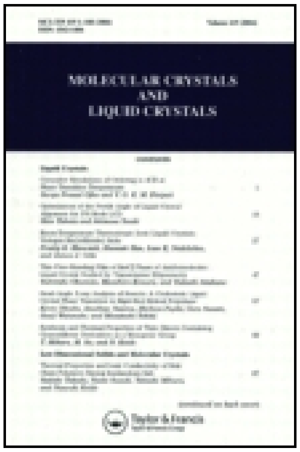

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Synthesis, Characterization and Some Aspects for Application of Polymer Liquid Crystals

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To cite this article: Naoyuki Koide (1986): Synthesis, Characterization and Some Aspects for Application of Polymer Liquid Crystals, Molecular Crystals and Liquid Crystals, 139:1-2, 47-80

To link to this article: http://dx.doi.org/10.1080/00268948608079599

Mol. Cryst. Liq. Cryst., 1986, Vol. 139, pp. 47–80
0026-8941/86/1392-0047/$30.00/0

Synthesis, Characterization and Some Aspects for Application of Polymer Liquid Crystals

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(Received November 26, 1985; in final form December 24, 1985)

Recent developments of thermotropic liquid crystalline polymers are reviewed. The characterizations of thermotropic liquid crystalline polymer for the type and thermal properties are discussed through the use of differential scanning calorimetry, polarizing microscopy and small and wide angle X-ray diffraction. The recent works with the order parameter, the alignment and the effects of an electric field of liquid crystal polymers are also described.

Some aspects for applications of thermotropic liquid crystalline polymers are illustrated: (1) storage or memory materials, (2) photoelastic liquid crystal, (3) immobilization of liquid crystal structure, and (4) coloured liquid crystal polymers.

Keywords: liquid crystal polymers, thermotropic polyesters, order parameter, alignment of liquid crystal polymers, electric-optic phenomena

INTRODUCTION

Polymer liquid crystals can be divided into two categories, lyotropic and thermotropic. The lyotropic polymer liquid crystals exhibit an ordered solution above a critical concentration in the appropriate solvents, and their liquid crystalline characteristics are dependent on concentration as well as temperature. Poly(γ-methyl-L-glutamate) and poly(γ-benzyl-L-glutamate), synthesized by Elliot and Ambrose[1] in 1950, gave liquid crystalline solutions in dioxane or methylene chloride. More detail studies of these solutions were carried out in 1956 by Robinson[2] who proved that these solutions show a cholesteric liquid crystal. After the discovery and the development of *p*-linked aromatic polyamides in the lyotropic systems exhibiting anisotropic and nematic solutions by Kwolek[3] and Morgan,[4] many polymer researchers, both academic and industrial groups, are becoming active in the field of liquid crystal polymers.

Polymer researchers have also been considerably interested in the thermotropic liquid crystal polymers which show a liquid crystal nature in the molten state having a possibility of high tensile strength and modulus being processing and spinning without strong protonating solvents. The first paper on thermotropic liquid crystal polyesters appeared in patented work in 1973 by Jackson, Jr. and Kuhfuss,[5] who described the random copolyesters prepared from *p*-acetoxybenzoic acid and poly(ethylene terephthalate). One year before, in 1972, Economy and others[6] patented a high-melting aromatic copolyester which exhibits melt anisotropy, although this behavior was not reported by them in the patent. The liquid crystal nature of oxybenzoate oligomers has already been reported by Vorlander[7] (in 1923). After their discovery of thermotropic polyester (Aromatic/Aliphatic copolyester, X7G), the majority of research has been concentrated on synthesis and establishment of the property-structure relationships. Recently, the rigid or semi-rigid type copolyesters are freely available for commercial use in some companys.

The incorporation of mesogenic rigid-rod units into the side-chain of acrylate, methacrylate or siloxane polymers gave also the thermotropic liquid crystal nature.[8,9] These side-chain type liquid crystal polymers which combine the polymeric character and liquid crystal properties lead to an interesting field of potential use for many applications such as display devices, memory devices and so on, due to their control of molecular arrangements being similar to their low molecular weight liquid crystals.

This paper will at first briefly discuss the synthesis and the characterization of thermotropic liquid crystals. The second part is concerned with their physical properties, such as order parameter, electric field effect and also with what the possibility of applications is for thermotropic polymers?

SYNTHESIS OF LIQUID CRYSTAL POLYMERS

Thermotropic liquid crystal polymers can be classified into fundamental types of structure. One is the main chain type liquid crystal polymer constructed with either the connection of rigid parts (mesogenic parts) itself or the combination of mesogenic and flexible sequences. The other is a side-chain polymer in which the mesogenic group is attached to the polymeric backbone, e.g., polyacrylate, polymethacrylate, or polysiloxane, with or without a flexible spacer. These chemical constitutions of liquid crystal polymers are schematically presented in Figure 1.

The main chain type liquid crystal polymers (e.g., aromatic polyesters), have been prepared by several methods, such as melt polycondensation, low temperature interfacial polycondensation, and high temperature solution polymerization. In the case of melt polycondensation, the high melting point of the polymer is an important factor in getting a high molecular weight polyester because such rigid-rod polyesters have very low solubility in reaction solvents. To overcome the limiting factor, two-step polycondensation reactions have been carried out. In the first reaction step an oligomer is obtained by either a homogeneous solution polymerization reaction or a melt polymerization reaction. After removal of the solvent, the final polycondensation reaction is followed in the solid state polymerization under a high pressure and high temperature slightly below its melting point, with or without a catalyst.

The low temperature interfacial polymerization has been broadly

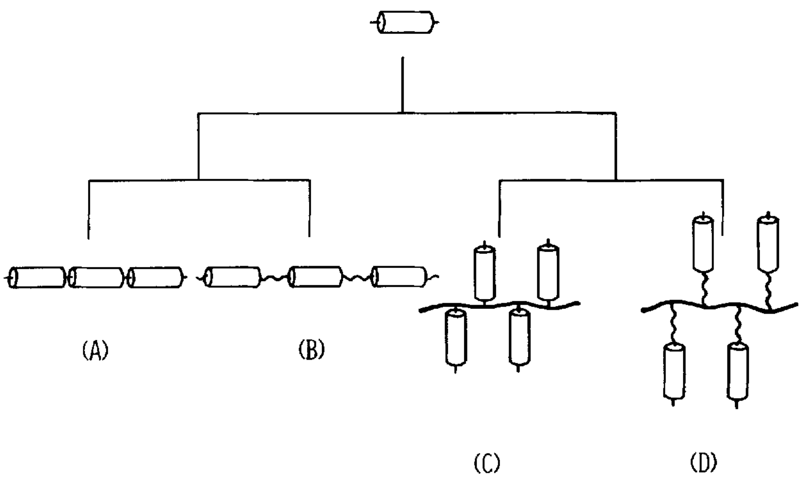
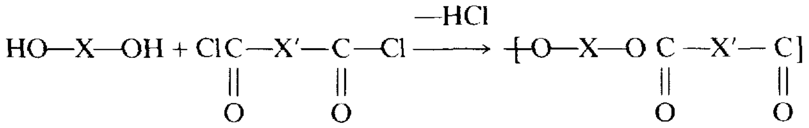


FIGURE 1 Schemes of main-chain type and side-chain type liquid crystalline polymers. (A) rigid, (B) semi-rigid: mesogenic group is attached to the polymeric backbone via (with (D) and without (C)) a flexible spacer.

mesogenic unit, (▭) : flexible spacer unit, ∿∿∿

applied, especially in the preparation of aromatic polyesters derived from the aromatic dihydroxy compound and diacid chloride.



$$\mathrm{HO{-}X{-}OH} + \mathrm{Cl}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{X'}{-}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{Cl} \xrightarrow{-\mathrm{HCl}} \left[\mathrm{O{-}X{-}O}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{X'}{-}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\right]$$

where X and X′ are aromatic or aliphatic.

The interfacial polycondensation reaction is markedly catalyzed by small amounts of quaternary ammonium or sulfonium compounds.

In these polycondensation reactions, two important factors must be considered to form aromatic polyesters of an intermediate molecular weight or polymers of high molecular weight. One is the purity of each starting material, and the other is the selection of a good solvent for the resulting polyester. Four examples of polycondensation are discussed by Lenz[10]: the Schotten-Baumann reaction of an aromatic acid chloride with phenol, an ester exchange reaction in the molten state at high temperatures, the oxidative esterification reaction or aromatic carboxylic acid with a phenol in the presence of a phosphorous compound and a chlorocarbon solvent, and polymerization reactions involving the use of mixed sulphonate-carboxylate anhydride.

