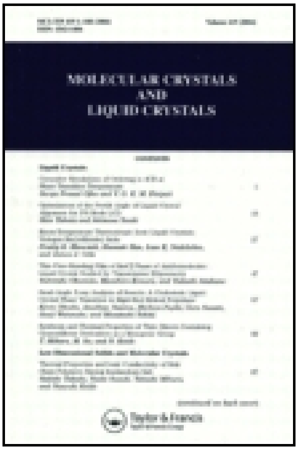

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Spiropyrans as Counterions in Photochrome-Containing Polyelectrolyte

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SPIROPYRANS AS COUNTERIONS IN PHOTOCHROME-CONTAINING POLYELECTROLYTE

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Abstract Synthesis and properties of polycation with spiropyran salt as counterion were investigated. The photochromic group was connected to the main chain of polymer (polycation bromide) by ion-exchange in polar solution. The new system shows negative photochromism. The existence of N^+-cation as part of the polymer changes kinetic properties the thermocoloration. The ring closuring reaction influences thermal properties of the polyelectrolyte chain.

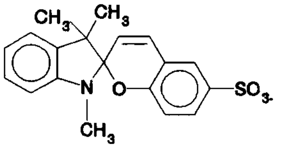
INTRODUCTION

Low molecular colorants can greatly modified both bulk and local physical properties of materials such as refractive index, optical absorption, nonlinear optical effects, conductivity, fluorescent properties etc. The most useful materials with respect to these parameters seems to be glass-forming organic polymers, which offer several advantages over inorganic glasses. Combination of charged polymers with colorants as counterions bounded by coulombic interactions seems to be simple way for preparation of polymeric materials. Such polyelectrolyte glasses based on polycations with anionic dyes as counterions were recently prepared[1] and their optical and thermal properties were reported[2,3].

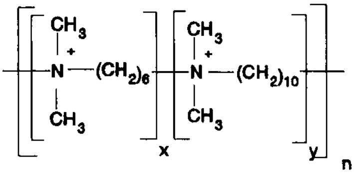
This report deals with preparation and investigation of the new type of polymer electrolyte functionalyzed with anionic spiropyran with a sulphonate group on the phenyl ring as counterions.

EXPERIMENTAL

Reverse photochromic 1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline]-6-sulphonic acid (Sp) was synthesized according to Sunamoto et al.[4]. NMR, IR and mass spectroscopy analysis confirmed the expected structure of this compound. Spiropyran-containing polyelectrolyte (PEL-Sp) with the desired molar ratio was obtained by ion-exchange starting from statistical polymer (PEL) prepared as the bromide by the same procedure as describes previously[1]. The salt of the polymer containing both types of counterions was precipated from the mixture.



Sp



PEL

Thus polyelectrolyte glasses with varying amounts of chromophores were obtained. The polymer is soluble in polar solvent like DMF, MeOH, H_2O and was cast from this solvents to provide optically clear films. The actual concentration of the spiropyran (8 wt.-%) was determined by ^1H NMR method.

Photochemical reaction was induced by irradiation with 300 W Xe lamp thorough the 400-480 nm transparent filter and followed taking UV-vis spectra (HP 8452A diode array spectrophotometer). The glass transition temperature (T_g) was determined by DSC (Du Pont 910) method. A scanning rate of 10 °C/min was used over the temperature range from 0 to 80 °C. The T_g was taken as the temperature of the inflection point on the heat capacity changes.

RESULTS AND DISCUSSION

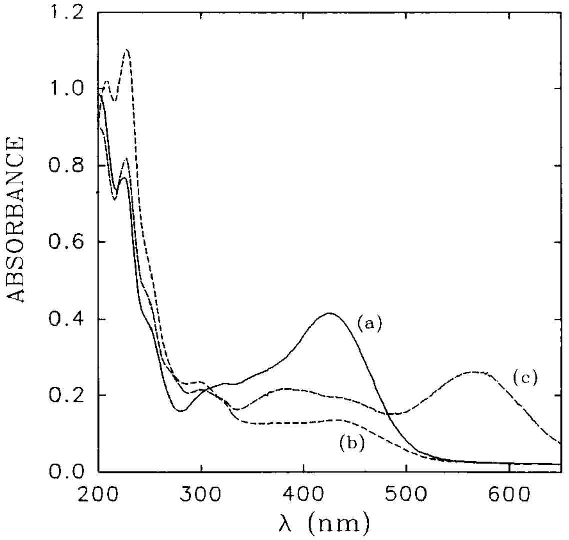


Fig.1 Changes in absorption spectra of thin glassy films of PEL-Sp (a) caused by 400-480 nm light irradiation (b) and after exposure to NH_4OH vapour (c).

