of orientational properties of the starting monomeric compounds is of special significance: determination of the possibility of developing different types of orientation of LC compounds upon their interaction with the surface, comparative study of orientation parameters at different temperatures and upon photopolymerization in the surface-aligned LC state.

The possibility of obtaining homeotropic orientation of acrylate molecules on the surface of KBr plates with the retention of orientation during subsequent *in situ* photopolymerization in smectic phase has been shown previously[4] for two LC acrylates.

In this work, we studied four LC acrylates on specially treated KBr plates by the IR dichroism technique. These acrylates have smectic phases of different types and exhibit a tendency for both homogeneous and homeotropic orientations. The preparation of homogeneously aligned LC samples along with homeotropically aligned samples makes it possible to study comparatively the orientational properties of acrylates with different types of orientation and to determine the angle between the vibrational transition moment and the long axis of the mesogenic group for a series of analytical absorption bands. No approximate values of the angles, which are often used in their calculation, are necessary with the use of these data for determination of orientational parameters.

Table 1. Structural formulas and schemes of phase transitions of compounds $CH_2{=}CHCOO{-}X$

Acrylate	X	Temperature of phase transitions/°C
1	$(CH_2)_6OC_6H_4COOC_6H_4OC_6H_{13}$	C 50.4 (32) S_A 56.9 N 62.3 I
2	$(CH_2)_6OC_6H_4COOC_6H_4OOCC_6H_{13}$	C 49.8 (34) S_A 58.5 N 68.7 I
3	$CH_2C^*(CH_3)HCH_2CH_2COOC_6H_4C_6H_4OC_8H_{17}$	C 41.0 (23.4) S^*_I 67.2 I
4	$CH_2C^*H(CH_3)CH_2CH_2COOC_6H_4C_6H_4OOCC_7H_{15}$	C 31.2 (−5) S^*_H 73.5 I

Note. Phases: C is crystalline, N is nematic, S_A is smectic *A*, S^*_I and S^*_H are chiral smectic *I* and *H*, and I is isotropic. Crystallization temperatures are indicated in parentheses.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 319—323, February, 1999.

1066-5285/99/4902-0318 $22.00

Experimental

4-Hexyloxyphenyl-4′-acryloyloxyhexyloxybenzoate (**1**), 4-octanoyloxyphenyl-4′-acryloyloxyhexyloxybenzoate (**2**), (*S*)-4-(5-acryloyloxy-4-methylpentanoyloxy)-4′-octyloxybiphenyl (**3**), and (*R*)-4-(5-acryloyloxy-4-methylpentanoyloxy)-4′-octanoyloxybiphenyl (**4**) (Table 1) were studied. All compounds were synthesized according to procedures described previously.[4,5]

Textures of the LC phases were optically observed, and temperatures of phase transitions were determined on a Leitz Ortholux Pol-BK polarization microscope with a Mettler FP900 thermosystem.

Homogeneously and homeotropically aligned samples, whose long axes of mesogenic groups of the monomer were oriented parallel to the same direction in the support plane or perpendicular to the surface, respectively, were prepared by development of the orienting microrelief on the surface of KBr plates. To achieve the homogeneous orientation, the plates were polished in one direction with finely ground chromium oxide. To prepare LC cells, the plates were connected in such a way that the directions of polishing coincided. To obtain the homeotropic orientation, the plates were subjected to uniform fast polishing with chromium oxide with addition of ethanol. This treatment creates a porous surface,[6] whose relief favors the homeotropic orientation of molecules of LC placed between the plates. In both variants, the samples were heated to a temperature of 5 °C higher than that of isotropization and cooled slowly to the LC phase. The optical anisotropy arisen in the samples was quantitatively estimated from measurements of IR spectra in polarized light for the homogeneous orientation and in unpolarized light for the homeotropic orientation.

IR spectra were recorded on a Specord M-80 spectrophotometer with a thermostatted cell with a rate of temperature change of 0.1 °C min^{-1} and an accuracy of thermostatting of ±1 °C. An LC layer with a thickness of ~10 μm and a surface area of 2 cm^2 was studied. The intensity of bands was measured from the optical density in a maximum of the absorption band. The error of determination of the homeotropic orientation parameter was 2%, and that for the homogeneous orientation was 10% due mainly to birefringence in the sample.[7] Measurements were carried out on cooling of samples from the isotropic phase during three cycles. No indications of thermal polymerization of acrylates were observed: the intensities of the bands of the vinyl group did not decrease, and no bands characteristic of polymers appeared. Photopolymerization of acrylates was initiated by the UV radiation of a DRK-120 mercury-quartz lamp during 60 s with an intensity of the light flow of $\sim 8 \cdot 10^{-3}$ J cm^{-2}.

