Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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PHOTO- AND THERMO-CHROMIC LIQUID CRYSTAL POLYMERS WITH SPIROPYRAN GROUPS

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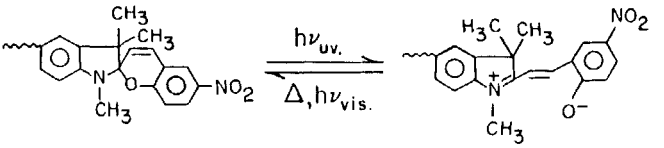
Abstract Side chain liquid crystal polymers containing spiropyran and mesogenic units give photo- and thermo-chromic mesophases. Structural changes of the mesomorphic systems can be induced by the reversible spiropyran- merocyanine dye conversion.

INTRODUCTION

The possibility of inducing structural and optical changes in photosensitive liquid crystals is one of the topics of great interest to those working on the development of new photoimaging technology. Recently, liquid crystal polymers have become a subject of considerable interest because the high viscosity and glassy nature of the mesophases can be well exploited when they are combined with photoactive compounds. Indeed, the synthesis of liquid crystal copolymers containing dye and mesogenic units[1] has opened up interesting possibilities to obtain materials with a multifunctional character. Thus, groups which confer some desirable property can be incorporated in a copolymer.

Spiropyrans are one class of compounds which can be used to generate structural changes in a mesomorphic system.[2,3] These compounds have an additional advantage in the development of light-sensitive liquid crystals because they are photo- and thermo-chromic:[4] by u.v. irradiation or heat they are reversible converted to a merocyanine dye



(SPIROPYRAN) A (MEROCYANINE) B

Our purpose in the present paper is to describe representative results which demonstrate that incorporation of spiropyran side groups in side chain liquid crystal polymers leads not only to photo- and thermo-chromic mesophases but changes the physical properties of the polymers.

MATERIALS AND METHODS

Liquid crystal polyacrylates were prepared according to the scheme shown in the Fig. 1. The detailed synthesis and free radical polymerization of the monomers were described earlier.[5] Liquid crystal polysiloxanes were obtained via active ester-mesogenic copolymers, which were prepared by addition of mesogenic and hydroxysuccinimide-ester olefines to Si-H containing polymers[6] (Fig. 2).

The liquid crystalline behavior and the transition temperatures of the polymers were investigated by polarization microscopy and differential scanning calorimetry (DSC). A wild M8 polarizing microscope with a Ernst Leitz GmbH wetzlar hot stage was used. The DSC measurements were performed with a Mettler TA 3000 calorimeter. Irradiation of the films was performed with an Osram HBO 200 mercury lamp. The optical absorption measurements were performed on a Varian 2200 spectrophotometer with a heating-cooling attachment. The composition of the copolymers was determined by elemental analysis or spectrophotometry of their solutions.

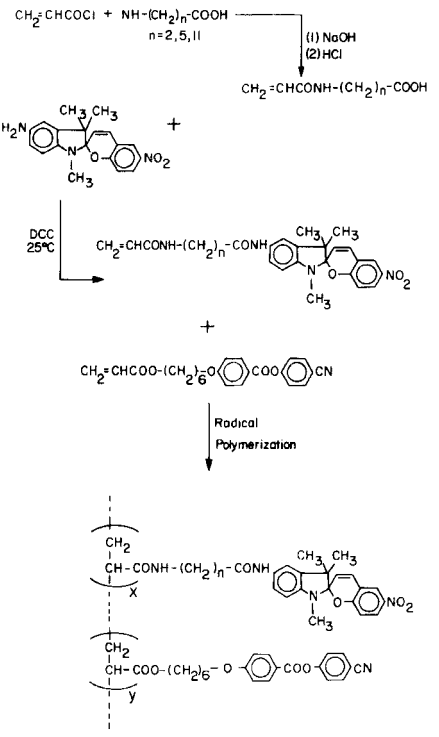


FIGURE 1. Reaction scheme for the synthesis of photochromic polyacrylates.

RESULTS AND DISCUSSION

Thermo- and photo-chromic properties

Observation with a polarizing microscope revealed that the clearing points of the copolymers are lower the higher the content of spiropyran units in the copolymer. Typical phase transition temperatures and composition for polyacrylate and polysiloxane copolymers are given in Figs. 3 and 4.

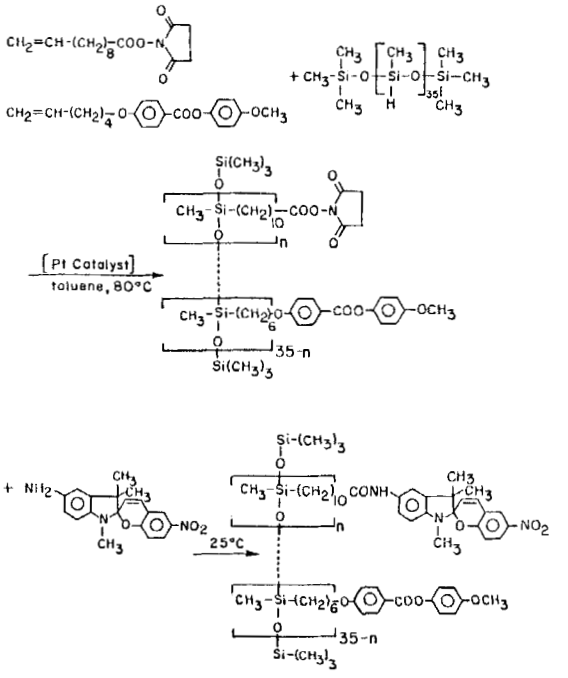


FIGURE 2. Synthetic route for preparation of photochromic polysiloxanes.

