

# Photoalignment of Liquid-Crystal Systems

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Kunihiro Ichimura graduated from Gakushuin University (Tokyo), Department of Chemistry, in 1963 and received both his M.Sc. and Ph.D. degrees from Tokyo Institute of Technology, Department of Chemistry. From 1968 to 1982, he was a researcher at the Research Institute for Polymers and Textiles, belonging to the Ministry of International Trade and Industry division, and became the Senior Officer of Research Planning of the Institute in 1989. He was promoted to Head of Research Department of the Institute in 1990 and was concurrently appointed as Professor in the Research Institute of Resources Utilization, Tokyo Institute of Technology, where he has been a full-time Professor since 1991. His representative research works cover photosensitive polymers, photochromic materials, photoresponsive liquid crystals, and ultrathin organic films.

on photochromic behavior and the effect of photochromic behavior on the matrix. In the former, efficiencies of photochromism are more or less affected by the microenvironmental properties of matrices including polarity, free volume, molecule-to-molecule interactions, etc. On the other hand, the latter effect involves reversible property changes of matrices as a result of structural transformation of photochromic guest molecules, leading to the orientational alteration of host molecules or residues embedded in matrices which surround the guests. It follows that the orientational changes of matrices triggered by photochromic molecules provide versatile photofunctional materials and devices based on the photogenerated physical as well as chemical modification of matrices. A typical example is a visual sensory system which is triggered by the photoisomerization of a retinal tethered to a protein molecule to modify the high-dimensional conformation of the biomolecule, giving rise to the subsequent molecular events.

It is worthy to mention that this type of effect of photochromic molecules on matrix properties is accompanied by marked molecular amplification because the number of host molecules exhibiting orientational transformations is much larger than that

## I. Introduction

Photochromic molecules are usually embedded in solid matrices for both fundamental and practical studies so that photochromism suffers from multiple matrix effects.<sup>1,2</sup> It should be noticed that the matrix effect has a dual meaning: the effect of the matrix

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of photochromic molecules as a photoreceptor.<sup>3</sup> Liquid crystals (LCs) form supramolecular assemblies with unidirectional orientations of the molecular axis in nature to give rise to optical anisotropy.<sup>4</sup> There are several types of LCs which differ in the details of molecular order, molecular shape, and molecular weight.<sup>5,6</sup> Consequently, the significance of the combination of LC systems with photochromism arises from the phototriggered amplification derived from the molecular order, resulting in the remarkable transformation of optical properties, displaying the photooptical effect. The photooptical effect comes from photoinduced changes in the level and the direction of alignment of LC molecules.<sup>1</sup>

There have been many studies on photoinduced changes of liquid-crystalline phases<sup>1</sup> since the first report on the change of cholesteric pitch bands of a mixture of cholesteryl iodide and cholesteryl nonanoate due to the photodecomposition of the iodide.<sup>7</sup> The photoisomerization of azobenzene as well as stilbene in a cholesteric LC results in reversible cholesteric color changes.<sup>8</sup> When nematic LCs are doped with stilbenes<sup>9</sup> or azobenzenes,<sup>10</sup> their *E/Z* photoisomerization results in mesophase change between nematic and isotropic phases. In these systems, the marked transformation of the molecular shape of the photochromic guests from the rodlike shape of the *E* isomer into the *Z* isomer, which leads to the destruction of ordered mesophase structures because the bent form of the *Z* isomer acts as an impurity. The photoinduced phase transition has a practical significance in applications to optical switching and information storage.<sup>11</sup> The other class of photoresponsive LC systems involves the rapid photoswitching of ferroelectric LCs doped with azobenzenes<sup>12–14</sup> and a thioindigo.<sup>15</sup> Although this kind of photoinduced alteration between ordered and disordered states of LC systems has been attracting extensive interest, the major aim of this article is to review the alignment control of LC systems triggered by photochromic molecules, maintaining mesophase structures before and after photoirradiation. In other words, this article deals predominantly with LC systems where orientational directions of mesophasic molecules referred to as LC directors are controlled by photochromic molecules simply by photoirradiation.

Thus, the photoalignment of the LC means here that the orientational directions of LC molecules is controlled or manipulated by photoirradiation as a result of the photogeneration of optical anisotropy of photochromic layers or films. The optical anisotropy stems from the photoinduced molecular orientation of photochromic units. To make the definition of terms as well as processes used in this research field much clearer, the photochemical behavior of azobenzene is briefly mentioned. The irradiation of a thin film of a polymer with azobenzene side chains with UV light results in the formation of a photostationary state containing the *Z* isomer as a major component, which is reversed to the *E* isomer under illumination with blue light. The *Z* isomer has an opportunity to reverse to the *E* isomer under irradiation with red light at 633 nm.<sup>16,17</sup>

When the light is linearly polarized, photons are absorbed by azobenzene molecules according to  $\cos^2 \theta$ , where  $\theta$  is the angle between the electric dipole transition moment and the electric-field vector of the light used to undergo the photoselection<sup>18</sup> leading to the molecular reorientation. Systematic studies on the photoorientation have been described.<sup>19</sup> The following processes cause photoorientation: photochemical *E* to *Z* isomerization, photochemical *Z* to *E* isomerization, thermal *Z* to *E* isomerization and angular redistribution, connected by rotational diffusion resulting from thermally induced Brownian motion.<sup>20,21</sup> A model has been given to interpret the dependence of the photoorientation upon irradiance and temperature.<sup>22</sup> A portion of the azobenzene with the transition moment parallel to the electric vector of the light is reduced so that the polymer film exhibits optical anisotropy unless the molecular mobility of the azobenzene is efficiently suppressed to retard the thermal randomization of the molecular orientation. Consequently, heat treatment of an amorphous polymer incorporating photooriented azobenzene above the glass-transition temperature ( $T_g$ ) removes the optical anisotropy. Note that the photoinduced dichroism can be generated by linearly polarized light irradiation even though a photochemical reaction takes place irreversibly to result in angular-selective photochemistry which is termed destructive photoorientation<sup>18</sup> to give the Weigert effect.<sup>23</sup> Owing to the reversible process of azobenzene chromophores, the repetition of *E/Z* photoisomerization induced by linearly polarized light in a polymer film causes the alteration of the molecular axis to give rise to dichroism, which is sometimes called photodichroism, as a result of nondestructive photoorientation. The predominant contribution of the aromatic ring system to the refractive index makes the polymer film birefringent. When the photoirradiated film is subsequently exposed to the linearly polarized light with an electric-field vector different from that of the initial light, the molecular axis of the azobenzene chromophores is transformed to be perpendicular to the electric vector of the second light to display photoreorientation. In this context, photochromic molecules are able to undergo *photoreorientation* because of the reversible process whereas the reversibility of a photochemical process is not always the necessary requirement to achieve *photoorientation*.

There are two ways to achieve the photoalignment of LC systems. The first one consists of LC doped with photochromic guests. Because a photogenerated aligned state of low-molecular-weight LCs is readily relaxed due to the mobility of LC molecules, predominant studies have been done on polymeric LCs to suppress the molecular motion, leading to the enhanced stability of photoaligned states.<sup>2</sup> The second way has been referred to as surface-assisted LC photoalignment and is performed by fabricating LC cells using substrate plates, the surface of which is modified with photochromic molecules.<sup>24,25</sup> Changes in chemical structures as well as orientational directions of photochromic molecules at a surface layer trigger the transformation of LC alignment. This sort of photoactive surface has been called a *command*

surface,<sup>24,25</sup> emphasizing the fact that the alignment of a large number of LC molecules is determined by a photochromic monolayer attached to a substrate surface.

The working principles of the photoalignment induced by photochromic molecules depend crucially on the LC systems employed. In cases of dye-doped LCs, many studies have been performed on the photocontrol of the azimuthal direction of the systems by illumination with linearly polarized light. Light absorption by photochromic molecules is achieved under exclusive requirements including coincidence of the electric vector of actinic light with the electric dipole transition moment of ground-state chromophores. Consequently, axis-selective light absorption takes place to cause the generation of optical anisotropy such as dichroism and birefringence. On the other hand, no light absorption occurs when a transition moment of a chromophore molecule lies in parallel with the propagation of the light, irrespective of whether the light is polarized. This condition enables us to open a novel route to manipulate the optical axis of LCs three-dimensionally since the orientational direction can be principally determined by the incident direction of light. It should be emphasized again here that LC systems are very convenient for photoalignment control because of their self-assembling nature, which amplifies the photoinduced orientational states of photochromic molecules and stabilizes sufficiently the photoresponsive systems, in particular, consisting of polymeric materials.

## II. Liquid Crystals Doped with Photochromic Molecules

### A. Low-Molecular-Weight Liquid Crystals Doped with Dye Molecules

Nematic LCs give rise to marked changes of the refractive index upon light illumination under electric-field application to display the so-called optical Freédericksz effect<sup>26</sup> without mesophase change because of the ease of the reorientational motion of LC molecules.<sup>27–29</sup> It was reported that the addition of guest dye absorbing actinic light remarkably enhances the optical Freédericksz effect to lead to spatial refractive index modulation.<sup>30–32</sup> The holographic exposure of this kind of a cell filled with a dye-doped LC enables one to carry out reversible grating formation. A guest dye such as a diaminoanthraquinone exhibits no photochemical structural change, therefore, the mechanism connected with photoconductivity and local electric-field-induced reorientation of LC directors has been discussed.<sup>33,34</sup> A photochemically induced reorientation mechanism may not be excluded, however, when a diazo guest dye is employed in this system.<sup>35,36</sup>

### B. Liquid Crystals Dispersed in Azobenzene Polymer Networks

Whereas the photoalignment of dye-doped nematic LC systems provides potential applicability to photonic devices based on real-time holography, the

spatial modulation is rather transient so that long-lived recording is hard when low-molecular-weight LCs are used. On the other hand, a quite stable photoaligned state is obtained when low-molecular-weight nematic LCs are dispersed in polymer networks tethering azobenzene side chains as a photo-receptor.<sup>37</sup> A photoresponsive LC/polymer composite cell was prepared by the thermal radical polymerization of an azobenzene acrylate monomer with diacrylate as a cross-linker dissolved in an LC. The exposure of the cell to linearly polarized blue light for the  $n, \pi^*$  excitation of the azobenzene generates a large birefringence with excellent thermal stability. The photogeneration of the optical anisotropy arises from the photoreorientation of azobenzene side chains as a result of the repetition of *E/Z* photoisomerization induced by irradiation with the linearly polarized light, as discussed in detail in section III.B, leading to the reorientation of bulk LC molecules owing to the *command effect* of the photoaligned azobenzene. The LC cell displays rewritability by changing the electric vector of the light so that clear photoimages are available and visualized by a couple of polarizers at a crossed position.

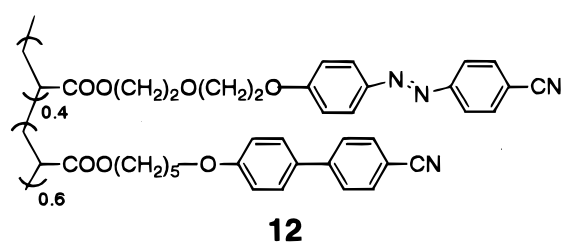
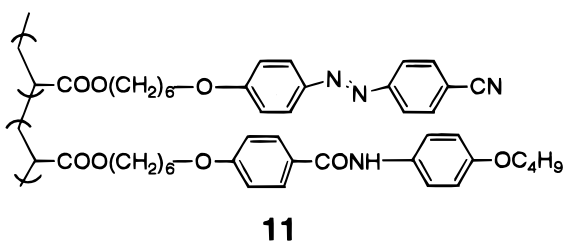
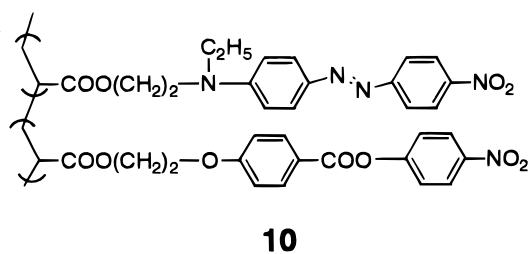
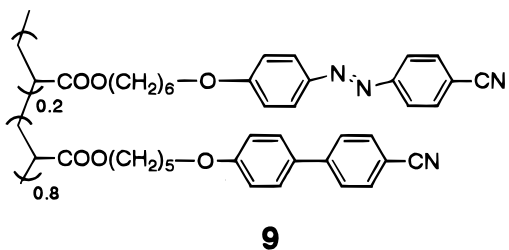
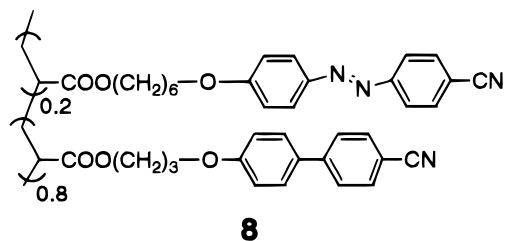
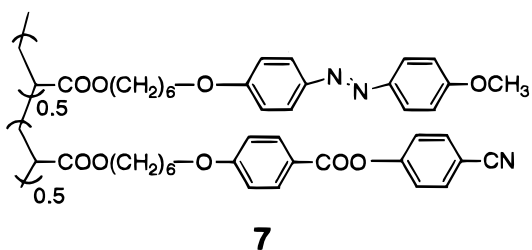
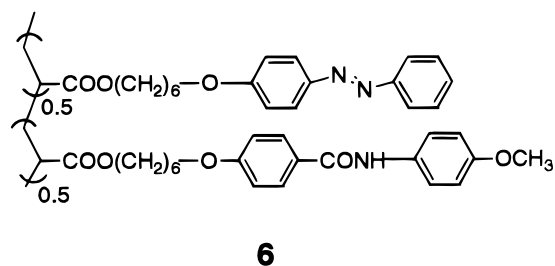
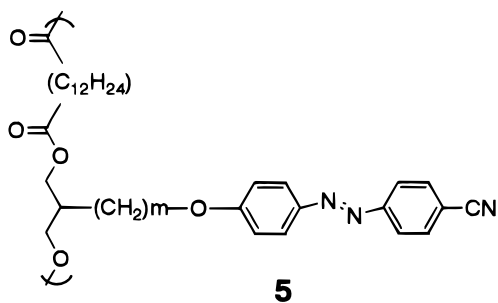
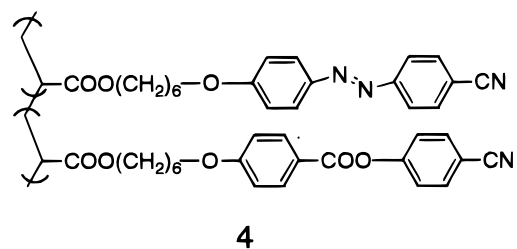
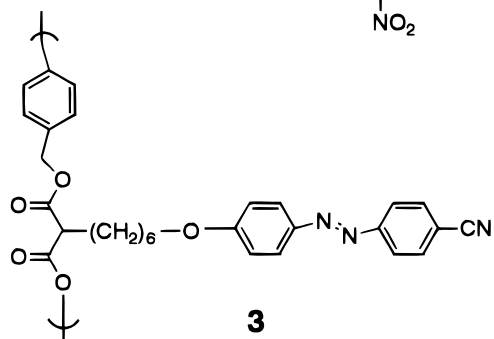
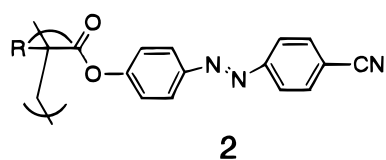
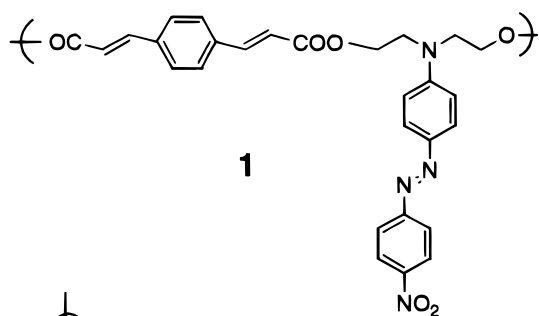
The irradiation of the composite LC cell with nonpolarized light results in a quite different event.<sup>38</sup> Whereas LC directors in a polymer network are distributed in a random fashion, an LC layer displays homeotropic alignment with a perpendicular orientation of LC molecules when the cell is illuminated with the blue light from surface normal. When the cell is irradiated with the light at an incident angle, for instance at 30° from surface normal, an optical axis of the LC layer moves to a direction in line with the incident direction of the light. This phenomenon is closely related to the previous finding,<sup>39,40</sup> as described later in section IV.E, that the uniaxial orientation of an LC filled in a cell fabricated by using substrates surface-modified with an azobenzene monolayer is determined by the incident plane angle of actinic light.

