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PHOTOSENSITIVE POLYMERS

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The present summary covers photophysical and photochemical processes in polymers and their applications; photopolymerization is not included. The main research interests in the field of photosensitive polymers has now shifted from fundamental studies on photophysical and photochemical processes to the area of applications such as photoresponsive polymers, image forming and optical memory materials.

Photophysical Processes in Polymers

Luminescence spectroscopy can give information concerning sequential distribution of a monomer unit in a copolymer. Although the copolymer of 2-vinylnaphthalene (2VN) and maleic anhydride (MAN) has been assumed to form an ideally alternating copolymer, the copolymer was found using the luminescence spectroscopy to contain a small but significant fraction of both the 2VN–2VN and MAN–MAN diad sequence depending on the monomer feed ratio (Y. Morishima, S.H. Lim *et al.*, 3435). On the basis of steady state and time dependent fluorescence data on 2VN-dimethyl maleate (MMA) copolymers derived from the 2VN-MAN copolymers, they concluded that the excimer observed in the copolymer can be mainly attributable to the emission from 2VN–2VN diad sequence in the copolymer. The relatively strong intensity of the excimer fluorescence, in comparison with the relatively small number of 2VN–2VN sites in the copolymers was attributed to the efficient energy migration to 2VN–2VN sites from photon absorbing naphthalene residues in the 2VN-MMA alternating sequences.

Luminescence spectroscopy has also been used to measure oxygen concentration in water or in gas phase (M. Kaneko, T. Asakura *et al.*, 3649), Ru(bpy)₃ was used in this study as a luminescence probe. Nafion or silk fibroin membranes containing the complex were immersed into a water sample and excited with 460 nm light. The emission intensity at 600–610 nm were found to depend on the oxygen concentration in the water. By using a

calibration curve, the oxygen concentration was calculated from the emission intensity.

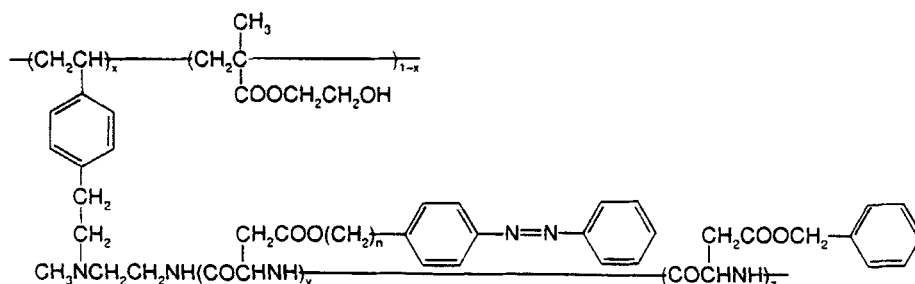
TICT (twisted intramolecular charge transfer) fluorescence is a useful probe to obtain information concerning local segment mobility, when TICT molecules are introduced in the polymer (Tazuke, R.K. Guo, 2845). A trace amount of dimethylaminobenzoate (DMBA) connected to poly-(methyl methacrylate) with different spacer length was investigated and it was found that the emission intensities from TICT excited state and planar local excited states were measured. The relative TICT intensity provides information on the effect of polymer microenvironment on the torsional motion of DMBA chromophores in solid state. The TICT intensity decreased with decreasing the spacer length between the DMBA group and the main chain. The result clearly demonstrated that the side chain mobility depends on the distance from the main chain.

Photoresponsive Polymers

Several new attempts to construct artificial photoresponsive systems by incorporating photoisomerizable chromophores into polymers have been reported. The polymers change their physical and chemical properties upon photoirradiation.

S. Kobayashi, M. Tabata *et al.* (3399) prepared polyphenylacetylene with pendant triphenylmethane leucohydroxide groups. The leuco-hydroxide is known to dissociate into an ion pair upon ultraviolet irradiation. This means that hole injection into the polymer is attained out by photoirradiation. They found that the radical concentration of the polymer changes upon photoirradiation by as much as 15–20%. Although the mechanism is not clear, the photogenerated positive ions in the pendant groups are considered to perturb the delocalization of radicals along the main chain. The rapid relaxation process observed after switching off the light, however, suggests the possibility of photo-heating effect to the process.