Results and Discussion

The ratio between the molecular ordering in the sample, which is measured by the dichroic ratio of the absorption band and the transition moment of the corresponding vibration, was determined from the model of partial axial orientation (Fig. 1). The direction of predominant orientation, that is, the optical axis of the sample, coincides with axis *z*.

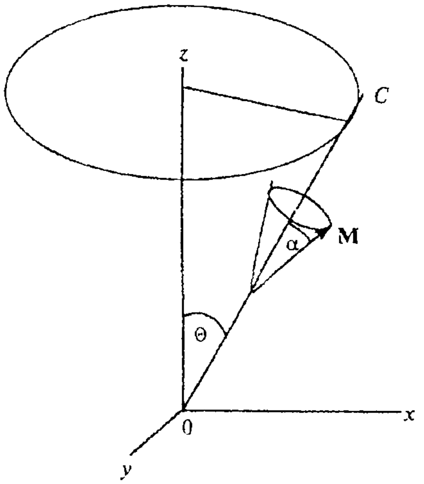

Fig. 1. Scheme of the model of partial axial orientation; 0C is the direction of the long axis of the molecule forming the θ angle with axis *z*, and **M** is the transition moment of the given vibration directed at the α angle to the long axis of the molecule.

For the homogeneous orientation in the sample, the radiation is directed along axis *y*. The dichroic ratio of the absorption band measured at two positions of the polarizer with the electric radiation vector parallel and perpendicular to axis *z*, according to the IR dichroism theory,[8,9] is determined by the equation:

$$R = A_z/A_x = \frac{4\cos^2\alpha\langle\cos^2\theta\rangle + 2\sin^2\alpha\langle\sin^2\theta\rangle}{2\cos^2\alpha\langle\sin^2\theta\rangle + \sin^2\alpha\langle\cos^2\theta\rangle + \sin^2\alpha}. \qquad (1)$$

For the homeotropic orientation, the unpolarized radiation is directed along axis *z* coinciding with the direction of orientation of LC molecules in the sample. In this case, the dichroic ratio was obtained by comparison of the intensities of the bands in the spectra of the LC and isotropic phases. To rule out the effect of phase and temperature changes in the density of the substance on the results of the measurements, the "dichroic ratio" was conventionally determined as a quotient of the division of the ratio of intensities of two absorption bands in the LC phase (A_1/A_2) by the same ratio in the isotropic melt ($A^{\text{I}}{}_1/A^{\text{I}}{}_2$). For the ratio of intensities of two bands due to vibrations of the same structural element, we obtain:

$$A_1/A_2 = \frac{\text{M}_1^2(2\cos^2\alpha_1\langle\sin^2\theta\rangle + \sin^2\alpha_1\langle\cos^2\theta\rangle + \sin^2\alpha_1)}{\text{M}_2^2(2\cos^2\alpha_2\langle\sin^2\theta\rangle + \sin^2\alpha_2\langle\cos^2\theta\rangle + \sin^2\alpha_2)}. \qquad (2)$$

Since the sum of the components of the absorption intensity in three mutually perpendicular directions is equal to M^2, and for the isotropic medium $A_x = A_y = A_z = (\text{M}^2)/3$, then for the same two bands in the spectrum of the isotropic phase

$$A^{\text{I}}{}_1/A^{\text{I}}{}_2 = \text{M}^2{}_1/\text{M}^2{}_2. \qquad (3)$$

Thus, according to Eqs. (2) and (3), the dichroic ratio for the homeotropic orientation has the following form:

$$R = A_1A_2^{\perp}/A_2A_1^{\perp} =$$

$$= \frac{2\cos^2\alpha_1\left\langle\sin^2\theta\right\rangle + \sin^2\alpha_1\left\langle\cos^2\theta\right\rangle + \sin^2\alpha_1}{2\cos^2\alpha_2\left\langle\sin^2\theta\right\rangle + \sin^2\alpha_2\left\langle\cos^2\theta\right\rangle + \sin^2\alpha_2}, \quad (4)$$

$$\text{or } \left\langle\sin^2\theta\right\rangle = \frac{\sin^2\alpha_1 - R\sin^2\alpha_2}{R(1 - 1.5\sin^2\alpha_2) - (1 - 1.5\sin^2\alpha_1)}.$$

The orientation parameter in the LC phase was estimated according to the equation[10]

$$P = 1 - \langle 1.5\sin^2\theta\rangle. \quad (5)$$

The orientation parameter characterizes the degree of ordering of LC molecules in the macroscopically oriented sample and, unlike the order parameter, depends not only on the nature of the substance and temperature, but also on the external orienting action.

