Liquid-Crystalline Polymer Gels. 3. Facile and Reversible Cholesteric Ordering of Dye Molecules Doped in Poly(γ-benzyl L-glutamate) Gels

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ABSTRACT: Azobenzene derivatives carrying alkoxy groups of different lengths were doped in cross-linked gels of poly(γ-benzyl L-glutamate) (PBLG) that possess cholesteric liquid-crystalline (CLC) order. Azobenzene derivatives with long alkoxy groups showed positive induced circular dichroism (ICD), indicating a preference of parallel orientation to the helix of PBLG. The dye molecules could be doped in and washed out repeatedly. Thus, the CLC gel was shown to provide a facile medium for obtaining an oriented dye system. Azobenzene groups linked to α-carbons of a polypeptide chain through a single methylene spacer showed strong preference for perpendicular orientation in the CLC. The most intense ICD was observed when the azobenzene-linked polypeptide was mixed in a CLC that is not cross-linked. The magnitude of the latter ICD was on the same order as the theoretical value calculated assuming a perfect alignment of the helical polypeptides in the CLC.

Polymer gels with liquid-crystalline order have been prepared by the cross-linking of a liquid-crystalline solution of poly(γ-benzyl L-glutamate) (PBLG). Polymer gels with cholesteric liquid crystalline (CLC) order have been prepared, and they showed cholesteric–isotropic reversible transition accompanied by the helix–coil transition of PBLG molecules.[1] Polymer gels with nematic liquid-crystalline order have also been prepared by cross-linking under a magnetic field. The nematic gel showed anisotropic swelling and shrinking induced by the solvent and temperature.[2] In this paper, optical anisotropy of the CLC gels doped with dye molecules is reported. It is shown that dye molecules are reversibly incorporated in the CLC gel, and they are oriented along the helical PBLG molecules. Therefore, the CLC gel provides a facile technique to obtain oriented dye systems, which may be utilized as display materials, photorecording materials, and so on. A further advantage of the CLC gel is its stability to keep the Grandjean texture, in which the axis of the cholesteric structure is normal to the surface.[3] For example, in the usual lyotropic CLC of PBLG, the Grandjean texture cannot be maintained for more than 1 day and it returns to a focal conic texture. The cross-linking stabilizes the CLC structure not only in the molecular level but also in the macroscopic texture.

The orientation of dye molecules in a CLC is known to induce strong circular dichroism (CLCICD).[4-13] The sign and the magnitude of CLCICD depends on the optical properties (linear birefringence and linear dichroism) of a quasi-nematic layer that constitutes the CLC and on the structural properties (the sense of the twisting and the pitch) of the whole CLC.[7] In the CLC gel, the structural parameters cannot be varied because of the cross-linking. The only parameter that can be varied after cross-linking is the linear dichroism of the single quasi-nematic layer, which may be controlled by doping a variety of dye molecules in the CLC gel. In this study, a variety of dye molecules, especially azobenzene derivatives carrying different alkoxy groups, were incorporated in the CLC gel, and their CLCICD were measured to clarify their preferred orientations.

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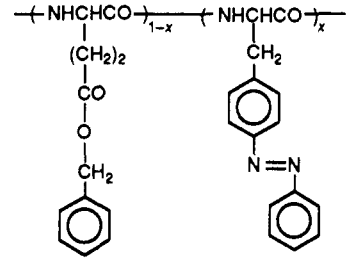
The orientation of dye molecules will be most rigidly fixed, if they are covalently linked to a polypeptide main chain. In the latter part of this study, a random copolypeptide carrying azobenzene groups linked to α-carbons through a single methylene spacer (I) was synthesized.



poly[Glu(OBzl)-*co*-azoAla] (I, $x = 0.25$)

The CLCICD of the linked azobenzene was measured and compared with a theoretical value considering the fluctuations of the azobenzene side group but neglecting the fluctuations in the orientation of helical PBLG in the CLC phase. A study of CLCICD from dyes that are linked to cholesteric gels of cellulose has been reported.[14]