New vinyl polymer membranes (1 and 2) grafted with azobenzene modified polyaspartate were synthesized (M. Aoyama, J. Watanabe *et al.*, 3748).



The membranes immersed in 1,2-dichloroethane showed CD spectra similar to those in solution. Upon ultraviolet irradiation, which causes the trans to cis isomerization of the azobenzene chromophores, the ellipticity at 222 nm of the membrane 2 was reduced to 30% of the original value, while any CD spectral change was not observed for the membrane 1. The spacer length between the photoisomerizable chromophores and the main chain is an important controlling factor in the photoresponsive polymers.

Photocontrol of membrane functions has been carried out by several research groups. M. Sato, T. Kinoshita *et al.* (2887) prepared polypeptide membranes composed of poly(L glutamic acid) containing triphenylmethane leucocyanide groups in the side chain. The membrane potential was shifted to a higher value upon ultraviolet light irradiation. The effective fixed charge density of the membrane was estimated to be 1.20×10^{-2} mol/l in the dark and 3.89×10^{-2} upon ultraviolet irradiation. The ion permeability through the membrane was also affected by photoirradiation. Ultraviolet irradiation increased the KCl permeability by as much as 16 times.

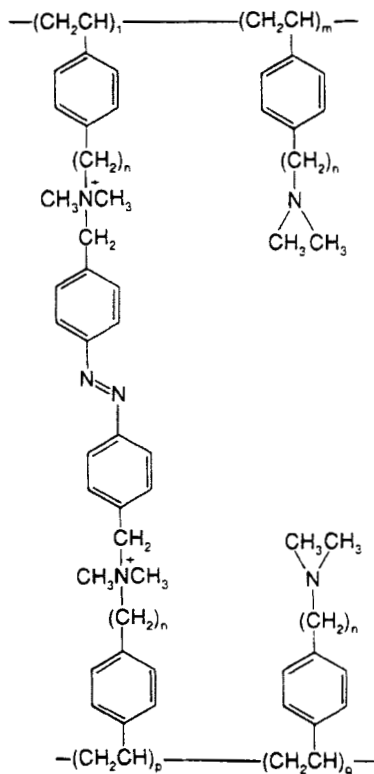
Photocontrol of the membrane permeability was also carried out by introducing spirobenzopyran chromophores into poly(vinyl chloride) membrane (J. Anzai, Y. Hasebe *et al.*, 2881). The membrane potential change of more than 100 mv was induced upon ultraviolet irradiation in the system. The potential change was observed even in the absence of salt concentration gradient between the two compartments. This is due to photo-generation of an asymmetric distribution of polar merocyanine forms in the membrane; the content of open form merocyanine is higher on the ultraviolet irradiation surface than on the non-irradiated surface.

Poly(N,N-dimethyl-4-vinylphenylamine)(PPA), poly(N,N-di-methyl-4-vinylbenzylamine)(PBA) and poly(N,N-dimethyl-4-vinylphenethylamine)(PPTA)(2) cross-linked with azobenzene groups were synthesized by M. Kijima, K. Se *et al.* (2291).

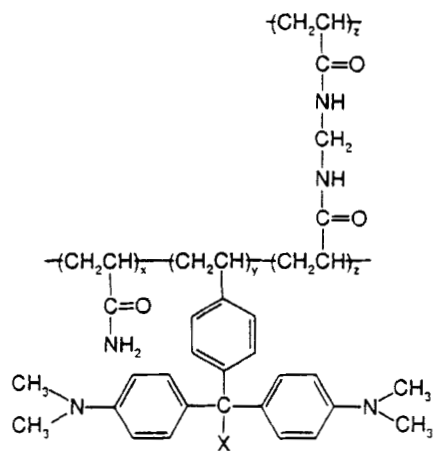
The films were prepared by casting from a THF solution of the polymers. The glass transition temperature of the polymers was found to be increased by the cross-linkings. Photoisomerization of the azobenzene chromophores in the film proceeded to about 10% conversion. The remains were considered to be fixed in the polymer network. The fraction could be controlled by introducing micro-domains of polystyrene into the polymer by block-copolymerization.