It is worthy to mention here that the alignment of an LC bulk is controlled by the dissolution of a tiny amount of poly(vinyl cinnamate) in an LC.<sup>41</sup> As shown in section IV.G in more detail, irradiation of a film of the photo-cross-linkable polymer leads to the generation of optical anisotropy, which triggers the surface-assisted in-plane LC photoalignment.

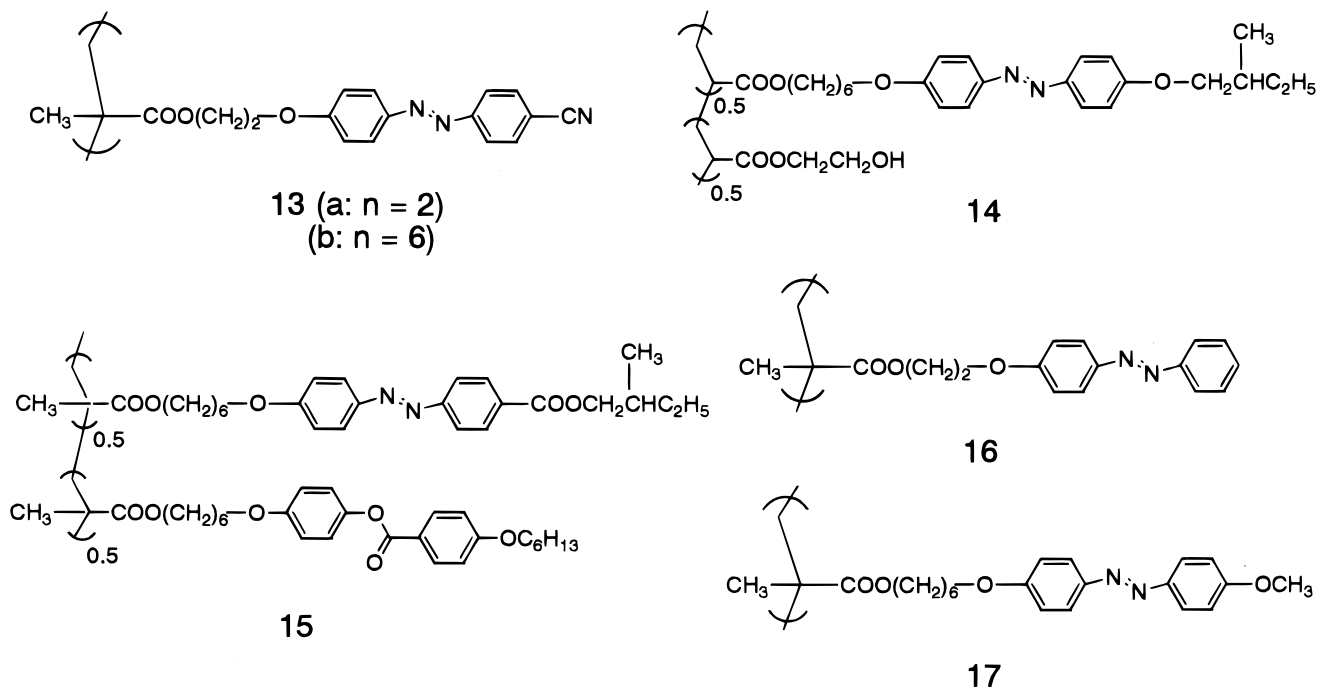
## III. Photochromic Liquid-Crystalline Polymers

### A. Background

The interaction of chromophores with linearly polarized light causes dichroism of a matter because of the axis-selective photochemical conversion bringing about the so-called the Weigert effect.<sup>23</sup> Michl suggested the photochromism by the molecular orientation induced by linearly polarized light as a potential photomemory principle.<sup>42</sup> Intensive studies have been carried out on the linearly polarized light-induced molecular reorientation of photochromic molecules embedded in polymer matrices. This type of photochemical processes is referred to here as polarization photochromism.







**Figure 1.** Azobenzene polymers for studies on photoreorientation.

There have been many reports on polarization photochromism in amorphous polymer films exhibiting optical anisotropy. Todorov et al. were the first to report the generation of photobirefringence by employing a film of poly(vinyl alcohol) doped with a water-soluble azo dyes such as methyl orange or methyl red to be subjected to the formation of holographic gratings.<sup>43,44</sup> They performed polarization holography, which stems from the molecular reorientation of the doped dye induced by linearly polarized light. Dichroism also emerges upon linearly polarized light irradiation of poly(methyl methacrylate) (PMMA) films of molecularly dispersed ferylfulgide,<sup>45</sup> 6-nitrospirobenzopyran,<sup>46,47</sup> and *p*-dimethylaminoazobenzene<sup>46,47</sup> and disappears by heating the films at a temperature above the glass transition temperature ( $T_g$ ) of PMMA. If photochromic molecules in a polymer solid are exposed to linearly polarized light to bring about both forward and backward reactions simultaneously, the photodichroism arises from the molecular reorientation as a result of a nondestructive mode. The extent of photoinduced dichroism depends on the nature of photochromic compounds and ingredient composition and viscosity of polymeric binders.

When compared with polymer films containing photochromic molecules physically, the covalent binding of photochromic units to polymer backbones results in marked enhancement of the stabilization of the molecular orientation induced by linearly polarized light irradiation.<sup>2</sup> Systematic studies have been achieved on the photoinduced molecular reorientation of azobenzene units to induce birefringence and dichroism of thin films of amorphous acrylate and methacrylate polymers with azobenzene side chains.<sup>48–53</sup> Photoorientation of azobenzenes occurs even in films of polyimides with a high  $T_g$ .<sup>54,55</sup> It is worthy to mention that the photoalignment of azobenzene polymer films is considerably enhanced by their

semicrystalline nature, as observed for a *p*-phenylenediacyrylate polyester incorporating a Disperse Red (*p*-nitro-*p*-aminoazobenzene moiety) side group (1)<sup>56</sup> and poly[4-(4-cyanophenylazo)phenyl methacrylate] (2).<sup>57</sup> On the other hand, the liquid crystallinity of polymers with azobenzene side chains plays a crucial role in the emergence of larger optical anisotropy and good thermal stability of the photoalignment induced by linearly polarized light irradiation, as stated in the following section. The azobenzene polymers mentioned in this section are shown in Figure 1.

## B. Two-Dimensional Photoorientation by Polarization Photochromism

### 1. Photogeneration of Optical Anisotropy

The first report on the polarization photochromism in LC polymers was made by Wendorff et al. who achieved the generation of holographic gratings in layers of LC polymers having azobenzene side chains (3, 4) using Ar-gas laser beams at 488 nm.<sup>58,59</sup> LC polyesters bearing azobenzene side chains (5), which possess low  $T_g$  values close to room temperature, are also applied to hologram formation with high resolution and excellent storage stability.<sup>60</sup> Holograms thus formed are thermally stable upon prolonged storage at an ambient temperature below the  $T_g$  because of strong molecular interactions of *p*-cyanoazobenzene mesogen to form aggregates<sup>61</sup> and erased either by heating to temperatures above the  $T_g$  or by light irradiation. The polarization holography is performed not only by linearly polarized light, but also by circularly polarized light.<sup>62</sup> Theory and experiments of polarization holography of side-chain LC polyesters are discussed.<sup>63</sup> Note that diffraction efficiencies are not only due to the photobirefringence, but also to the physical formation of surface-relief gratings, which are mentioned later. The polarized visible light

for the  $n-\pi^*$  transition of azobenzene moiety brings about the reorientation of azobenzene chromophores to give the photodichroism and photobirefringence.<sup>63</sup> Consequently, azobenzene chromophores in a layer of a photoirradiated LC polymer (**4**) show, for instance, an order parameter of one order of magnitude ( $S = 0.56$ ) greater than those of amorphous polymers with an order parameter  $S = 0.03$ .

Polarized light irradiation of a layer of the other azobenzene LC polymer (**6**) with a homeotropic (perpendicular) alignment gives rise to the emergence of birefringence due to a homogeneous orientation even at temperatures below  $T_g$ .<sup>64</sup> In connection with the photoinduced reorientation mechanism, factors affecting the photobirefringence were investigated.<sup>65</sup> The temperature effect is remarkable. Photoinduced birefringence is only slightly influenced by temperature below  $T_g$ , whereas a considerable increase of the photobirefringence with values one order of magnitude higher takes place above  $T_g$ . Much higher temperatures result in the reduction of the values, and photoinduced birefringence disappears at a clearing temperature to give an isotropic melt. It should be noticed that the generation of optical anisotropy consists of two fast and slow processes: axis-selective photoisomerization involving one-way  $E$ -to- $Z$  photoisomerization and subsequent photoreorientation of the molecular axis.<sup>66,67</sup> The second process takes place very slowly in a glassy state, when compared with the first one, because the sweep volume required for the rearrangement of a rod-shaped molecular axis is much larger than that for the photoisomerization.

The polyester with *p*-cyanoazobenzene side chains (**5**) was subjected to alternating exposure to 351 nm light from a Kr laser and 488 nm light from an Ar laser to evaluate the rewritability based on the photoreorientation.<sup>68</sup> The level of changes in the photobirefringence is reduced markedly in the early stage of the alternating irradiation due to the perpendicular reorientation of the azobenzene, while 10 000 cycles are possible. The photoinduced optical anisotropy of films of LC azobenzene polymers can be removed thermally by annealing at temperatures higher than a clearing point or photochemically by irradiation with circularly polarized light,<sup>69</sup> which was employed first for the erasure of photobirefringence of films of amorphous azobenzene polymers.<sup>48</sup> It was observed for a photoaligned film of an LC azobenzene polymer that photobleaching is generated by irradiation with circularly polarized light while photoinduced birefringence is erased.<sup>69</sup> This photobleaching effect is interpreted in terms of the reorientation of azobenzene chromophores toward the incident direction of the light. The bleaching is removed by heating the sample at a temperature close to the clearing point of the LC polymer. It should be mentioned that the irradiation of a film of an LC polyester with *p*-cyanoazobenzene side chains (**5**) with circularly polarized light at 488 nm brings about circular anisotropy.<sup>70</sup> Optical activity  $> 10^4$  deg/cm is generated.

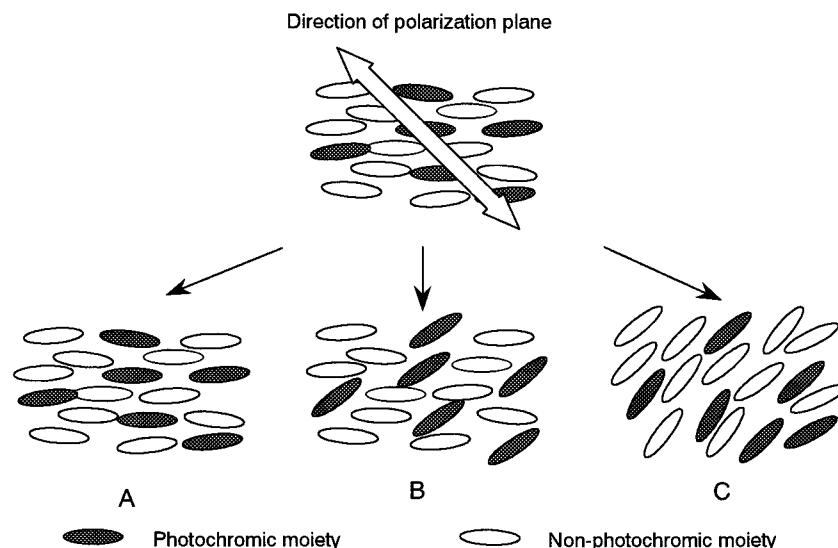
In conjunction with the polarization holography based on the photoorientation of azobenzenes, a novel

phenomenon exhibiting mass transfer in polymer films giving rise to surface-relief gratings is described briefly here.<sup>71</sup> When films of polymers substituted azobenzenes are subjected to interfering laser irradiation to perform holographic exposure, volume holograms are formed at the beginning as a result of the photogeneration of birefringence to give the difference in refractive indices in alternative domains.<sup>43,44</sup> Interestingly, massive movement of the polymers takes place subsequently to produce surface-relief gratings exhibiting microscale depth profiles during the irradiation.<sup>72,73</sup> Surface relief gratings are formed in a film of the LC polyester even after an exposure time of 5 ns.<sup>74</sup> A variety of polymers with azobenzenes in side chains and even in main chains have been employed for the fabrication of the photoinduced surface-relief gratings, irrespective of whether the polymers are amorphous<sup>72,73</sup> or liquid crystalline.<sup>75</sup> Oligopeptides bearing azobenzene side chains are designed to ensure the reversibility of the formation of surface-relief gratings.<sup>76</sup> It is worthy to note that the level of the mass transfer is influenced strongly by the types of polarization of the laser beams.<sup>77-79</sup> *s*-Polarized light gives better results when compared with *p*-polarized light, while the circular polarization of interfering Ar laser beams gives rise to a relief grating with much steeper microgrooves. Some models for the creation of surface-relief gratings including pressure gradients caused by the difference in photoisomerization rates between two domains<sup>80</sup> have been proposed,<sup>81-83</sup> but an appropriate explanation for all of the observations achieved so far is not yet available. The observation has been made on the formation of surface-relief gratings in a film of an LC polymer with styrylpyridine side chains, which are protonated to make them sensitive to 488 nm Ar laser beams.<sup>84</sup> In contrast to the cases of azobenzene-based polymers, the styrylpyridine polymer, which exhibits both  $E/Z$  photoisomerization and  $(2+2)$  photodimerization, requires heat treatment after the holographic exposure to create surface-relief gratings.