Polyelectrolyte-containing spiropyran molecules (PEL-Sp) show revers photochromism in liquid solutions as well as in glassy films. Fig.1 presents changes in UV-vis absorption spectra of PEL-Sp film induced by light irradiation or exposure of the film to ammonia vapour. The occurrence of the isosbestic points at 308 nm for photoirradiation and at 490 nm during the increase pH indicates that the ring closure reaction is the only photochemical change.

The existence of the culombic interaction between spiropyran-counterion and the ionene does not change the position of the absorption maximum of the merocyanine (Mc) species. As in the case of free spiropyran molecules the λ_{max} position can be related to the solvent polarity[4]. The absorption maximum shows a blue shift with the solvent polarity (Table 1). The absorption spectrum for PEL-Sp film suggests that the polarity of the microenvironment of Mc species corresponds to that of ethanol. Contrary to the same position of the absorption maxima, the thermocoloration kinetics of PEL-Sp shows changes as compared with non bounded spiropyran molecules in the same solvents. It was found that the first-order rate constants for the thermocoloration in polar solvents decrease about 2 times compared with that observed for free molecules[4] (see Table 1). The higher values for conversion rate from Sp to Mc for PEL-Sp can be interpreted in terms of stabilization of the ionic product of Mc by additional solvation with N^+-cations as part of polymer chain. This means that although absorption spectra does not monitor the increase in polymer-dye interaction the kinetic of thrmocoloration does. The formation of this interaction could be applied to the control of physical processes driven by light.

TABLE 1 Absorption and kinetic parameters for polyelectrolyte-containing spiropyran.

environment	λ_{max}, nm	rate constant, s^{-1}
H_2O (neutral)	408	0.00049
MeOH	425	0.00037
EtOH	430	0.00031
film (solid)	430	0.000048

The photochromic properties of PEL-Sp can also be monitored by changes in thermal properties. Fig.2 shows DSC thermograms for PEL. The curves correspond to the fresh sample and samples being subjected to light irradiation and heat. One can note a significant shift of the T_g value from 17.8 °C to 36.6 °C after visible light irradiation for 1 hour. The T_g for the sample after heat treatment at 40 °C for 15 min. was found to be at 32.0 °C. Further increase of irradiation time increases also a T_g value. This suggests that the increase of T_g upon irradiation arises from the interaction between the photochromic molecules and the polymer matrix. Similarly as for ionenes with different size of dye-counterions[2], this fact can be elucidated by the change of the photochrome volume during Mc->Sp phototransformation (Mc has a lower volume than the Sp form) and by the change negative charge distribution on pyran ring.

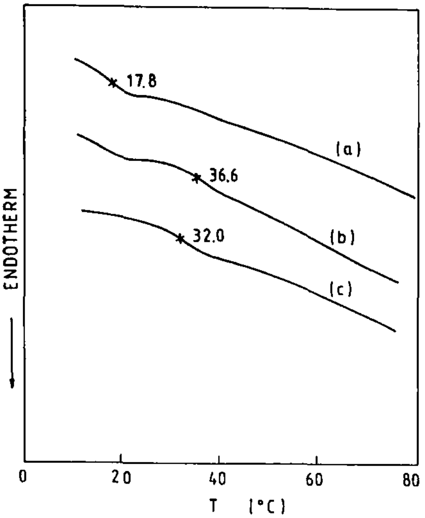


Fig.2 DSC spectra of (a) fresh PEL, (b) after visible light irradiation and (c) heat treatment.

In conclusion, we designed a photochromic polyelectrolyte with spiropyran molecules as counterions. This system shows negative photochromism in solution and solid films. Thermocoloration rate of the photochromic polymer system is higher as compared to non bounded spiropyran molecules.

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