

# Drastic metal-ion enhancement in photoinduced aggregation of copolymers carrying crown ether and spirobenzopyran moieties

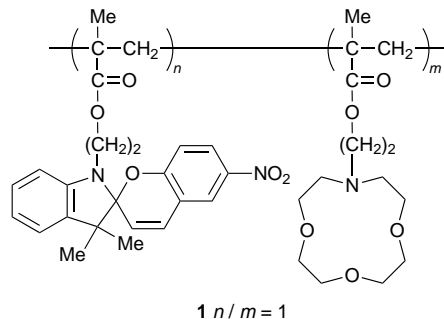
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Metal ion complexation of the crown ether moiety of crown ether–spiropyran copolymer **1** brings about the enhanced aggregation of its merocyanine moiety, formed by photoisomerization of its spiropyran, which results in reversible polymer precipitation.

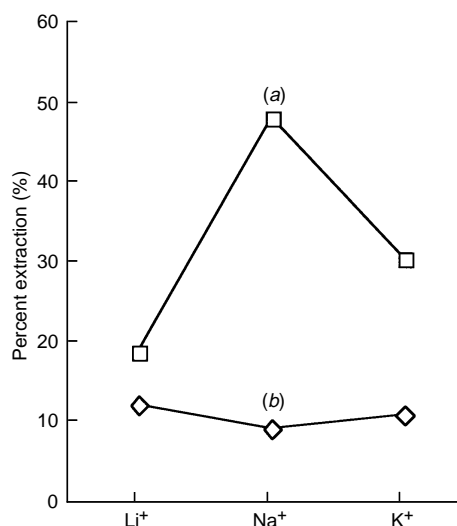
Spirobenzopyran derivatives, typical photochromic compounds,<sup>1</sup> when isomerized to their corresponding merocyanine forms, tend to aggregate.<sup>2</sup> The aggregation of the merocyanine isomers is enhanced in polymers carrying spirobenzopyran moieties on their side chains.<sup>3</sup>

Spirobenzopyran derivatives incorporating a monoazacrown ether moiety are attractive materials which can realize photochemical control of cation complexation.<sup>4,5</sup> Since an easy way to combine a spirobenzopyran moiety with a crown ether moiety is copolymerization of vinyl monomers carrying their corresponding functional moieties, we have designed such polymers **1** carrying side chains with monoaza-12-crown-4 and spirobenzopyran moieties. During the course of investigating the cation complexation and photochromism of the crown ether–spiropyran copolymer **1**, we have discovered an intriguing phenomenon. Herein we report the reversible photoinduced aggregation and precipitation of polymer **1** enhanced dramatically by cation complexation of its crown ether moieties.

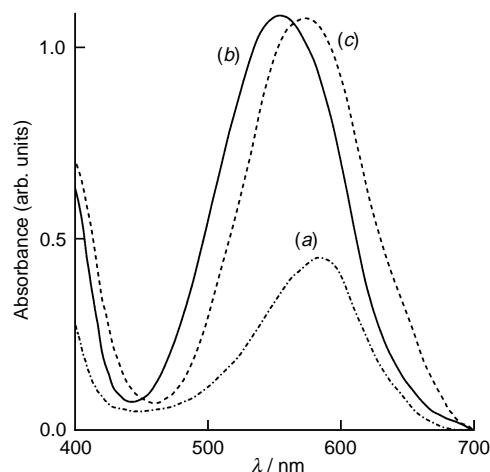


Radical copolymerization of an equimolar amount of the corresponding vinyl monomers of monoaza-12-crown-4 and spirobenzopyran<sup>6</sup> afforded crown ether–spiropyran copolymer **1** which possessed a composition of almost 1:1 (spiropyran–crown ether unit) and a number average molecular weight of  $1.3 \times 10^4$  (polystyrene standard). The cation complexing ability of **1** toward alkali metal ions, which was estimated by a conventional solvent extraction technique, is in the order  $\text{Na}^+ > \text{K}^+ > \text{Li}^+$ , as shown in Fig. 1. The crown ether–spiropyran copolymer **1** has a very different ion selectivity from its corresponding monomeric crown ether, *N*-benzylmonoaza-12-crown-4 (10-benzyl-1,4,7-trioxa-10-azacyclododecane). The higher cation complexing ability toward  $\text{Na}^+$  and  $\text{K}^+$  than  $\text{Li}^+$  is probably due to the easy formation of intrapolymer 2:1 (crown ether ring–metal ion) complexes with  $\text{Na}^+$  and  $\text{K}^+$  by cooperative action of two neighbouring crown ether rings, as was the case with poly(12-crown-4) derivatives.<sup>7</sup> Intrapolymer sandwich-type complex formation promotes cation binding and thereby cation extraction.