Two synthetic routes can be considered to get side-chain liquid crystal polymers. One type is that a mesogenic molecule is attached to the monomer, a methacrylate or an acrylate. A number of side-chain mesogenic monomers are summarized by Blumstein[11] and by Shivaev.[12] The other type can be prepared by the addition of suitable reactive vinyl mesogenic monomers to poly[oxy(methylsilylene)] using the platinum catalysts reported by Finkelmann.[13]

Side-chain liquid crystal polymers are easy to prepare. A side-chain liquid crystal polymer which connected the mesogenic group to the polymer backbone via a flexible spacer would be easy to orient under an application of external field like the low molecular weight liquid crystal. In this case the role of the flexible spacer is that the motions of the polymer backbone decouples with those of the mesogenic groups. Under these conditions the mesogenic side group can be anisotropically ordered. A simple synthetic route for a typical mesogenic side chain-polymer with a flexible spacer, an alkyl chain, is illustrated for a polymethacrylate[14] as shown in Figure 2. It is supposed that a direct-linkage polymer, in which rigid mesogenic side groups are directly attached to a polymer backbone without a spacer,

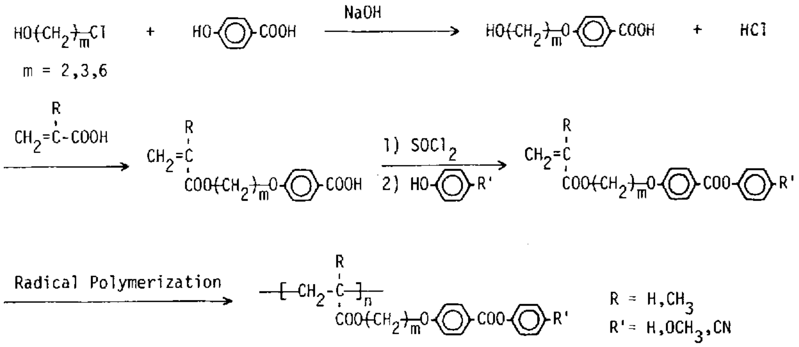
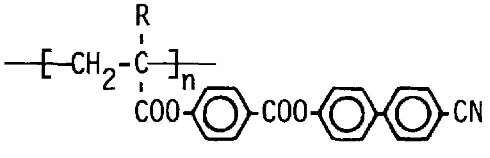


FIGURE 2 Scheme of synthesis for side-chain type liquid crystalline polymer. Ref. from 14.

is not effective to form a liquid crystal polymer, because the motions of the backbone may hinder the liquid crystalline ordering of the pendant mesogenic group. But by choosing the proper length and anisotropic property of the rigid mesogenic group, it is possible to obtain a side-chain liquid crystal polymer without a spacer,[15] as shown in the following.



CHARACTERIZATION OF LIQUID CRYSTAL POLYMERS

After a few years of the first preparation of thermotropic polyalkanoates from *p*,*p*′-dihydroxy-α-α′-dimethyl-benzalazine and appropriate acylchloride by Roviello and Sirigu[16] in 1975, many research groups have synthesized the new liquid crystal polymers, e.g., Ringsdorf and Finkelmann,[8,17] Strzelecki,[18] Griffin,[19] Blumstein,[20] Noël,[21] Lenz,[22] Krigbaum,[23] and Iimura.[24] The assignment of the liquid crystalline mesophase is obtained with the aid of the classification of low molecular weight liquid crystal compounds. In many cases, the characterization of liquid crystal polymers is performed by thermal analysis, a polarized microscope with a heating stage, X-ray measurements, miscibility tests and determination of order parameter by ESR, NMR and IR dichroic techniques. The smectic, nematic and cholesteric phases are detected for both main-chain and side-chain polymers as well as for the low molecular weight liquid crystalline materials. Detailed discussions of these results have been reported by Noël,[25] Kothe et al.[26] and Martins et al.[27] In this part, we describe briefly the characterization of thermotropic liquid crystalline polymers.

THERMAL ANALYSIS

In polymer liquid crystals, differential scanning calorimetry (DSC) measurements are a popular method to determine the thermal nature, including transition temperature and transition entropy which have a parallel relation to the order parameter of the liquid crystal polymers.[28] Typical DSC curves for the main-chain liquid crystal polymers and the side-chain liquid crystal polymers are shown in Figures 3 and

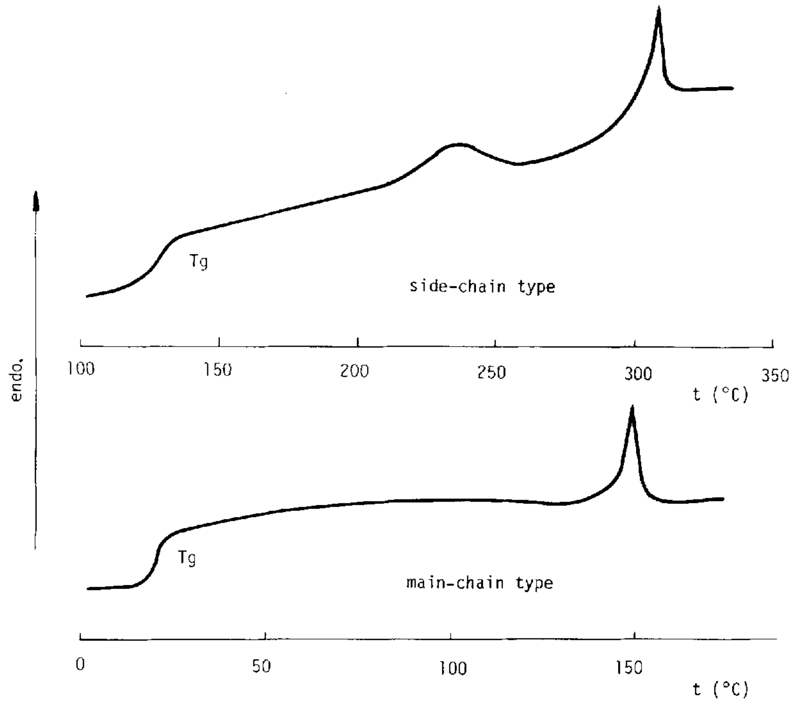


FIGURE 3 Some examples of DSC curve for main-chain type and side-chain type liquid crystalline polymer.

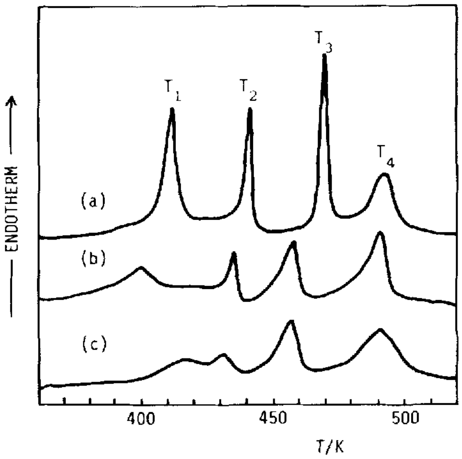


FIGURE 4 DSC curves of main-chain type liquid crystalline polymer. Scanning speeds 10 K/min. (a) annealed at 446 K for 20 h. Ref. from 16.

4, respectively. Their thermal transition behaviours are usually similar to that of the low molecular weight liquid crystals. As shown in Figure 3, the DSC curve of side-chain liquid crystal polymers exhibits a glass transition temperature characteristic of the polymeric backbone, and a phase transition from the mesophase to the isotropic phase due to the mesogenic side chain. The optical texture observed in the liquid crystal state of the polymer can be frozen without change in the glassy state. The transition energy from the solid to the mesophase is usually larger than that from the mesophase to the isotropic phase.

The thermal behaviour of liquid crystal main-chain polymers is complicated, especially in that they are constructed with only rigid mesogenic components without flexible parts. For the measurements of the transition temperature and transition enthalpy there must be careful examinations being used in polymer science, such as thermal treatments[19] and so on,[29,30] as shown in Figure 4. In the case of polymeric materials, another important factor is the molecular weight dependence on the transition temperature, as shown in Figure 5.[30] The transition temperature of isotropization increases rather dramatically with increasing molecular weight, and reaches a constant value above the molecular weight of approximately 10000. The entropy of isotropization also has the same dependence upon the molecular weight (both the side-chain[31] and the main-chain liquid crystal polymers).[32] A higher molecular weight liquid crystal polymer would, therefore, have a more thermal stability.