Accordingly, polarization holography using polymers with azobenzene side chains has been studied, taking into consideration the types of polarization of laser beams<sup>85</sup> and the macroscopic surface morphology. The factors determining diffraction efficiencies can be separated into optical anisotropy based on the molecular orientation and surface reliefs to discuss the effects of film thickness, exposure dose, and laser intensity.<sup>86</sup>

## 2. Command Effect on Photoorientation

The photoreorientation of azobenzene chromophores induces the cooperative reorientation of nonphotoactive mesogens as copolymer units. There is a cooperative effect in the nematic phase of the LC copolymers to result in the reorientation of both the azo units and the photoinactive mesogenic units as a result of photoselected rotational diffusion of these residues. Subsequent studies revealed that the linearly polarized light-induced reorientation of molecules in LC polymer layers is classified into three types, as sketched in Figure 2.<sup>87</sup> In case A, the



**Figure 2.** Three types of molecular reorientation of photochromic liquid-crystal polymers irradiated with linearly polarized light:<sup>51</sup> (A) No photoreorientation, (B) selective photoreorientation of photochromic mesogens; (C) cooperative photoreorientation.

reorientation is almost completely suppressed because of the very stable orientational order of a mesophasic matrix. This is the case for polymer **7**. Case B shows that the reorientation takes place solely at azobenzene residues without the reorientation of nonphotochromic side groups. Polymer **8** belongs to this case. In case C, the reorientation of the photochromic moieties of polymers **9** causes a continuous reorientation of nonphotochromic mesogenic groups even below  $T_g$  to exhibit a large optical anisotropy. Note that the structural difference between **8** and **9** is solely the spacer length in the mesogenic unit. The extent of molecular reorientation of nonphotochromic residues has been monitored by following a stretching vibration of the CN group attached to mesogenic units in a polarized IR measurement.<sup>87,88</sup>

This kind of cooperative reorientation of both push–pull-type azobenzene moieties and nonphotoactive phenyl benzoate groups occurs even though polymer **10** is amorphous in nature.<sup>89</sup> Either dipolar interactions of the photoactive and nonphotoactive groups or steric effects or the combination of both can explain the cooperative motion.<sup>90</sup> The same situation may play a role in the cooperative orientation phenomenon of the LC polymers (**11**) substituted with highly polar *p*-cyanoazobenzene residues.<sup>91</sup> The photoorientation of azobenzenes resulting from the alteration of their molecular axis induces the rearrangement of polymer chains. Selectively D-labeled LC polyesters with *p*-cyanoazobenzene side chains were prepared to monitor the orientation behavior of main-chain and side-chain alkylene spacers by means of polarized FT-IR measurements.<sup>92</sup> The photoorientation of the azobenzene leads to the cooperative orientation of both main and side chains. The level of molecular order of the spacer chains induced by photoirradiation is also discussed with respect to the influence of the morphology of the polyesters.

### 3. Thermal Enhancement of Photoorientation

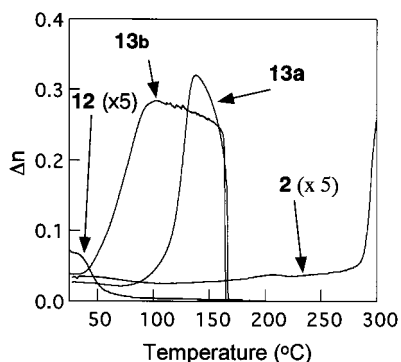
Irradiation of LC polymers with azobenzene side chains with linearly polarized light has been oc-

asionally carried out by filling them in a cell to generate a large optical anisotropy. The photoorientation of azobenzene chromophores in LC polymers requires large exposure doses; the reduction of exposure doses is crucial from a practical viewpoint since this sort of photoreorientation is of great significance in application to rewritable optical memories. It was observed that annealing of films of LC polymers with azobenzene side chains markedly enhances the order parameter of the films even though exposure doses are much smaller than those needed for saturated values of optical anisotropy.<sup>67,91</sup>

This kind of thermal enhancement of photoalignment is due to the self-aggregation of mesogenic azobenzenes studied by using spin-cast films of LC polymers.<sup>93</sup> Note that films of LC polymers prepared by the spin-coating technique are amorphous since the random molecular orientation of the polymers in solution is frozen by the rapid removal of solvent. Polarized light irradiation of amorphous films of LC copolymers with azobenzene side chains below  $T_g$  gives relatively large birefringence, indicating the physical reorientation of nonphotochromic mesogenic residues triggered by the photoinduced reorientation of azobenzene groups.<sup>94,95</sup> When films of LC copolymers with *p*-cyanoazobenzene side chains and phenyl benzoate mesogenic residues are subjected to annealing at temperatures 20 K higher than  $T_g$  after linearly polarized light irradiation, a considerable increase in optical anisotropy is generated. The lower the content of the photochromic groups, the larger the enhancement of the photoinduced order parameter of both the azobenzene and the nonphotochromic mesogen. It was revealed that 10% loading of the azobenzene is sufficient to result in the amplification of optical anisotropy.<sup>96</sup>

The changes in the photoalignment of polymer films with *p*-cyanoazobenzene side chains were followed by measuring the photobirefringence upon heating. Whereas the optical anisotropy generated in a film of the amorphous polymer decreases monotonically and disappears completely above the  $T_g$ ,





**Figure 3.** Continuous changes of photobirefringence of thin films of polymers with *p*-cyanoazobenzene side chains (**2**, **12**, **13a**, and **13b**) generated by irradiation with linearly polarized 436 nm light upon heating. **2** and **12** are semicrystalline and amorphous, while both **13a** and **13b** are liquid crystalline (Table 1).

**Table 1.** Physical Properties of Azobenzene Polymers

Polymer	$T_g$ (°C)	$T_{sl}$ (°C)	$M_w \times 10^{-4}$	$M_w/M_n$
<b>2</b>	185		4.3	3.3
<b>12</b>	73			
<b>13a</b>	109	160	2.6	2.9
<b>13b</b>	61	168	3.4	3.6

films of an LC polymer with azobenzene side chains (glass 75 °C, smectic 102 °C isotropic) exposed to linearly polarized light at room temperature displays a gradual increase in the photobirefringence upon heating and a marked increase at ca. 80 °C, followed by the thorough disappearance at 100 °C.<sup>67</sup> Changes of optical anisotropy of photoaligned ultrathin films of azobenzene polymers (**2**, **12**, **13a**, and **13b**) can be monitored continuously by using ellipsometry as a function of temperature rise.<sup>97</sup> The properties of the polymers are listed in Table 1. The results shown in Figure 3 reveal that photobirefringence of the amorphous polymer (**12**) is reduced at temperatures close to  $T_g$  and disappears completely above  $T_g$ , while the annealing of photoirradiated films of both of the LC polymers (**13a** and **13b**) enhances the photobirefringence. It is worth noting that the semicrystalline polymer (**2**) exhibits extreme thermostability of the photobirefringence even at temperatures above 250 °C.<sup>57</sup>

### C. Three-Dimensional Photoorientation by Slantwise Photoirradiation

As mentioned in the Introduction, no light absorption occurs when the transition moment of a chromophore molecule lies just in parallel with the propagation of the light. In principle, this condition provides a way to manipulate the optical axis of photochromic molecules three-dimensionally, being determined by the propagation direction of light.<sup>18</sup> This kind of three-dimensional photocontrol of molecular orientation by irradiation with nonpolarized light is mentioned above in the case of a composite system consisting of a nematic LC and cross-linked

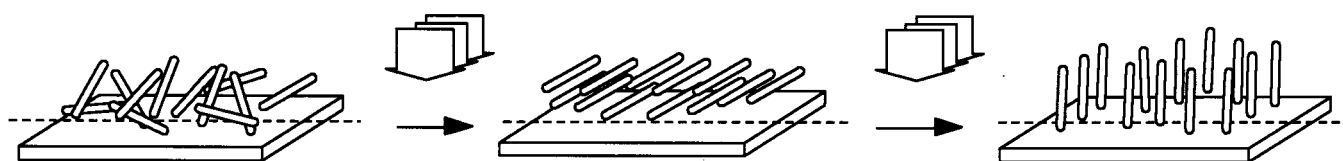
polymer networks tethering azobenzene side chains.<sup>38</sup> Since the transition moment of azobenzene lies approximately in parallel with the longitudinal molecular axis, the reduction of  $\pi, \pi^*$  absorbance leading to photobleaching of thin films of photochromic polymers should be observed upon prolonged photoirradiation of a film of a polymer incorporating azobenzene when the light comes from surface normal.

Although numerous studies have been, so far, made on the photochemical behavior of polymers containing azobenzenes either bound covalently or dissolved physically, no clear indication of such photobleaching has been reported until quite recently, to the author's knowledge. For example, Stumpe et al. observed that a Langmuir–Blodgett multilayer of the amphotropic polymer with azobenzene side chains (**14**) demonstrates a reduction of the  $\pi, \pi^*$  absorbance upon irradiation with unpolarized visible light,<sup>98</sup> suggesting that the spectral changes are ascribable to the homeotropic (perpendicular) reorientation of the azobenzene chromophores. Wang et al. mentioned photobleaching upon irradiation of a layer of the azobenzene LC polymer (**15**) with circularly polarized light and insisted the photoreorientation of azobenzene chromophores in the direction of the light propagation,<sup>69</sup> while the reduction of photobirefringence upon alternate exposure for monitoring the rewritability was assumed to be ascribed to perpendicular reorientation.<sup>68</sup>

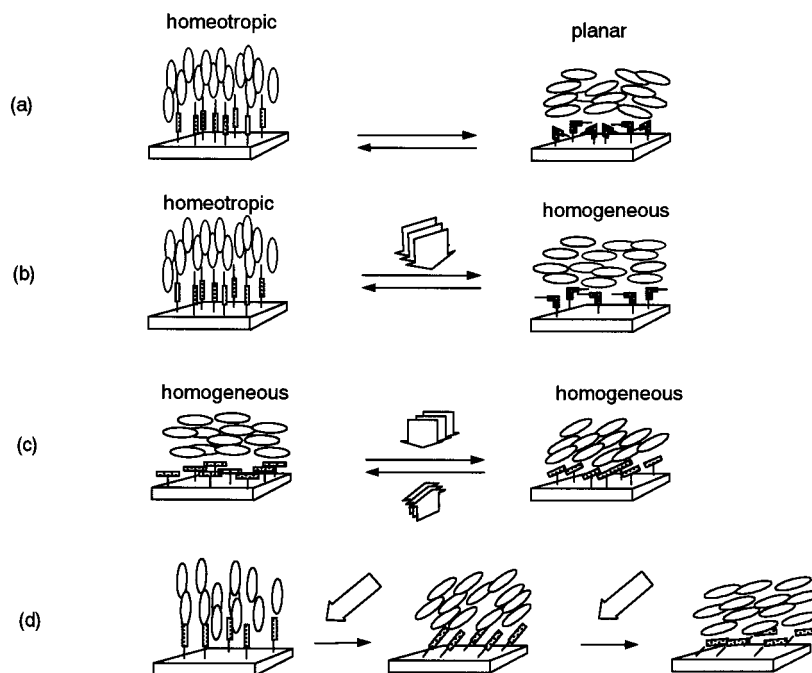
Spectroscopic evidence for the photoreorientation of azobenzene determined by the light propagation was presented first by using a film of the amorphous polymer with azobenzene side chains (**16**).<sup>99</sup> Slantwise photoirradiation of the film with unpolarized light resulted in tilting the molecular axis of the azobenzene tethered to polymer backbones toward the direction of light incidence. Unequivocal observation was performed by using the azobenzene LC polymer (**17**).<sup>100</sup> When a spin-cast thin film of the polymer is exposed to nonpolarized light, the molecular axis of azobenzene groups aligns in line with the propagation direction of the light, accompanied by the formation of H-aggregation. The results provide a convenient way to manipulate the three-dimensional orientation of the photochromic molecules solely by selecting the incident direction of light for photoisomerization. A similar observation was made by using a conoscopic microscope.<sup>101</sup>

As stated above, major interest in the photoreorientation induced by irradiation with linearly polarized light has been focused on the photocontrol of azimuthal alignment of photochromic molecules, which arises from the angular-selective light absorption. It was revealed that the biaxial reorientation of azobenzene results from irradiation of a film of an LC polymer with azobenzene side chains with linearly polarized light at higher temperatures, maintaining a mesophase.<sup>102</sup> Azimuthal photoreorientation in the direction perpendicular to the electric vector of the light takes place easily, followed by gradual reorientation toward the propagation direction of the polarized light, as sketched in Figure 4.





**Figure 4.** Illustrative representation of successive reorientation of azobenzene moieties tethered to an LC polymer backbone displaying in-plane reorientation, followed by homeotropic reorientation, upon irradiation with linearly polarized 436 nm light.



**Figure 5.** Illustrative representation of surface-assisted photoalignment control of LC molecules triggered by photochromic molecules tethered to a substrate surface. (a) Out-of-plane LC photoalignment between homeotropic and planar modes triggered by *EZ* photoisomerization of photochromic surface molecules upon alternate irradiation with nonpolarized light UV and visible light. (b) Out-of-plane LC photoalignment between homeotropic and homogeneous modes triggered by alternate irradiation with linearly polarized UV light and nonpolarized light. (c) In-plane photoalignment by irradiation with linearly polarized light. (d) Tilt-angle generation with slantwise photoirradiation.

#### IV. Surface-Mediated Photoalignment Control of Nematic Liquid Crystals

##### A. Versatility of Surface-Assisted Photoalignment of Liquid Crystals

The orientation direction of the molecular axis (director) of LCs relative to a surface plane of a substrate is critically determined by the nature of the surface.<sup>103</sup> There are two extremes of LC orientation: homeotropic alignment, where the LC director is perpendicular to a substrate surface, and planar one, which displays the LC director parallel to a substrate whereas the molecular direction is randomly distributed. Note that homogeneous alignment with practical significance is referred to as a uniaxially aligned state having an orientation parallel to the surface. Homeotropic alignment is readily available by modifying the surface with amphiphilic molecules or long-chain alkyl silylating reagents.<sup>104</sup> On the other hand, a typical method to yield a homogeneous (unidirectionally parallel) alignment is based on the rubbing treatment of a polymer thin film covering a substrate. Suitable modification of substrate surfaces provides LC directors with tilt angles with respect to the surface, maintaining uniaxial orientation.

When a substrate surface is modified with photochromic molecules to alter the chemical structures and molecular orientation of the uppermost surface (command surface) in molecular levels, the alignment of nematic LC is controlled reversibly by alternate irradiation.<sup>24,25</sup> Thin films of polymers active for LC photoalignment have been called command layers sometimes. This kind of phototriggered control of LC alignment was first reported in 1988.<sup>105</sup> The photoalignment is performed by substrate surfaces modified with photochromic units of a surface density of 1 unit/nm<sup>2</sup> or less.<sup>105,106</sup> Such photoactive surfaces have been referred to as 'command surfaces' since each photochromic unit brings about the reversible alignment transformation of about 10<sup>4</sup> LC molecules.<sup>24,25,105–107</sup>

There are four modes of the LC alignment controlled by command surfaces, as illustrated in Figure 5. The first one called 'out-of-plane alignment' photocontrol involves the reversible alignment change between homeotropic and planar modes. When UV actinic light is linearly polarized to lead to the polarization photochromism of azobenzenes on surfaces, a planar alignment becomes uniaxial to give a homogeneous alignment which reverses to the homeotropic alignment due to the backward isomeriza-

**Table 2. Command Layers for LC Photoalignment**

Layer	Photochemistry	Representative chromophores
Molecular films — LB films — SAM films	E/Z photoisomerization	Azobenzene Stilbene $\alpha$ -Hydrazono- $\beta$ -ketoester Cinnamate
	Electrocyclic reaction	Spiropyran
Polymer films — Spin-cast — Adsorption — LB deposition — Surface-selective modification	E/Z photoisomerization	Azobenzene Cinnamate Benzylidene-phthalimidine
	Photodimerization	Cinnamate Coumarin Benzylidene-phthalimidine Benzylideneacetophenone
	C=O photochemistry	Imide

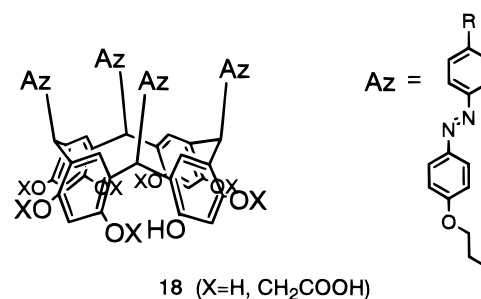
tion. Slantwise exposure with nonpolarized UV light also gives rise to a homogeneous alignment.<sup>39,40</sup> This is the second type. The third one is referred to as the 'in-plane alignment' photocontrol which has been achieved by irradiation with linearly polarized light for photochromic reactions of surface molecules. The fourth consists of the control of tilt angles of an LC director by an appropriate choice of photoactive molecules at the uppermost surfaces, which is subjected to slantwise photoirradiation.