UV irradiation (300–400 nm) causes isomerization of the spiropyran moiety of **1** to its corresponding merocyanine form, which in turn brings about aggregation of the resulting zwitterionic merocyanine moieties. This phenomenon was suggested in absorption spectral changes of a THF solution of crown ether–spiropyran copolymer **1**. The behaviour of the merocyanine aggregation of **1** in the presence of an equimolar amount of alkali metal perchlorate is distinct from that in the absence of any metal salt, as illustrated by the absorption maximum difference for its merocyanine moiety after 5 min of UV irradiation (Fig. 2). In the absence of metal ions, the photoirradiation caused an increase in the absorption peak around 600 nm assigned to the non-aggregated merocyanine moiety, which shifted gradually to shorter wavelength (560 nm) after prolonged photoirradiation. The blue shift of the merocyanine absorption peak can be attributed to the formation of H-type aggregates.<sup>3</sup> Further UV irradiation caused little change in the absorption spectrum. In a solution containing  $\text{Li}^+$  ions, on the other hand, the absorption around 560 nm attributed to H-type aggregation appeared after only 5 min of irradiation, with a colour change of the solution from colourless to purple. Further irradiation decreased the absorption with a slight red shift, and then purple-coloured polymer started to precipitate from the solution. The modest blue shift in a solution containing  $\text{Na}^+$  ions indicates that the H-type aggregate formation is sluggish in the system containing  $\text{Na}^+$  ions as compared with that containing  $\text{Li}^+$  ions. Since, in a solvent in which they are moderately soluble (*e.g.* THF), polymer molecules of **1** generally cast in a contracted form in the absence of metal ions, the photoisomerized merocyanine moieties are likely to form intramolecular aggregates in a polymer chain. In the presence of



**Fig. 1** Cation extraction (a) by crown ether–spiropyran copolymer **1** and (b) comparison with *N*-benzylmonoaza-12-crown-4. Aqueous phase:  $0.1 \text{ mol dm}^{-3}$  alkali metal hydroxide,  $7 \times 10^{-5} \text{ mol dm}^{-3}$  picric acid. Organic phase:  $2.1 \times 10^{-3} \text{ mol dm}^{-3}$  crown ether unit in 1,2-dichloroethane. Extracted for 15 min in the dark.



**Fig. 2** Absorption spectra of crown ether-spiropyran copolymer **1** in THF (a) without metal ion, (b) with  $\text{LiClO}_4$ , and (c) with  $\text{NaClO}_4$ , after UV irradiation for 5 min. Polymer **1** and metal perchlorate:  $4 \times 10^{-4}$  mol  $\text{dm}^{-3}$  each in THF. UV light: 300–400 nm.

metal ions, however, the polymer chains carry positive electric charges due to cation complexation with its crown ether moieties, and therefore the polymer chains expand due to intramolecular electrostatic repulsion among the cationic charges.<sup>8,9</sup> The expansion of the polymer chains increases the probability of formation of an interpolymer merocyanine aggregate while suppressing the intramolecular (intrapolymer) one. Thus, the interpolymer merocyanine aggregation induces crosslinking of **1**, finally leading to the polymer precipitation.

Very interestingly, the polymer precipitate formed on UV irradiation in the presence of the metal ion can be dissolved again by subsequent visible light irradiation (for 20 min), leaving the solution almost transparent. This means that the UV-induced precipitation and visible light-induced dissolution of polymer **1** in the presence of  $\text{Li}^+$  ions is quite reversible. This is also the case in the presence of  $\text{Na}^+$  ions, although the UV-induced merocyanine aggregation and precipitation is not as

easy as in the  $\text{Li}^+$  system. This is probably because polymers carrying a 12-crown-4 moiety at the side chain tend to form intramolecular 2:1 (crown ether ring-metal ion) complexes with  $\text{Na}^+$ .<sup>7,10</sup> This intramolecular formation of the sandwich-type complexes suppresses more or less the polymer chain expansion which is required for the interpolymer merocyanine aggregation.

Thus, reversible photocontrol in the precipitate formation of crown ether-spiropyran copolymer **1**, based on cation complexation-induced merocyanine aggregation, has been realized in THF solutions containing metal ions. Further studies are now under way to elucidate the properties of the polymer precipitate.

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#### Footnote

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