Experimental Section

A CLC gel of PBLG was prepared from PBLG (M_w = 420 000) by using triethylenetetramine as a cross-linker in dioxane.[1] The mole fraction of the cross-linker was 0.1 with respect to the BLG unit. A concentrated dioxane solution of PBLG (25 wt %) containing 10 mol % of the cross-linker was placed between a pair of glass plates separated by a spacer of 25 μm. The sample was left standing at room temperature for 7 days. At this stage, the CLC was in the Grandjean texture, i.e., the axis of cholesteric structure was perpendicular to the glass plates. The cross-linking was carried out at 70 °C for 20 days. During this period the solvent was evaporated off gradually. The gel was peeled off in the form of a thin membrane. The full pitch of the CLC was estimated to be 11–16 μm, from a microscopic observation of the fingerprint pattern of a thick gel prepared separately under the same condition using a thick spacer (200 μm).

4-Methoxyazobenzene was synthesized by a diazo coupling of *p*-anisidine with nitrosobenzene in acetic acid. Other azobenzene derivatives carrying different alkoxy groups were synthesized by refluxing 4-hydroxyazobenzene or 4,4′-dihydroxyazobenzene with 1.5 equiv of *n*-alkyl bromide in ethanol containing KOH for

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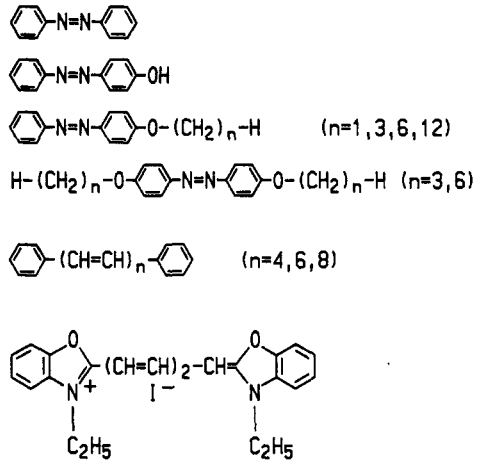
Chart I



about 7 h. Other dye compounds are used as received. The chromophoric compounds used in this study are listed in Chart I.

The cross-linked gel was immersed in a dye solution. The CLC gel doped with dye molecules was placed between a pair of glass plates, and absorption and CD spectra were measured. A Jasco J-500 instrument interfaced to an NEC PC9801 personal computer was used for the CD measurement.

A random copolypeptide of BLG and L-*p*-phenylazophenylalanine (azoAla)[15-17] was synthesized by a copolymerization of the corresponding *N*-carboxyanhydrides (NCA's) using *n*-hexylamine as initiator in dimethylformamide. The unnatural amino acid containing an azobenzene group was synthesized according to Goodman and Kossoy.[17] The mole fraction of azoAla was 0.25, and the NCA/*n*-hexylamine ratio was 240. The copolypeptide was purified by repeated reprecipitation from methanol. The copolypeptide was mixed with PBLG homopolypeptide and co-cross-linked to obtain a membranelike CLC gel. The final fraction of an azoAla unit in the gel was 0.016.

Conformational analysis on the fluctuation of an azobenzene group in an azoAla unit was carried out by using a program coded by one of the authors (M.S.).[16] The energy parameters and the geometry of amino acids are taken from the ECEPP system.[18] Those of the azoAla unit have been reported previously.[16]

Results and Discussion

Induced Circular Dichroism of Azobenzene Derivatives. Figure 1 shows CD spectra of 4-(dodecyloxy)azobenzene and a cyanine dye (3,3′-diethyl-2,2′-oxadicarbocyanine iodide) doped in the CLC gel. The CD band around 260 nm has been assigned to a CLCICD of phenyl groups in the side chains of PBLG. It is known that the positive CD at this band indicates a right-handed screw sense of the cholesteric structure.[12,13] A negative CD with approximately the same intensity has been observed for a CLC gel of poly(γ-benzyl D-glutamate). At 348 nm, a positive CD band is seen for the azobenzene derivative that is assignable to the CLCICD of an azobenzene $\pi\pi^*$ transition. The CLCICD is strong even though the content of azobenzene derivatives is very low (1.6%). When the cyanine dye is doped in the CLC gel, positive CD is observed at the position of its absorption peak (588 nm).