## B. Preparation of Command Surfaces

The materials that have been employed, so far, for the LC photoalignment control are classified into two groups: molecular films and polymeric films (Table 2). Since the photoalignment is performed by photo-reactive molecules or residues localized at a topmost surface of a substrate plate, even monolayered molecular films work sufficiently to achieve the LC photoalignment. Whereas the Langmuir–Blodgett (LB) technique consisting of transferring a floating monolayer on a substrate plate on water under surface compression is one of the conventional ways to provide precisely designed monolayers, closely packed monolayers derived from photochromic amphiphiles are rather unsuitable for the preparation of command surfaces. This is because photochromic reactions such as *E/Z* photoisomerization are accompanied by relatively large sweep volumes, which are required for the structural transformation to result in the marked reduction of the level of photochromic reactions. In this context, the crown conformer of calix[4]resorcinarene derivatives substituted with azobenzene residues (**18**) was designed to ensure efficient *E-to-Z* photoisomerizability of the chromophore even in densely packed LB monolayers<sup>108</sup> because the occupied area of this kind of cyclic

amphiphiles is determined not by a cross-sectional area of by the azobenzene, but specifically by the base area of the cyclic skeleton.

Modification of the surface of silica plates with photochromic silylating reagents was used extensively to make the surface photoactive, however.<sup>106–108</sup> A general procedure involves the immersion of a fused silica plate in a solution of photochromic compounds substituted with an alkoxy-silyl residue, followed by heat treatment of a wet plate at an elevated temperature to fix the photochromic unit covalently. Another convenient approach is to modify a substrate surface by adsorption technique to fabricate self-assembled monolayers. For example, a thin film of poly(acrylic acid) is spin cast on a substrate plate, followed by immersing the plate in a solution of an azobenzene bearing an amino residue which interacts with carboxyl groups of the polymer film.<sup>109</sup> Surface plasmon spectroscopy provides a novel method to monitor the response of the photochromic molecular ultrathin layers.<sup>110</sup>



Polymer films are good candidates for preparing command layers. Whereas polymers doped physically with photoreactive guest dye molecules are occasionally employed, polymers with photochromic side

chains bound covalently are extensively used for the fabrication of command layers. Thin films of photochromic polymers are prepared by spin coating, LB deposition, and surface adsorption. Spin coating is the most frequently used technique to provide command layers, while the LB deposition of monolayers of amphiphilic photochromic polymers is of significance in the elucidation of the relationship between the chemical structures of command surfaces and their ability to control the LC photoalignment.

The most conventional way to fabricate photoreponsive LC cells is to put a nematic LC between two surface-modified substrate plates. A hybrid cell is occasionally assembled with a photochromic plate and a substrate plate, which brings about homogeneous or homeotropic alignment caused by conventional surface treatments. Photoinduced alignment alteration is followed by monitoring the transmitted light intensity of a linearly polarized He-Ne laser beam passed through an LC cell and a polarizer at the crossed position. The azimuthal orientational direction of LC molecules as a result of linearly polarized light irradiation, as illustrated in Figure 5b,c, is conveniently determined by measuring the dichroism of a dichroic guest dye dissolved in the LC.

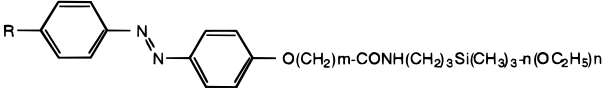
### C. Out-of-Plane Photoalignment

#### 1. Silica Surfaces

Because of their good availability and acceptable photofatigue resistance, azobenzene derivatives have been extensively used for surface photofunctionalization. Azobenzene displays a marked transformation of molecular shapes upon photoirradiation between the rodlike *E* isomer and the V-shaped *Z* isomer, accompanied by a marked polarity change. Consequently, *E/Z* photoisomerization of azobenzene residues tethered to substrate plates through silylation induces a drastic change in LC alignment between homeotropic and planar alignment, as sketched in Figure 5a. The photoalignment is influenced critically by the chemical structures of silylating reagents incorporating azobenzene, as shown in Table 3.<sup>106</sup> Table 4 summarizes the photoalignment control by azobenzenes tethered to a silica surface, which is modified with 3-aminopropyltriethoxysilane in advance, by the Michael addition of acrylated derivatives<sup>111</sup> or Schiff base formation with the corresponding aldehydes. The results compiled in both of the tables display the important role of the *para*-substituent (R) in the photoalignment. Hydrophobic long-chain alkyls and cyclohexyl residues at the *p*-position favor homeotropic alignment, whereas hydrophilic substituents including chloro and cyano are not appropriate for the out-of-plane photoalignment control because of the generation of planar alignment before UV irradiation.

The spacer effect is also to be taken into account. Whereas no photoalignment is induced by *p*-methoxyazobenzene when the chromophore is tethered to a silica surface through silylation (Table 3), the same moiety attached to an aminated silica surface through the Michael reaction exhibits the ability to result in the out-of-plane photoalignment (Table 4). A longer

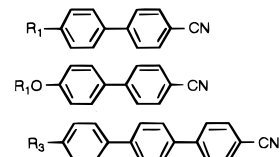
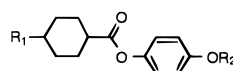
**Table 3. Structural Effect of Azobenzene Silylating Reagents on the Out-of-Plane Photoalignment**



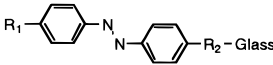
R	m	n	Alignment	Photocontrollability	
				DON-103	RO-571
H	5	3	p	-	-
Cl	5	3	p	-	-
CH <sub>3</sub> O	5	3	p	-	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> O	5	3	p	-	-
CN	5	3	p	-	-
CNC <sub>6</sub> H <sub>4</sub> OCO	5	3	p	-	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	1	3	h	+	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	2	3	h	+	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	3	3	h	+	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	5	3	h	+	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	5	2	p	-	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	5	1	h	-	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	10	1	h	+	-
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub>	5	3	h	+	-
cyclohexyl	5	3	h	+	-

DON-103

RO-571



**Table 4. Structural Effect of Azobenzenes Tethered to an Aminated Silica Surface on LC Photoalignment<sup>a</sup>**



R <sub>1</sub>	R <sub>2</sub>	Alignment	Photocontrollability
CH <sub>3</sub>	OCO(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	p	-
CH <sub>3</sub> O	OCO(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	h	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	OCO(CH <sub>2</sub> ) <sub>2</sub> NH(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	h	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	O(CH <sub>2</sub> ) <sub>2</sub> O-C <sub>6</sub> H <sub>4</sub> -CH=N-(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	h	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	O(CH <sub>2</sub> ) <sub>5</sub> O-C <sub>6</sub> H <sub>4</sub> -CH=N-(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	h	+
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	O(CH <sub>2</sub> ) <sub>10</sub> O-C <sub>6</sub> H <sub>4</sub> -CH=N-(CH <sub>2</sub> ) <sub>3</sub> Si(O-) <sub>3</sub> -	h	+

<sup>a</sup> Abbreviations used: p, planar; h, homeotropic; +, positive photocontrol; -, no photoalignment.

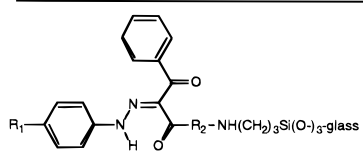
spacer such as a decamethylene unit seems to be favorable for the photocontrol of LC alignment; the photocontrollability of the silica surfaces is dependent on the spacer length when azobenzene units are attached to the surface by using the azobenzenes bearing a monoethoxysilyl group (Table 3).

Modification of the silica surface with binary mixtures of an azobenzene silylating reagent with a photochemically inert long-chain alkyl silylating reagent occasionally affects the photocontrollability.<sup>112</sup> Whereas the silylating reagent having unsub-

**Table 5. Structural Effect Of photochromic Units on Out-of-Plane LC Photoalignment**

Photochromic moiety	Alignment <sup>a</sup>	Photocontrollability
19	h	+
20	p	-
21	h	-
22	p	-
23	h	-
24	p	-
25	h	+ <sup>b</sup>

<sup>a</sup> Abbreviations used: H, homeotropic; p, planar. <sup>b</sup> One-way photoalignment.

**Table 6. Out-of-Plane Photoalignment by  $\alpha$ -Hydrazone- $\beta$ -ketoester Groups**


Substituent (R <sub>1</sub> )	Spacer (R <sub>2</sub> )	Alignment <sup>a</sup>			
		Initial	UV	VIS	Heating <sup>b</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-	h	h	h	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-OCH <sub>2</sub> CO-	h	p	p	h
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-O(CH <sub>2</sub> ) <sub>5</sub> -	h	p	p	h
CH <sub>3</sub> O	-OCH <sub>2</sub> CO-	h	p	h	h
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-O(CH <sub>2</sub> ) <sub>2</sub> OCOCH <sub>2</sub> CH <sub>2</sub> -	h	p	h	h
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-O(CH <sub>2</sub> ) <sub>6</sub> OCOCH <sub>2</sub> CH <sub>2</sub> -	h	p	h	h
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	-O(CH <sub>2</sub> ) <sub>11</sub> OCOCH <sub>2</sub> CH <sub>2</sub> -	h	p	h	h
CH <sub>3</sub> O	-O(CH <sub>2</sub> ) <sub>6</sub> OCOCH <sub>2</sub> CH <sub>2</sub> -	r	r	r	

<sup>a</sup> Abbreviations used: h, homeotropic; p, planar; r, random. <sup>b</sup> Heated at 65–70 °C.

stituted azobenzene is not photoactive for the out-of-plane alignment control because of the generation of planar alignment,<sup>106</sup> as shown in Table 3, the co-modification with dodecyltriethoxysilane makes the LC alignment homeotropic, leading to reversible LC photoalignment control under an appropriate choice of the molecular ratio of both components.

The photoalignment is influenced by the nature of LC molecules. The behavior of a cyanobiphenyl-type LC (RO-571) with a positive dielectric anisotropy is quite different from that of DON-103 with a negative dielectric anisotropy,<sup>113</sup> as seen in Table 3. Since the former LC aligns homeotropically due to the polar CN headgroup interactive with a polar surface, it is significant to choose a suitable azobenzene surface modifier and an optimal mixing ratio of the azobenzene and a long-chain alkylation reagent.

Photochromic units other than azobenzenes were examined by using photochromic silylating reagents. The results are summarized in Tables 5 and 6. Among the photochromic reactions tested, the geometrical photoisomerization of a stilbene (**19**)<sup>114</sup> and

$\alpha$ -hydrazone- $\beta$ -ketoesters (**26**)<sup>115</sup> displays the ability to manipulate the out-of-plane photoalignment reversibly. The stilbene is substituted with 4-octyloxy residue.  $\alpha$ -Hydrazone- $\beta$ -ketoesters exhibit quite a similar substituent effect. The *p*-hexyl substituent makes the LC alignment homeotropic so that UV irradiation at 365 nm results in the transformation into a planar alignment. On the other hand, no out-of-plane alignment was generated by the introduction of *p*-methoxy when the photochromic unit is attached through silylation. It should be mentioned here that reversibility of the LC alignment is crucially influenced by spacer groups. Whereas the reversible out-of-plane LC alignment is achievable by alternate irradiation with 365 and 440 nm light when the photochromic unit is introduced by the Michael addition of the corresponding acrylate derivatives to an aminopropylated silica surface (from the fifth to the eighth samples in Table 6), the reverse process from planar to homeotropic alignment occurs only by heating when a silica surface is modified with  $\alpha$ -hydrazone- $\beta$ -ketoester units through silylation (from the first to the fourth samples in Table 6). The other photoisomerizable moieties including *p*-dimethylaminocinnamylidene (**20**), retinylidene (**21**), and spiro-pyrane (**22**) groups do not work for the LC photoalignment since they bring about planar alignment before photoirradiation.<sup>114</sup> Although a hemithioindigo substituted with a hexyloxy group (**23**) exhibits homeotropic alignment,<sup>114</sup> no planar alignment is induced because of the irreversible consumption of the chromophore upon UV irradiation. A chalcone bearing a 4-octyloxy substituent gives rise to a planar alignment, though the process is irreversible probably due to the photodimerization.<sup>116</sup>

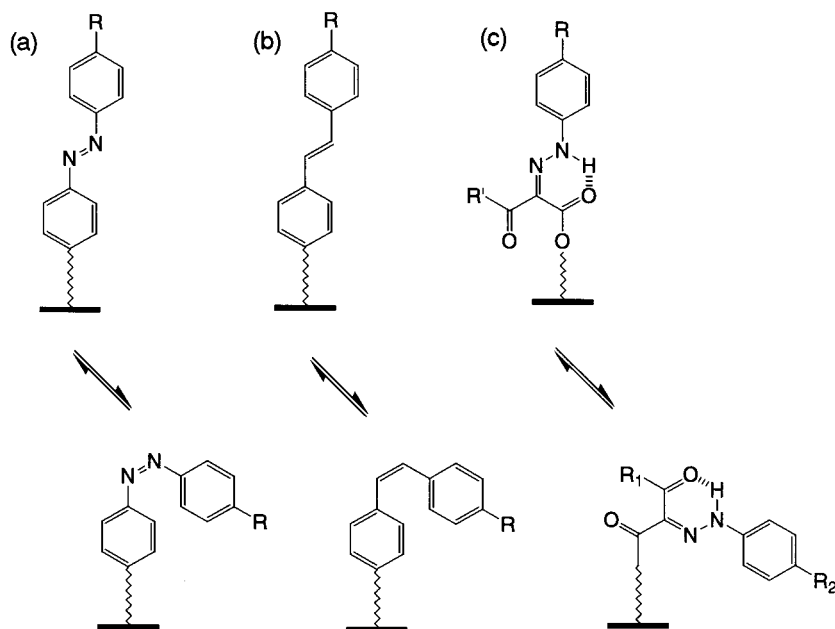
In summary, there is a common feature in chemical structures among the *E/Z*-photoisomerizable moieties having the ability to lead to the out-of-plane photoalignment. They exhibit reversible changes between rodlike and V-shaped forms (Figure 6). UV irradiation causes the drastic shape change to trigger the reorientation of LC molecules to give rise to planar alignment. Appropriate introduction of a hydrophobic alkyl substituent to these photochromic chromophores results in homeotropic alignment so that reversible out-of-plane orientation is performed.

## 2. Photochromic Polymer Surfaces

Alternating irradiation with UV and blue light for the photoisomerization of azobenzene side chains attached to vinyl polymers induces the reversible out-of-plane transformation of LC alignment (Figure 5a) when LC cells are made of a couple of substrate plates which are spin-coated with the azobenzene polymers.<sup>117,118</sup>

Some of the kinds of polymers that have been prepared are shown in Figure 7. The first type (**27**) is derived from PVA by partial esterification, while the second one is prepared by the radical polymerization of acrylated or methacrylated azobenzenes (**28**).<sup>118</sup> Acrylamide-type polymers have also been prepared. It is noteworthy that the azobenzene chromophores attached to side chains of vinyl polymers sometimes display a blue shift in their UV





**Figure 6.** Photochromic units exhibiting the out-of-plane LC photoalignment.

absorption band due to the  $\pi-\pi^*$  transition because of the formation of chromophoric aggregates. For example, heat treatment of a thin film of a PVA substituted with an azobenzene (**27**;  $m = 5$ ,  $n = 1$ ) results in a spectral change due to aggregation of the azo chromophore, which reverses again to the monomeric form after one cycle of alternating UV and visible light irradiation.<sup>117</sup> Novel ladder-like polysilsesquioxanes bearing azobenzene side chains (**29**) were prepared to demonstrate the out-of-plane photoalignment.<sup>119</sup>

The functionality of photochromic thin films to give rise to the out-of-plane photoalignment is complicated and dependent on the structure of the polymers, and sometimes no photoresponse is induced. The results are summarized in Table 7. Although distinct photocontrol of the out-of-plane LC alignment is achieved by using a thin film of an azobenzene-modified PVA (**27**),<sup>117</sup> occasionally no photoalignment is obtained until the cells are heated to an isotropic melt of nematic LCs when substrates are covered with poly(acrylates) and poly(methacrylates) bearing azobenzene side chains.<sup>118</sup> These facts indicate that microscopic mixing at an interface region between an LC layer and the surface of an azobenzene polymer film must be a key step to establish the photoresponsiveness.

