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Photosensitive Polymers

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Photosensitive Polymers

MASAHIRO IRIE

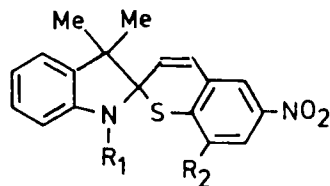
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The present summary covers photophysical and photochemical processes in polymers and their applications; photopolymerization is not included. Research interests are now shifting from the photoresist materials to optical memory materials, and nonlinear optics materials. Researches concerning these topics are included.

OPTICAL MEMORY MATERIALS

Organic materials have several attractive characteristics as components of optical data storage media in comparison with inorganic ones.^{1,2} They are less subject to degradation caused by air and moisture, and generally less toxic. They can be prepared by spin coating, leading to lower fabrication cost. In addition, organic media have the potential of being used for photon-mode recording. Photon-mode recording is advantageous in the sense of resolution, speed of writing, and multiplex recording capability. Because of these characteristics, there is an increasing interest in using organic materials for write-once as well as rewritable media. Candidates for the organic recording media are photochromic and photochemical hole burning (PHB) materials.

A. Miyashita, M. Hirano *et al.* (3387, E1339) developed photochromic spirobenzothiopyran polymers, which has sensitivity at laser wavelengths (780–830 nm). The polymers were synthesized by copolymerizing the following monomers with styrene or MMA.



- 1a : $R_1 = \text{CH}_3$, $R_2 = \text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$
1b : $R_1 = \text{CH}(\text{CH}_3)_2$, $R_2 = \text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$
1c : $R_1 = \text{C}_{18}\text{H}_{37}$, $R_2 = \text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$
1d : $R_1 = \text{C}_{18}\text{H}_{37}$, $R_2 = \text{CH}_2\text{OCO}(\text{CH}_2)_{20}\text{CH}_3$

Poly(1c-co-MMA) changes color from light yellow to green upon irradiation with ultraviolet light. The green color is due to the merocyanine form. The absorption maximum of the merocyanine form was observed at 665 nm and the edge extended to 900 nm. The green color was easily bleached out upon exposure to light with wavelengths longer than 700 nm or heating above 70°C. The merocyanine forms of spirobenzothiopyran chromophores dispersed in MMA were thermally unstable and they decayed easily at room temperature. In contrast with this behavior, the merocyanine form of the chromophores in the pendant groups became thermally stable. 79% of the colored forms remained stable for more than 190 days at 23°C. The polymer film had the sensitivity at diode laser wavelength and its colored state was thermally stable.

Not only the color change but also the geometrical structure change of photochromic compounds can be used for optical data storage. This was achieved by introducing photochromic azobenzene chromophores onto the surface of substrates of a liquid crystal cell (Y. Kawanishi, T. Tamaki *et al.* 3393, E1341). Trans-cis photoisomerization of the azobenzene monolayers on the surfaces caused the reversible change in the molecular alignment of nematic liquid crystals without any aid of external field. When the cell was exposed to conventional non-polarized ultraviolet light, the alignment changed from homeotropic to parallel which has low homogeneity. On the other hand, the parallel alignment became highly homogeneous when the linearly polarized light was used as the light source. The axis of the homogeneous alignment was found to be perpendicular to the direction of the polarized light. The photo-stimulated alignment changes of liquid crystals are applicable for optical data storage media as well as for display devices. The effect of irradiation with polarized light was also studied for the dimerization reaction of bis-anthracene chromophores dispersed in PMMA (Q. Tran-Cong, N. Togoh, *et al.* 3381, E1337).

4,4'-Bipyridinium ion is known to change color by photo-chemical reduction. T. Nagamura, Y. Isoda (3453, E1361) synthesized a photochromic polymer by introducing 4,4'-bipyridium salt with tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate anion into the polytetrahydrofuran backbone and examined the thermal stability of the colored form. Upon irradiation, the polymer film changed color from pale yellow to blue. The decay behavior of the colored form depended on temperature. Below 10°C, the blue color remained constant, while it decayed above this temperature. The decay rate at 20°C was, however, 20 times slower than that observed in microcrystals or in monolayer assemblies. This result suggests the possibility of increased color stability by selecting appropriate polymer matrices.

Another promising approach of photon-mode recording is PHB. PHB was first developed as a spectroscopic technique to detect homogeneous line widths in dyed solid systems.³ The method is applicable to wavelength multiplex optical memory. The memory system has a memory density over 10^3 times higher than the existing heat-mode recording systems.

H. Suzuki, T. Shimada *et al.* (3411, E 1347) developed a highly sensitive PHB system, which is composed of PMMA doped with tetraphenylporfin and halogenated anthracene derivatives. Holes were produced at 5.2 K in PMMA containing tetraphenylporfin and 9-bromoanthracene by irradiation with two short (2.5 ns) and low power (60 pJ/cm²) pulses. They measured the hole generation efficiency by using various halogenated aromatic derivatives with different reduction potentials, and

confirmed that two-photon donor-acceptor electron transfer via a stable photo-product is responsible to the hole generation.