According to the optical theory developed by De Vries[4] and Chandrasekhar,[5,6] an absorption transition polarized parallel to the molecular axis (director) of the quasi-nematic layer in a right-handed CLC shows positive ICD, and those perpendicular to the molecular axis shows negative ICD. The $\pi\pi^*$ transition of azobenzene[19] and that of cyanine dye are polarized nearly parallel to the long axis. Therefore, the positive ICD's in Figure 1 indicate that those rodlike chromophores are oriented parallel to the molecular axis of a PBLG helix.

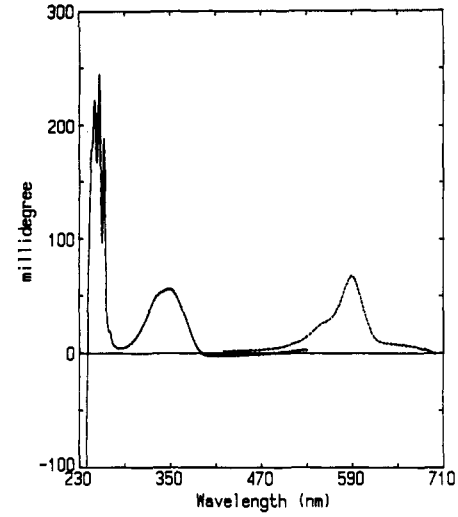


Figure 1. CD spectrum of 4-(dodecyloxy)azobenzene doped in the CLC gel in dioxane (—) and that of 3,3′-diethyl-2,2′-oxadicarbocyanine iodide doped in the CLC gel in DMF (- - -). Thickness of the gel = 25 μm, absorbance of an azobenzene derivative = 1.242 (348 nm), absorbance of a cyanine dye = 0.917 (588 nm), at room temperature.

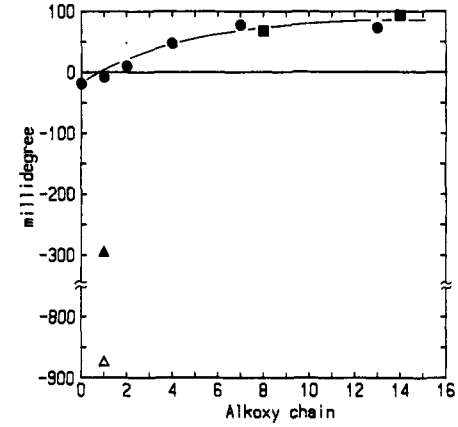


Figure 2. Relative intensity of CLCICD of azobenzene derivatives doped in a CLC gel plotted against the chain length of an alkoxy group of azobenzene derivatives listed in Chart I: (●) monosubstituted azobenzenes, (■) disubstituted azobenzenes, (▲) polypeptide I co-cross-linked with PBLG, (△) polypeptide I doped in a non-cross-linked PBLG. The gels are equilibrated with dioxane; thickness = 25 μm. The intensity of ICD was normalized by the absorbance of an azobenzene group at the $\pi\pi^*$ band.

The magnitude of the ICD of various azobenzene derivatives was plotted as a function of the length of an alkoxy chain (Figure 2). In the figure, the magnitude of the ICD was normalized first to reproduce the ICD of a phenyl group at 256 nm (252 mdeg) and then divided by the absorbance of an azobenzene group at the peak of a $\pi\pi^*$ band. The ICD is weak and negative when unsubstituted azobenzene or *p*-hydroxyazobenzene is doped in the CLC gel. Positive ICD is observed when other azobenzene derivatives were doped in the CLC gel, and its intensity becomes higher with an increase in the chain length of an alkoxy group. The magnitude of ICD is about the same for monosubstituted and disubstituted azobenzenes, if the total chain lengths of the alkoxy chains are the same.