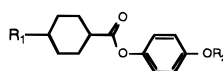
Since the photoalignment is caused by the structural alteration of monolayered photochromic units at a topmost surface, thick polymeric films are not required for the film thickness to be considerably reduced. For this purpose, adsorption of azobenzene polymers on substrate surfaces is one of the methods for photoalignment control.<sup>117,118</sup> Photoresponsive cells are simply assembled by sandwiching a nematic LC between a couple of substrate plates, after dissolving an azobenzene pendant polymer in the LC.<sup>117</sup> The polymer is adsorbed spontaneously to make the silica surface photoactive. Another method to make polymer surfaces photoactive for LC alignment control involves the surface adsorption of low-molecular-

**Table 7. Out-of-Plane Photoalignment Control by Azobenzene Polymers<sup>a</sup>**

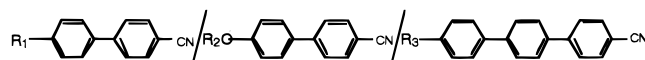
Polymers	Aggregation of Az		Induced alignment change	
	Before	After	DON-103	RO571
	baking			
<b>43</b> ( $m=5, n=1$ )	-	++	P	
<b>44a</b>			N	N
<b>44b</b>			N	N
<b>44c</b>			N	N
<b>44d</b>			N	N
<b>44e</b>	-	+	N	N
<b>44f</b>	-	+	N	P
<b>44g</b>	-	++	N	P
<b>44h</b>	-	-	N	N
<b>44i</b>	++	++	P	
<b>44j</b>	-	-	N	N
<b>44k</b>	-	-	N	N

<sup>a</sup> Abbreviations used: -, No aggregation; +, slight aggregation; ++, prominent aggregation; N, negative response; P, positive response.

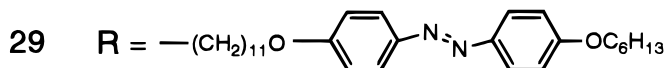
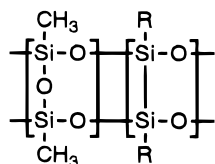
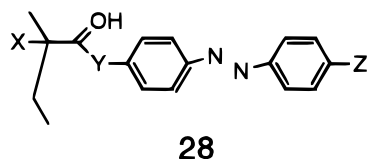
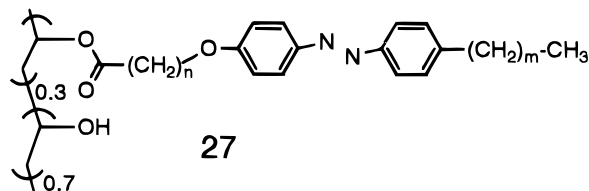
DON-103



RO571



weight azobenzenes.<sup>120</sup> Aminoalkylated azobenzenes are conveniently used for adsorption on surfaces of a fused silica plate and a thin film of poly(acrylic acid) spin cast on a substrate plate.<sup>120</sup>



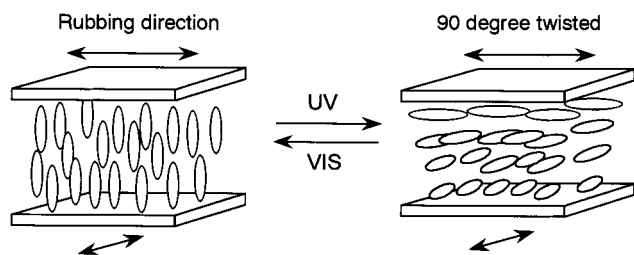
	X	Y	Z
<b>28a:</b>	H	O	H
<b>28b:</b>	H	O	CH <sub>3</sub>
<b>28c:</b>	H	O	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> -
<b>28d:</b>	H	O	CH <sub>3</sub> O-
<b>28e:</b>	CH <sub>3</sub>	O	H
<b>28f:</b>	CH <sub>3</sub>	O	CH <sub>3</sub>
<b>28g:</b>	CH <sub>3</sub>	O	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> -
<b>28h:</b>	CH <sub>3</sub>	O	CH <sub>3</sub> O-
<b>28i:</b>	CH <sub>3</sub>	-O(CH <sub>2</sub> ) <sub>11</sub> OCO-	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> -
<b>28j:</b>	H	NH	H
<b>28k:</b>	CH <sub>3</sub>	NH	H

**Figure 7.** Azobenzene polymers suitable for the out-of-plane photoalignment control.

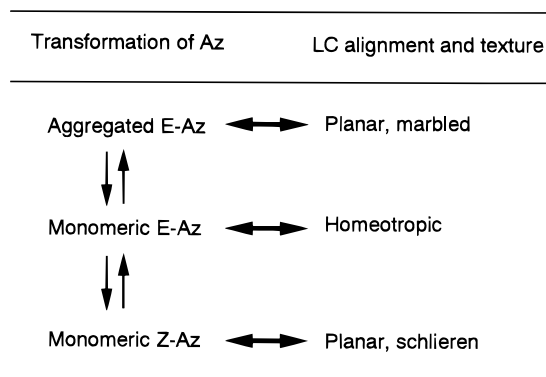
Analogous to surface modification of silica substrates, a thin film of poly(vinyl alcohol) (PVA) was subjected to surface-selective esterification with *p*-hexylazobenzene acid chlorides or acetalization with *p*-hexylazobenzene aldehydes in benzene.<sup>121</sup> The surface-modified PVA thin films are subsequently rubbed to fabricate LC cells exhibiting homeotropic alignment. Upon UV irradiation, a homeotropic alignment is converted into a homogeneous one when a cell is made by placing a nematic LC between a couple of plates covered with the modified PVA. These results imply that uniaxially oriented, homogeneous LC alignment arises from two factors: the planar LC alignment due to the formation of *Z* isomers and the uniaxial alignment owing to the rubbing effect. Guest–host cells are assembled by dissolving dichroic dyes in LCs to visualize photoimages with the use of a single polarizer. A photoresponsive twisted nematic

(TN) cell can be assembled by setting the rubbing direction of the two plates in a crossed position (Figure 8). Note that the working mode is quite similar to that of conventional LC display devices driven by the electric-field application.

The photoinduced alignment alteration described so far takes place reversibly between bistable states: homeotropic and planar states (Figure 5a). An extraordinary photoalignment change is observed when a thin film of a polymethacrylate substituted with *p*-hexylazobenzene in the side chain through a long alkylene spacer (**28i**) is used (Figure 9).<sup>122,123</sup> Before irradiation, a nematic LC shows a marbled texture corresponding to a planar alignment. UV irradiation results in the alignment change to form a transient homeotropic mode in the early stage of the irradiation, followed by the formation of a schlieren texture exhibiting another type of planar alignment. This



**Figure 8.** Light-driven TN cell of a nematic LC placed between a couple of substrate plates, the surface of which is coated with a PVA film, followed by surface-selective chemical modification with an azobenzene and by rubbing treatment. The cell assembly is made in such a way that the rubbing direction of both plates is at a crossed position. Homeotropic alignment is generated by the *E* isomer of the azobenzene, while UV irradiation of the cell leads to a 90° twisted state as a result of *E*-to-*Z* photoisomerization.



**Figure 9.** Photoalignment changes among three states induced by a film of the azobenzene polymer **28i**.

kind of alignment transformation between the marbled and schlieren textures through a homeotropic state occurs reversibly, while the transient homeotropic state is stable in the dark. This unique phenomenon is interpreted in terms of the microscopic modification of a polymer thin film. The azobenzene homopolymer having a long spacer exhibits a blue-shifted  $\pi-\pi^*$  transition band owing to the aggregation of the *E* isomer even at room temperature. It follows that the aggregated state of the *E* form is destroyed in the early stage of UV irradiation by the partial formation of the bent *Z* isomer to bring about a homeotropic alignment, followed by formation of a photostationary state containing *Z* isomer as a major component to give a schlieren texture. This process proceeds reversibly upon illumination of a UV-exposed film with blue light, resulting in the transient recovery of the monomeric *E* form, which is converted into the aggregated state upon further illumination to regenerate a marbled texture.

Because photochromic reactions such as the geometrical photoisomerization of azobenzenes and stilbenes are accompanied by marked changes in the molecular structures, a sufficient free volume is required in LB films embedding these kinds of photochromic moieties. In fact, the photoisomerizations accompanied by the expansion of occupying areas of photochromic amphiphiles are severely suppressed in their LB films.<sup>124,125</sup> Polymeric amphiphiles incorporating photochromic units are good candidates to give photoactive LB films applicable to

**Table 8. Surface-Assisted In-Plane Reorientation of a Nematic Liquid Crystal by Linearly Polarized UV Light Irradiation of the LB Layers of Azo-Modified PVAs (43)<sup>a</sup>**

Tail length (m)	Spacer length (n)	Number of Layers				
		1	3	5	7	9
0	10	○	△	n. d.	n. d.	//
1	10	○	△	n. d.	n. d.	//
4	10	○	△	n. d.	n. d.	//
6	10	○	△	n. d.	n. d.	//
8	10	○	△	n. d.	n. d.	//
10	10	○	△	n. d.	n. d.	//
12	10	×	△	n. d.	n. d.	//
6	1	×	×	//	//	//
6	5	×	○	△	//	//
6	10	○	△	//	//	//

<sup>a</sup> Abbreviations used: ○, Sufficient reorientation; △, insufficient reorientation; ×, no reorientation; //, LC molecules align in parallel with the dipping direction and show no reorientation; n.d., not determined.

command surfaces because occupying areas are determined not by photochromic units, but by hydrophilic polymeric backbone chains which possess larger occupying areas.

A family of PVAs substituted with azobenzenes in the side chains (**27**) have been prepared in order to obtain photochromic LB films which are active for alignment photoregulation. Owing to the partial esterification of hydrophilic PVA, the polymers with azobenzene side chains exhibit an amphiphilic character based on hydrophilic vinyl alcohol units and hydrophobic azobenzene units substituted with a long-chain alkyl tail. Employment of an appropriate surface pressure during the deposition of a polymeric monolayer on a plate enables ones to control the average density of azobenzene-containing chromophores on substrate surfaces. A minimum density of the photochromic units for the LC photoalignment is approximately 1.0 unit/nm<sup>2</sup><sup>126</sup> and quite in line with the value (0.83 unit/nm<sup>2</sup>) obtained by the covalent adsorption method through the silylation.<sup>106</sup> Similar to other deposited LB films, multilayered azobenzene-containing polymers demonstrate molecular orientation during the dipping procedure to lead to a homogeneous liquid-crystal alignment with a direction parallel to the dipping.<sup>126</sup>

Using these novel LB films, systematic studies have been carried out to elucidate factors of molecular structures of azobenzenes governing the photoinduced LC alignment switching.<sup>126-130</sup> The effects of spacer length (*n*) and tail length (*m* + 1) on the photoresponse of LC cells are summarized in Table 8. It should be stressed here that a cumulative layer is positive for the photocontrol whereas no photoalignment is observed by a monolayered film of a

PVA with azobenzene side chains (**27**;  $m = 5$ ,  $n = 1$ ). The ability to perform the out-of-plane photoalignment is influenced not only by the spacer length, but also by the tail length. The longer the tail is, the slower the photoresponse becomes. This slower response reflects the reorientation of photoisomerized azobenzene chromophores embedded in LB films resulting from the subsequent interaction of the chromophore with LC molecules after a sufficient relaxation period. These facts imply that photochromic units with suitable lengths of both spacer and tail interact with LC molecules intimately at a surface to bring about perpendicular arrangement of the command molecules to result in a homeotropic alignment. The photoisomerization of command molecules takes place rapidly to induce the reorientation of the LC surrounding them. The photoinduced switching of LC out-of-plane alignment at a surface region is followed by using optical waveguide structures containing an LC film held between two photoresponsive LB films.<sup>131,132</sup>

Electronic absorption spectra of LB monolayers are markedly dependent on the averaged density of the azobenzene chromophores, which is influenced by the level and mode of molecular aggregations. The spectral shape and absorption maximum of monolayered azo-modified PVA (**27**;  $m = 5$ ,  $n = 1$ ) are roughly in line with those in a solution when the monolayer is transferred at a surface area of  $1.02 \text{ nm}^2$ , showing that the azo chromophores are oriented in a random fashion without any specific interaction among the chromophores. On the contrary, a remarkable hypsochromic shift of the absorption band for the  $\pi-\pi^*$  transition is observed when the film deposition is made at a surface area of  $0.30 \text{ nm}^2$ , indicating aggregation of the azobenzene moieties through the side-by-side interaction due to a dense packing. Further studies on the molecular orientation of LB films of the amphiphilic azobenzene-containing PVA have been carried out with the aid of FT-IR measurements to obtain further information concerning the surface-induced alignment change of LC molecules.<sup>133</sup> The frequencies of the  $\text{CH}_2$  stretching bands are sensitive to the conformation of the hydrocarbon chains and afford crucial information on the ordered structure of the LB films. The results show that the hydrocarbon chains in a monolayered film is *trans*-zigzag to imply an ordered structure whereas those in multimonolayered films contain *gauche* conformers, indicative of disordered structures. The disordered structure is favorable for molecular interactions between the azobenzene and LC molecules to display the photoalignment.

As illustrated in Figure 5a, the out-of-plane photoalignment takes place between two extreme states through continuous orientational changes, determined by the extent of *E/Z* photoisomerization of surface molecules, leading to continuous alteration of retardation of LC layers filled in photoresponsive cells. In other words, tilt angles of LC molecules are controllable by the level of isomerization of photochromic molecules.<sup>134</sup> In fact, it was observed that tilt angles are continuously transformed from perpen-

dicular to parallel orientations by using LB films of azobenzene polymers.<sup>135</sup>

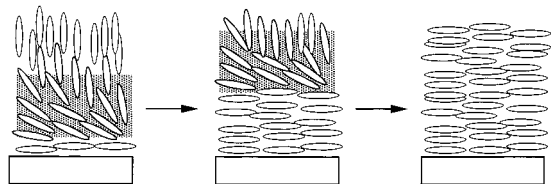
### 3. Working Mechanism

On the basis of the results stated above, the factors affecting the out-of-plane photoalignment are summarized as follows. (1) Monolayers or even submonolayers of suitable photochromic molecules are able to command the reversible changes of LC alignment. (2) Photochromic residues such as azobenzene, stilbene, and  $\alpha$ -hydrazono- $\beta$ -ketoesters active for the photoalignment display the marked alteration between rodlike and V-shaped forms to generate homeotropic and planar LC alignment, respectively. (3) The introduction of hydrophobic alkyl substituents at the *p*-position of the photochromic chromophores is favorable for the generation of homeotropic alignment. (4) There are critical occupied areas ( $S$ ) of photochromic units in the range of  $\text{ca. } 0.4 \text{ nm}^2 < S < \text{ca. } 1.0 \text{ nm}^2$  to realize the LC photoalignment. (5) The level of photoisomerization determines the tilt angles of LC molecules. (6) The surface-mediated LC photoalignment is influenced by the nature of LCs, whereas even an LC with an extremely low dielectric anisotropy is also subjected to the photoalignment control.