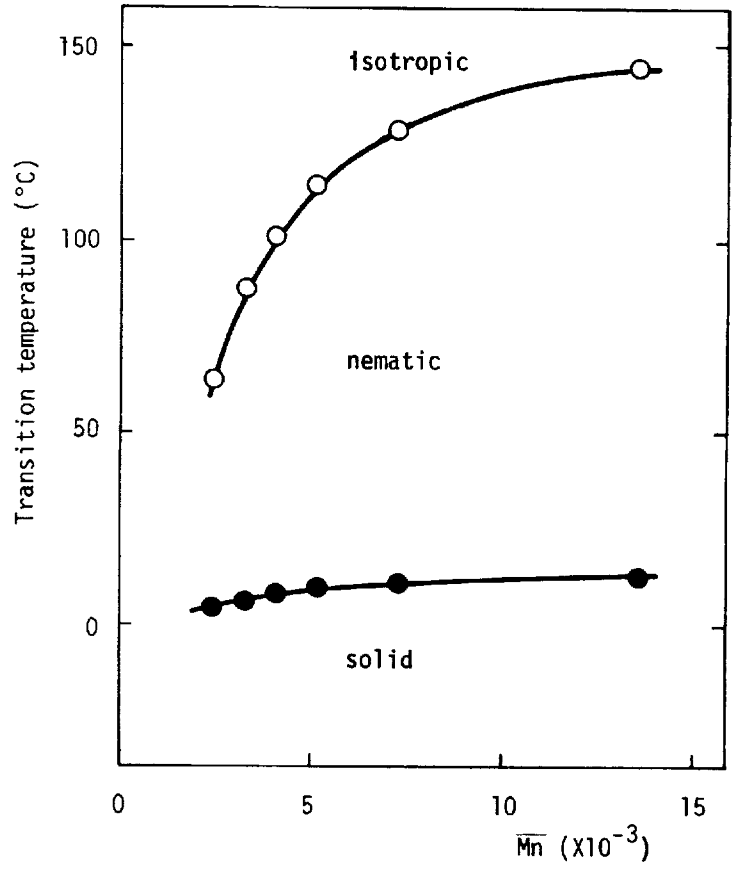
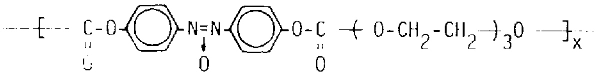


FIGURE 5 Molecular weight dependence of transition temperature for polycarbonate (POEAOBC-3),


$$-[-\underset{\|}{\overset{}{C}}{\text{-}}O{-}C_6H_4{-}\underset{\downarrow}{N}{=}N{-}C_6H_4{-}O{-}\underset{\|}{C}{-}(O{-}CH_2{-}CH_2)_3O-]_x-$$

(●): glass transition temperature, (○): isotropic temperature.

TEXTURAL OBSERVATIONS WITH POLARIZING MICROSCOPE

Typical liquid crystalline textures are observed under the polarizing microscope with a hot stage. In the nematic polymers, a schlieren texture characteristic for low molecular weight nematic liquid crystals is usually observed for the semi-rigid liquid crystal polymers, whereas a nematic threaded texture or very small particle texture appears sometimes in careful observations for the rigid-mesogenic liquid crystal polymers as shown in Figures 6 and 7.

Smectic fan-shaped textures with focal conics and fan-shaped textures of smectic A and C modifications similar to the conventional low molecular liquid crystal are also observed in both semi-rigid main-chain and side-chain liquid crystal polymers. Polyesters of bis-4,4′-(1,4-cyclohexanedicarbonyloxy) benzoate exhibit a Batonnetes texture indicative of smectic A and C phases.[33] We have reported[24] that the polyesters prepared from 4,4′-azoxydibenzoic acid and oligo-ethyleneglycol exhibit a fan-shaped texture of Smectic A as shown in Figure 8.

Polymeric cholesteric phases are identified by the observation of an oilystreak pattern or a finger print texture[34–36] and by the fan-shaped texture[37,38] in non planar textures. Microscopic observations are fundamental techniques to determine the type of liquid crystalline

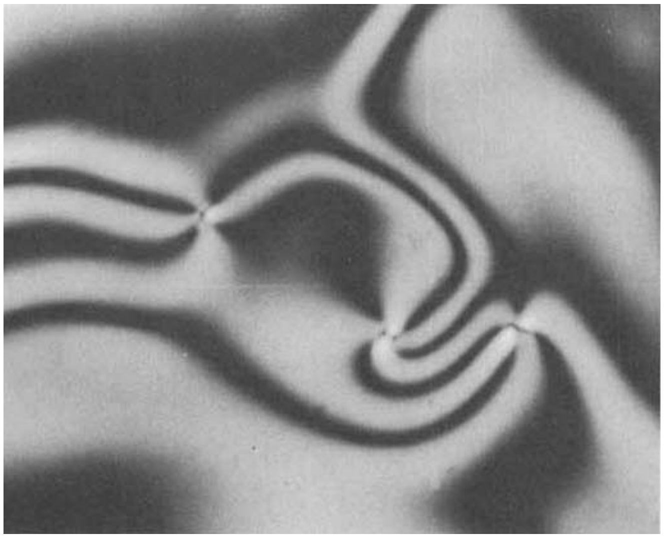
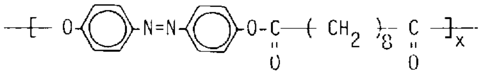


FIGURE 6 Typical nematic schlieren texture for polyester,



Crossed polarizers, ×200. See Color Plate X.

FIGURE 7 Nematic threaded texture for × 7 G. Crossed polarizers, X200. See Color Plate XI.

FIGURE 8 Typical smectic fan-shaped texture with focal conics for copolyester. Crossed polarizers, ×200. See Color Plate XII.

phase both in low and high molecular weight liquid crystal compounds, but it is necessary to assign the liquid crystal phase using a combination of different kinds of physical methods, e.g., mutual miscibility and x-ray diffraction, because whether the texture of liquid crystal polymers always exhibits the texture similar to the low molecular weight liquid crystal compounds is questionable. The monograph of optical textures by Demus and Richter,[39] and also the book by Gray and Goodby[40] are valuable guides to identify the liquid crystal polymer phases.

X-RAY MEASUREMENTS

The X-ray measurements can offer a lot of information about the liquid crystal arrangements and the degree of the order. X-ray diffraction would be one route to reach, especially, an identification of mesomorphic orientation. Generally, low molecular weight polymers can be easily oriented by the weak external fields, e.g., electric or magnetic fields, while high molecular weight polymers are difficult to orient.[41] Oriented samples can be prepared by cooling them from their isotropic fluid to the mesophase under a high magnetic field. The orientational order depends on the molecular weight in the case of polymeric liquid crystals, that is to say, the high magnetic field is necessary to orient completely the higher molecular weight liquid crystal polymers. Orientation of most of liquid crystal polymers may be preserved easily on cooling from the mesophase to the solid state.

It is possible to distinguish the nematic phase from the smectic phase of polymeric liquid crystals by x-ray diffraction patterns of powder samples as shown in Figure 9. There are two diffraction patterns of a powder sample having inner rings at the small-angle diffraction region and outer rings at the wide-angle region. The inner rings represent the longer layer spacings, and one or more outer rings correspond to the lateral packing arrangements of the molecules. At small-angle regions, a diffuse halo is observed in the nematic orientation which indicates that there is no order in the direction of the long axis of the molecule, whereas the smectic A and smectic C phases show a sharp diffraction pattern corresponding to the layer spacings, while at the wide-angle regions there is only one diffuse outer halo which relates to the disordered lateral arrangement in the nematic, smectic A and smectic C orientations. Consequently, the difference between the smectic A and the smectic C arrangement cannot be identified by the powder sample, whereas oriented samples of smectic A or smectic C differ from their photographs in the small-angle diffraction patterns as shown in Figure 9-b. In the smectic A arrange-

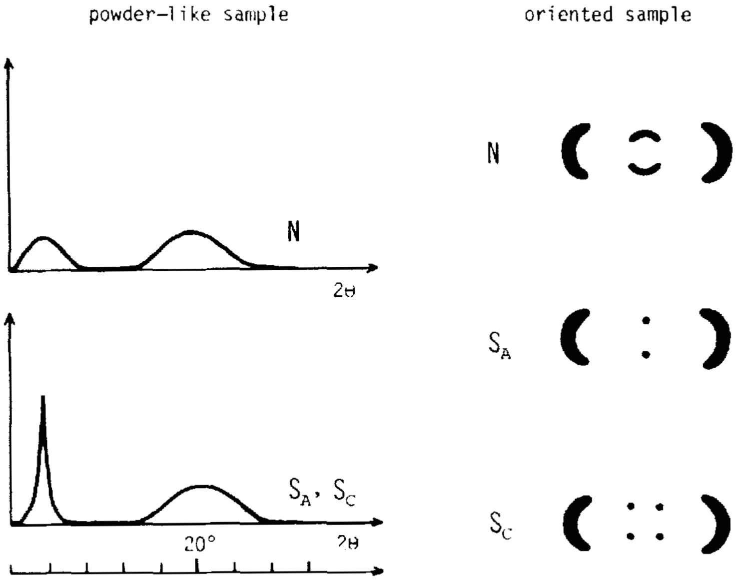


FIGURE 9 Schematic X-ray patterns of oriented and unoriented mesophases.

ment, two sharp spots on the meridional arcs at the lowest angle are observed, whereas the meridional reflections at the lowest angle split up into four sharp spots which are attributed to the tilted orientation of smectic C layer.[42]

ORDER PARAMETER

The orientation of the molecules in liquid crystal polymers can be described by the order parameter S.

$$S = 1/2\langle 3\cos^2\theta - 1\rangle$$

where θ is the angle between the molecular axis and the orientational axis of the domain, and the blanket indicates the average in the domain under consideration. The order parameter can be determined experimentally by various methods, such as the measurements of IR[43] and UV spectra,[44,45] nuclear magnetic resonance,[46-50] electron spin resonance,[50-53] polarized fluorescence,[54] x-ray scattering,[43,55] and refractive indices.[8,56]

