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PHOTOCHROMIC POLYMERS

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Abstract Studies on photochromic polymers with spiro-type photochromic side groups indicate that properties of the polymers are substantially different from the properties of similar polymer-photochrome blends.

INTRODUCTION

Applications of photochromism are mainly based on polymers containing photochromic dyes. Here, we define the photochromic polymers as polymers with photochromic dyes chemically incorporated in a macromolecule. The photochromic groups are usually side groups connected to a main chain through a flexible spacer (Fig. 1). In such polymers, a very high concen-

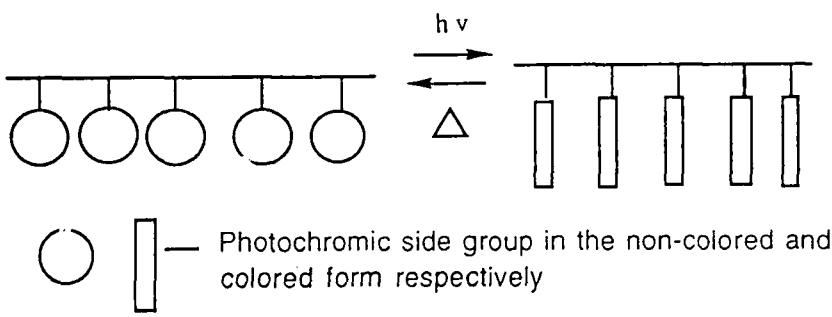

FIGURE 1 Schematic structure of photochromic polymers

tration of a photochrom in a polymer matrix can be achieved, which makes them indispensable for preparing thin films with high optical density of a colored form. If each unit of a macromolecule contains a photochromic group, concentration of the photochrome reaches 100%. In this paper, we

treat the subject by considering the characteristic features of photochromic polymers based on the most comprehensively investigated photochromic dyes, spiropyranes and spirooxazines[1,2] (Fig. 2)

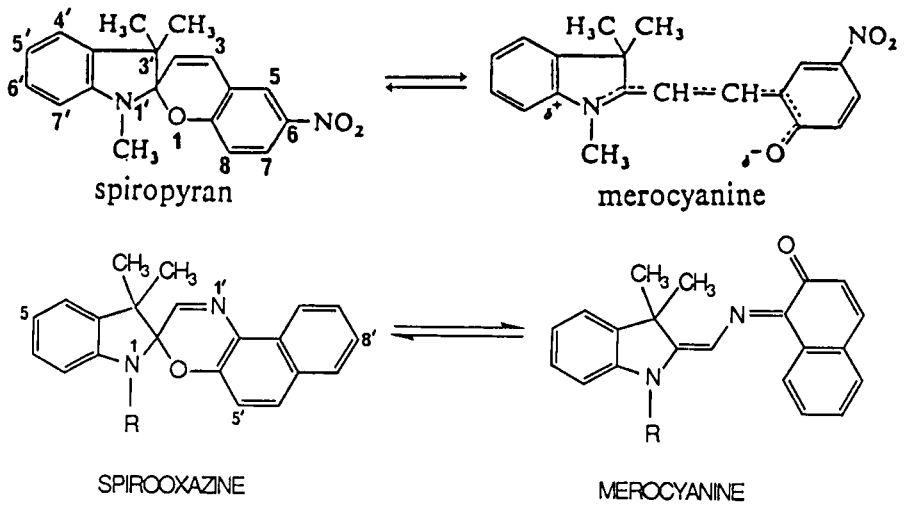

FIGURE 2 Examples of spiro-photochromes

Preparation of the polymers with polyvinyl (polyacrylic, polymethacrylic, polystyrene) and polysiloxane backbones and spiro-type photochromes by free radical or polymer analogous reactions was reported by us elsewhere[3-5].

Photochromic transformations of the polymers with closely spaced side groups are hindered by steric factors, since these transformations are connected with substantial conformational changes of the dye molecules. For example, polysiloxanes with spirooxazine side groups reveal retardation of the thermal decoloration reaction, which is stronger when the content of spirooxazine in the molecule is higher, and when the spacer which connects the photochromic group to the main chain[5] is shorter (Fig. 3).

In polymers containing spiropyrans with NO_2 groups (Fig. 2), the main factor leading to retardation of the thermal color decay is interaction of merocyanine groups formed on UV-irradiation[6]. The merocyanine dyes are known to have a very strong tendency to aggregation, due to the high polarizability and the large dipole moment of the molecules[7]. The

aggregation leads to reversible physical crosslinking of the macromolecules and to network formation. However, in the vinyl polymers, rigidity of the polymer matrix restricts the degree of aggregation.