LC alignment determined by the nature of substrate surfaces has been interpreted in terms of the surface energy of the substrates and the physical deformation of surfaces. According to Jérôme, there are three classes of microscopic origin of macroscopic anchoring of LC molecules on surfaces.<sup>136</sup> They include smooth surfaces of glass plates and polymer films, interpenetrable layers prepared by grafting long alkyl chains at substrate surfaces, and surfaces having a certain topology such as a microgrooved morphology. The latter is not involved in the surface-assisted LC photoalignment, since the photoactive surfaces prepared by the procedures mentioned above have no chance to cause the deformation of the surface morphology. Though the relationship between the surface free energies and whether LC molecules are in a homeotropic or planar alignment mode has been claimed to be adequately applied to the interpretation of LC alignment,<sup>103</sup> this is not the case for the surface-mediated photoalignment control. Whereas the wettability of surfaces tethering azobenzenes is more or less modified by photoisomerization because of the marked polarity change of the chromophores,<sup>107</sup> the out-of-plane photoalignment is achieved even though essentially no alteration of the wettability of azo-modified plates is induced photochemically. On the other hand, no photoalignment is observed for a substrate plate modified with a spiropyran unit, which results in observable changes in the wettability.<sup>137</sup> Consequently, it is reasonably concluded that the out-of-plane photoalignment cannot be interpreted by the conventional theories.

All of the results described above support that intimate interactions between photochromic surface residues with LC molecules play a critical role in the photoalignment. In connection with this point, the generation of homeotropic alignment as a result of the intermolecular interactions was confirmed by





**Figure 10.** Illustrative representation of LC reorientation induced by a command surface. The gray zones indicate that the alignment of LC molecules is distorted.

spectroscopic alteration of azobenzenes at surfaces upon contact with LC layers.<sup>107,126</sup> The transition moment for the  $\pi, \pi^*$  excitation of azobenzene lies approximately in parallel with the molecular axis. This situation allows one to estimate the orientational direction of the chromophores localized at surfaces. It was observed that  $\pi, \pi^*$  absorbances of azobenzenes attached covalently to a silica surface or embedded in LB monolayers are reduced considerably upon contact with LC molecules.<sup>126</sup> These results mean that the chromophore units reorient perpendicularly with respect to a surface due to the interaction with the LC to give homeotropic alignment, whereas the orientational direction of the azobenzenes before wetting with the LC is randomly distributed.

Clearer evidence was obtained by fabricating hybrid LB monolayers comprised of an amphiphilic PVA with *p*-hexylazobenzene side chains (**27**;  $m = 5$ ,  $n = 10$ ) and a nematic LC, 4-cyano-4'-amylbiphenyl (5CB).<sup>138</sup> An equimolar mixture of the polymer and 5CB forms a floating monolayer with excellent homogeneity and is assumed to be an interfacial model. An LB film of the binary hybrid shows the marked reduction of both of the  $\pi, \pi^*$  absorption band of the azobenzene and absorption due to 5CB, showing that both molecules align perpendicular to a surface. Upon UV irradiation, the absorption due to 5CB increases, synchronizing with the *E*-to-*Z* photoisomerization. Thus, the out-of-plane photoalignment involves three steps consisting of the photoisomerization, the reorientation of LC molecules surrounding the photochromic residues, and the subsequent reorientation of bulk LC molecules. As illustrated in Figure 10, the photoisomerization of surface molecules gives rise to the orientational distortion of LC molecules at the interface so that the domino effect to spontaneous reorientation of the bulk LC layer emerges to minimize the elastic energies.

Intermolecular interactions at the interfacial region are discussed by using LB monolayers of cellulose and polypeptide derivatives with azobenzene side chains and LCs with positive, negative, and negligibly small dielectric anisotropy, respectively.<sup>135</sup> Note that the main chains of the biopolymers exhibit rigidity due to the helical structures. It was concluded that polar interaction between the photoformed *Z* isomer of azobenzene with a large dipole moment and LC molecules plays a significant role in the photoalignment from a homeotropic to planar mode, since an LC with a negative dielectric anisotropy displays the fastest photoresponse among the three types of LCs. Taking into account the facts that even stilbenes with a smaller dipole moment change give rise to the

photoalignment<sup>114</sup> and that the reorientation of an LC with a very small dielectric anisotropy takes place, it is hard to determine if the polar interaction plays a predominant role in the photoalignment. It is reasonable to attach more importance to van der Waals interactions between photochromic residues and LC molecules.

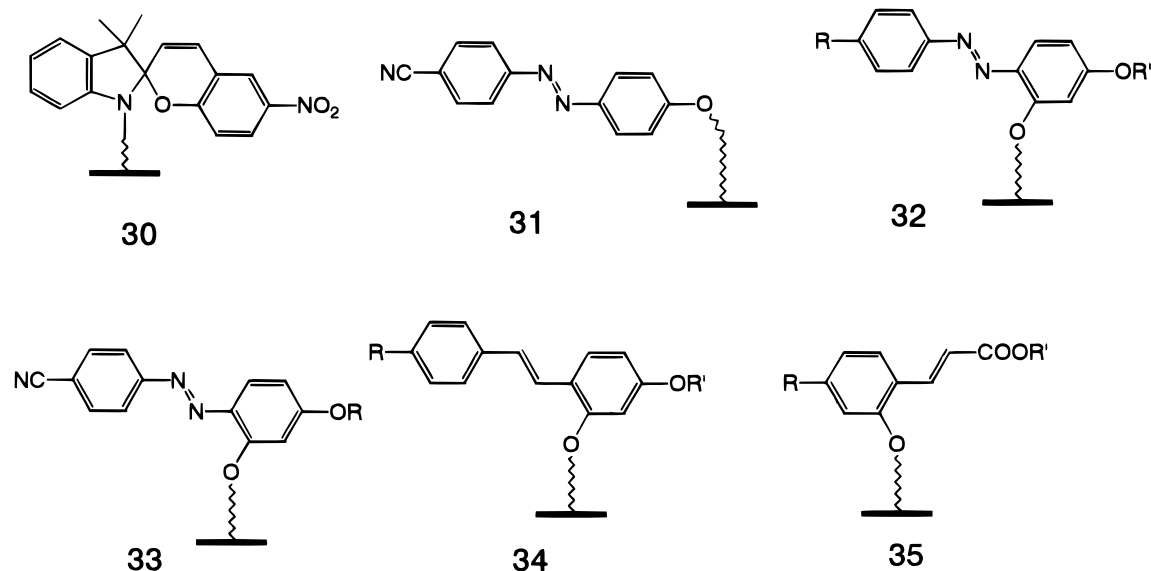
We recently observed that the ability to control the LC photoalignment from a homeotropic to homogeneous state triggered by a self-assembled monolayer of calix[4]resorcinarenes with azobenzene substituents (**18**)<sup>108,139</sup> is closely related with wetting hysteresis defined as the difference between advancing and receding contact angles of nematic LCs.<sup>140</sup> According to Fadeev and McCarthy, who stress a significant role of molecular-level topography and rigidity of monolayered surfaces in wettability, the hysteresis is small when alkyl chains in monolayers are flexible or packed densely to form smooth surfaces but larger when the monolayers are rigid and have a decreased ability to form smooth surfaces.<sup>141</sup> On the basis of this interpretation, it is reasonably concluded that the molecular-level roughness of the outermost surface leading to intimate interactions between LC molecules and surface azobenzenes plays a critical role in the photocontrol of LC alignment.

Concerning the working mechanism, a novel technique was applied to reveal the molecular reorientation of polymeric LB monolayers by measuring the generation of the Maxwell displacement current across a single layer of the amphiphilic PVA with *p*-hexylazobenzene side chains (**27**;  $m = 5$ ,  $n = 10$ ).<sup>142</sup> The displacement current of a monolayered film stems from three factors, including orientational changes of polar molecules, changes in the molecular density, and changes in surface potentials. The displacement-current measurements were made on a mixture of the polymer with nematic LCs in order to obtain information about the reorientational event of molecules at the surface.

## D. In-Plane Photoalignment

### 1. Molecular Films

Conventional LC display devices are assembled by using substrate plates with a transparent electrode, the surface of which is covered with rubbed thin films of a polyimide for LC-aligning films to give homogeneous alignment. The application of an electric field results in an electrooptical effect which stems from the reorientation of LC molecules with a positive dielectric anisotropy to form homeotropic alignment. When actinic UV light is linearly polarized to lead to the polarization photochromism of azobenzenes on a surface of substrates, giving rise to a homogeneous LC alignment, a similar alignment change displaying good reversibility is attained without any electric-field application for an LC cell, the wall of which is modified with azobenzenes. Homeotropic alignment is regenerated by the backward isomerization (Figure 5b).<sup>109,110,126</sup> While nonpolarized UV irradiation generates a planar alignment with a schlieren or marbled texture as stated above, a single domain exhibiting excellent optical quality is obtained by linearly polar-



**Figure 11.** Photochromic units attached to a silica surface for the in-plane LC photoalignment.

ized UV light. The photoaligned direction is just perpendicular to the electric vector of linearly polarized UV light, indicating that the optical axis of an LC layer is manipulated simply by changing the electric vector of the light. In fact, the photoaligned homogeneous alignment alters its azimuthal direction reversibly by rotating the electric vector of the UV light. It was confirmed that azobenzene monolayers display dichroism upon irradiation with linearly polarized UV light.<sup>143</sup>

When the orientation of LC molecules lies in parallel with a substrate surface before and after photoirradiation, the in-plane photoalignment is attainable (Figure 5c). A thin film of a polyimide doped with a dichroic azo dye in a relatively high concentration (33 wt %) was first used to demonstrate this kind of the photoalignment.<sup>143</sup> Irradiation of a nematic LC cell modified with the film with an Ar laser beam brings about the reorientation of LC molecules with an azimuthal direction perpendicular to the electric vector of the linearly polarized light. Similarly, the in-plane photoalignment is generated by linearly polarized light irradiation of a thin film of PVA dissolving methyl orange which shows *E/Z* photoisomerization.<sup>145</sup>

Systematic studies were made by using photochromic monolayers covalently attached to a silica surface (Figure 11), taking notice of the requirements for the in-plane LC photoalignment, LC molecules align parallel with photochromic surfaces before and after photoirradiation. As shown in Table 5, a spiroopyran monolayer (**30**) is not suitable for the out-of-plane photoalignment because of the formation of a planar alignment before UV photoirradiation.<sup>108</sup> This behavior is favorable for the in-plane photoalignment by irradiation with linearly polarized UV light.<sup>146</sup> The irradiation of an LC cell, the walls of which are treated with a spiroopyran silylating reagent, with linearly polarized UV light results in homogeneous alignment with the orientation perpendicular to the electric vector of the light. The photoinduced homogeneous alignment is stable on storage at ambient temperature.

Table 3 shows that azobenzenes with polar *p*-substituents such as a *p*-cyano group are inadequate to perform the out-of-plane photoalignment in the case of spiroopyran.<sup>106</sup> However, a planar alignment induced by the *p*-cyanoazobenzene (**31**) becomes homogeneous upon irradiation with linearly polarized blue light for  $n-\pi^*$  excitation.<sup>147</sup> It is noteworthy that the LC reorientation is markedly enhanced by heating a cell above  $T_{NI}$  of an LC. Rotation of the electric vector of the linearly polarized light leads to control of an azimuthal orientation at will.

A more sophisticated molecular design of the azobenzenes was undertaken to fulfill the requirements for the in-plane photoalignment. The azobenzenes (**32**) bear alkyl residues at both *para*-positions to mimic the size and shape of LC molecules.<sup>148,149</sup> The chromophores are tethered to a silica surface at the *ortho*- or *meta*-position so that the long molecular axis lies approximately in parallel with the surface. It was confirmed that the exposure of a plate modified with the azobenzene monolayer to linearly polarized blue light displays dichroism. Perpendicular reorientation of an LC is induced by irradiation with the light. Generation of the in-plane photoalignment is again enhanced dramatically by elevating cell temperatures above  $T_{NI}$  of the LC during the photoirradiation. A prominent feature of this type of rewritable cell is the anomalous stability toward heat and light. The extraordinary thermostability of the photoalignment implies that the thermal as well as photochemical randomization of the photoaligned state of the laterally attached azobenzene is considerably suppressed, probably because of the formation of supramolecular structures consisting of the azobenzene residues and LC molecules at the interface.

The effect of positional isomerism of the attachment of azobenzenes to a silica surface was studied by comparing the in-plane photoalignment induced by a head-on-type *p*-cyanoazobenzene (**31**) with that induced by the side-on-type counterpart (**23**).<sup>149</sup> Remarkable differences in the surface-mediated photo-reorientation of LC molecules were observed between both types of azobenzenes. Exposure doses required

for the photoreorientation are greatly reduced by the introduction of *p*-cyanoazobenzene in a side-on manner; the reorientation is complete at exposure energies of less than 50 mJ cm<sup>-2</sup> for the side-on type, whereas about 200 mJ cm<sup>-2</sup> exposure doses are required for the head-on type. A re-aligned angle after re-illumination of the side-on-type azobenzene with the polarized light levels off at an angle perpendicular to the electric vector of the light, but the head-on type exhibits a much smaller re-aligned angle, displaying the effectiveness of side-on-type attachment for the achievement of the in-plane photoalignment.

The in-plane photoalignment is performed similarly by using monolayers on a silica surface of *E/Z* photoisomerizable residues other than azobenzenes. Stilbenes (**34**)<sup>150</sup> and cinnamates (**35**)<sup>151</sup> were introduced to a silica surface at the *ortho*-position to achieve the side-on-type attachment since the head-on type results in the out-of-plane photoalignment, as mentioned above. Both types of molecules bring about the in-plane photoalignment, though they exhibit marked wavelength-dependence. In the case of the stilbenes (**34**), better photoalignment is generated by irradiation with linearly polarized 330 nm light, when compared with that obtained by polarized irradiation at 260 nm.<sup>150</sup> It was concluded that the photoalignment arises from a photostationary state containing the rodlike *E* isomer as a major component. In other words, the in-plane alignment is determined specifically by *E* isomer, while *Z* isomer bearing a bent structure plays no role in the photoalignment. Irradiation of side-on-type cinnamate (**35**) with linearly polarized 313 nm light induces no homogeneous alignment.<sup>151</sup> In a sharp contrast to this, linearly polarized 259 nm light results in homogeneous alignment, the orientational direction of which is switchable by changing the electric vector of the light. The interpretation of the wavelength dependence can be made as follows. Photoirradiation with 313 nm leads to the formation of *Z* isomer and (2 + 2) cycloadduct(s), both of which have no ability to align LC molecules, probably owing to their molecular shapes which are inconvenient for intermolecular interactions with rod-shaped LC molecules. On the other hand, irradiation with 259 nm light results in photocleavage of cyclobutane adduct(s) to regenerate the *E* isomer, which is active for the in-plane photoalignment. As described later, these results provide novel clues to elucidate the working mechanism for photoalignment triggered by thin films of polymers with photodimerizable side chains, which are of practical significance.

## 2. Polymer Films

Linearly polarized UV irradiation of LC cells made up of silica plates covered with LB films of amphiphilic azobenzene PVAs (**27**) yields the in-plane LC alignment to perform the second type of surface-assisted alignment photoregulation shown in Figure 5b.<sup>126</sup> Table 8 shows the structural effect of the LB films on the ability for the azimuthal reorientation control of LCs. The table tells us that the photoreponsive behavior is dependent on the number of

accumulated layers. In particular, azimuthal reorientation can be achieved specifically by monolayered films in general, although there are some exceptions. On the contrary, multilayered films cause the homogeneous alignment in parallel with the dipping direction, and no azimuthal reorientation is induced by irradiation with linearly polarized UV light. This shows that the conformational orientation of the polymer main chains wins over the photoinduced orientation of azo chromophores.