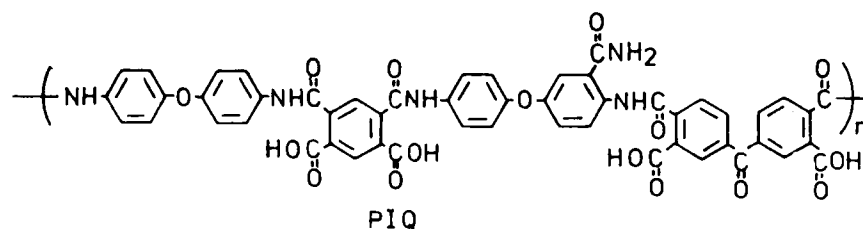
K. Sakota, M. Maeda *et al.* (3402, E1344) studied the effect of deuterium substitution of the central hydrogens of tetraphenylporfins on the quantum yield of hole burning. The deuterated porfins reacted 18–40 times less efficiently than the non-deuterated porfins. This confirmed that the hole burning in tetraphenylporfin is due to tautomerization of hydrogens in the central part. Deuterium substitution of the dyes as well as polymer matrices has the possibility of control of the thermal stability of holes at higher temperature.

NONLINEAR OPTICS MATERIALS

Certain organic conjugated π -electron systems have extraordinary nonlinear optical and electro-optic properties. Organic nonlinear materials offer potentially significant advantages over conventional inorganic nonlinear crystals.^{4,5} Many efforts have been made to seek new organic molecular materials exhibiting large second as well as third order susceptibilities.

For second order nonlinear process, macroscopic non-centrosymmetric alignment of organic molecules is required. Organic molecules with high second order hyperpolarizability, however, tend to make centrosymmetric crystals because of their dipole-dipole repulsive forces. To avoid the difficulty in making suitable crystal structures, the dye-polymer system was developed. Nonlinear active dyes in glassy polymer matrices can be aligned in non-centrosymmetric order by electric field poling. For such systems, there are many possible combinations between matrix polymers and dyes which are known to exhibit high hyperpolarizability. In order to hold high second order susceptibility, however, the alignment of dyes should be thermally stable. The key issues, therefore, are enhancement of the orientation order and stability of the poled state.

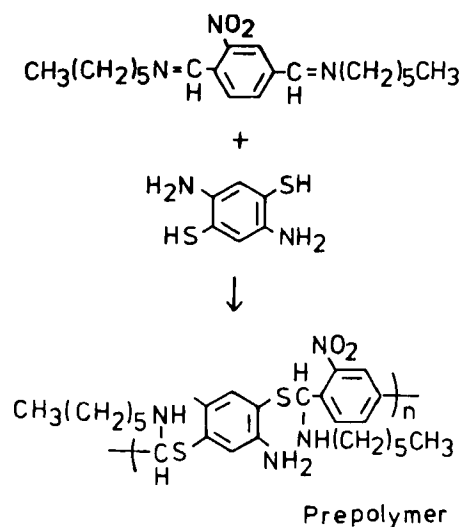
H. Okawa, T. Wada *et al.* (3477, E 1369) introduced polar diamine chromophores into the polyimide network in attempting to fix them thermally stable. A polyamic acid (PIQ) doped with 1,4-diamino-2-nitrobenzene was spin-coated on a substrate and heated at 250°C under poling. The heat treatment converted the amic acid groups into imides.



By poling the absorption at 420 nm due to phenylenediamine decreased. This indicates that the chromophores are oriented along the electric field. The dye-polymer system has the thermal stability and good optical properties useful for waveguides.

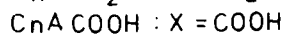
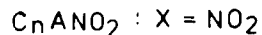
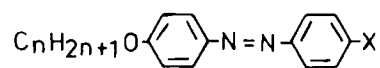
T. Wada, G. Zheng (3474, E1368) compared poling dynamics and stability of poled dyes in molecularly dispersed state and attached in the polymer pendant groups. They prepared PMMA doped with 10% of azo dye, disperse red 1, and polyurea containing 4-nitrostilbene in the pendant groups. The dynamics was followed by absorption measurements during poling procedure. The poling rate of the dyes dispersed in PMMA was 5 times faster than the dyes attached to the pendant groups. Both polymers showed sharp absorption intensity changes above T_g due to the relaxation of the dye alignment.

Another approach to align dyes in non-centrosymmetric structure is to use non-symmetric interfaces, such as the water-air interface. T. Senoh, T. Koike *et al.* (3462, E1364) synthesized poly(benzothiazole) prepolymer containing nitro groups in the polymer backbone by surface polycondensation reaction.



The ultra-thin film was transferred onto the substrate by the Langmuir-Blodgett (LB) technique, and the second harmonic generation abilities of the multilayer prepolymer film and the heat treated poly(benzothiazole) film were measured. Although the prepolymer film had the ability to produce second harmonic light efficiently, the intensity decreased to 1/40 by heat treatment above 200°C. Decrease of IR intensity due to alkylamine group by heating correlated well with the decrease of the second harmonic light intensity. This suggests that the decrease of second harmonic light intensity is caused by thioazole ring formation in the polymer backbone. Calculation of hyperpolarizability of the prepolymer and the thiazole structures predicted the decrease as much as 1/30.

The LB method was also applied to align polar molecules with large hyperpolarizability into a non-centrosymmetric structure. The high order orientation is, however, often reduced by the dipole-dipole repulsive forces between polar molecules. K. Nakamura, M. Era *et al.* (3465, E1365) improved the orientational order of polar molecules in LB films by mixing with less polar homologous amphiphiles. Polar azobenzene-linked amphiphiles C_nANO_2 was mixed with C_nACOOH with the same



chain length n , in various molar ratios and the mixed monolayer was transferred onto silica substrates.

Second harmonic light intensity in a single component monolayer was negligible. On the other hand, high intensity was observed from the mixed LB films. This result shows that in the mixed film polar C_nANO_2 molecules are oriented in the non-centrosymmetric structure. Molecular dilution of polar amphiphiles with less polar homologous molecules is a useful method to align molecules in a non-centrosymmetric structure.

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