



Molecular amplification of photochemical events

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Abstract

The commander–soldier (C–S) concept proposed by the present author is discussed to review photoresponsive systems exhibiting molecular amplification of photochemical events, which are categorized into two groups; the trigger-type and catalysis-type. As exemplified by the surface-assisted photoalignment control of nematic liquid crystals (LCs) as soldier molecules, the trigger-type C–S scheme results intrinsically in marked enhancement of signal/noise ratios and was expanded to achieve the alignment photocontrol of lyotropic LCs, chiral nematic LCs and discotic LCs. The other molecular amplification scheme referred to as the catalysis-type is kicked off by a photogenerated acid- or base-catalyst to bring about the subsequent acid- or base-catalyzed reaction(s), leading to the improvement of photosensitivity. Acid or base proliferation reactions consisting of autocatalytic formation of acidic or basic catalyst molecules are mentioned to highlight their significant roles in improving photosensitivity characteristics of photopolymers consisting of chemical transformations induced by photogenerated acidic or basic species.

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1. Introduction

Because a quantum efficiency for photoinduced structural modification of a molecule cannot exceed unity in general, a minimum exposure dose required for inducing property changes of materials solely in a chemical way to fulfill practical performances is of a critical value. For example, if a photochemical reaction to form a colored substance is applied to record visible images, a minimum exposure dose needed for the image formation is strictly determined by the quantum efficiency. If a film coated with a layer of this kind of a photosensitive material is set in a camera to take a picture in a sunny place, an exposure time should be longer than 10 min, whereas it takes 1 ms or shorter for silver halide photography, which is based on photochemistry and thermal chemistry. Visual sensory systems exhibit extremely high photosensitivity so that we can see substances even under lunar light, though no photoimage can be recorded on a conventional photographic film without assistance of a flash lamp. Why do they display enormously high photosensitivity without aid of electronic as well as photonic amplification? Taking notice of ever increasing importance of photosensitive organic as well as polymeric materials for versatile practical applications in industries and of deeper understand-

ing of photobiological phenomena [1], systematic studies on principles of molecular amplification of photochemical events of organic materials are essentially needed. On the other hand, various types of photoresponsive molecular systems exhibiting photoinduced material property alterations have been developed extensively by appropriate combinations of photochemical reactions and the subsequent chemical as well as physical transformations which are triggered by the photoreactions.

The author proposed previously the concept of commander–soldier (C–S) schemes to grasp versatile types of molecular amplification systems, focusing on how to link photochemical reactions to the subsequent chemical or physical events to constitute materials or systems exhibiting molecular amplification phenomena [2]. This was motivated by our previous finding that the alignment of a numerous number of nematic liquid crystal (LC) molecules is dramatically controlled by *E/Z* photoisomerization of monolayered azobenzene tethered to a substrate surface [3,4], which is referred to as a command surface. The C–S concept was discussed in the previous paper [2] to classify photoresponsive systems into two groups including the trigger-type and the catalysis-type, showing representative examples comprised of suitable combinations of photochemical reactions with consequential molecular events. The purpose of this paper is to follow up the validity of the C–S concept with slight modification on the basis of our current studies on two types

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of molecular amplification systems; the surface-assisted photocontrol of LC systems other than low-mass nematics and novel photopolymers incorporating autocatalytic formation of acidic and basic molecules initiated by photogenerated acidic or basic species. Note that the former belongs to the trigger-type, whereas the latter photopolymer systems are made up from the catalysis-type schemes.

2. Result and discussion

2.1. C–S schemes consisting of two chemical processes

Fig. 1 shows four types of representative C–S systems consisting of two elementary processes. The following technical terms was proposed to describe the schemes. First, it should be mentioned that the systems consist of two kinds of molecules; commander (C) and soldier (S) molecules. A C molecule absorbs a photon to be transformed to a molecule (C'), which is able to lead to chemical alterations of numerous numbers of molecules as S molecules interactive with C'. The chemical structure of C' is different from that of C as a consequence of the corresponding photochemistry, while the transformation of S into S' means not only a change of the chemical structure of S, but also the modification of a physical state of S including molecular orientation, aggregation and so on, accompanied by no

molecular structural change. Second, there are two types of molecular amplification schemes on the basis of differences in the nature of molecular interplay between C' and S; trigger-type and catalysis-type. As illustrated in Fig. 1, the former trigger-type transformation of S into S' is initiated by C' photogenerated from C (Fig. 1(a)), whereas the conversion of S into S' catalyzed by C' generated from C is referred to as the catalysis-type (Fig. 1(b)). Note here that the trigger-type involves essentially a domino effect so that C' induces structural or orientational changes of a single S molecule to give S', which triggers the subsequent change of the other S molecules without the interplay with C', whereas C' in the catalysis-type interacts with every S molecule to play a role as a catalyst. In order to stress and depict the difference in the molecular interplays, two elementary processes involved in the trigger-type are connected by a straight arrow, whereas a circle arrow is used for the catalysis-type to link two elementary processes. The third C–S scheme shown in Fig. 1(c) involves an autocatalytic process, where S is equivalent to C, as exemplified by silver halide photography. The fourth scheme shown in Fig. 1(d) belongs also to autocatalytic process, but is different from the third one in the fact that C is not the same as S, whereas both C and S produce C' molecules to attain the autocatalysis. Acid or base proliferation reactions proposed by us [5] and described below in detail belong to this scheme. The n in Fig. 1 stands for the number of S and consequently corresponds to a level of molecular amplification.