The results of Figure 2 show that the azobenzene derivatives are incorporated in the CLC gel with a preferred orientation depending on their molecular shapes. Azobenzene and *p*-hydroxyazobenzene are randomly dispersed in the CLC gel, with a small preference for the perpen-

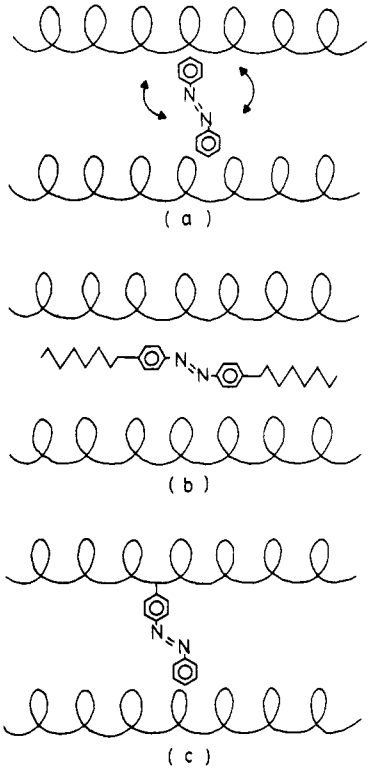


Figure 3. Schematic illustration of the preferred orientation of azobenzene derivatives in a CLC gel. (a) Azobenzene and hydroxyazobenzene are randomly oriented with a little preference for the perpendicular orientation. (b) Azobenzene derivatives carrying long alkoxy groups are oriented parallel to the helices of PBLG. (c) Azobenzene groups linked to a polypeptide chain are oriented perpendicular to the helices.

dicular orientation. The azobenzene derivatives with long alkoxy groups are oriented parallel to the molecular axis of PBLG or to the director of the quasi-nematic layer. The orientations of the doped azobenzene derivatives are schematically illustrated in Figure 3.

It is noted that the data in Figure 2 were collected by using the same CLC gel repeatedly. A CLC gel doped with an azobenzene derivative was washed with dioxane until no trace of azobenzene absorption was detected and then immersed in the solution containing the next azobenzene derivative. In this way the CLC gel could be used repeatedly for the doping of azobenzene derivatives and other dye molecules.

In order to examine the effect of cross-linking, the CLCICD observed in the CLC gel was compared with that in non-cross-linked CLC of PBLG having about the same cholesteric pitch and the same thickness. No significant difference was observed in the magnitude of ICD in the two systems. However, as will be shown later, this does not indicate that the original order of PBLG molecules in the CLC is maintained in the CLC gel. The order of azobenzene derivatives may not be very high, and, therefore, the disorder in the alignment of PBLG molecules induced by the cross-linking does not affect the average orientation of azobenzene derivatives significantly.

Induced Circular Dichroism of Azobenzene Groups Covalently Linked to a PBLG Chain. In order to find the largest or intrinsic ICD that can be attained in the CLC gel and in the non-cross-linked CLC, a copolypeptide with pendant azobenzene groups (I) was synthesized. In the copolypeptide, azobenzene groups are linked to an α-carbon atom by the shortest spacer (single methylene unit), so that the rotational freedom of the side group is minimized. Co-cross-linked CLC gel and non-cross-linked

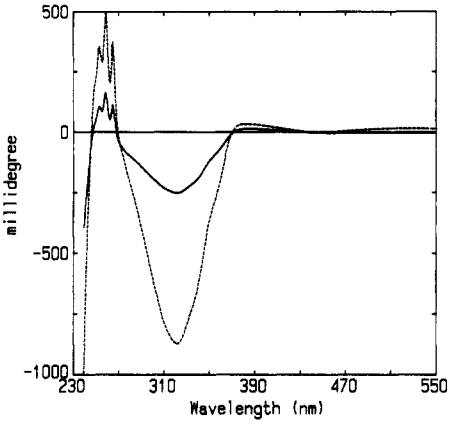


Figure 4. CLCICD of azobenzene groups covalently linked to a polypeptide chain (copolypeptide I): (—) co-cross-linked gel of I and PBLG, (- - -) non-cross-linked CLC containing I. The thickness of the gel = 25 μm.