The first results of the temperature dependence of the order parameter with polymer liquid crystals were reported by Finkelmann et al.[8] directly from birefringence measurements on side-chain liquid crystal polymers which exhibited a typical nematic phase. The values of the order parameter for some main-chain and side-chain liquid crystal polymers are listed in Tables I and II, respectively. If we discuss the order parameter of liquid crystal polymers, the molecular weight dependence of *S* must be considered. The order parameter for polycarbonates having different molecular weights are shown in Figure 10. The order parameter of the oriented polycarbonate increases with increasing molecular weight and decreases steadily as the temperature is raised. From the experiment on the samples with a different length of flexible spacer, it was found that the *S* of polycarbonates having a shorter flexible spacer is of a higher value than that of polycarbonates having a longer flexible spacer. This can be explained by the fact that the polymer with a shorter flexible spacer aligns itself more easily under the magnetic field. A quite opposite result was reported by Liebert et al.[18] with linear polyesters aligned

TABLE I

Values of order parameter for LC main-chain polymers

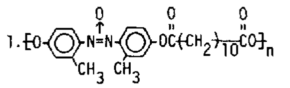
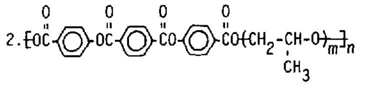
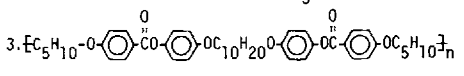
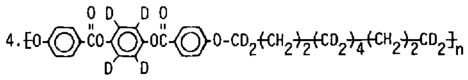
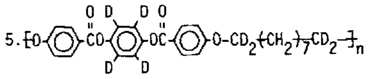
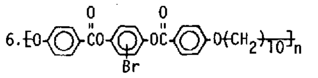
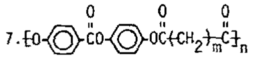
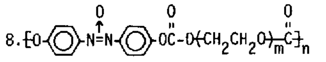
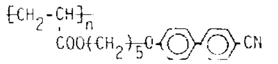
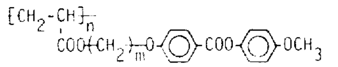
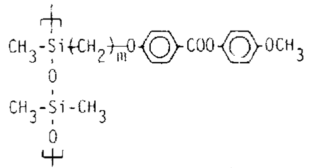
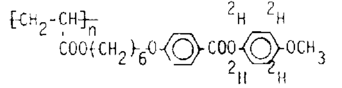
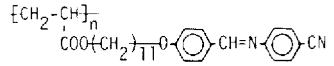
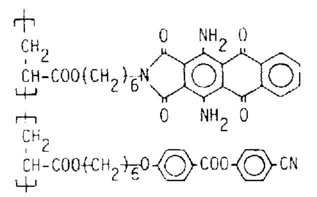
Structure	Type of meso-phase	Order para-meter	Method	Ref.
	N	0.69-0.84	^{1}H NMR	41
	N	0.60	^{1}H NMR	50
	N	0.60	MS	58
	N	0.85	^{2}H NMR	49
	N	0.77	^{2}H NMR	49
	N	0.81	ESR	57
	N	0.54	X-Ray	55
	N	0.79	ESR	53

TABLE II

Values of order parameter for LC side-chain polymers

Structure	Type of meso-phase	Order para-meter	Method	Ref.
1. 	N	0.45	^{1}H NMR	46
2. 	m=2 N m=6 S	0.65 0.92	ESR ESR	51
3. 	m=3 N m=6 N	0.65 0.60	:n :n	56
4. 	S	0.85	^{2}H NMR	47
5. 	S	0.50	UV	45
6. 	N	0.58	UV	44

in a magnetic field of 3KG for 24 h. The order parameter of an oriented nematic polyester was found to be 0.64, having an inherent viscosity of 0.29 dlg^{-1}, and 0.54 for a sample having a higher inherent viscosity of 0.54 dlg^{-1}. Large values of S in the range of 0.8–0.9 of main-chain polymers were obtained by Mueller et al.[57] from ESR measurement. Volino et al.[48] also deduced an order parameter ranging from 0.64 to 0.84 from NMR spectra. It is interesting to note that the nematic order parameter of main-chain polymers changed with the molecular weight[48] and dropped in the vicinity of the nematic-isotropic transition.[41,48,58] In the side-chain liquid crystal polymers, the values of S for the nematic phase are in the range of 0.28 to 0.65, and for smectic polymers S is 0.85 to 0.92 except for No. 1 and No. 5 polymers in Table II. The ordering in both smectic and nematic polymers is less ordered than their low molecular weight smectic

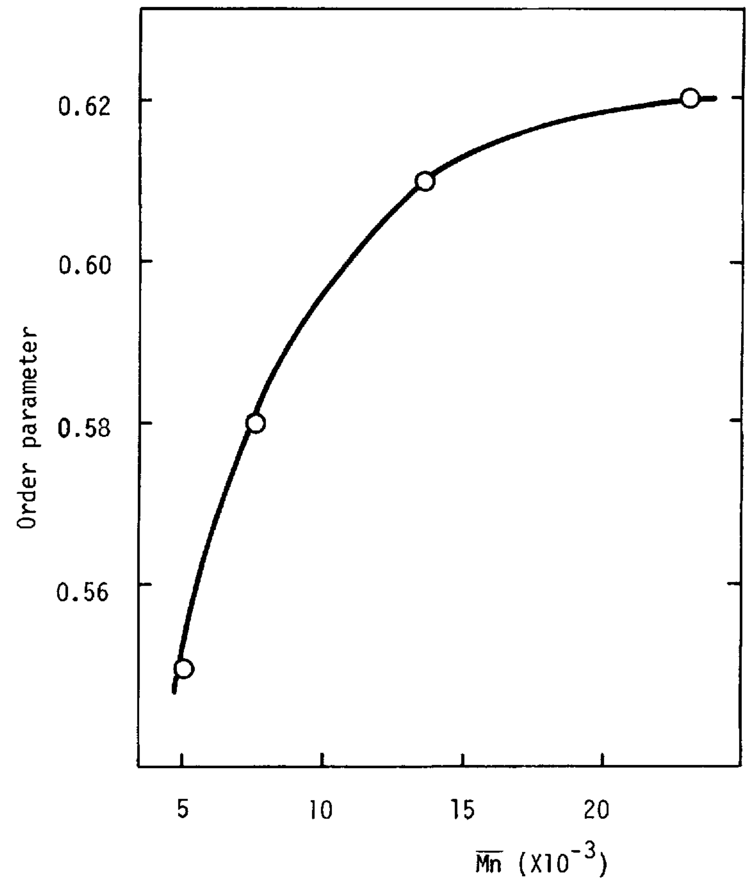


FIGURE 10 Molecular weight dependence of order parameter *S* for polycarbonate (POEAOBC-3).

and nematic analogues. The *S* alters with temperature, and the change in ordering is profoundly influenced by the chemical constitution of the molecule and by the length of the flexible spacer. The effect of temperature on *S* is similar to that of low molecular weight liquid crystals, e.g., *S* decreases with increasing temperature, whereas *S* increases with a longer flexible spacer.

ALIGNMENT OF LIQUID CRYSTAL POLYMERS

The low molecular weight liquid crystal compounds should be aligned by surface treatment, external fields, e.g., electric or magnetic fields, and viscous flow. In comparison to the low molecular weight liquid crystals, the alignment of the liquid crystal polymers is more complicated. The cell preparation and surface treatment can be achieved by a method similar to that for low molecular weight liquid crystals. In homeotropic alignments, the long molecular axes of the liquid crystal molecules are perpendicular to the glass surface. Sometimes homeotropic alignment appears when liquid crystal polymers are heated at high temperature between the slide glass without any surface treatments.[59–61]

The cell preparation for liquid crystal polymers is achieved by the known procedure for low molecular liquid crystals.[62] The homeotropic alignment for the liquid crystal polymer can be conducted by the following methods.[63] The cleaning of the glass surface is done with chromic-sulphuric acid, washing with distilled water, acetone and methanol, and rinsing with distilled water. Then the glass is rinsed in an ultrasonic technique with distilled water for 10 min and dried in a desiccator. Another method[64] is that the glass plates are coated with In_2O_3/SnO_2 and then foiled with polyimido film. The cleaned glass plates are rubbed with a styropor wheel. Main-chain liquid crystal nematic polymers[65] are introduced by the capillary method into the glass plates. After 2 days of annealing at 190°C, the sample becomes homeotropically aligned. The nematic solutions are also aligned homeotropically by using lecithin for surface treatment. Under crossed polarizers completely homeotropic orientation appears to be black. And verification of the alignment is proved by the conoscopic observations, and the uniformity of the alignment is determined by using a quater wave plate. With the aid of conoscopic observations, Noël et al.[63] discovered the optically positive uniaxial character of the main-chain liquid crystal copolymer, and Finkelmann[66] also determined the same character for the side-chain liquid crystal polymers.