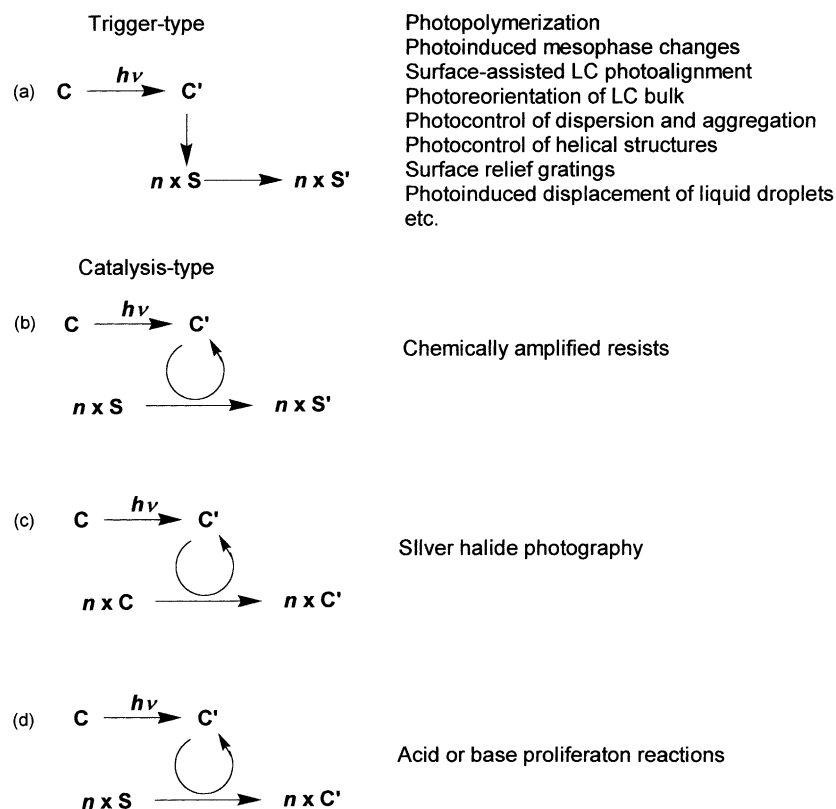


Fig. 1. C–S systems consisting of two processes.

Some typical examples for the schemes are also given in Fig. 1. Radical as well as cationic photopolymerizations [6] belong to the trigger-type, since radical or cationic species as C' generated by the photolysis of a photoinitiator denoted as C reacts with a monomer molecule (S) to form an active species, which initiates the propagation of the corresponding polymerization. Photoinduced mesophase changes [7], surface-assisted LC photoalignment [3], photoreorientation of LC bulk [3], reversible photocontrol of dispersion and aggregation of colloidal silica particles [8] and of helical structures of polymer main chains [9] illustrated as trigger-type scheme are all triggered by photoisomerized molecules or residues and discussed in the previous article [2]. The other example exhibiting marked levels of molecular amplification include the formation of surface relief gratings (SRGs) inscribed in polymer films incorporating azobenzene chromophores exhibiting E/Z photoisomerization, which gives rise to a driving force for the SRG formation [10]. We have observed recently that SRG is obtained by using a film of a polymer bearing stilbazole side chains [11]. It is noteworthy that stilbazole residues undergo not only E/Z photoisomerization, but also photodimerization so that this type of a polymer film suffers from photocross-linking to give a networked structure. The light-guided movement of liquid droplets placed on a surface modified with a monolayered azobenzene derivative is an alternative system disclosing a tremendous level of molecular amplification [12]. It should be stressed that both systems attracting current interest display the displacement of massive materials triggered by photoisomerization as a molecular-level event.

2.2. Surface-assisted LC photoalignment as trigger-type amplification

2.2.1. Lyotropic LCs

LCs can be classified into lyotropic and thermotropic ones, depending on whether they contain solvent molecules or not. As mentioned above, the surface-assisted photoalignment has been applied predominantly to low-mass nematic LCs, which are thermotropic [4]. Molecular-level structural changes of photosensitive molecules tethered to topmost substrate surfaces induce the modification of molecular orientation of thermotropic nematic LCs to bring about macroscopic optical property alterations. Three types of photocontrol of orientation changes of LC molecules

have been established using photoreactive molecular as well as polymer thin films; out-of-plane alignment changes between homeotropic and planar modes, in-plane alignment changes induced by linearly polarized light irradiation and tilt orientation triggered by oblique photoirradiation [4]. They are of great significance not only for practical applications, but also for fundamental studies on interfacial phenomena involved by LC molecules. This situation led us to carry out systematic investigation of photoalignment of LCs other than low-mass nematics.