CLC were prepared from the mixture of PBLG and the copolypeptide. A Grandjean texture was observed for the two CLC systems.

CLCICD of the co-cross-linked CLC gel and that of the mixed CLC are shown in Figure 4. The magnitudes of the CLCICD are also plotted in Figure 2. A very strong negative ICD appeared at the azobenzene absorption band in the two CLC systems. The negative ICD indicates a perpendicular orientation of the azobenzene group with respect to the PBLG molecules as shown schematically in Figure 3 (bottom). In contrast to the case of doped azobenzenes, the magnitude of ICD was much stronger in non-cross-linked CLC than in the co-cross-linked CLC gel. The difference shows that the order of PBLG molecules is disturbed considerably by the cross-linking. The magnitude of ICD of the non-cross-linked CLC was –0.873° for the CLC of 25 μm thickness. The full pitch of the CLC may be 11–14 μm as estimated from microscopic observation of much thicker CLC that showed a fingerprint texture.

It should be noted that the ICD of the non-cross-linked CLC disappeared after about 1 day, indicating the instability of the Grandjean texture. On the other hand, the ICD remained unchanged even after several months or more for the cross-linked CLC gels.

The co-cross-linked gel of copolypeptide I and PBLG were photoirradiated with UV light (312 nm) to induce trans to cis photoisomerization of the azobenzene groups. The CLCICD was markedly reduced in the cis form. The ICD appeared again by the irradiation of visible light (455 nm) that induces cis to trans isomerization. It is shown that the ICD is photoreversibly controlled. The photoreversible chiroptical property may be utilized as a chiroptical photorecording/reading system.

Theoretical Evaluation of Induced Circular Dichroism from Conformational Analysis of Azobenzene Side Group. The ICD can be calculated according to the optical theory developed by Chandrasekhar.[5,6] The Jones vectors after right and left circularly polarized light (CPL) passed through m quasi-nematic layers of CLC are expressed as

$$\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \frac{1}{\sqrt{2}} \mathbf{J}_m \begin{bmatrix} 1 \\ i \end{bmatrix} \text{ for right CPL} \quad (1)$$

$$\begin{bmatrix} B_1 \\ B_2 \end{bmatrix} = \frac{1}{\sqrt{2}} \mathbf{J}_m \begin{bmatrix} 1 \\ -i \end{bmatrix} \text{ for left CPL} \quad (2)$$

According to Chandrasekhar, the Jones matrix $\mathbf{J}_m$ is given by

$$\mathbf{J}_m = \mathbf{S}^m(\mathbf{G}\mathbf{S}^{-1})^m \tag{3}$$

where $\mathbf{S}$ represents the rotation of the principal axis by β and $\mathbf{G}$ represents a complex retardation matrix multiplied by an extinction factor $\exp(-\alpha)$, for a single quasi-nematic layer.

$$\mathbf{S} = \begin{bmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{bmatrix} \tag{4}$$

$$\mathbf{G} = \exp(-\alpha)\begin{bmatrix} \exp(-i\hat{\gamma}) & 0 \\ 0 & \exp(i\hat{\gamma}) \end{bmatrix} \tag{5}$$

β is a small angle between the directors of two successive layers and is calculated from the pitch P and the thickness of a single layer p, $\beta = 2\pi p/P$. $\hat{\gamma}$ is a complex quantity defined as

$$\hat{\gamma} = \pi\Delta n p/\lambda - i\Delta k p/2 \tag{6}$$

where Δn is the linear birefringence of a single layer and Δk is the linear dichroism of the single layer of thickness p. The p is arbitrarily taken as 10 nm; therefore, the number of the layers m is calculated from the thickness d of the sample as $m = d/p$. The final result was not changed when p was taken to be 20 nm.