Homogeneous alignment was achieved by Noël,[63] using surface deposition of hexadecyltriethyl ammonium bromide on glass substrate or by using a freshly cleaned mica surface for a liquid crystal main-chain polymer.[43] A good homogeneous alignment of a liquid crystal side chain polymer is also obtained by the polishing method with a diamond paste,[67] or by the Chatelain rubbing technique with the use of a cotton swab. Unfortunately, challenges to orient liquid crystal main-chain polymers using the rubbing technique itself were unsuccessful.[68,69] It would be possible to align liquid crystal polymers only by surface treatments with a combination of a number of the techniques mentioned above, especially the coating of polymer film, inorganic film and rubbing techniques.

Applying electric field to liquid crystal polymers

By applying an electric field to the low molecular weight liquid crystal at its mesophase, the orientational order characteristics for the mesogenic molecule changes to another orientational state. These phenomena can be explained as follows. In general, a liquid crystal polymer consists of long rod-like molecules linked by mesogenic or flexible molecules. These long rod-like molecules have an anisotropic nature, (refractive index, dielectric, magnetic susceptibility), parallel or perpendicular to the rigid-rod molecular axis. In low molecular weight liquid crystals, the application of an electric field leads to preferential alignment owing to the dielectric anisotropy of the molecules. The dielectric anisotropy ($\Delta\epsilon$) is the difference between parallel dielectricity ($\epsilon_{\parallel}$) and a perpendicular one ($\epsilon_{\perp}$) to the molecular axis. Owing to the dipole anisotropy, liquid crystal polymers can be easily oriented by an external field as is known for low molecular weight liquid crystal compounds.

After the discovery of flow instability phenomena for the low molecular weight *n*-type ($\epsilon_{\parallel} - \epsilon_{\perp} < 0$) nematic liquid crystal by Heilmeier in 1968[70] liquid crystal research has stimulated much interest in the potential for use in electro-optic devices. Whereas, the majority of the research on liquid crystal polymers over the last five years has concentrated on their synthesis and characterization. The recent work on the effects of electric fields on nematic phases by Ringsdorf,[71,72] by Finkelmann[73] on side-chain polymer liquid crystals, and by Krigbaum et al.[74] on main-chain liquid crystals has demonstrated many more possibilities for applications to the electro-optic phenomena.

The next three basic parameters must be taken into consideration when applying an electric field to liquid crystal polymers: dielectric constant ($\Delta\epsilon$), elastic constant [K_{ii}, splay (K_{11}), bend (K_{33}) and twist (K_{22})], and a viscosity (η_i) similar to low molecular weight liquid crystals. In the electro-optical phenomena of liquid crystals, the response time (τ) can be expressed by the following equation[75]:

$$\tau = \eta_i(\epsilon_{\circ}\Delta\epsilon V^2 - k_{ii}q^2)^{-1} \tag{1}$$

where η_i and k_{ii} are the viscosity parameter and the elastic constant, respectively, $\Delta\epsilon$ is the dielectric anisotropy of the polymers ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, the subscripts $\parallel$ and $\perp$ denote the dielectric constant of parallel and perpendicular to the director respectively), $\epsilon_{\circ}$ is the permittivity of vacuum, V is the strength of applied voltage and q is the variable wave vector. The wave vector of q is given by approximately π/d for the nematic liquid crystal when the cell thickness is d. Consequently, the rise time (τ_r) and the decay time (τ_d) for the twist nematic (TN), guest host (GH), and dynamic scattering modes (DS) can be expressed by the following.

$$\tau_r = \eta_i d^2(\epsilon_\circ \cdot \Delta\epsilon V^2 \cdot k_{ii}\pi^2)^{-1} \tag{2}$$

$$\tau_d = \frac{\eta_i d^2}{\pi^2 k_{ii}} \tag{3}$$

The rise time is defined as the time scale with intensity of the transmitted light of 90% when applying an electric field to liquid crystal polymers, while the decay time is defined as the time scale with intensity of 90% from the maximum transmitted light when switching off an electric field as schematically shown in Figure 11. The threshold voltage (V_{th}) for a planar cell is given as the following equation.[77]

$$V_{\text{th}} = \pi\left(\frac{k_{11}}{\epsilon_\circ \Delta\epsilon}\right)^{1/2} \tag{4}$$

The effects of electric fields upon polymeric nematic material have been reported by Finkelmann,[73] Ringsdorf,[71] Hasse,[77] Plate,[78] Krigbaum,[68,69,74] Blumstein.[79] Corazza et al.[80] have reported the first study of the effect of an applied electric field to a polymeric cholesteric phase. Recently, Coles et al.[81] have studied the effects of electric fields upon a polymeric smectic phase.

The first electro-optical effect upon the side-chain type liquid crystal polymers was reported by Finkelmann et al.[73] These electro-optical effects exhibiting an electric field induced flow instabilities of nematic polymers are similar in behaviour to those known for the conventional low molecular weight liquid crystal. As expected, their response time was much longer than those of the low molecular weight nematics because of the high viscosity of the polymeric phases, as can be seen in equations 2 and 3. The homeotropic orientation in the nematic polymers was obtained by application of a dc field at the nematic state. The rise-time was about 10 sec under the dc field of 8 V. The homeotropic orientation was changed to a turbulence state above this applied voltage.

In general, polymeric materials have a high viscosity compared with the low molecular nematogen of chemically equivalent struc-

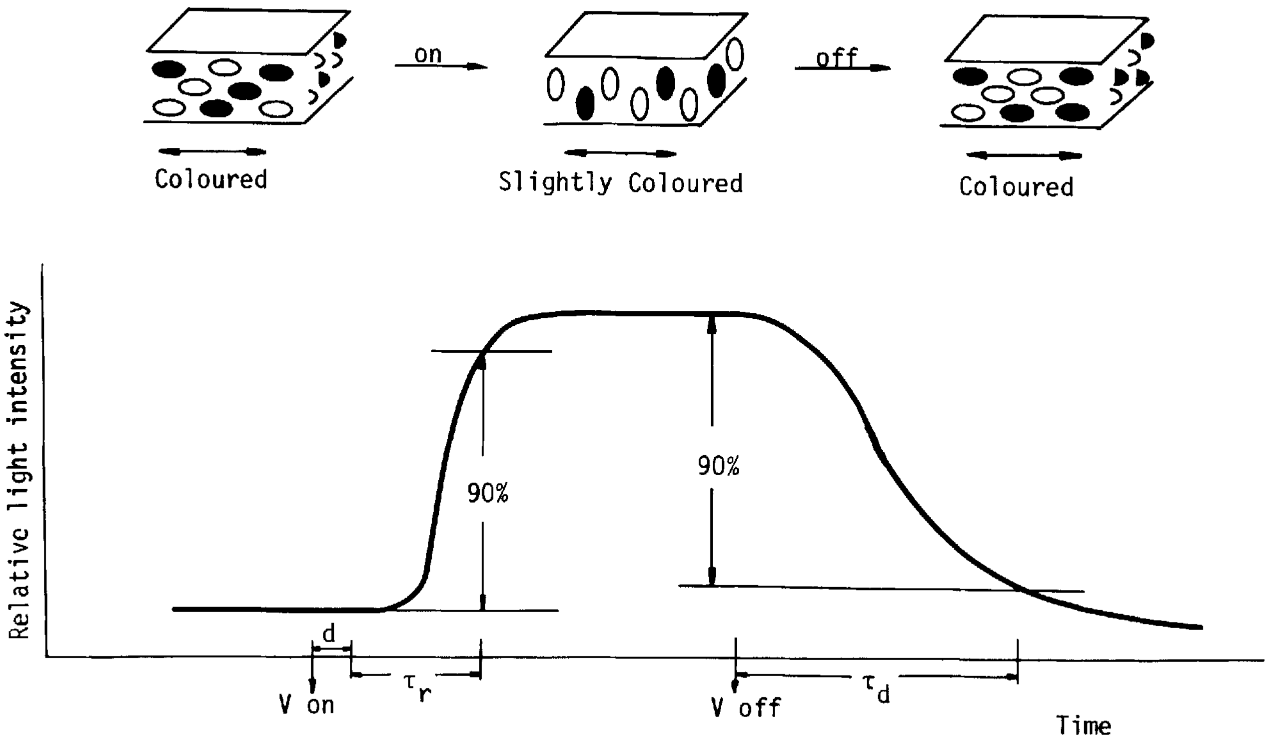
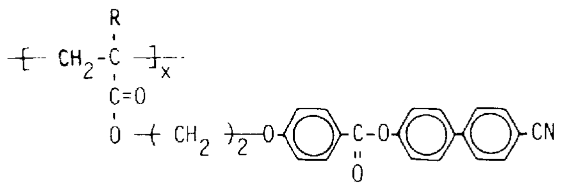


FIGURE 11 Schematic electro-optical effects of guest-host systems for a Heilmeier cell, ○: mesogenic unit, ●: dye molecule, ⟷: polarization plane, d: delay time, τ_r: rise time, τ_d: decay time.

tures. Consequently, a rapid response time can not be expected for liquid crystal polymers. But Finkelmann et al.[82] have tried to realize a rapid response time using new polysiloxane polymers containing a high cyanobiphenyl side group. If the temperature of the experimental conditions is much higher than the glass transition temperature, the response times below 200 ms can be achieved. The important features of the siloxane polymer are the large dielectric anisotropy of the pendant group and their elasticity due to the flexibility of the siloxane backbone. The spacer length between the polymer backbone and the mesogenic group has an important influence on the threshold voltage. In comparison with the threshold voltage at a constant reduced temperature T^* ($T_m/T_c = 0.98$, T_m being the measuring temperature and T_c the phase transition temperature from liquid crystal to isotropic phase), it was found that the threshold voltage (V_{th}) increases with decreasing spacer length as $V_{th} = 5$ V for $m = 6$, 12.5 V for $m = 5$ and $V_{th} > 50$ V for $m = 4$. The same results were reported with the other side-chain liquid crystal polymers.