Compared with thermotropic LCs containing no solvent, researches on lyotropic LCs as mesophasic solutions have been out of the main stream of LC sciences and technologies, and there have been only few reports on their alignment control by surfaces, although they play critical roles, in particular, in biological systems [13]. We reported previously that a dichroic dye molecular film is readily obtained by spin-coating of an aqueous solution of a water-soluble dye on a thin film of a polymer with azobenzene side chains, which is exposed to linearly polarized light before the spin-coating [14]. Our subsequent reports described that the dye aqueous solution exhibits lyotropic mesophase, implying that the orientation of dye molecules on the polymer film arises from the alignment of the aqueous solution exhibiting lyotropic mesophase, followed by the evaporation of water as a solvent to give an optically anisotropic dye film [15]. Consequently, the possibility to achieve the photoalignment of lyotropic LCs was determined by the following procedure. Lyotropic LCs used here were prepared by dissolving a water-soluble diazo-dye, C. I. Direct blue 67 [13], and disodium chromoglycate (DSCG) [16] as an anti-asthmatic drug (Fig. 2), respectively, in the presence of a small amount of a nonionic surfactant to give about 10 wt.% solutions exhibiting nematic phase at room temperature. An empty cell fabricated by using a couple of glass plates, in side walls of which were coated with thin films of a polymethacrylate with azobenzene side chains, was subjected to irradiation with linearly polarized light to cause photoorientation of the azobenzene, followed by filling with a lyotropic LC solution. It was found that optical anisotropy is generated in aqueous solutions exhibiting lyotropic mesophase for both the dye and the drug [17]. One of the example is shown in Fig. 3. A homogeneous alignment of an aqueous solution of the dye was generated by a thin film of a polymer with azobenzene side chains under exposure to linearly polarized

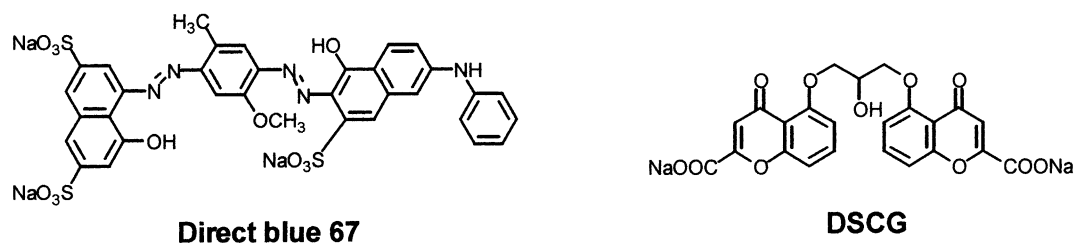


Fig. 2. The water-soluble dye and the drug giving lyotropic LCs.

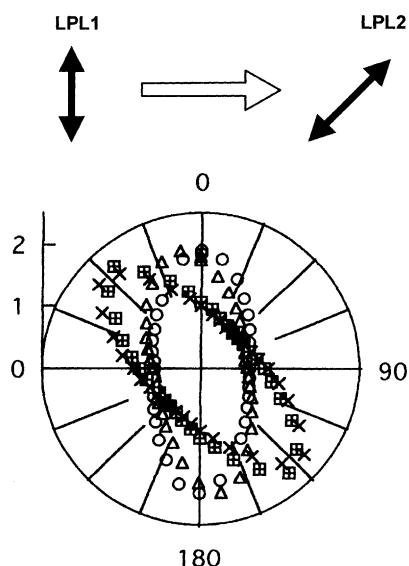


Fig. 3. Circular diagrams of polarized absorbances of a cell filled with an aqueous solution of the dye exposed to linearly polarized 436 nm light. The cell walls were coated with thin films of an azobenzene polymer, which were irradiated first with the light (LPL1) of a $1\text{J}/\text{cm}^2$ dose (circles), followed by irradiation with the light (LPL2) of the electric vector perpendicular to that of LPL1 of exposure doses of $1\text{J}/\text{cm}^2$ (triangles), $3\text{J}/\text{cm}^2$ (crossed-squares) and $10\text{J}/\text{cm}^2$ (crosses), respectively.

light. The orientation direction was modified by changing the electric vector of the polarized light, as shown in Fig. 3.

2.2.2. Smectic and chiral nematic LCs

Mesophases are usually divided into three groups; nematic, smectic and cholesteric (chiral nematic) mesophases. We revealed at the early stage of our systematic studies on command surfaces that no photocontrol of alignment of a smectic LC is achievable between homeotropic and planar modes [18], when an azobenzene monolayer is used as a command surface, so that we assumed that nematic mesophase is one of the necessary conditions for photoalignment control. On the other hand, it has been reported recently that the irradiation of a photosensitive liquid-crystalline polymer with linearly polarized light leads to the alignment control of chiral smectic LCs, ferroelectric LCs, which is applicable to ferroelectric LC displays [19], suggesting that command surfaces are workable for the orientation modification of smectic LC layers under appropriate choices of smectic LCs, cell assembly, photoirradiation conditions and photoaligning films.