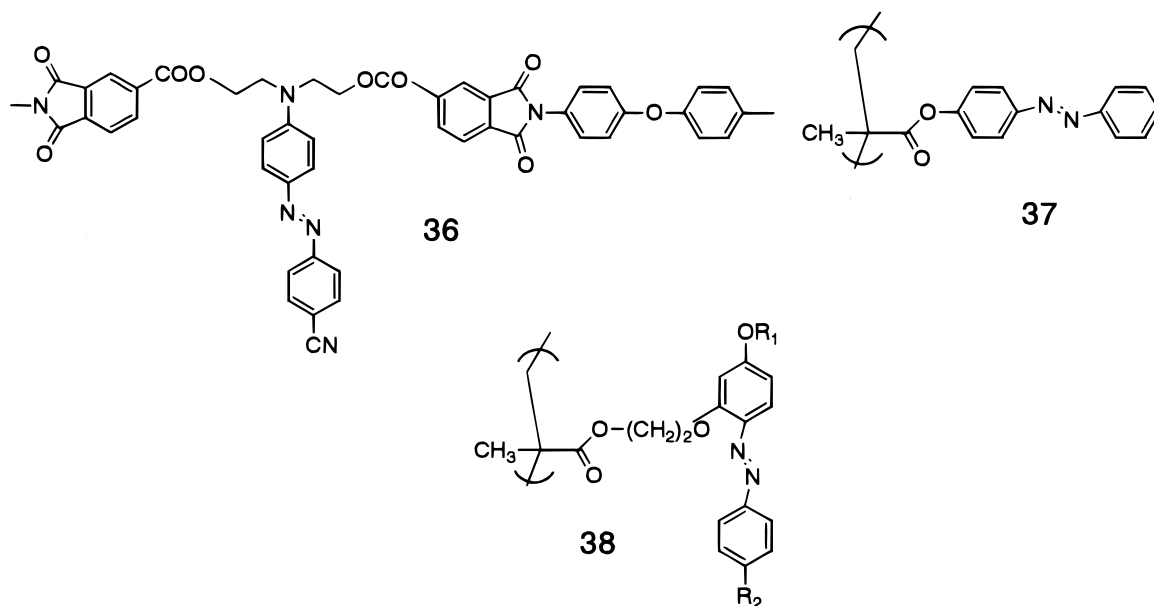
The third type of the alignment photoregulation (Figure 5c) using single-polarized light has been performed extensively by substrate surfaces covered with spin-cast films of polymers doped with dichroic dyes,<sup>144,145</sup> as mentioned already above, and polymers with azobenzene side chains.<sup>152,153</sup> This section deals with polymers bearing photochromic residues covalently. The generation of dichroism of films of photochromic polymers by irradiation with linearly polarized light has been described in section III.B in detail.

As revealed by experiments of the photoinduced in-plane alignment control by silica plates surface-modified with azobenzenes,<sup>148,149</sup> the azimuthal reorientation of LCs is achieved by the uniaxial conformational change of command molecules localized at a topmost substrate surface. This situation was confirmed by the following systems. The first consists of the chemical modification of PVA thin films. Careful treatment of PVA films with azobenzene acid chlorides in hexane yields the surface-selective introduction of the chromophores with a reasonable surface coverage of 2–3 units/nm<sup>2</sup>.<sup>154</sup> The second system is based on the deposition of a single LB monolayer of a polyimide-bearing *p*-cyanoazobenzene side chains (**36**) on a silica plate.<sup>155</sup> Homogeneous alignment is obtained for both cases.

Spin-coated films of polymers with pendant azobenzenes are other candidates for the azimuthal alignment photocontrol of LCs (Figure 12). When a homopolymer of 4-methacryloyloxyazobenzene (**37**) is spin-coated on a silica plate and exposed to linearly polarized light, followed by the cell assembly, a homogeneous alignment is obtained.<sup>152</sup> The uniaxial orientation of the mesophase fades away gradually even in the dark, however. This probably arises from the permeation of LC molecules into the polymer film to relax the photooriented state of the azobenzene moiety. This suggests that the combination of LCs with azobenzene polymers plays an essential role in the persistence of the photoinduced in-plane alignment of LCs. In fact, the storage stability of photoinduced homogeneous alignment was considerably enhanced by using thin films of poly(methacrylates) having laterally attached azobenzene side chains (**38**)<sup>153</sup> or poly(methacrylates) tethering azobenzene groups through a spacer (**16**).<sup>156</sup>

In a marked contrast to the case of the head-on-type azobenzene polymer (**37**), a homogeneous alignment induced by polarized light irradiated thin films of the side-on-type azobenzene-based polymers (**38**) displays excellent storage stability in the dark. These types of azo polymers show the following peculiarities. First, the reorientation of the azo chromophore





**Figure 12.** Azobenzene polymers for the in-plane photoalignment.

requires a polarized exposure energy of approximately  $100 \text{ mJ/cm}^2$ , whereas the exposure energy to complete the photoisomerization of azobenzene groups of the head-on-type polymer (**37**) amounts a few  $\text{J/cm}^2$ . Second, although the photodichroism of the chromophore in a polymer film is thermally labile so that about 25% was lost in 30 min, the homogeneous alignment is essentially not altered upon prolonged storage in the dark. It is very likely that the enhanced stability of the photoalignment arises from the molecular interaction between the azobenzene molecules and LC molecules to form a kind of supramolecular aggregate at the interface. The stabilized photoalignment generated by the polymer thin films enables one to achieve reversible reorientation of LCs by rotating the electric vector of polarized actinic light. It is noteworthy here that the reorientation of LCs requires 1 order of magnitude greater exposure energy of more than  $1 \text{ J/cm}^2$ . Thus, the molecular aggregation constituted by surface azobenzene residues and LC molecules shows a suppressive effect on the photoinduced reorientation of the command molecules.

In connection with the elucidation of the working mechanism of the in-plane photoalignment controlled by linearly polarized light irradiation, the experimental results are summarized as follows. (1) The in-plane LC photoalignment emerges upon irradiation of photochromic residues localized at the uppermost surfaces with linearly polarized light as a result of the photoreorientation of the photochromic moieties to give optical anisotropy, which is transferred to nematic LC layers. (2) Photochromic moieties capable of performing the in-plane photoalignment include azobenzene, stilbene, cinnamate, and spiropyran. (3) Larger exposure doses of linearly polarized light are required for the photoreorientation of LC molecules after cell assembly, when compared with those needed for the generation of optical anisotropy of films of photochromic polymers in absence of an LC. (4) The rate of photoreorientation of an LC assisted by photochromic monolayers at-

tached to a silica plate through silylation is markedly enhanced by heating the LC cell at temperatures above  $T_{\text{NI}}$  of the LC. (5) Photoalignment behavior of an LC brought about by azobenzene polymer films is crucially influenced by the chemical structures of azobenzenes.

A novel technique to achieve LC photoalignment was recently reported by using surface-relief gratings, which are described in section III.B.1.<sup>157</sup> As mentioned in section IV.C.3, LC alignment is generated not only by molecular-level interactions at the interfacial region between a surface and an LC layer, but also by the macroscopic deformation of the surface morphology including microgrooves.<sup>136</sup> A film of an azobenzene polymer spin cast on a substrate surface was exposed to circularly polarized Ar laser beams at 488 nm to fabricate a surface-relief grating as a microgroove. Nematic LC molecules placed in a cell assembled by the substrate plates display a uniform alignment, the direction of which is parallel to the microgrooves.

### E. Photocontrol of Tilt Angles

An alternate route to photogenerated homogeneous alignment consists of slantwise irradiation with nonpolarized light, the propagation direction of which is tilted from surface normal.<sup>39,40</sup> The azimuthal direction is in parallel with the direction of an incident plane, and the order parameter of the photoaligned LC layers is not far from that induced by irradiation with linearly polarized UV light. Conoscopic observation of the LC cell subjected to slantwise UV irradiation reveals that a cross point in conoscopic images, which represents the optical axis of an LC, moves to the incident direction of the UV light. By alternating irradiation with UV and visible light, the cross point can be intentionally moved back and forth reversibly.<sup>40</sup> This means that the slantwise exposure provides the uniaxial orientation axis with tunable tilt angles. In fact, tilt angles of an LC layer are altered continuously during



slantwise photoirradiation of a cell, as illustrated in Figure 5d.<sup>99</sup>

As stated in the previous sections, the orientational direction of azobenzenes tethered to polymer backbones is determined by the propagation direction of actinic light.<sup>99,100</sup> The tilt angle generation in the surface-assisted LC photoalignment evidently stems from this kind of three-dimensional orientational photocontrol of azobenzene chromophores. This implies that intermolecular interactions of LC with tilted azobenzene moieties at an uppermost surface brings about tilt angles of an LC layer. The level of tilting of LC directors depends not only on the extent of photoisomerization, but also on the excitation wavelength and the chemical structures of azobenzenes. Whereas very small tilt angles are generated by slantwise photoirradiation of films of a polymer with unsubstituted azobenzene side chains, the substitution of azobenzene chromophore with a *p*-trifluoromethoxy group give rise to much large tilt angles.<sup>158</sup>

Since the photogeneration of tilt angles of LC layers is of great significance from a practical viewpoint, other photosensitive systems will be mentioned later in connection with applications of surface-mediated photoalignment techniques.

## F. Surface-Assisted Photoalignment of Liquid Crystals Other Than Low-Molecular-Weight Nematics

Because the surface-assisted photoalignment of nematic LCs provides a novel technique to transfer photoaligned molecular information of surface layers to bulk LC layers with marked molecular amplification, the extension of this procedure to other mesophasic systems attracts great interest from both a fundamental and practical viewpoint. On the basis of the types of molecular order, LCs are usually classified into three groups: nematic, smectic, and cholesteric LCs.<sup>5,6</sup> The photoalignment assisted by command surfaces has been performed, so far, exclusively for nematics of small molecules, so that the application of this procedure to obtain monodomain textures of the other types of LCs is of great significance from both a fundamental and practical viewpoint.

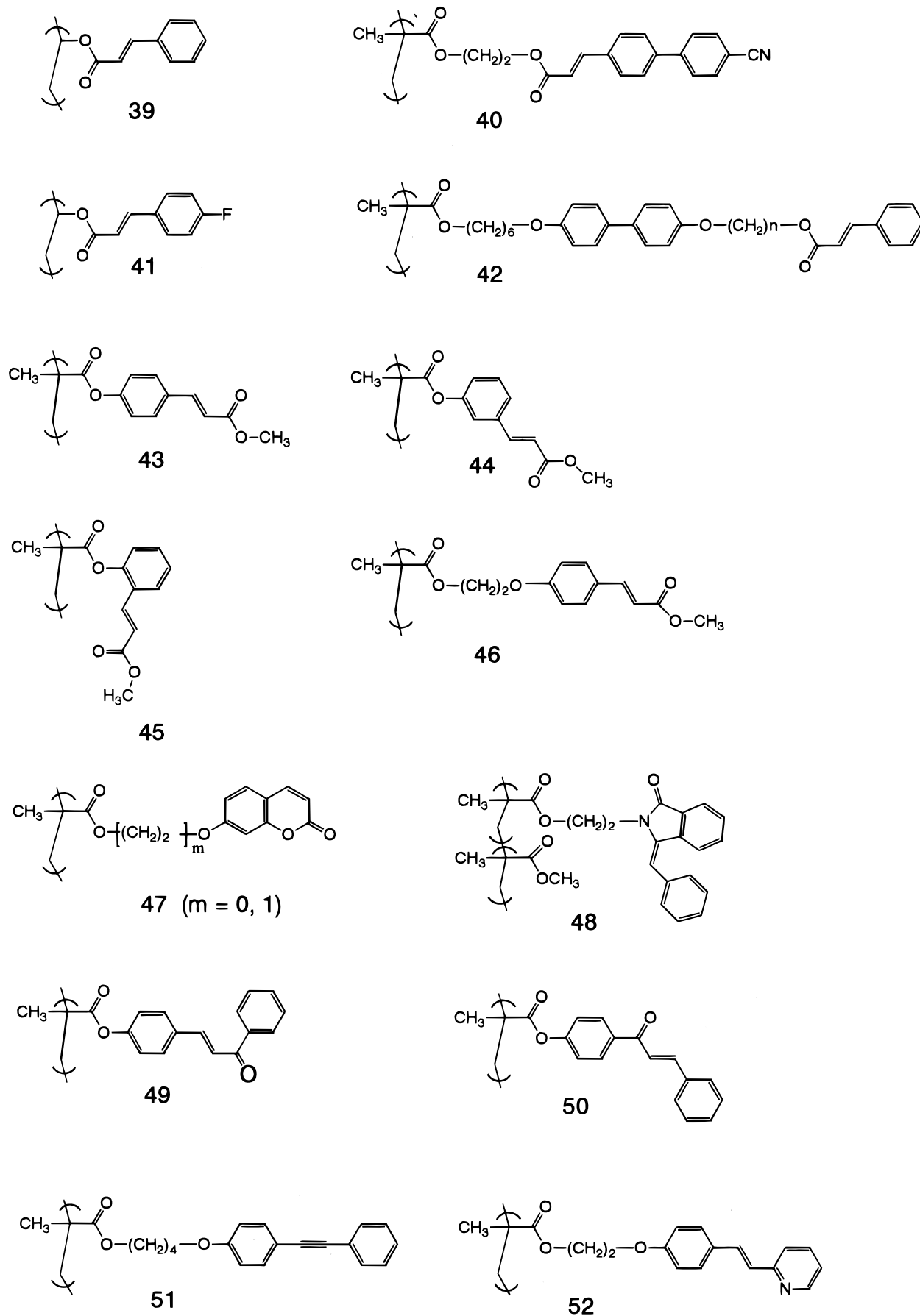
A polymeric LC with a nematic phase is alignable on a thin film of a polymer with azobenzene side chains, which is exposed to linearly polarized light.<sup>159</sup> Since a thin film of a polymer LC is prepared by spreading its solution on a film of the azobenzene polymer and the reorientation of polymeric LC requires annealing at temperatures close to its clearing point, the photogenerated alignment of a film of the azobenzene polymer should be stable toward solvent and heat. Polymethacrylate with *p*-cyanoazobenzene side chains (**2**) fulfills these requirements.<sup>160,161</sup> Uniaxially aligned films of a polymer LC exhibiting a nematic phase is fabricated by spin coating a solution of the LC polymer on a thin film of the polymer (**2**), which is exposed to linearly polarized light in advance, to be annealed at a temperature slightly lower than the clearing point of the LC polymer.

The surface-assisted photoalignment of LCs has been extended to the formation of uniaxially aligned dye molecular films to open a novel way to produce optical polarizers.<sup>162</sup> The procedure is quite simple, although the mechanism is quite complex. A thin film of an azobenzene polymer (**37**) coated on a substrate plate is exposed to linearly polarized blue light, followed by spin coating of an aqueous solution of a water-soluble azo dye. An aqueous solution of the dye exhibits a lyotropic LC phase, so that the orientation of the lyotropic LC is determined by the photoaligned film of azobenzene polymer in the same manner as in the case of low-molecular-weight nematic LCs.<sup>163</sup> The removal of water from the dye layer gives aligned dye molecular films, where dye molecules align parallel to the polarization plane of actinic light. Since the orientational direction of the azobenzene chromophore is regulated intentionally by changing the polarization plane, polarized photoimages can be made in an azobenzene polymer film using photolithographic technique. Observation of surface morphology by atomic force microscope suggests that the dye molecular films are assembled by fibrous supramolecular aggregates of the dye, in line with the presence of lyotropic mesophase.<sup>164</sup> Polarized patterns of anisotropically aligned dye molecular films are thus obtained and visualized with a polarizer.