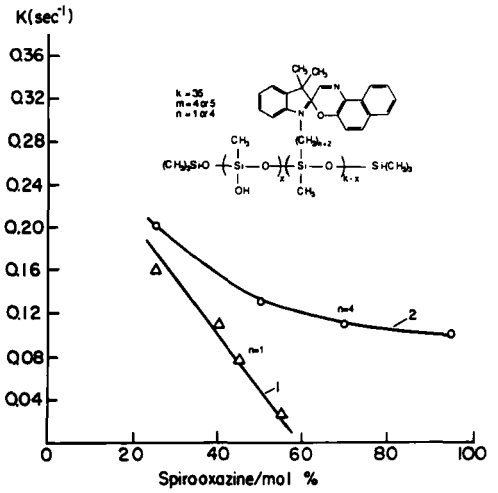

FIGURE 3 Dependence of decoloration rate constants on the photochrome content in the polisiloxane polymers. Curve 1, n = 1; curve 2, n = 4.

Plastification or swelling of the polymers in a solvent increase segmental mobility of the macromolecules and promote aggregation, which can occur even thermally without irradiation[8-10]. For some spiropyran homopolymers (100% photochrome concentration) crystallization of merocyanine groups were observed to have up to 40% degree of crystallinity. Discrete X-ray and electron diffraction patterns of such polymers indicate three-dimensional crystals formed by merocyanine groups while the atactic backbones remain amorphous (Fig. 4).

The crystallization proceeds as a cooperative process: it brings the photochromic groups closer together and promotes thermal spiropyran-merocyanine conversion, which in turn sustains crystallization. We have called this process "zipper crystallization".

Other functional groups can be incorporated in a macromolecule

together with photochromic groups, and this opens up new possiblities for tailoring multifunctional polymers. We synthesized a variety of photochromic liquid crystal po;ymers (PLCP) by incorporating both meso-

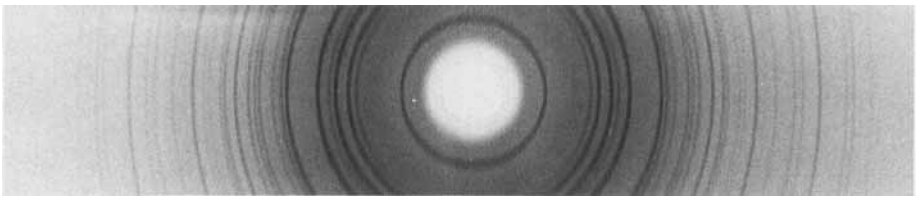

FIGURE 4 Powder X-ray diffraction pattern of 100% polyspiropyran-methacrylate after swelling in THF.

genic and photochromic side groups in a macromolecule[11-15] (Fig. 5). Such polymers respond reversibly not only to light but also to electric and magnetic fields, which may be important for laser-related technologies[2].

Molecular design of PLCPs can be diversified by changing a macromolecular backbone, for example, by going from relatively rigid polyvinyl macromolecules to very flexible polysiloxanes. Molecular weight of a polymer, length of spacers, relative concentration of different functional groups, etc. are factors which also control properties of PLCPs. Synthetic methods of preparation of PLCPs were substantially varied[11,13].

The temperature range of mesophase decreased with increasing concentration of such bulky groups as spiropyran or spirooxazine in the copolymers[12,14-16]. Rather large fractions (more than 40% in some cases) of these bulky groups can be incorporated in a macromolecule and mesophase still remained preserved. This was explained by separation of the photochromic and mesogenic sites in such copolymers, i.e. the photochromic groups and mesogenic domains "avoid" each other[14].

Aggregation of merocyanine groups formed on irradiation or heating of PLCPs containing spiropyrans leads to crosslinking of macromolecules and results in so-called "rheo-optical effect", dynamic ordering of mesomorphic macromolecules and appearance of transient birefringence in response to a very weak mechanical disturbance above the clearing temperature[11-13].

Aggregation of merocyanine groups in photochromic polymers is a

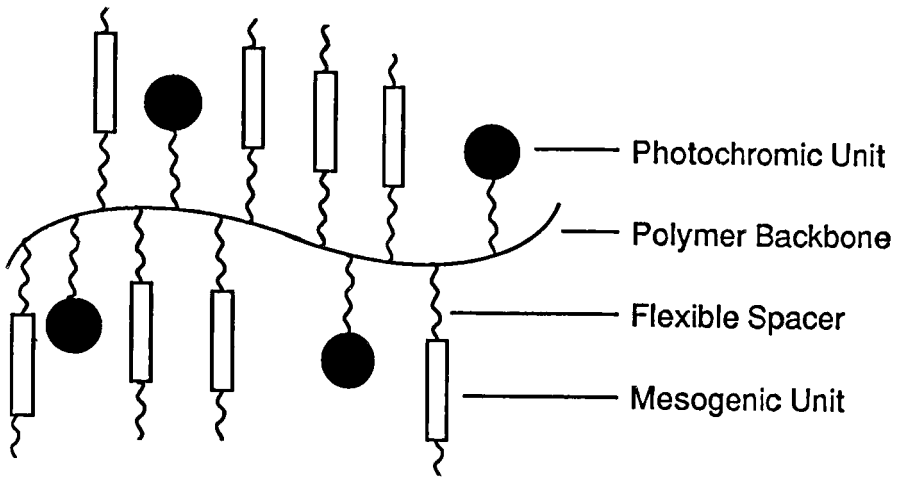

FIGURE 5 Structure of PLCP

source of another new and promising optical effect, two dimensional second-order nonlinearity[16-20].