Cholesteric (chiral nematic) LCs exhibit multi-farious textures so that the control of alignment of this type of LCs plays a critical role in practical applications for display and memory devices. We attempted previously to control the alignment of a cholesteric LC derived from cholesterol derivatives by using an azobenzene monolayer [20], which results in reversible orientation changes of nematic LCs between homeotropic and planar modes. But it failed. Our recent reexamination has revealed that the photoalignment of

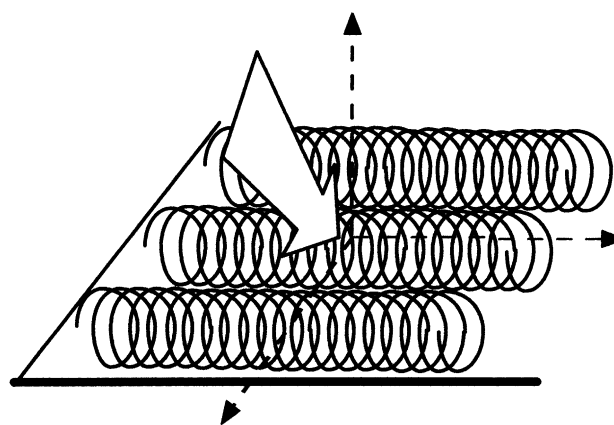


Fig. 4. Illustrative presentation of photoalignment of a chiral nematic LC achieved by oblique irradiation with nonpolarized light.

chiral nematic LCs is able to be performed under appropriate conditions, as follows [21]. A film of a polymer with *p*-fluoroazobenzene side chains gives rise to the generation of homeotropic alignment of nematic LCs thanks to the fluoro-substituent so that inclined orientation with a high pretilt angle is generated by oblique photoirradiation with nonpolarized blue light. When an empty cell was fabricated with a couple of glass substrates coated with the polymer films and exposed obliquely to nonpolarized light, a chiral nematic LC comprised of a nematic LC and a chiral dopant filled in the cell exhibited a homogeneously aligned texture. It was found that the direction of helical axis of the LC is perpendicular to the incident direction of the light, as shown in Fig. 4.

2.2.3. Discotic LCs

LCs are also classified by their molecular shapes of mesogens. Conventional LCs referred to as calamitic LCs (CLCs) are commonly comprised of rod-shaped cores as mesogens, while discotic LCs (DLCs) possess disk-like rigid cores, which are substituted with flexible alkyl chains at their periphery positions [22]. DLCs have been attracting current interest because of unique photonic as well as electronic properties owing to their disk-shaped π -electronic structures and have been applied to optical elements for LC display devices based on their particular molecular arrangement. On the other hand, when compared with CLCs, scarce study has been carried out on surface-mediated alignment control of DLCs, and the photoalignment technique by command surfaces has not yet been applied to DLCs. Because DLCs display usually high transition temperatures and high viscosity in mesophases, materials and procedures for CLC photoalignment are not always employed for DLCs. For example, no photoalignment was demonstrated by using conventional polymers with azobenzene side chains, while they act as photoaligning films for low-mass nematics, since a photooriented state of films of the polymer is deteriorated by heating at higher temperatures needed for the generation

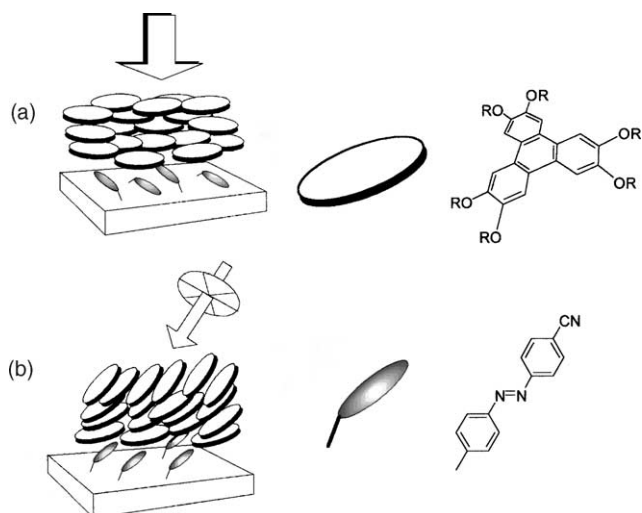


Fig. 5. Photoalignment of a DLC on a pMAzCN film: (a) homeotropic alignment by irradiation with linearly polarized light; (b) homogeneous hybrid alignment.

of discotic mesophase. In this respect, we picked out poly[(4-cyanophenylazo)phenyl methacrylate] (pMAzCN), taking notice of the excellent thermostability of a photooriented state of the polymer, which is demonstrated by irradiation of a film of the polymer with linearly polarized photoirradiation and the subsequent annealing at 250 °C or higher to enhance and fix the optical anisotropy [23,24].

After a thin film of pMAzCN was exposed to linearly polarized blue light, followed by heating at a higher temperature, a solution of a discotic triphenylene-type LC exhibiting discotic nematic (N_D) phase was spin-cast on the film to give an LC film, which was subsequently annealed to generate N_D phase. Contrary to our anticipation, we observed only homeotropic but no homogeneous alignment (Fig. 5(a)). On the other hand, when irradiation of the polymer film was carried out obliquely with nonpolarized blue light to induce inclined photoorientation of the azobenzene moieties in the film, followed by annealing the film at a higher temperature, a hybrid alignment of the DLC was generated, when a DLC layer was spin-cast on the polymer film and heated to give rise to N_D phase [25]. The photoaligned DLC film was stable even after cooling down at an ambient temperature and stored for long time without any deterioration of the LC orientation. As illustrated in Fig. 5(b), the molecular arrangement of the DLC film belongs to the so-called hybrid alignment, where DLC molecules close to the polymer surface are tilted, while tilt angles of the molecules in a bulk DLC film increase continuously from the bottom to the uppermost surface. The highest tilt angle at the air/LC interface comes from the fact that DLC molecules at the topmost surface align in such a way to minimize a surface energy of a free-standing LC film.