The copolymers exhibit thermochromic properties i.e change of color progressively with temperature. The electronic absorption spectra of the polyacrylic copolymer films (see Fig. 5) show an increase of visible absorption with temperature rise. The transition from amorphous to liquid crystalline phase is accompanied by formation of a broad plateau in the range 460-585 nm. The optical density in this range does not change with

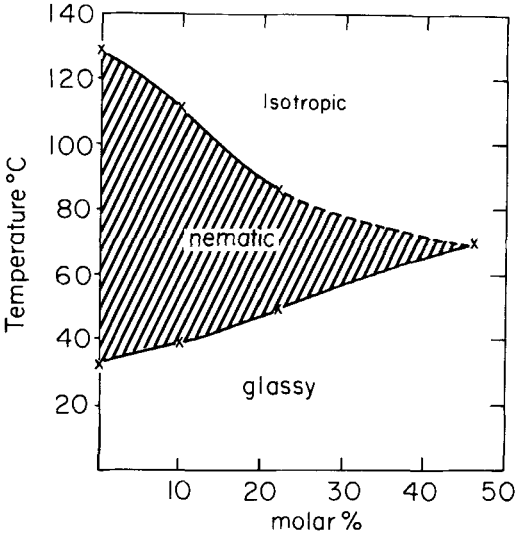


FIGURE 3. Phase behavior of the spiropyran containing polyacrylates with n=5 in Fig. 1

temperature up to the clearing point. The transition from mesophase to isotropic phase coincides with the appearance of an absorption band with a $\lambda(\max) = 585$ nm (a correction for the light scattered by the mesophase was made when the spectra were plotted). The band vanishes reversibly on cooling.

The copolymer films acquire a pink color at room temperature. Irradiation with visible light ($\lambda > 500$ nm) brings about a pale yellow color, while irradiation of the yellow film with u.v. light ($\lambda = 365$ nm) at temperatures below the glass transition temperature results in a blue color. If the yellow film is irradiated with u.v. light at temperatures around

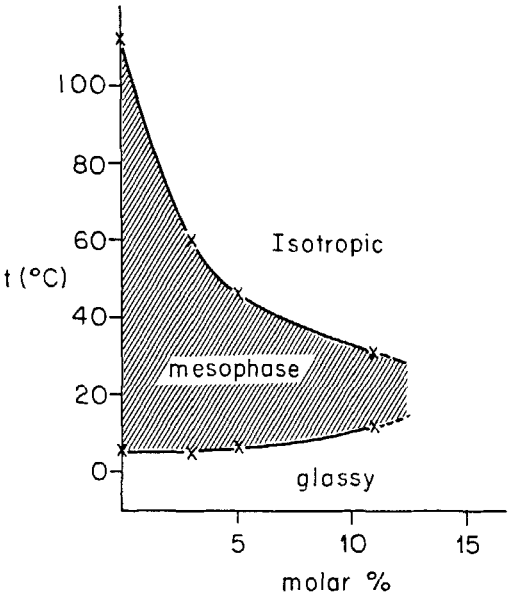
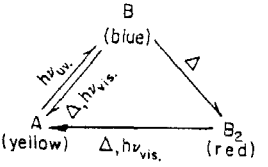


FIGURE 4. Phase diagram of the polysiloxane copolymers with spiropyran groups.

and above the glass transition temperature it turns deep red. The yellow color can be restored by irradiation of blue or red films with visible light.

Characteristic absorption spectra of irradiated and non-irradiated polysiloxane films are given in Fig. 6. The maximum at 550 nm (red) corresponds to aggregated merocyanines, while the maximum at 580 nm (blue) was ascribed to isolated merocyanine groups.[7] The yellow color (λ(max). $\approx$ 370 nm) corresponds to the spiropyran absorption.