The observed CD ψ is calculated from the Jones vectors for right and left CPL

$$I_R = |A_1|^2 + |A_2|^2, \quad I_L = |B_1|^2 + |B_2|^2 \tag{7}$$

$$A_R = -\log I_R, \quad A_L = -\log I_L \tag{8}$$

$$\psi = 32.98(A_L - A_R)\ (\text{deg}) \tag{9}$$

Therefore, the magnitude of CLCICD can be calculated from the full pitch P, the linear birefringence Δn, the linear dichroism Δk, and the sample thickness d. The birefringence of the CLC of PBLG has been tabulated by Robinson.[20] For the CLC in dioxane, the Δn was $-0.0218 \times$ (volume fraction of polypeptide). On substitution of the volume fraction of PBLG (0.22), the Δn value was calculated to be -0.0047. The wavelength dependence of the Δn value may be neglected at least over the range from 436 to 644 nm. We will use the same Δn value at 348 nm, with a reservation that the Δn value may be a little larger in magnitude at 348 nm.

The linear dichroism Δk was evaluated from a conformational analysis of side-chain orientation of azobenzene groups using empirical potential energy, under an assumption that the PBLG helix is perfectly aligned along the director of the layer. The azobenzene unit in the side chain of copolypeptide I may fluctuate around side-chain rotational angles $\chi_1(C^\alpha\text{–}C^\beta)$ and $\chi_2(C^\beta\text{–}C^\gamma)$. A side-chain energy contour map was calculated for an Ac-Ala_{10}-azoAla-Ala_{10}-$NHCH_3$ molecule, assuming a perfect α-helical conformation ($\phi = -62.5°$, $\psi = -42.3°$, $\omega = 180°$). For simplicity, all Glu(OBzl) units were replaced by alanine (Ala) units. The energy contour map is shown in Figure 5. There are two energy minima, corresponding to a syn and anti orientation of an azobenzene unit with respect to the main chain. However, the area allowed for the fluctuations of an azobenzene group around room temperature (thermal energy = ca. 1 kcal/residue) is small. From the contour map, the distribution of the orientation of an azobenzene group was calculated. The $\pi\pi^*$ transition moment of azobenzene is tilted by 14° from the C(aromatic)–N(azo) bond.[19] Then, the orientational distribution of the $\pi\pi^*$ transition moment was calculated to give a dichroic ratio, k(parallel)/k(perpendicular), of 1.475 at 25 °C. From the dichroic ratio, the linear dichroism was calculated to be 0.000 018 (nm^{-1}) for a single layer, when the total absorbance of the CLC was 1.0 for 2500 layers (thickness = 25 μm). When the linear dichroism Δk is substituted into eq 6, and eqs 2–9 are used, the magnitude of ICD was calculated to be $\psi = -1100$ (mdeg) for $P = 11$ μm and $\psi = -1400$ (mdeg) for $P = 14$ μm. These values are somewhat larger in magnitude than the value experimentally observed (−873 mdeg) for the non-cross-linked CLC containing a small amount of copolypeptide I. The smaller experimental ICD might indicate that the PBLG molecules are more or less disordered in the CLC phase. The orientational order of PBLG in the CLC state has been evaluated by Abe and Yamazaki.[21] The order parameter S was very high (0.932) in dioxane. Therefore, the disorder of the PBLG molecules may not be essential in the present case. We believe that the agreement between experimental and observed data is satisfactory, since there can be several factors that may reduce the observed ICD, other than the disorder in the molecular level. For instance, the disorder in the Grandjean texture may also reduce the observed ICD. The smaller magnitude of an ICD of the co-cross-linked gel indicates that the CLC order is somewhat disturbed by the cross-linking. However, the ICD is still very large compared with those observed for doped dyes.