A cinnamate polymer is also workable for the hybrid photoalignment of DLCs in the same fashion, when a film of the polymer is exposed obliquely to nonpolarized UV light

to give rise to tilted molecular orientation [26]. No thermal treatment is necessary in this case, since the thermostability and resistance to solvent treatment of photooriented state of the cinnamate polymer is markedly enhanced by cross-linked network formation. The hybrid molecular arrangement in a photoaligned DLC film was confirmed by measuring polarized fluorescence intensity of a DLC film as a function of incidence angle of excitation light [27].

2.2.4. Summary for LC photoalignment

As stated above, LC materials can be classified according to the four factors; the absence or presence of solvent, the nature of mesophase, the molecular shape of mesogens and the molecular weight. LCs employed for conventional LC display devices belong to thermotropic, calamitic, low-mass nematic LC and, strictly speaking, occupy only a narrow area in the LC world. In other words, the photoalignment of various types of LCs according to the C–S scheme illustrated in Fig. 1(a) opens way to multiple research fields in LC science and technology. In addition to conventional low-mass nematic LCs, we have already confirmed that a LC polymer with nematic phase is subjected to photoalignment by using a pMAzCN film exposed to linearly polarized light. Ferroelectric LCs is also photoalignable, as mentioned above. The results described here reveal in this context that the command surface technique to generate uniform LC orientation can be applied to wide ranges of LCs under appropriate choices of irradiation conditions and photoaligning films, as summarized in Fig. 6. Note again that the LC photoalignment belongs to the trigger-type molecular amplification to enhance signal/noise ratios. This situation can be visualized by a uniaxially aligned dye molecular film, which is formed on a film of an azobenzene polymer with a relatively small dichroism after exposure to linearly polarized light.

2.3. C–S schemes consisting of three chemical processes

2.3.1. Doubled photoorientation

Fig. 7 shows three kinds of C–S schemes comprised of three elementary chemical events connected by trigger and catalysis processes. The first of them (Fig. 7(a)) consists of the combination of two trigger-type amplification, whereas the second and the third (Fig. 7(b) and (c)) involve two catalysis-types and both of a trigger-type and a catalysis-type, respectively. To the author's knowledge, there has been no systematic study on these sorts of molecular amplification systems based on such multiple steps so that it is hard to present examples suitable for each scheme except for our following systems.

The amplification scheme illustrated by the combination of two trigger-type processes (Fig. 7(a)) may be exemplified by the improvement of performances for LC photoalignment using liquid-crystalline as well as semi-crystalline azobenzene polymers. It has been known that photogenerated optical anisotropy of thin films of polymers with

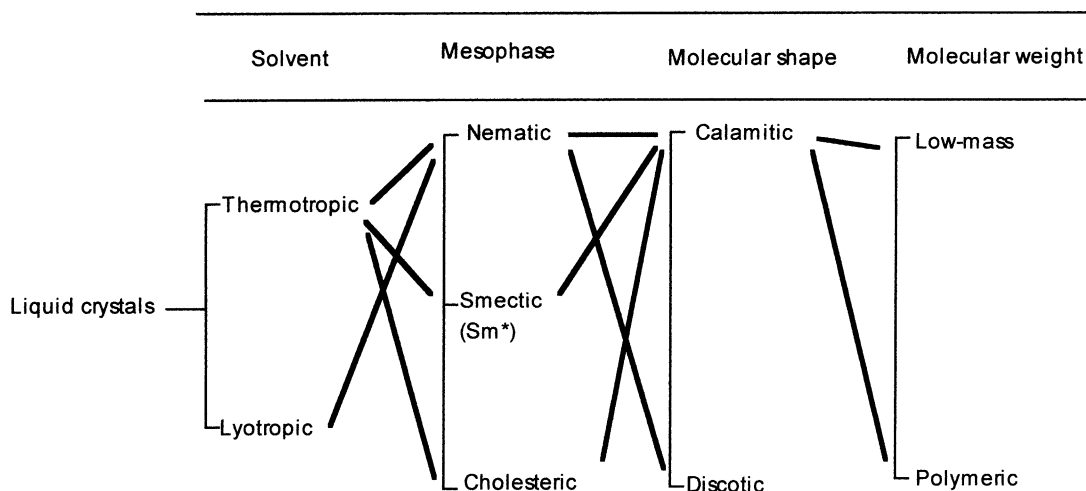


Fig. 6. Photoalignment control of versatile LCs by command surfaces.

azobenzene side chains is considerably enhanced by thermal annealing of their spin-cast films after photoirradiation when polymers are liquid-crystalline or semi-crystalline [4]. Glassy films of these classes of polymers cast from their solutions are anisotropic so that they exhibit relatively small optical anisotropy under irradiation with linearly polarized light ($C \rightarrow C'$ in Fig. 7(a)). On the other hand, subsequent thermal annealing of photoirradiated films results in considerable enhancement of optical anisotropy due to the command effect, which comes from liquid crystallinity as

