Novel Photochromic Polymer Films Containing Ion-pair Charge-transfer Complexes of 4,4′-Bipyridinium Ions for Optical Recording

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Elastic polymer films containing 4,4′-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as part of the main chain showed persistent and reversible colour changes due to photoinduced electron transfer upon excitation of an ion-pair charge-transfer band (λ_{ex} >365 nm) *in vacuo* with the lifetime of the coloured state markedly dependent on temperature.

Photochromic systems employing polymers or Langmuir–Blodgett films have recently attracted much interest in view of their promising applicability in high-speed and high-density optical memory devices. The photochromism reported so far involves changes of chemical bonds such as heterolytic cleavage or *cis–trans* isomerization. These reactions might limit the thermal or cyclic stability and the response time for optical recording especially in the solid state. Recently we have reported novel photochromism in organic solutions,[1] microcrystals[2,3] and monolayer assemblies[4–6] which was due only to electron transfer *via* the excited state of specific ion-pair charge-transfer (CT) complexes[7,8] of 4,4′-bipyridinium ions with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[9] (TFPB$^-$). We also showed that the molecular orientation of 4,4′-bipyridinium cation radicals could be controlled in monolayer assemblies.[6] The photochemical colouring and thermal fading were highly reversible in all these systems.[1–6]

Kamogawa *et al.* recently reported the 'photomemory' of 4,4′-bipyridinium copolymers with *N*-vinyl-2-pyrrolidone.[10] Their system used UV irradiation for writing and oxygen for

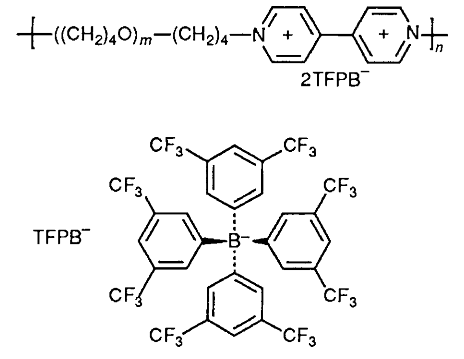

Fig. 1 The structure of the elastic polymer containing 4,4′-bipyridinium ions and the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion

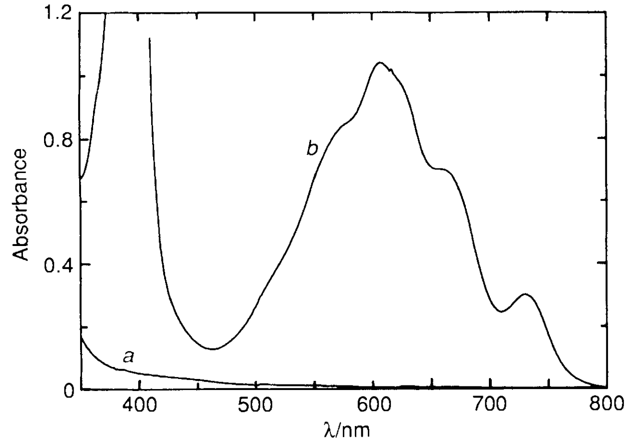

Fig. 2 Absorption spectra of polymer films (*a*) before and (*b*) after irradiation *in vacuo* at 30 °C for 45 min

erasing. The former would be accompanied by undesirable side reactions and the latter includes irreversible reactions.[11] We now report reversible and persistent photochromic polymer films in which the lifetime of the coloured state photochemically formed can be controlled by temperature to construct optical recording systems. We also show that the present polymeric system is superior to the corresponding monolayer assemblies recently reported by us[4–6] with respect to film preparation and the lifetime of the coloured state.