A pronounced advancement of the science and technology of LC materials has been made due to the industrial development of LC displays, which employ rod-shaped calamitic LCs. Recently, extensive attention has been paid on discotic LCs,<sup>165</sup> which are generally comprised of disk-shaped rigid cores surrounded by flexible side chains at the peripheral positions so that systematic studies on the alignment control of this class of LC have been required. It was found recently that a discotic LC is alignable on a photoaligned film of the polymer **37** to give a monodomain LC film with excellent optical quality when a solution of the LC is cast on the film, followed by heat treatment.<sup>166</sup>

## G. Durable LC Photoalignment

The reversibility of photochromic reactions of molecules localized at the uppermost surface essentially ensures the rewritability of LC cells driven by the surface-assisted alignment photocontrol.<sup>24,25</sup> Occasionally, the fixation of the photoalignment is highly needed for practical applications including the production of LC-aligning films, which is one of the key materials in industrial manufacture of LC display devices.<sup>167–169</sup> A photoaligned state of thin films of photosensitive polymers should not be altered at all toward heat and light and also maintained unchanged even under application of electric fields. Furthermore, LC-aligning films should generate pretilt angles for application to LC display devices. So far, three types of polymeric materials exhibiting durable photoalignment have been developed. The first involves the photoirradiation of thin films of polyimides with irradiation with linearly polarized light<sup>170–172</sup> or slantwise irradiation with nonpolarized light.<sup>173</sup> The second is based on the photo-crosslinkable polymers substituted with (2 + 2) photo-



**Figure 13.** Representative photosensitive polymers applied to durable LC photoalignment. dimerizable side chains such as cinnamates (**39**–**46**),<sup>174,175</sup> coumarins (**47**),<sup>169,176</sup> benzylidene-phthal-imidines (**48**),<sup>177</sup> benzylideneacetophenones (**49**, **50**),<sup>178</sup> diphenylacetylene (**51**),<sup>179</sup> and stilbazoles (**52**)<sup>180</sup> (Fig-

ure 13). Although these functional groups are not sufficiently photochromic and exhibit irreversible photochemical reactions except for *E/Z* photoisomerizable derivatives, the LC photoalignment induced by thin films of these kinds of photo-cross-linkable polymers is mentioned here, since the photoalignment mechanism performed by command layers of these polymers is closely related to that of photochromic layers. The third one is provided by the fixation of photoorientation generated by photoisomerization of azobenzenes.<sup>159,181–183</sup>

The photoalignment control by UV irradiation of polyimide thin films possesses practical significance for application to LC-aligning films required for LC display devices.<sup>173</sup> The UV irradiation cleaves chemical bonds anisotropically in polyimides including those in the imide ring to induce the polarizability of polyimide units.<sup>171,172</sup>

Extensive studies have been made on the photoalignment induced by thin films of polymers with photodimerizable side chains predominantly from a practical viewpoint. The photodimerizable units are classified into two groups. The first group, including cinnamates, benzylidenephthalimidines, benzylideneacetophenones, and stilbazoles, demonstrates both *E/Z* photoisomerization and photodimerization, while coumarins and diphenylacetylenes belonging to the second one display solely photodimerization. It should be stressed that the orientational direction of an LC determined by thin films of the polymers exposed to linearly polarized light sometimes depends on exposure doses and the chemical structures of the polymers. For example, whereas poly(vinyl cinnamates) (**39**) result in a perpendicular orientation,<sup>174</sup> parallel alignment, where an LC director is in line with the electric vector of linearly polarized light, is generated by polymers with mesogenic side chains bearing cinnamate residues.<sup>175</sup> Interestingly, a polymer with cinnamate side chains without a spacer unit (**43**) exhibits the transformation of photoalignment from a perpendicular into a parallel direction during irradiation with linearly polarized light.<sup>184</sup> On the other hand, parallel alignment is obtained throughout the photoirradiation for a polymer bearing the same cinnamate residues through a spacer (**46**).<sup>184</sup>

Such complicated behavior in the photoalignment is interpreted in terms of the involvement of two photochemical reactions.<sup>184</sup> The perpendicular orientation stems from the *E/Z* photoisomerization, whereas cyclobutane formation determines the parallel orientation. As discussed in section IV.D.1 dealing with the photoalignment determined by command surfaces modified with cinnamate monolayers, the *Z* isomer of cinnamate seems to play no role in the photoalignment.<sup>151</sup> In the early stage of irradiation with linearly polarized light, the *E* isomer with a transition moment parallel to the electric vector of the linearly polarized light is consumed preferably so that the perpendicular orientation is induced as a result of intermolecular interactions between LC molecules and unreacted *E* isomer side chains. Upon further photoirradiation, the content of the *E* isomer decreases because of the irreversible photodimerization to reduce the commanding ability of the *E* isomer,

leading to reversion to a parallel orientation. The parallel direction is determined by cyclobutane adduct(s). Reversion of the LC director is also observable for some polymers with benzylideneacetophenone and may be interpreted in the same manner.

The predominant role of a rod-shaped isomer of *E/Z*-photoisomerizable moieties in the in-plane photoalignment was decisively presented by the experiments using polymers with benzylidenephthalimidine side chains.<sup>177</sup> Note here that the *Z* isomer of this chromophore has a form equivalent to *trans*-stilbene while the *E* isomer is similar to *cis*-stilbene. Benzylidenephthalimidines display both photoisomerization and (2 + 2) photodimerization, similar to cinnamates, although quantum yields for the photodimerization in the film are very low when compared with polymers with cinnamate side chains.<sup>177a</sup> Polymers with benzylidenephthalimidine side chains (**48**) demonstrate a marked dependence of the LC photoalignment on the excitation wavelength of linearly polarized light. Essentially no homogeneous LC alignment is generated by irradiation with linearly polarized 313 nm light; uniaxial alignment with excellent optical quality is attained by using 365 nm light. These amazing results are interpreted in terms of isomer ratios at photostationary states. The formation of the *Z* isomer related to the *trans* form of stilbene favors illumination with 313 nm light, whereas a predominant component under irradiation with 365 nm light is the *E* isomer (*cis* form). This wavelength effect reveals that the in-plane alignment arises specifically from the *Z* isomer.

On the other hand, the photoalignment reversion from a parallel into a perpendicular orientation occurs for a polymer substituted with coumarin side chains without spacer (**47a**).<sup>176</sup> In the early stage of irradiation with linearly polarized light, the axis-selective photodimerization lead to the formation of cyclobutane adduct(s), which determine the parallel orientation. As the polarized dimerization proceeds, the level of remaining coumarin units with a molecular axis perpendicular to the electric vector of the light exceeds that in parallel with the electric vector. Because of the stronger intermolecular interactions of the coumarin with LC than that of the cyclobutane adduct(s), the overall commanding ability of the remaining coumarin rings wins over that of the cycloadduct(s) at critical exposure doses to transform the LC director into a perpendicular orientation.

The enhancement of thermostability of the photoaligned state of azobenzene polymers is achieved by the formation of cross-linking by using a bisazide photo-cross-linking reagent, resulting in an increase in the thermal stability of photoinduced homogeneous alignment.<sup>181</sup> Anomalously thermostable photoalignment of polymer films is attained by employing polymethacrylate with *p*-cyanoazobenzene side chains (**2**) even though no covalent cross-linking is provided. When a thin film of the polymer is exposed to linearly polarized light, followed by heating at elevated temperatures, extremely stable photoalignment is obtained due to the semicrystalline nature of the polymer.<sup>159</sup> When a film of a polyamic acid incorporating azobenzene units in the main chains is ex-

posed to linearly polarized light to induce optical anisotropy, followed by annealing for the imidization, the resulting polyimide film displayed excellent thermal and photochemical stability.<sup>182</sup> This technique is applicable to generate pretilt angles of LC layers by slantwise photoirradiation of a precursor polyamic acid with nonpolarized light.<sup>183</sup>

Systematic studies have been carried out by Kawatsuki et al. on the photoorientation of LC homopolymers as well as copolymers with cinnamate side chains.<sup>175,185–190</sup> While thin films of these kinds of polymers become optically anisotropic upon irradiation with linearly polarized UV light, the optical anisotropy is enhanced by heating after photoirradiation in a manner quite similar to LC polymers with azobenzene side chains.<sup>189</sup> The tilt angles are induced by slantwise irradiation with linearly polarized light.<sup>190</sup> Slantwise photoirradiation of a film of the LC cinnamate polymer with nonpolarized light provides the opportunity to control tilt angles of the chromophores.<sup>189</sup> The orientational direction of the mesogenic groups is perpendicular to the propagation direction of UV light to give rise to a coplanar orientation of the mesogenic residues. Consequently, the LC photoalignment control of low-molecular-weight LCs is attained by irradiation both with linearly polarized light and with nonpolarized light.

Taking notice of the practical significances of the durable photoalignment by using irreversible systems, the results are summarized as follows. (1) Irradiation of thin films of photosensitive polymers with linearly polarized light brings about surface-assisted in-plane LC alignment, although photochemical reactions are irreversible, indicating that even irreversible axis-selective photochemistry induces the in-plane alignment. (2) The orientational direction of homogeneous LC alignment is determined by various chemical species involving not only photoproduct(s), but also unreacted photosensitive groups. The *E/Z*-photoisomerizable isomer with a bent structure plays no role in the photoalignment. (3) Photo-cross-linkage of polymer backbones enhances the thermal stability of photoaligned states. (4) Tilt angles of an LC can be generated by slantwise photoirradiation of these types of polymer films.

## V. Applications

The LC photoalignment control can be reasonably applied in two ways, taking notice of the active and passive photofunctions. In the former, the reversibility of the photoinduced alignment alteration is put to practical uses including erasable optical recordings of various types,<sup>191</sup> laser-addressed display devices, spatial light modulators in optical computing systems, image processing, etc.<sup>192,193</sup> The in-plane alignment photocontrol is, in particular, of great interest because the optical information is written-in and read-out simply by rotating the electric vector of polarized light from a single light source. In particular, the formation of a holographic grating is of practical significance owing to the potentiality for high-density photomemory exhibiting rewritability for both LC polymers<sup>58,59</sup> and command-surface-type LC cells.<sup>194</sup>

The passive function provides durable molecular orientation exhibiting optical anisotropy. One of the promising applications of surface-assisted photoalignment is to produce LC-aligning layers required for LC display devices, mentioned above.<sup>167–169</sup> Although uniaxial orientation of LCs in conventional display-device technology has been achieved by buffing a thin polyimide film to get homogeneous alignment, this technique has an essential drawback owing to the rubbing treatment which brings about static electricity of the polymer film to cause the attraction of dust particles to deteriorate precise devices. In this respect, the azimuthal photocontrol of LCs by means of thin films of photochromic polymers is of great significance from a practical viewpoint. Some other applications of the surface-assisted LC photoalignment including optical data storage<sup>168,169</sup> and various optical elements including interference color filters are proposed.<sup>195</sup> To apply the surface-assisted photoalignment to optical elements, photoaligned LC layers are immobilized by radical<sup>196</sup> and cationic<sup>197</sup> photopolymerization of LC acrylate monomers and epoxide monomers, respectively.

As mentioned in section IV.F, even lyotropic LC is photoalignable to give anisotropic dye molecular films, which are of potential applicability for multi-axis polarizers.<sup>162</sup> The photoalignment control of self-assembled molecular systems other than nematics seems to be a promising way to open versatile applications.

## VI. Summary and Outlook

One of the outstanding features of photoalignment of LC systems comes from marked molecular amplification. Let us take into account the degree of amplification in photoresponsive LC systems. LC copolymers with azobenzene side chains display azimuthal reorientation of the chromophores, which triggers the reorientation of photoinactive mesogenic side chains. About 10 mol % of loading is sufficient for this type of cooperative photoalignment under a suitable combination of the azobenzene and the mesogenic residues. Consequently, the degree of molecular amplification is assumed to be about 10. On the other hand, the degree of amplification of the photoalignment mediated by command surfaces amounts to approximately  $10^4$ , when a thickness of an LC layer is 10  $\mu\text{m}$ , because the photochemical alteration of structures and orientations of a monolayered photochromic unit causes orientational changes throughout the LC layer. In this context, it is not appropriate to call photoreceptor molecules in the photoalignment systems photochromic, since the photofunctionality does not arise from photoinduced color changes, but from the ability to command the reorientation of LC molecules or mesogenic residues. In this way, the photoreceptor molecule was proposed to be called a command molecule, while LCs are referred to as soldier molecules in order to stress the uniqueness of cooperative works of LCs.<sup>3</sup>

The prominent significance of photochromism in the photoalignment control of LC systems originates from the reversibility of structural transformations



of molecules capable of commanding LC molecules or residues. Let us consider the polarization photochemistry. The exposure of photoreactive molecules in polymer matrices or solid surfaces to linearly polarized light results first in axis-selective light absorption leading to the emergence of dichroism due to the preferential consumption of molecules, the transition moment of which is parallel to the electric vector of the light. If a photochemical reaction proceeds irreversibly, photoreactive molecules with a transition moment perpendicular to the electric vector have to suffer from a delayed photoreaction since the molecular axis fluctuates more or less even in polymer film or on a substrate surface. This means, in principle, that the photoinduced dichroism grows in the early stage of irradiation with linearly polarized light to reach a maximum value, followed by a gradual decline of the optical anisotropy upon further photoirradiation.

On the contrary, photochromic molecules may have a subsequent process to alter their molecular axis, exhibiting photoreorientation, because of the reversibility of chemical transformation. An excellent and rather exceptional example for the photoreorientation as a result of the repetition of the photochemical processes is presented by azobenzene photochromism, as reviewed throughout this article. Although the other photochromic molecules can exhibit this kind of alteration of their molecular axis upon irradiation with linearly polarized light, there has been no experimental evidence supporting that photoinduced dichroism of photochromic moieties demonstrating *E/Z* photoisomerization around C=C double bonds stems from the photoreorientation. This is because of the balance between the suppression of and the optimum freedom for the molecular motion of photoalignable molecules in matrices. Whereas the molecular motion should be suppressed more or less in order to make photoaligned states free from orientational relaxation, a free volume should be ensured for the photoinduced rearrangement of the molecular axis. In the author's opinion, the ability of azobenzenes to display the photoreorientation may arise from their inversion mechanism, which requires a smaller space for the *E*-to-*Z* isomerization to be favorable for photoinduced molecular reorientation, while the *E*-to-*Z* photoisomerization of unsaturated chromophores having a C=C double bond such as stilbenes needs a larger free volume owing to the rotation mechanism.

The photoalignable LC systems developed so far are comprised by the following two types, as mentioned above. The first, consisting of LCs doped with photochromic units, is operated as a result of the photoinduced reorientation of the photochromic chromophores, leading to the generation of large optical anisotropy. To make the photoresponsive systems liquid-crystalline, phototrigger molecules or residues have to be mesogenic. In this respect, photochromic azobenzenes have been extensively employed as phototriggers due to the mesogenic nature. Because the *Z* isomer with a nonmesogenic structure usually acts as an impurity to deteriorate mesophases to result in photoinduced mesophase changes, the ir-

radiation of LC systems with blue light for  $n, \pi^*$  excitation to give a photostationary state containing the mesogenic *E* isomer as a major component has been commonly used.

The second LC system, which is workable by command surfaces, involves the transfer of photoaligned states of photochromic molecules attached to substrate surfaces to bulk LC layers. In contrast to the doped LC systems, the surface-assisted photoalignment is operative even though the levels of photogenerated optical anisotropy are quite minute. This situation provides the versatility of the employment of photochromic units to fabricate this kind of LC photoresponsive system and opens a way to photoalignment control even by using irreversible photochemistry. In other words, the surface-assisted photoalignment of LCs is performed not only by photochromic molecules in these cases.

Finally, it should be emphasized again that the precise and sufficient photocontrol of molecular orientation described in this article is based on the combination of the reversibility of photochromic reactions with a long-range order of LC molecules. A prominent example is the photogeneration of large birefringence of LC systems by irradiation with linearly polarized light. Furthermore, the three-dimensional photocontrol of molecular orientation induced by azobenzene chromophores incorporating LC systems is amazing. These results provide promising ways to fabricate novel types of optical elements and devices for photonic applications.

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