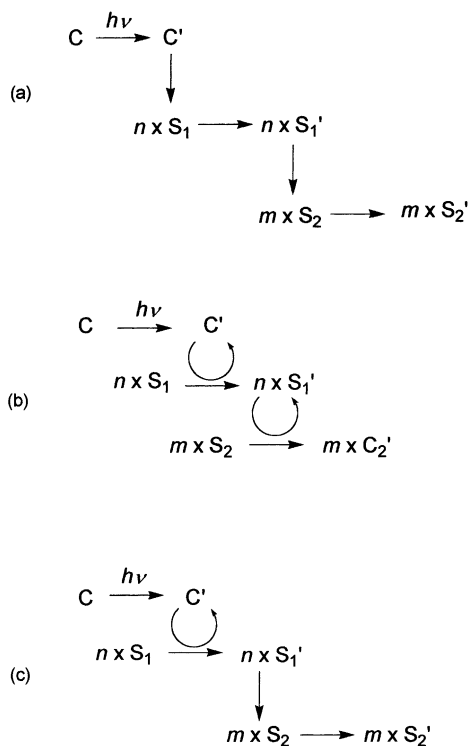


Fig. 7. C–S systems consisting of three processes.

well as semi-crystallinity of the polymers [28]. In particular, a semi-crystalline polymer with *p*-cyanoazobenzene (pMAzCN) [24,28] or *p*-trifluoromethoxyazobenzene (pMAzF) [29] side chains exhibits remarkable enhancement and thermostability of photoaligned state, when photoirradiated thin films of these polymers are annealed at high temperatures ($n \times S_1 \rightarrow n \times S_1'$ in Fig. 7(a)). As mentioned above, a thermally enhanced photooriented film of pMAzCN is very suitable for the photoalignment of DLCs ($m \times S_2 \rightarrow m \times S_2'$ in Fig. 7(a)) because of the solvent-resistance of thermostability of the photooriented state. In a similar manner, thermally enhanced photooriented films of pMAzF is workable for LC-aligning films giving high pretilt angles necessary for the fabrication of vertically aligned (VA)-mode LC display devices, which are of practical significance due to the presentation of wide-view angles [30].

The latter two of the schemes shown in Fig. 7 contain catalytic reaction(s) as a result of photochemical reactions, which initiate subsequent chemical processes. Good examples for these classes can be presented by the autocatalytic generation of acidic or basic molecules referred to as acid or base proliferation reactions, which have been developed by us [5]. The following sections deal with novel photopolymer systems incorporating this type of nonlinear organic reactions to increase concentrations of catalytic molecules.

2.3.2. Photopolymers based on acid proliferation reactions

As stated above briefly, the trigger-type amplification as exemplified by the surface-assisted LC photoalignment exhibit considerably enhanced levels of signal/noise ratios, but photosensitivity itself required for attaining the C–S systems is essentially not much improved since they involve no catalytic process. On the other hand, chemically amplified photoresists (CAP) display usually photosensitivity higher than that of conventional photoresists employed for submicron-photolithography due to the participation

of acid-catalyzed deprotection reactions [31]. But the enhancement of their photosensitivity of CAP seems to be restricted because of the deactivation of photogenerated acid- or base-catalyst molecules and the considerable suppression of molecular diffusion in resist films. These facts motivated the author to verify the possibility of enhancing the photosensitivity of CAP by the involvement of the autocatalytic formation of acidic species from acid-sensitive compounds referred to as “acid amplifiers” [32,33]. The process can be illustrated as shown in Fig. 1(d) and has been proposed to call an acid proliferation reaction to stress the nonlinearity in kinetics. An acid amplifier referred to as S in Fig. 1(d) is decomposed by an acid expressed as C' generated from a photoacid generator (C) to give new

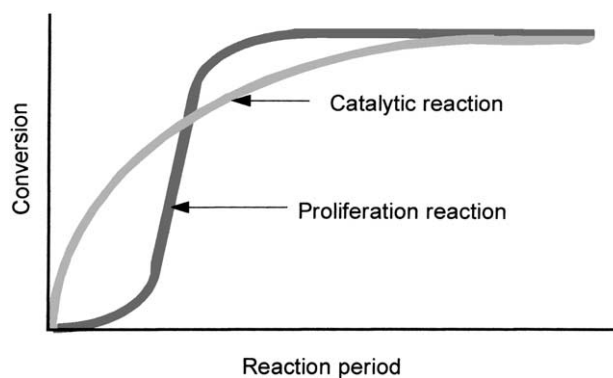


Fig. 8. Time courses of a catalytic reaction and an acid proliferation reaction.