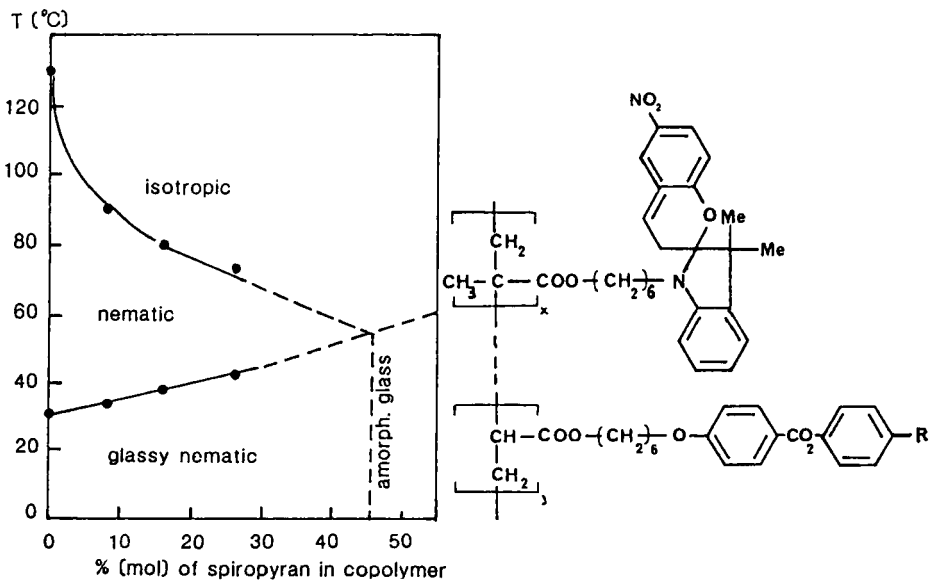

FIGURE 6 Phase diagram for one of PLCP

A polymer film containing merocyanine groups and cast on a glass slide was poled between two thin metal electrodes, deposited on the slide by evaporation (Fig. 7). Second harmonic generation (SHG) measurements

revealed that the film generated two SH signals, one with light polarized parallel to the electrostatic field and another which was polarized perpendicular to the field. The first SHG was conventional and stemmed from merocyanine molecules oriented along the field. The second SH signal was unconventional and could not be explained by orientation of the dye molecules in the field. The second order susceptiblity parameter for the unconventional nonlinearity became two orders of magnitude higher than the conventional one when the field was increased.

Further detailed studies showed that SHG perpendicular to the field was originated by charges injected in the polymer film from the electrodes and trapped by merocyanine aggregares[19,20]. Asymmetric geometry of the sample (thin electrodes situated on the interface between the polymer film and the glass) was apparently important for asymmetric distribution of charges in the film.

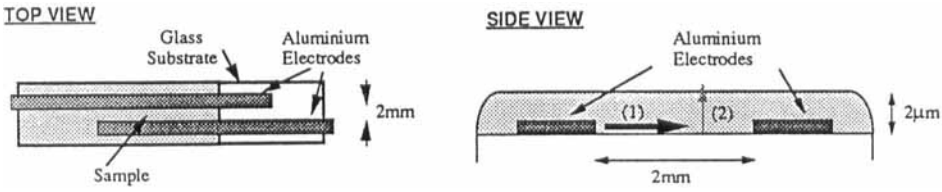

FIGURE 7 Geometry for "in-plane" poling. Charge injection (1) during application of voltage across the electrodes sets up a charge gradient (2) along the direction perpendicular to the electric field. The strongest optical nonlinearity is measured in this direction.

CONCLUSIONS

Incorporation of spiropyran and spirooxazine photochromic dyes in a macromolecule as side groups allowed not only for substantially increasing the photochrome concentration in a polymer matrix but also for controlling the photochromic process and tailoring other properties of the macromolecules. This is connected with the close location of the photochromic groups in the macromolecules and with strong interactions between them. Reversible crosslinking and even crystallization of macromolecules by virtue of these interactions were observed in the polymers with spiropyran–merocyanine groups.

Functionalization of the polymers with mesogenic side groups in addition to photochromic ones resulted in photochromic liquid crystal polymers.

Merocyanine groups and their aggregates in the photochromic polymers poled in an electrostatic field revealed two-dimensional second-order nonlinearity, which opened new possibilities for application of such polymers.

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