Photo-deformable polymer gels can be produced by incorporating triphenylmethane leucocyanide groups into a polyacrylamide gel (3).

Although the gel showed a large deformation, the deformation rate was very slow. To improve the deformation rate, electric field effects were examined (M. Irie, Y. Kobayashi *et al.* 3107). In an electric field the photostimulated deformation rate was accelerated by as much as 60 times. The addition of salts into the external aqueous solution further increased the deformation rate. The most pronounced acceleration effect was observed by the addition of $MgCl_2$.



$n = 0$; PPA
 1 ; PBA
 2 ; PPTA

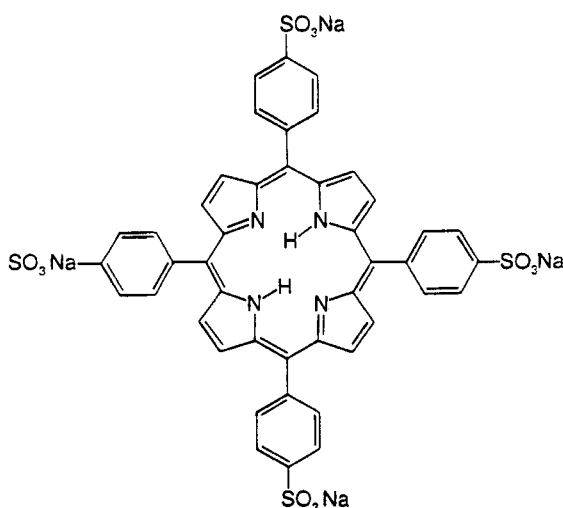


Optical Memory Materials

Recent advances in optical recording materials have introduced a new technology competing with the present magnetic recording systems. The signal density in the optical recording medium is one or two order of magnitude greater than that of magnetic recording media, while erase and rewrite capability is not yet satisfactory. At present, extensive studies are being undertaken to develop optical recording media. For this reason, a session concerning recording media was organized. Among various media reported in the session, here is concerned with photochemical hole-burning (PHB) as the system for a future recording system.^{1,2}

PHB was first developed as a spectroscopic technique to deduce molecular absorption lines burned in inhomogeneously broadened absorption band of dye-doped solid systems. The method is applied to wavelength multiplex optical memory. In principle, the memory-system overcomes the limiting storage density of the present optical disk system and achieves values over 10^3 times higher.

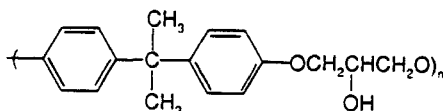
M. Yoshimura, T. Nishimura *et al.* (2854) developed multi-layered PHB systems to expand the wavelength region for hole formation and increase the hole multiplexing. The guest molecules were 1,4-dihydroxyanthraquinone (DAQ) and 4-amino-2,6-bis(4-butylphenoxy)-1,5-dihydroxyanthraquinone (ABDAQ) and the host matrices were PMMA and poly(2-hydroxyethyl methacrylate) (PHEMA). The samples were mounted in a cryostat at 4.2K and PHB was caused by irradiation with light from a dye laser. They were able to make more than 300 multiplex holes in a single layered PHB system, ABDAQ/PHEMA. By using a double layered system, ABDAQ/PHEMA and DAQ/PHEMA, the number of holes increased to 600.



In addition to the number of hole multiplicity, another important requirement of PHB is to develop new materials, which possess higher thermal stability. K. Sakota, K. Kominami *et al.* (2863) found that the holes burned in ionic porphin(4)-doped polyvinylalcohol have higher thermal stability.

The hole remained up to 120K. The holes could be burned above the liquid nitrogen temperature in these ionic porphin-doped polyvinyl alcohols.

K. Horie, T. Mori (2866) also reported a new matrix, which stabilizes the holes up to 80K. The matrix is phenoxy resin (polyhydroxyether)(5).



The low polarity and stiff molecular structure of phenoxy resin without bulky side groups are supposed to suppress the hole broadening due to electron-phonon interaction.

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