Analytical bands were chosen according to their assignments based on the analysis of spectra of related compounds and published data.[11–13]

We established that, depending on the relief of the support surface, molecules of acrylates **1** and **2** in the LC phases can be aligned both homogeneously and homeotropically. Molecules **3** and **4** are aligned only homeotropically regardless of the method of treatment of the supports. As seen in Table 1, the smectic *A* phase of acrylates **1** and **2** appears from the nematic phase, whereas the highly organized smectic *I** and *H** phases of acrylates **3** and **4**, respectively, are formed upon cooling of the isotropic phase. Probably, this determines the difference in the orientational behavior of acrylates.

The possibility of obtaining homogeneously aligned samples and the presence of the smectic *A* phase with the orthogonal arrangement of molecules to the plane of smectic layers makes it possible to calculate the angles formed by the vibrational transition moment with the long axis of the mesogenic group for a series of absorption bands of the phenylbenzoate (PB) group. These data are useful, because the PB group is a fragment of mesogenic groups of many LC compounds.

The measurements showed that for both homogeneous and homeotropic orientations of the molecules of acrylate **1**, the absorption bands of the PB fragment at 1608, 848, and 764 cm^{-1} are characterized by the highest dichroism. The homogeneous orientation parameter (P_{hm}) was pre-calculated for the bands at 1608 and 848 cm^{-1} on the basis of commonly accepted values of the angles α = 0° and 90°, respectively, and α = 90° for the band at 764 cm^{-1}. In the whole temperature range, the P_{hm} values calculated from the band at 764 cm^{-1} are higher than those for the first two bands. For example, at the temperature of 35 °C corresponding to the highest degree of orientation in the smectic *A* phase, the P_{hm} value calculated from the band at 764 cm^{-1} is equal to 0.83, whereas the calculation from the bands at 1608 and 848 cm^{-1} gives 0.77. This divergence is related to the difference of the α values for the ν(C—C) and ρ(C—H) bands of the benzene rings in the PB group from the commonly accepted values. Taking into account the assignment of the band at 764 cm^{-1} to the out-of-plane deformational vibration γ(C—C=O) and its strong perpendicular polarization, we took the α angle for this band equal to 90° as the basis for calculations. The values of the α angles calculated according to Eq. (1) for several absorption bands of the PB group are presented in Table 2. The calculations were performed from the spectra of the samples obtained at the temperature (35 °C) corresponding to the highest P_{hm} value in the LC phase. For the bands at 1608 and 848 cm^{-1} that are most often used for the determination of orientational parameters in IR spectroscopy of LC compounds, the average values of the α angle are 13° and 79°, respectively. The calculated values of the angles indicate that the difference of them from the commonly accepted values is determined by the structure of the PB group in the acrylate molecule rather than by the deviation of the transition moments from the 1,4-axis of the benzene rings. The axis of the PB group is the line connecting the centers of the benzene ring, whose deviation from collinearity for some phenylbenzoate derivatives, according to the XDA data, reaches 5°.[14] In this case, the values of the α angle for the γ(C—C=O) vibration equal to 90° and approximately equal deviations of the α angles from 0° and 90° for the ν(C—C) and ρ(C—H) vibrations, respectively, are quite reasonable. Based on the calculated values of the α angles according to Eqs. (1) and (5), we determined the P_{hm} values in three cycles. In the case of homeotropic orientation, P_{ht} was calculated by Eqs. (4) and (5) using the data on the bands at 764 and 1608 cm^{-1}, respectively, taking the α angle equal to 90° and 13°, respectively. The temperature dependences of P_{hm} and P_{ht} are not affected by the type of orientation; they are well reproducible in three cycles (Fig. 2). The orientational parameters in the smectic phase reach 0.85 in both cases.