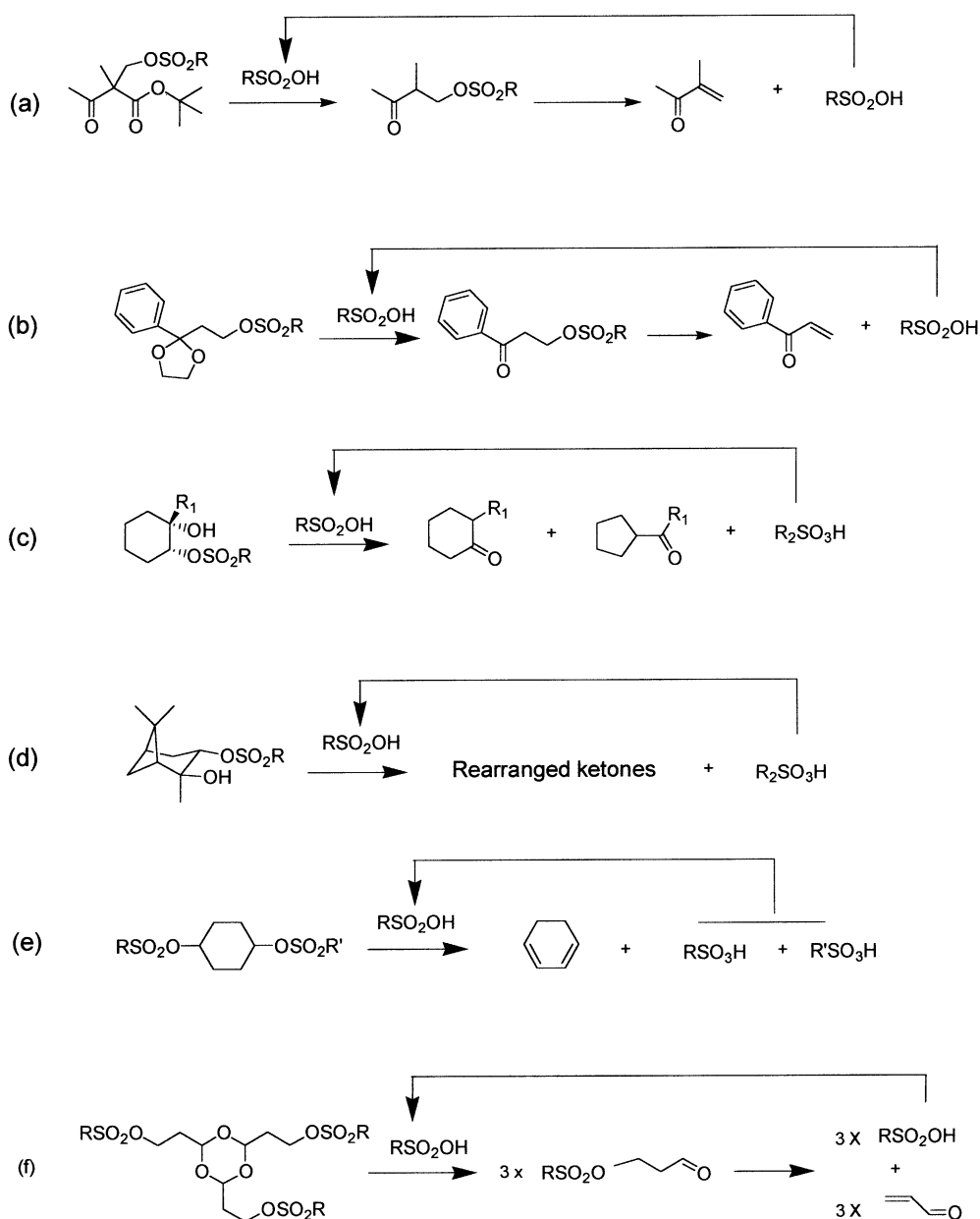


Fig. 9. Acid proliferation reactions.

acidic molecules (C') so that rates of subsequent acidolytic reactions may be significantly enhanced. Note again that the autocatalytic generation of acidic species from an acid amplifier results in the incrementation of concentrations of catalytic species to realize nonlinear organic reactions in a sharp contrast to conventional catalytic reactions (Fig. 8). Consequently, when acid proliferation reactions are coupled with acidolysis reactions, as illustrated in Fig. 8, we can develop versatile photopolymer systems exhibiting nonlinear catalytic transformations.

Fig. 9 summarizes some representative acid proliferation [5]. The acid amplifiers shown in Fig. 9 are decomposed acidolytically to give sulfonic acids, which are able to catalyze the decomposition of the parent molecules so that the reactions proceed in nonlinear manners. The first two acid amplifiers shown in Fig. 9(a) and (b) suffer from the bi-eliminations, while the third and fourth undergo the acid-catalyzed pinacol rearrangements (Fig. 9(c) and (d)), together with the liberation of sulfonic acids. Aiming at further enhancement of the generation of strongly acidic species, acid amplifiers giving multiple acidic molecules have been developed. The fifth acid amplifier gives rise to two molar amounts of a sulfonic acid [34], while three molar amounts of the acid is liberated in the last reaction [35]. The combination of these types of acid proliferation reactions (Fig. 1(d)) with CAP systems (Fig. 1(b)) provides acid proliferation-type photoresists, the principle of which is sketched in Fig. 7(b). It has been shown that photosensitivity of conventional CAPs is in fact improved by the addition of acid amplifiers [33,36,37] and that acid proliferation-type photoresists are applicable for submicron photolithography [38,39].

Cationic photopolymerizations are initiated by strong acidic species so that it is in principle possible to construct the C-S scheme is shown in Fig. 7(c), which consists of the photogeneration of strong acid, the proliferation of the acid and the polymerization of monomers. Cationic

polymerizations of vinyl ethers as well as epoxides as a trigger-type amplification corresponding to the scheme shown in Fig. 1(a) are suppressed by nucleophilic reactions [6]. Therefore, it is a prerequisite condition for performing the enhanced cationic photopolymerization that the nucleophilicity of the counteranion of a photogenerated acidic species has to be minimized. One of the candidate for this purpose is a disulfonate of 1,4-cyclohexanol ($R = p$ -tolyl, $R' = CF_3$ in Fig. 9(e)), which liberates autocatalytically trifluoromethanesulfonic acid as an organic superacid able to initiate cationic polymerization [34].