The mechanism for these transformations is summarized below



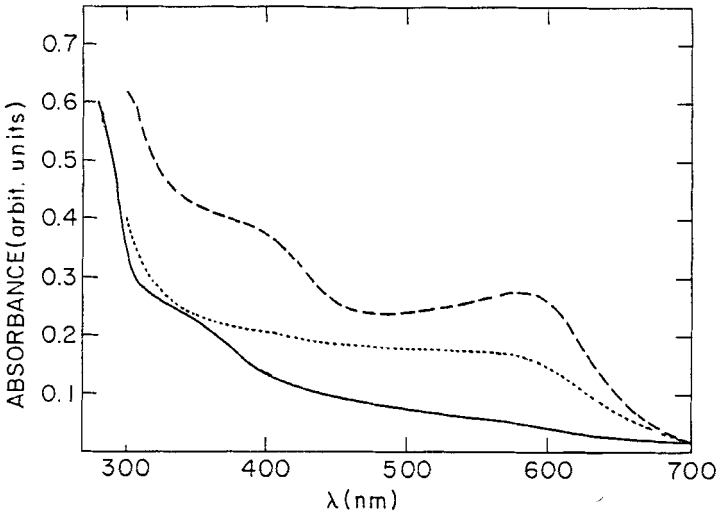


FIGURE 5. Absorption spectra of polyacrylate (n=5) containing 22% of spiropyran units: (—) amorphous film at 26 °C; (···) mesomorphic film at 82 °C; (– – –) isotropic film at 95 °C.

Apparently at temperatures below the glass transition the thermal dimerization of the merocyanine groups is impossible because of the limited segmental mobility.

Rheo-optical properties

A very remarkable feature of the isotropic films formed above the clearing point by the copolymers is their very strong transient translucence between cross polarizers when they are squeezed between two glass slides or even lightly touched with the tip of a spatula.

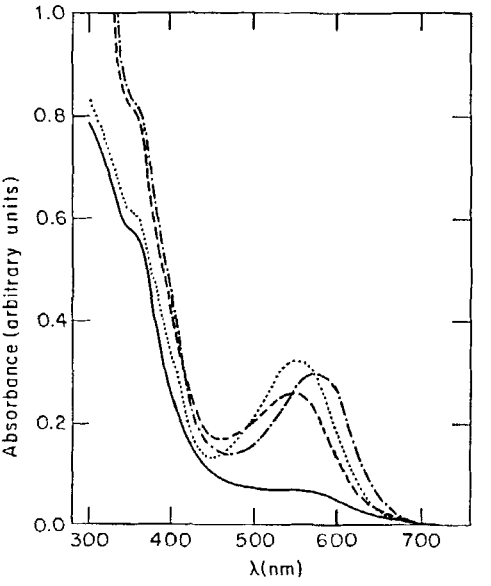


FIGURE 6. Absorption spectra of polysiloxane with 11% of spiropyran units: (—) yellow film at 25° C; (···) red film at 25° C; (- · -) blue film at −20° C; (– – –) red film obtained by heating the blue film to 25° C.

The liquid crystal homopolymers, which do not contain spiropyran, do not exhibit this effect.

Usually such instant birefringence during mechanical disturbance is considered as an indication of homeotropic (orthogonal to solid surface) orientation of mesogenic molecules.[8] Therefore, one could conclude that instead of nematic-isotropic transition at the clearing point we observe a transformation of orientation of mesogenic groups of macromolecules from parallel to perpendicular to the surface.

To check this, we treated the glass surface with cremophor[9] and nylon[10] which promote the planar orientation of liquid crystals and with 1-dodecanol[9] for the homeotropic alignment. We found no effect of the surface on the "sparkling phenomenon". A decisive experiment was performed with droplets of the copolymers in an isotropic phase having a relatively small area connected with a surface. For these droplets again even a very gentle touch gave remarkable sparkling though in this case the effect of the surface must be insignificant. This suggests that the transient brightening is caused by at least partial restoration of liquid crystalline order, induced by mechanical disturbance.

The DSC measurements give endothermic peaks at temperatures that coincide with the microscopic observation of the clearing points. This confirms that the static birefringence disappearance relates to the mesophase-isotropic phase transition.

The rheo-optical properties of the copolymer films as a function of temperature were investigated with a parallel-disk type rheometer with transparent glass disks.[11] The results revealed that introduction of relatively small portion of the spiropyran groups causes a drastic increase in the viscosity of the polymers. This indicates that the interaction of the merocyanine groups, formed on heating or irradiation, gives rise to the aggregation of macromolecules in a network with high viscosity.

The formation of such a network by physical crosslinking of the macromolecules due to dimerization of the merocyanine side groups is responsible for the appearance of the strong dynamic birefringence above the clearing point.

Presumably, the more rigid structure of the network favors the preservation by macromolecules of the conformation acquired in the mesophase even above the clearing point. This makes the dynamic ordering easier.

CONCLUSION

The synthesis of polyacrylate and polysiloxane liquid crystal polymers, containing spiropyran and mesogenic units leads to materials with thermo- and photo-chromic mesophases. Structural changes of the mesomorphic systems can be induced by the reversible spiropyran-merocyanine dye conversion. At temperatures below the glass transition, when the segmental mobility is limited, u.v. irradiation of the copolymers results in formation of isolated merocyanine molecules. At higher temperatures the aggregation of the dye moieties takes place, leading to a network formation and a very strong dynamic birefringence above the clearing point. The reverse photoconversion of merocyanines to spiropyrans occurs on irradiation with visible light.

The possibility to control with light and temperature the formation of the three primary colors combined with the physical properties of liquid crystal polymers may make these materials interesting for applications in the area of display and information storage technology.

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