In order to overcome the slow response time, Coles et al.[83] attempted to examine the response behaviour of new systems in a side-chain polymer liquid crystal, which dissolves low molecular weight nematic material (mentioned later).

The switching properties of either acrylic or methacrylic polymers with a cyanobiphenyl type pendant group shown below were studied.[84] The chemical structure of the polymer is,



(R=H, PCBAAB-2)

(R=CH_3, PCBMAB-2)

The dependence of the response time on the temperature for PCBAAB-2 is shown in Figure 12. By increasing the temperature, τ_r and V_{th} decrease. The methacrylate type polymers always exhibit a longer response time than that of the acrylic type polymers. The difference in the response time can be ascribed to the difference in the flexibility of the polymer backbone. Higher molecular weight polymers need a longer response time due to their high viscosity. A surprising result was obtained in these side-chain liquid crystal polymers when we applied an electric field above the threshold voltage at a low fre-

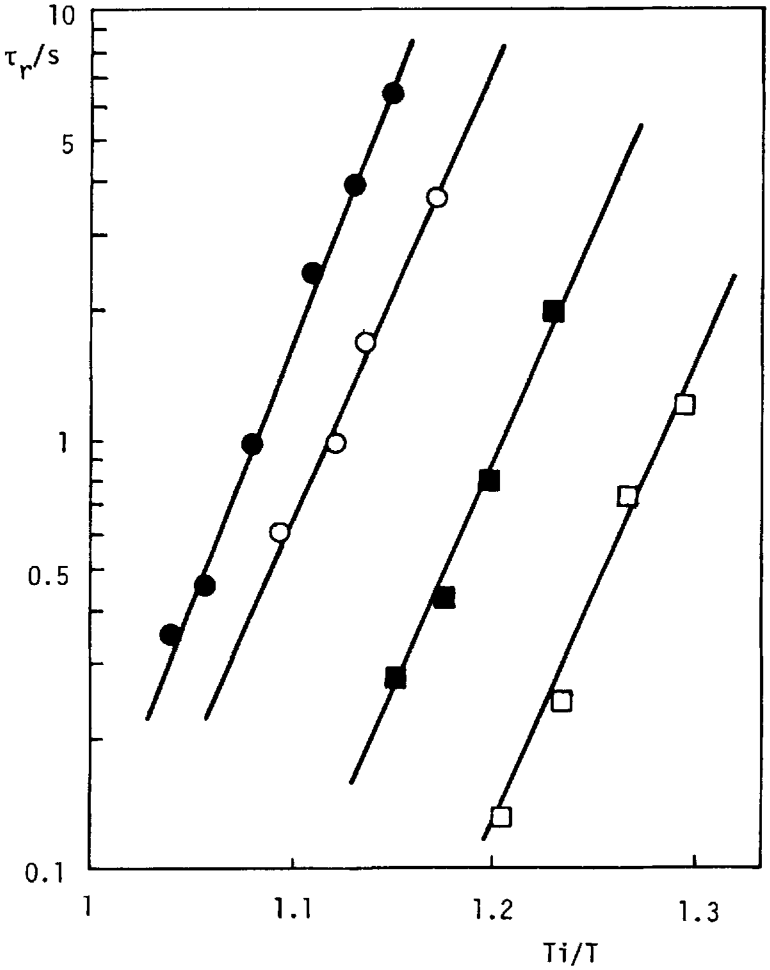


FIGURE 12 Response time (τ_r) as a function of T_i/T (T_i = isotropic temperature, T = measurement temperature) for PCBMAB-2 and PCBAAB-2. (—●—): PCBMAB-2 (*Mn* = 21500), (—○—): PCBMAB-2 (*Mn* = 9000), (—■—): PCBAAB-2 (*Mn* = 11300), (—□—): PCBAAB-2 (*Mn* = 6200).

quency. A clear Williams domain forms in a few minutes even in these side-chain liquid crystal polymers having a molecular weight of 90000, as shown in Figure 13.[84]

The role of an electric field on the polymeric nematic phase of main-chain polymers was first reported by Krigbaum et al.[68]

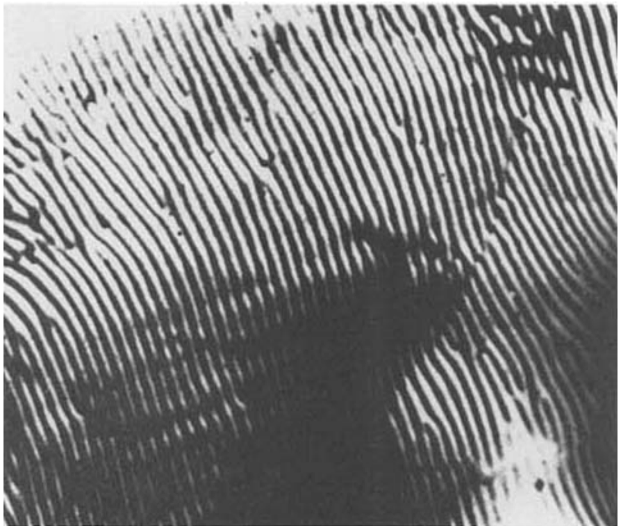
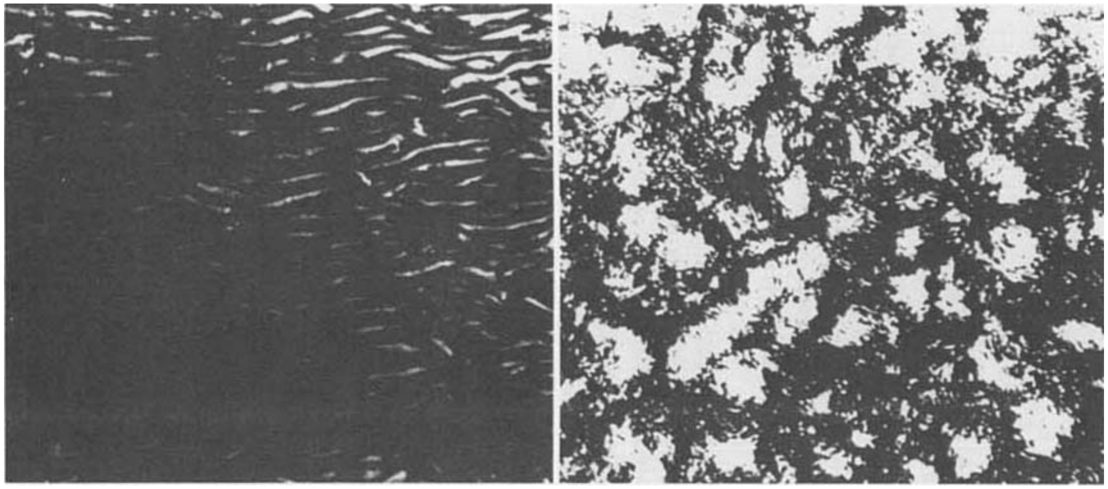


FIGURE 13 Williams domain of PMABMCS-6 ($Mn = 90000$), DC 3 V, 13 μm.

The Williams domain was observed in a moderately high molecular weight sample of Eastman Kodak copolyesters. The formation time of Williams domain patterns in this copolyester was of the order of 1 h, and the flow instability patterns have been preserved in the solid state on cooling to room temperature. Since high field turbulence was observed only within 1 min. at the nematic state, Krigbaum et al.[69] proposed that the applied electric field method to the polymer liquid crystal might provide a quick diagnostic test for a nematic phase. However, a different case was found for the nematic and smectic phases. The Williams domains were observed only in nematic polymers, and a high field turbulence was exhibited both in nematic and smectic phases, as shown in Figure 14.