Table 2. Dichroic ratio (*R*) and angles (α) calculated from the spectra of acrylate **1** in three (*1*—*3*) thermal cycles

Vibration	ν/cm^{-1}	R_{hm}			α/deg		
		1	*2*	*3*	*1*	*2*	*3*
ν(C—C)	1608	9.76	8.36	10.84	11.0	14	13
ν(C—C)	1510	7.44	6.27	8.24	17.5	20	18
β(C—H)	1008	7.10	6.35	8.30	18.5	20	18
ρ(C—H)	848	0.19	0.21	0.17	78.0	80	80
γ(C—C=O)	764	0.15	0.16	0.12	90*	90*	90*
χ(C—C)	690	0.31	0.36	0.28	73.0	71	74

* Accepted as the basis for calculation.

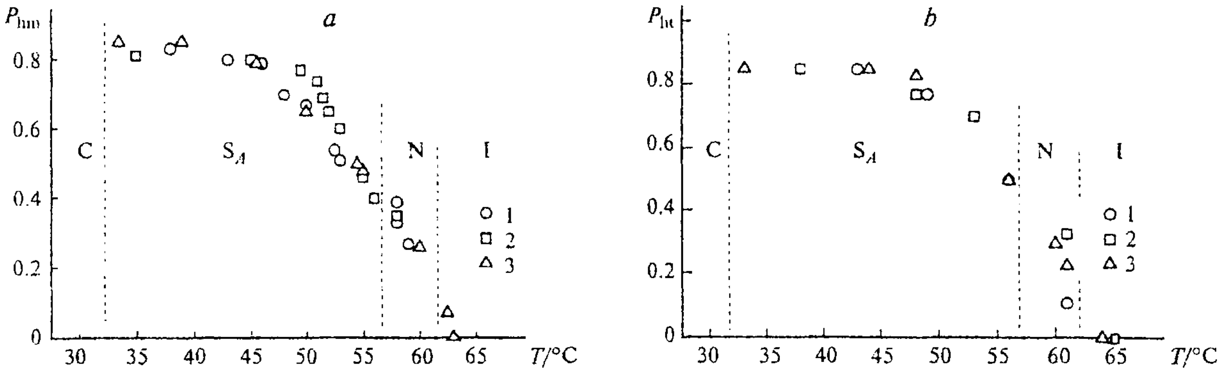

Fig. 2. Temperature dependences of the orientation parameters P_{hm} (*a*) and P_{ht} (*b*) in the LC phases of acrylate **1** in the first (*1*), second (*2*), and third (*3*) cycles.

The preparation of samples with a high degree of orientation is of interest, in particular, because of the possibility of forming aligned polymer films during the photopolymerization of acrylate. For this purpose, the homogeneously and homeotropically aligned samples were UV-irradiated at the temperature (46 °C) corresponding to the medium region of the smectic phase of acrylate **1**. After UV irradiation, the absorption bands corresponding to vibrations of the acrylate group (1635, 1408, 983, 964, and 808 cm^{-1}) disappeared completely, which indicates complete conversion of the monomer. The type of orientation was retained; the value of the orientation parameter decreased by 15% for both homogeneous and homeotropic orientations.

The P_{hm} and P_{ht} parameters for acrylate **2** were determined using the same analytical bands of the PB group at 764 and 1600 cm^{-1} and the α values equal to 90° and 13°, respectively. To determine P_{ht} for acrylates **3** and **4**, we chose the pairs of bands caused by vibrations of the biphenyl group ρ(C—H) and ν(C—C): 840 and 1600 cm^{-1} (**3**) and 840 and 1500 cm^{-1} (**4**). In the latter case, the choice of the band at 1500 cm^{-1} was determined by the fact that the band at 1600 cm^{-1} has a very weak intensity due to a high symmetry of the mesogenic group in molecule **4**. The α angle was taken equal to 90° for the ρ(C—H) vibration and 0° for ν(C—C). The temperature dependences of P_{hm} and P_{ht} in the LC phases of acrylate **2** are shown in Fig. 3. As seen in Fig. 3, the orientation parameter in the smectic *A* phase reaches 0.91 (P_{ht}) and 0.86 (P_{hm}). The value of the θ angle in the smectic *A* phase calculated by the IR dichroism method was 18° and 14° for acrylates **1** and **2**, respectively. These values of the θ angle, which are seemingly too high for smectic *A*, agree well with the