An elastic polymer containing 4,4′-bipyridinium salts as a part of the main chain was synthesized by a slight modification of the procedure reported by Kohjiya *et al.*[12] Dried tetrahydrofuran (24.45 g) was stirred in Ar for 15 min at room temperature in the presence of trifluoromethanesulphonic anhydride (1.40 g) as an initiator. The solution was then cooled to −70 °C and a tetrahydrofuran solution of 4,4′-bipyridine (0.53 g in 10 ml) was added. The mixture was stirred for 7 h at −70 °C and for 1 h at 2 °C to cause the reaction of 4,4′-bipyridine with living dicationic poly(tetrahydrofuran). The highly viscous products were purified by repeated precipitation and washing with water. The content of 4,4′-bipyridinium ions in this polymer was determined from the absorbance at 265 nm to be 4.3×10^{-4} mol g^{-1}. The counter-ions ($CF_3SO_3^-$) of the white polymer were exchanged in chloroform with TFPB$^-$ to yield a pale-yellow elastic polymer. The structure of this polymer is shown in Fig. 1, where *m* is estimated to be about 30 from NMR spectroscopy and elemental analyses (Found: C, 60.55; H, 9.59; N, 0.94%). This value of *m* corresponded to the above-mentioned content of 4,4′-bipyridinium ions within experimental error. Transparent polymer films were obtained by casting 1,2-dimethoxyethane solutions into a quartz plate.

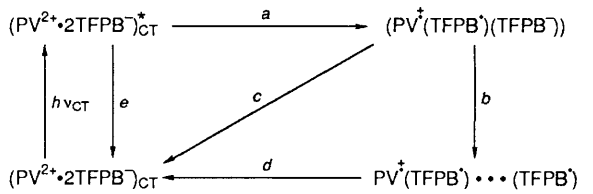

Fig. 3 A schematic representation of the electron transfer reaction responsible for the colour changes observed. PV^{2+}, $PV^{\cdot +}$, and TFPB$^{\cdot}$ stand for polymeric 4,4′-bipyridinium ion, its reduced form, and oxidized TFPB$^-$. The excited CT state is deactivated by the electron transfer to form geminate pairs (path *a*) or by radiative and nonradiative processes (*e*). Geminate pairs will form metastable charge-separated species $PV^{\cdot +}$ (TFPB$^-$)$\cdot \cdot \cdot$ $\cdot$(TFPB$^\cdot$) by path *b* or, *via* reverse electron transfer, revert to the original CT state (*c*). Metastable charge separated-species revert to the original CT state thermally (*d*).

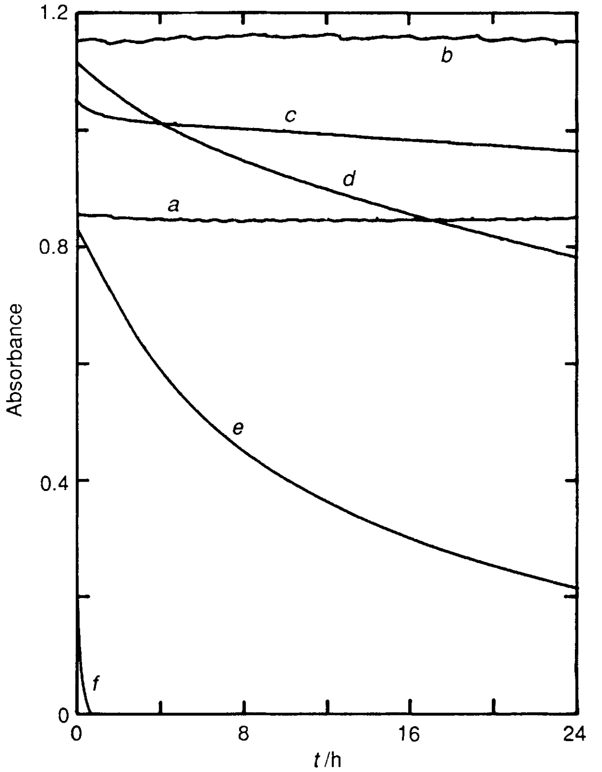

Fig. 4 Time-dependence of absorbance at 605 nm for polymer films irradiated *in vacuo* for 45 min at (*a*) −20, (*b*) 0, (*c*) 10, (*d*) 20, (*e*) 30, and (*f*) 80 °C

The films were thoroughly degassed in an Oxford DN1754 cryostat. These samples were irradiated *in vacuo* at controlled temperature by a Hamamatsu 150 W Xe–Hg lamp equipped with a Toshiba L-39 cut-off filter (λ >365 nm) and a 10 cm water filter to excite their CT absorption band alone.