Krigbaum et al.[74] were not able to obtain a well-aligned nematic sample using the Chatelain rubbing technique,[85] even for samples as thin as 4 μm. In the case of very low molecular weight polyesters, however, Williams domains perpendicular to the rubbing direction were observed in the conduction regime, and changed to broad domains similar to MBBA with increasing frequency above the critical one.[86] The broad domain texture was also observed, as well as a homeotropic Freedericksz transition, by Gilli et al.[87]

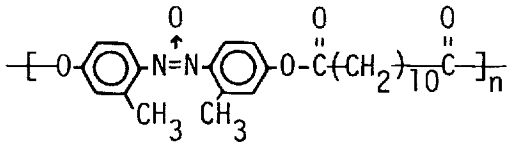
Blumstein et al.[88] have investigated the effects of molecular weight and temperature on the formation and on the relaxation of electro-



(1) (2)

FIGURE 14 Polarizing microphotograph, (1) Williams domain of PAOPA-8 (nematic liquid crystalline polymer), (2) Dynamic scattering mode of POEAOB-3 (smectic liquid crystalline polymer).

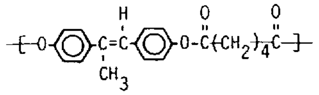
hydrodynamic instabilities with semi-rigid main-chain polymers by the following structural formula:



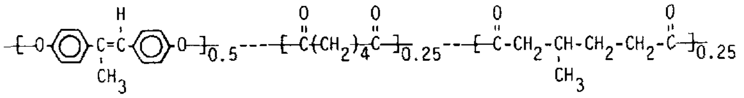
The time needed for the formation of Williams domains increases with the decrease of the applied voltage and temperature, and with increasing molecular weight. At a higher voltage a dynamic scattering mode appeared.

Corazza et al.[80] observed that copolyester having the following chemical structure (a) changes from a predominantly planar texture to a focal conic one when the electric field is applied to the helical axis of the planar texture. These phenomena were also observed in the following cholesteric polyesters (b). As can be seen in Figure 15, when voltage is applied, the planar texture containing the dark area grows into a brighter pattern within several minutes. Under high voltage, a dynamic scattering mode always appears.

(a)



(b)



The first comprehensive experimental study of the Frank elastic constant (K_{ii}) and the twist viscosity coefficient, γ_1, for liquid crystal polymers was reported by Casagrande et al.[67,89] They determine K_{11} and γ_1 from the dynamics of a Freedericksz transition with two different geometries. The splay elastic constant K_{11} and the twist viscosity coefficient η_1 were observed from planar geometry, whereas the bend elastic constant K_{33} is obtained from the homeotropic alignment. For a Freedericks transition the critical magnetic field strength (H_c) is given by the following equation.[90]

$$H_c = \frac{\pi}{d}\left(\frac{k_{11}}{\chi_a}\right)^{1/2} \tag{5}$$

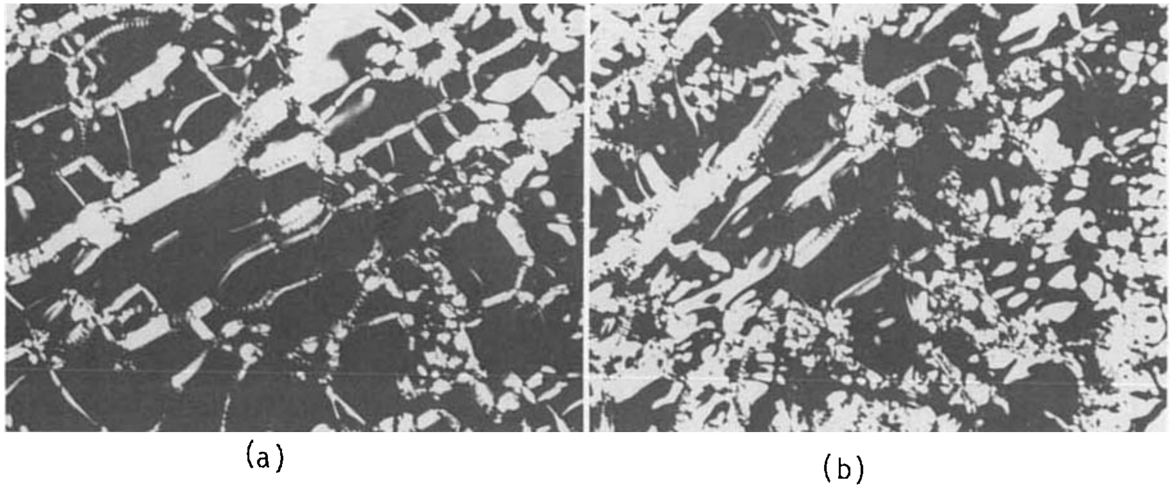
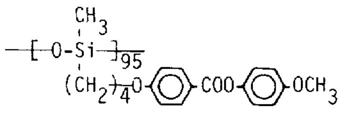
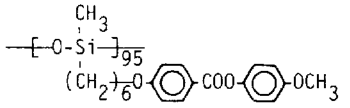
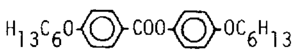
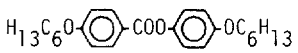


FIGURE 15 Transition pattern of cholesteric phase (CcDHCSA-8-(+)MA*) in electric field (DC 5 V, 13 m). (a) 10 minutes after the application of dc 5 V, (b) 15 minutes after the application of dc 5 V at 188.8 C. crossed polarizers.

TABLE III

Measurements of the Freedericks Transition in the magnetic field*

Formula	Hc (gaus)	τ (s)	$K11 \times 10^7$ (dyne)	γ_1 (poise)
	1500	5400		
	877	1800	7.8	2.90×10^2
	1250	0.93	15.8	2.48×10^{-1}
	964	3.48	9.4	6.60×10^{-1}

HC : critical field, τ : relaxation time, K11 : spray elastic constant, γ_1 : twist visocosity coefficient. * Ref. from 67.

where d is the sample thickness, χ_a is the diamagnetic anisotropy and K_{11} is the spray constant. The length of the polymer chain slightly influences both K_{11} and K_{33} but the length of the spacer plays a more pronounced role in the Frank elasticity, as shown in Table III. From Table III the response times of the polymers are several orders of magnitude larger than in low molecular weight nematics, due to the high magnitude of γ_1. With increasing length of the spacer K_{11} increased, while K_{33} decreased. As for the elastic constant K_{11} and K_{33}, they were of the same order of magnitude as those found in conventional liquid crystals.

Coles et al.[90] carried out Freedericksz transition measurements under magnetic and electric fields with a mixture of monomeric-polymeric nematic liquid crystals. They used a polysiloxane system with a pendant group of cyano-biphenyl and of benzoate ester because of its strong electro-optic response, and also because of its excellent thermal stability. They found that k_{11}, k_{33}, k_{33}/k_{11} and k_{22}/γ_1 decrease with increasing polymer concentration. K_{22} decreases with increasing polymer concentration. The twist viscosity, γ_1, of a mixture of monomeric-polymeric liquid crystals is eight times larger than that of 4-cyano-4′-pentyl-biphenyl. These changes suggest that by using a suitably thin cell, short response times below 200 ms can be realized at modest applied voltages.

ASPECTS OF APPLICATIONS

Recently, main-chain thermotropic polymer liquid crystals are considerably interesting because of their possibility of application to new technologies. Main-chain thermotropic polymers, mainly composed of rigid-mesogenic parts, can have great potential for the production of ultra-high modulus fibers similar to Kevlar and also for the application of coating materials on optical fibers.[91] Side-chain liquid crystal polymers can play a more important role in application than main-chain liquid crystal polymers at present. The combination of liquid crystals and polymeric properties can offer many possibilities for applications in other fields, e.g., high-strength and high modulus fibers, composite materials, electro-conductive liquid crystal polymers, photoconductive liquid crystal polymers, electro-optic storage devices and so on. In this section we will present a few examples of applications which have appeared recently in the literatures.

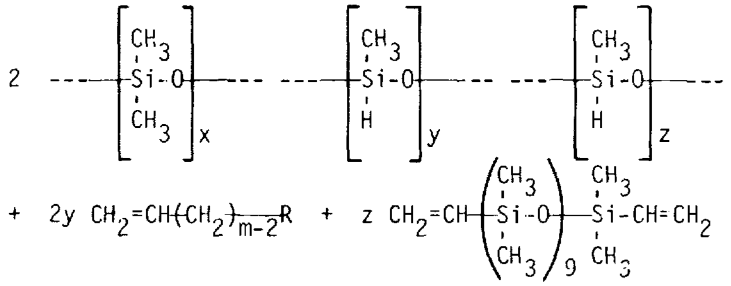
The first example is the application to storages or momery materials of liquid crystal polymers. The response time of liquid crystal polymers is very slow owing to their high viscosity. Liquid crystal polymers show new optical properties whose orientation can be controlled with the aid of external fields, and then this orientation texture can be durably frozen at the glassy state. These storage characteristics would be expected only from polymeric liquid crystal materials and can offer many probabilities for applications.

Platé et al.[92] have demonstrated the thermorecording liquid crystal polymer, which can be realized with the action of a focused helium-neon laser with a power of 10 mW as a source of light on the homeotropically-oriented nematic polymer film at a temperature slightly below the clearing temperature. The laser-recorded information as a randomly oriented domain can be stored for a long time below Tg. After applying an electric field again at the mesophase temperature under an electric field, the recorded information is completely wiped off in a few seconds.