2.3.3. Photopolymers based on base proliferation reactions

It has been recently revealed that the nonlinear liberation of basic molecules is in fact possible from base amplifiers derived from urethanes [40] and phenylsulfones [41,42]. Fig. 10 shows the base proliferations, which are expressed as the scheme shown in Fig. 1(c). They exhibit amine-catalyzed β -elimination as a result of deprotonation at β -carbon relative to the electron-withdrawing groups, leading to the formation of carbanions to produce the same aliphatic amine and carbon dioxide, displaying autocatalytic reactions. Though these reactions and compounds themselves are not novel and rather familiar, it should be stressed that there has been no report on such autocatalytic behavior of these compounds before our publications.

When compared with CAP incorporating acidolysis reactions, photoresists based on base-catalyzed deprotection are reported only scarcely probably because of the limitation of choices of photobase generators, which give basic species acting as a basic catalyst. Taking notice of high reactivity of aliphatic primary as well as secondary amines with epoxy groups, determination has been made to reveal the addition effect of the base amplifiers on photosensitivity characteristics of a negative-working photoresist consisting of poly(glycidyl methacrylate) and a photobase

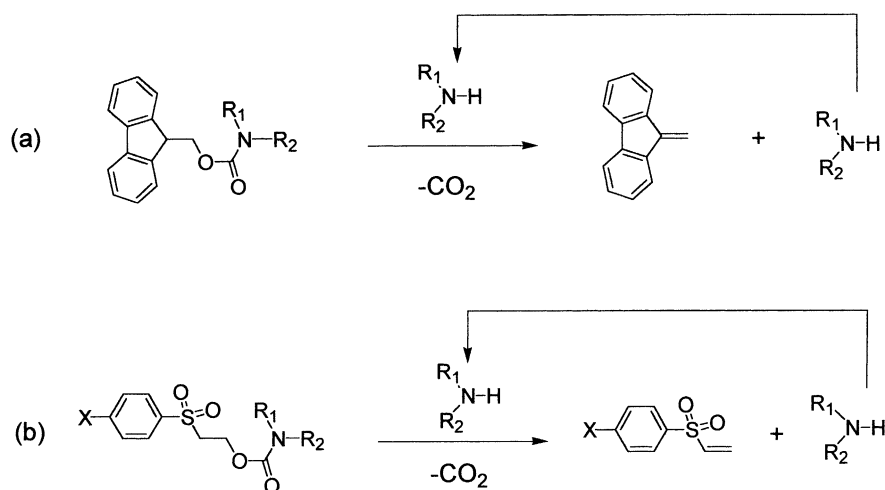


Fig. 10. Base proliferation reactions.

generator, which is insolubilized by cross-linking reaction between epoxy with amine residues. It was found that exposure doses required for the photoinduced insolubilization is markedly reduced by the addition of a difunctional base amplifier to display markedly enhanced photosensitivity, showing that the introduction of the base proliferation reaction plays a critical role in improving photosensitivity performances. These results indicate that the involvement of base proliferation reaction is of practical significance because of potential applicabilities for novel high performance resist materials, UV-curable materials for surface coatings, light-sensitive adhesives and so on.

In summary, a number of photopolymer systems with improved photosensitivity characteristics can be provided by the combination of acid as well as base proliferation reactions with the photogeneration of acidic or basic molecules and acid- or base-catalyzed reactions according to the scheme sketched in Fig. 7(b).

3. Concluding remarks

- (1) According to the C–S concept, molecular amplification schemes can be divided into two groups; trigger-type and catalysis-type. A transformed C molecule (C') triggers the transformation of S molecules exhibiting a domino effect in the former case, while in the latter a C' molecule as a catalyst encounters with every S molecule to result in the chemical transformation into S'. Considerable enhancement of photosensitivity is observed for the catalyst-type, whereas the trigger-type results in enhancing signal/noise ratios. Versatile molecular amplification phenomena for photochemical reactions can be categorized by the number of the both types involved.
- (2) Many chemical events are depicted by couples of donor and acceptor molecules in hydrogen bond formation, excited energy transfer and electron transfer processes, whereas host and guest molecules are commonly used to express the formation of supramolecular complexes. Couples of receptors and substrates are used for biological systems. These couples consist commonly of stoichiometrically defined numbers of component molecules. On the other hand, the combination of a C molecule with S molecules is not restricted by stoichiometrical molecular ratios at all so that a chemical change of an indefinite number of S molecule can be induced by a single C molecule. This is the essence of the C–S concept to express molecular amplifications.
- (3) Multi-step C–S schemes depicting molecular causality become workable to construct molecular cascade systems, when a transformed soldier molecule (S') in every elementary process can act as a commander for the succeeding elementary process. In this respect, visual

sensory systems triggered by the photoisomerization of retinals are regarded as one of the ultimate C–S systems comprised of numerous elementary processes, which are connected by both trigger-type and catalysis-type linkages, whereas extremely high photosensitivity of the systems arises from enzymatic reactions as catalytic processes.

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