Upon irradiation the colour of the polymer films changed from pale-yellow to blue. The UV/VIS absorption spectra are shown in Fig. 2 for polymer films (*a*) before and (*b*) after irradiation. The latter spectrum is characteristic of 4,4′-bipyridinium cation radical monomer.[13] This result indicates that the blue colour was caused by photoinduced electron transfer reactions *via* the excited state of ion-pair CT complexes as schematically shown in Fig. 3 (path *a*, *b*) in solid polymer films in a similar manner as that previously reported for TFPB$^-$ salts of 4,4′-bipyridinium ions in organic solutions, microcrystals and monolayer assemblies.[1–6] Kohjiya *et al.*[14] recently reported a colour change in a similar copolymer of tetrahydrofuran and 4,4′- bipyridinium salts with bromide or chloride upon UV irradiation (λ_{ex} >270 nm). Their spectrum after irradiation showed a large proportion of 4,4′-bipyridinium cation radical dimers with a peak at 540 nm[13] in addition to monomers. This is in contrast with our results and is most probably due to the structural difference of the counter-anions.

Coloured species photogenerated in polymer films decayed *in vacuo* in the dark reversibly with a rate depending on temperature as already reported for monomeric TFPB$^-$ salts of 4,4′-bipyridinium ions in other systems.[1–6] The time-dependence of the absorbance at 605 nm of polymer films after irradiation at various temperatures is shown in Fig. 4. It should be noted that no decay was observed after 24 h below about 0 °C. The coloured state was easily erased at elevated temperatures. The absorption spectrum after thermal decay of 4,4′-bipyridinium cation radicals was the same as that of the original polymer film. It was formed again upon excitation of the CT band at each temperature *in vacuo*. The lifetime ($\tau_{1/e}$) of 4,4′-bipyridinium cation radicals at 20 °C was about 72 h, which is about 18 times longer than that in microcrystals and monolayer assemblies reported previously.[3,4] We have shown that 4,4′-bipyridinium cation radicals escaping from the geminate reaction (path *c* in Fig. 3) immediately after the photoinduced electron transfer because of conformational changes (distance and/or orientation) (path *b*) became metastable owing to the bulk and chemical stability of TFPB$^-$ and also to the restriction of molecular motion by the microenvironment.[1,3,4] The much increased lifetime in the present polymer system compared with that in microcrystals or monolayer assemblies strongly suggests that the microenvironment in highly elastic polymers[12,14] facilitated the change of mutual orientation and/or distance of charge-separated species and also restricted the molecular motions leading to the reverse reaction (path *d*). Persistent storage of data below about 0 °C is most probably related to the endotherm observed at 0–30 °C in a differential scanning calorimetry thermogram of this polymer suggesting a crystalline melting of poly(tetrahydrofuran) units. A glass transition of this polymer was observed around −90 °C.

These results indicate that data written optically (λ >365 nm) can be stored in polymer films. These data can be read with a diode laser and can be erased thermally. The present photochromic polymer may be used as a new material for high-speed and high-density optical recording. Efforts are being made to measure the rate of colouring and also to obtain detailed information on the molecular mechanism controlling the fading process.

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References

1 T. Nagamura and K. Sakai, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3529.
2 T. Nagamura and K. Sakai, *J. Chem. Soc., Chem. Commun.*, 1986, 810.
3 T. Nagamura and K. Sakai, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 1432.
4 T. Nagamura, K. Sakai and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1988, 1035.
5 T. Nagamura, K. Sakai and T. Ogawa, *Thin Solid Films*, 1989, **179**, 375.
6 T. Nagamura, Y. Isoda, K. Sakai and T. Ogawa, *J. Chem. Soc., Chem. Commun.*, 1990, 703.
7 T. Nagamura and K. Sakai, *Chem. Phys. Lett.*, 1987, **141**, 553.
8 T. Nagamura and K. Sakai, *Ber. Bunsenges. Phys. Chem.*, 1988, **92**, 707.
9 H. Nishida, N. Takada, M. Yoshimura, T. Sonoda and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2600.
10 H. Kamogawa, K. Kikushima, and M. Nanasawa, *J. Polym. Sci. Polym. Chem. Ed.*, 1989, **27**, 393.
11 A. W.-H. Mau, J. M. Overbeck, J. W. Loder and W. H. F. Sasse, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 869, and references cited therein.
12 S. Kohjiya, T. Hashimoto, S. Yamashita and M. Irie, *Chem. Lett.*, 1985, 1497.
13 E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524.
14 S. Kohjiya, T. Hashimoto, S. Yamashita and M. Irie, *Makromol. Chem., Rapid Commun.*, 1989, **10**, 9.