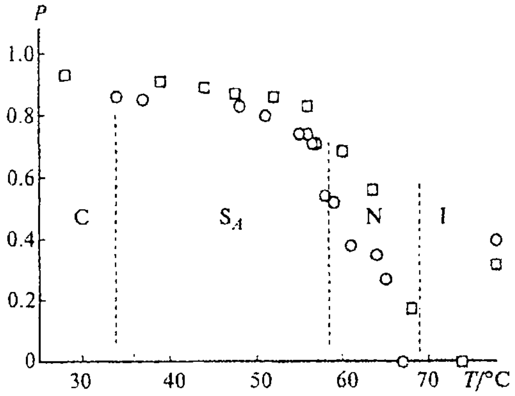

Fig. 3. Temperature dependences of the orientation parameters P_{hm} (*1*) and P_{ht} (*2*) in the LC phases of acrylate **2**.

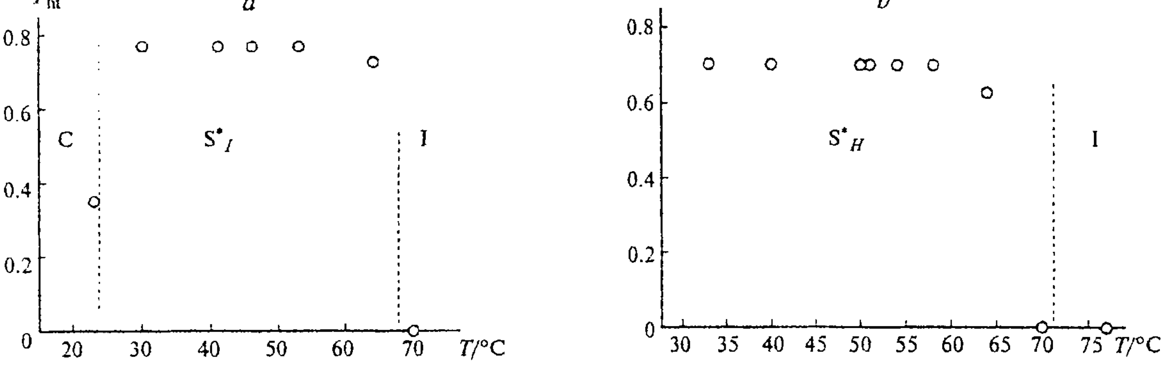

Fig. 4. Temperature dependences of the orientation parameter P_{ht} in the chiral smectic phases of acrylates **3** (*a*) and **4** (*b*).

theoretical and experimental values θ_{max} = 14.2° and $<\theta>$ = 19.3° and are the result of local distortions of the orthogonal arrangement of molecules in layers inherent in the smectic *A* phase.[15] The temperature dependences of P_{ht} for acrylates **3** and **4** presented in Fig. 4 indicate that the orientational parameters remain unchanged in a wide temperature range. It is noteworthy that the ability of the high-viscosity smectics *I** and *H**, appearing directly from the isotropic phase and continuing to the homeotropic orientation, was demonstrated for the first time. The calculated average values of the θ angle in the S^*_I and S^*_H phases are 24° and 27°, respectively. Assuming that smectic layers in the homeotropically aligned smectics *I** and *H** are parallel to the surface of KBr plates, we can consider that the θ values obtained correspond to the matched tilt angle of mesogenic groups in smectic layers. These θ values are comparable to those of the tilt angles of molecules in smectic layers of acrylates **3** (26°) and **4** (27°) calculated from the XDA data.[16]

The aligned samples of acrylates **2**—**4** were photopolymerized in the medium temperature region of the smectic state. Unlike the photopolymerization of acrylate **1**, accompanied by some distortion of ordering, the photolysis of acrylates **2**—**4** occurs with the complete retention of orientational ordering in the polymer films formed.

Thus, based on the procedure proposed for calculation of the homeotropic orientation parameter of the molecules and the values of the α angles calculated from the IR dichroism data, we determined the orientational ordering parameters in the nematic and smectic *A*, *I**, and *H** phases. We have shown for the first time the ability of the high-viscosity *I** and *H** smectics appeared directly from the isotropic phase to the homeotropic orientation that is retained during photopolymerization of acrylates upon their complete conversion.

It is noteworthy that the use of water-soluble orienting supports, such as KBr plates, with a wide spectral transmission region makes it possible to perform investigations in the visible, UV, and IR regions simultaneously and to create aligned polymer films with free surfaces.

This work was financially supported by the International Science Foundation INTAS (Grant 94-1482).

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Received March 11, 1998;
in revised form May 19, 1998