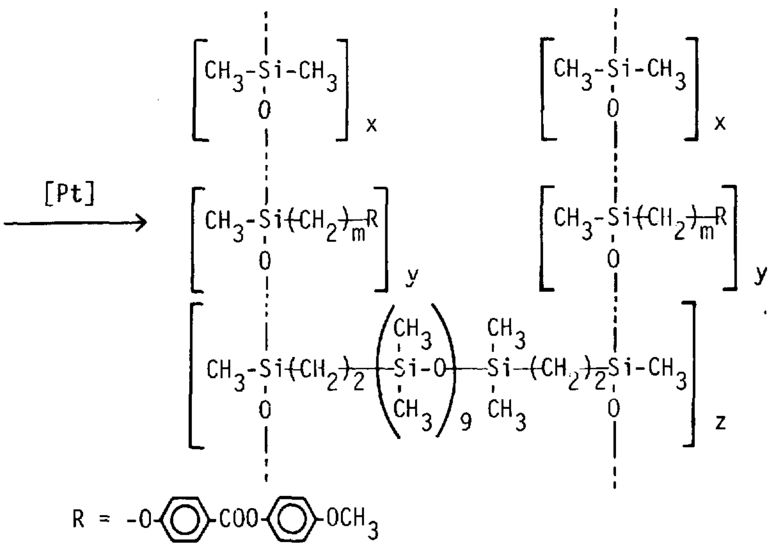
Another optical storage device has been examined with the smectogenic side-chain polymer by Coles et al.[93] The clear texture was stored in the smectic A phase above Tg and no deterioration of the optical quality has been observed over eighteen months. The storage effects would appear to be a result of the high viscosity and bistable nature of smectic polymers, similar to the low molecular weight smectic, which is a bistable storage medium when suitably addressed by thermal and electrical fields.[94] The texture of this smectic polymer developed a clear fan texture on annealing, which strongly scatters light. Application of a low dc electric field leads to field-induced scattering, while application of high dc voltages induced a pseudo-homeotropic alignment in the applied field region. The partially ordered area by an electric field was transparent and did not scatter. The contrast ratio between the clear and scattering regions was as high as $10^3:1$ to $10^4:1$ as compared with $10:1$ for monomeric smectic A materials.

The storage effects were also reported for the main-chain liquid crystal polymer by Gilli et al.[87]

The second example is the new field of liquid crystal polymer reported by Finkelmann et al.[95,96] e.g., the photoelastic liquid crystal side-chain polymers prepared by an addition reaction of the mesogenic vinyl compounds and the crosslinking agent via the following scheme: The viscous melt of the linear liquid crystal polymer is changed into an elastomer by crosslinking, and then liquid crystal properties are combined with rubber elasticity. The orientation of the liquid crystal elastomer differs according to the odd or even number of methylene units in the alkyl spacer. In the liquid crystal elastomer, with an odd number of spacers, the mesogenic side groups are oriented perpendicular to the direction of deformation, and in the case of an even number of spacers, parallel to this deformation. The mechanical deformation of these nematic elastomers causes a macroscopic orientation of the mesogenic side groups. They discussed the possibility for application of these liquid crystal elastomers to light modulation and linear polarizers having dichroic dyes dissolved or linked to the polymer.

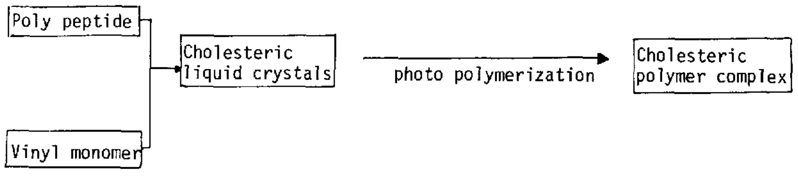


$$2\;\left[\text{Si}(CH_3)_2\text{-O}\right]_x\left[\text{Si}(CH_3)(H)\text{-O}\right]_y\left[\text{Si}(CH_3)(H)\text{-O}\right]_z + 2y\;CH_2{=}CH\text{-}(CH_2)_{m-2}\text{-}R + z\;CH_2{=}CH\text{-}\left(\text{Si}(CH_3)_2\text{-O}\right)_9\text{-}\text{Si}(CH_3)_2\text{-}CH{=}CH_2$$



The third example is the immobilization of liquid crystal structures, which can be obtained by the following three methods: 1. polymerization of the monomer in a lyotropic liquid crystal, 2. polymerization of the liquid crystal monomer, 3. frozen-in liquid crystal structure of a liquid crystal polymer. The frozen-in cholesteric liquid crystal (organizations) films are applicable as passive optical devices[97,98] such as circular polarizers, band pass filters, notch filters, and reflective displays.

Tsutsui et al.[99,100] have reported that the cholesteric organization can be easily immobilized in polypeptide-vinyl monomer liquid crystal mixed systems in which the vinyl monomer acting initially as a solvent forms a polymerized matrix, as shown in this schematic diagram:



A typical example is that poly(γ-butyl-L-glutamate) (PBuLG) dissolved in the triethylene glycol dimethacrylate system (TGDM). The irridescent cholesteric colors, through the entire visible spectral regions, can be controlled by either changing the PBuLG/TGDM ratio or the photopolymerization temperature, and since the polymeric material can be formed into a film, they need no supporting matter and are easy to handle.

Other routes to prepare cholesteric polymers are that the polymerization of a mesogenic monomer is attached to a chiral moiety, or the copolymerization of a mesogenic monomer with a chiral mesogenic or chiral non-mesogenic comonomer.[37,101,102,103] The wavelength of maximum reflectivity, λ_R is related to the pitch, P.

$$\lambda_R = nP \tag{4}$$

where n is the refractive index. The cholesteric pitch can be easily controlled by the content of the chiral moiety, and the cholesteric structure is also frozen in the glassy state without any change below the glass transition temperature. λ_R can be adjusted within 300 nm $< \lambda_R < \infty$. These cholesteric polymers can be easily coated on a given surface, or processed into the form of large-space film.

The fourth example is colored liquid crystal polymers obtained by copolymerization of mesogenic monomers with monomeric dyes, or by the mixing of a liquid crystal polymer and a dye material.[44,45] Dye molecules in liquid crystal media are oriented together with liquid crystal molecules by applying an electric field the schematic representation of which is shown in Figure 11. The oriented nematic structure can be frozen in below the glass transition temperature in contrast to low molecular weight guest-host systems. In this state, the nematic liquid crystal polymers can be used as durable polarizers.

MISCELLANEOUS

Highly orientational polymers, e.g., polyacetylene,[104] are obtained by polymerization in the presence of low molecular nematic liquid crystal materials.

Kajiyama et al.[105] have prepared a composite membrane which is composed of polymer and low molecular weight liquid crystalline materials, as shown in Figure 16. The permeability coefficient for hydrocarbon gases increases 100–200 times over several degrees in the mesomorphic temperature range. By application of an electric field to the composite membrane, gas permeability increases, depending on the magnitude of applied voltage.[106] The polymer/liquid crystal/fluorocarbon ternary composite membrane shows excellent oxygen permeability and permaselectivity.[107]

Chapoy et al.[108] have investigated the role of long-range order on

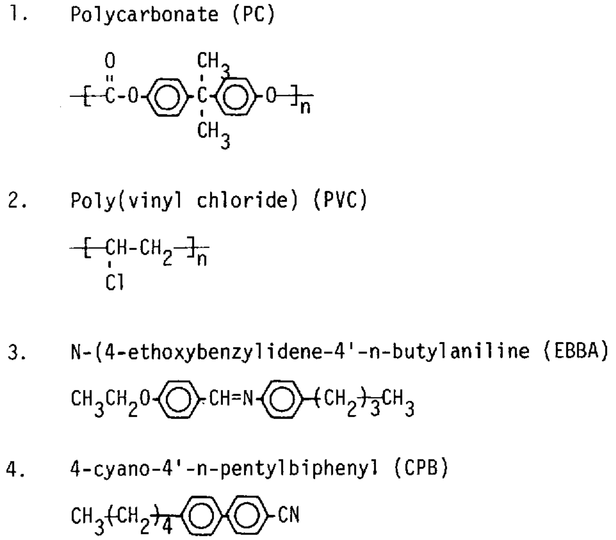


FIGURE 16 Chemical structures of polymers (1,2) and low molecular weight liquid crystals (3,4).

electrical properties as organic conductors through the use of a liquid crystal polymer and a helical poly-α-amino acid with a carbazole-substituted side-chain. To obtain effective photoconductive enhancement, it is necessary to align carbazole substituents in the nematic arrangement.

Another expected field for application of liquid crystal polymers is the use of gas chromatographic separation, because liquid crystal polymers exhibit properties of thermal stability, wide-range mesomorphic temperatures, low volatility and high selectivity.

Acknowledgment

I wish to thank Professor K. Iimura, Science University of Tokyo, for a critical reading of the manuscript.

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