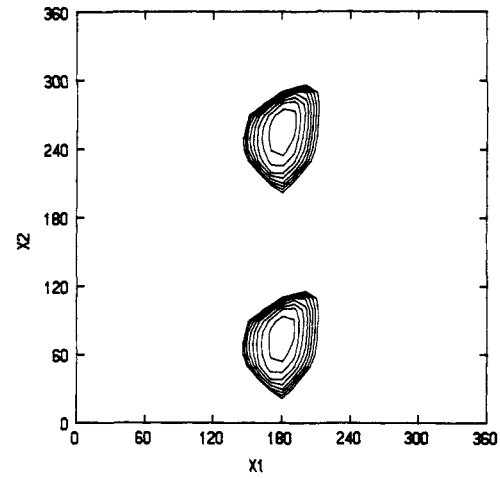


Figure 5. Side-chain energy contour map for an α-helical Ac-Ala_{10}-azoAla-Ala_{10}-$NHCH_3$ molecule ($\phi = -62.5°$, $\psi = -42.3°$, $\omega = 180°$). The interval of the contour lines is 0.5 kcal/amino acid unit.

Induced Circular Dichroism of Other Dye Molecules Doped in the Liquid-Crystalline Gels. Several other dye molecules were also doped in the CLC gel. For example, anthracene showed negative ICD at the ^1La band that is polarized perpendicular to the long axis, indicating that the long axis is oriented parallel to the helix axis of PBLG. A series of α,ω-diphenylpolyenes, 1,4-diphenylbutadiene (DPBD), 1,6-diphenylhexatriene (DPHT), and 1,8-diphenyloctatetraene (DPOT), were also doped in the gel. They showed positive ICD (parallel orientation), and the magnitude of the ICD increases with the molecular length of the polyenes (Figure 6). All dye molecules showed ICD's of reasonable signs, depending on the molecular shapes and the polarizations of the transition moment. Although the CLCICD of doped dyes in PBLG LC's have been reported by several authors, the present CLC gel is advantageous in the fact that dyes can be doped in the gel

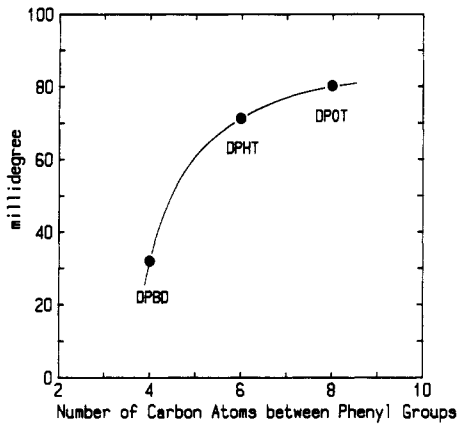


Figure 6. Relative intensity of CLCICD of a series of diphenylpolyenes with different numbers of polyene spacers. The ICD is normalized by the absorbance at the maximum of each compound (333 nm for DPBD, 357 nm for DPHT, and 378.5 nm for DPOT).

and washed out from the gel repeatedly and that the microscopic order of PBLG molecules and the macroscopic texture of the CLC are maintained during the dope and wash processes. There are several other systems that can be used repeatedly for oriented binding of dyes. Graphites and clays can intercalate molecules with a specific orientation.[22,23] Some host molecules can bind and release guest molecules in solution.[24] However, the present CLC gels may be more facile than the other systems to attain oriented molecular assemblies.

Concluding Remarks

The CLC gels can reversibly bind a variety of dye molecules with specific orientations. The orientational order of dye molecules may be more or less disturbed by the cross-linking. However, the cross-linking can immobilize the macroscopic texture (Grandjean texture), which otherwise disappeared within 1 day at room temperature.

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