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Alignment by Poling and Regioselective Photodimerization of Stilbazolium Ions Dispersed in Polyelectrolytes

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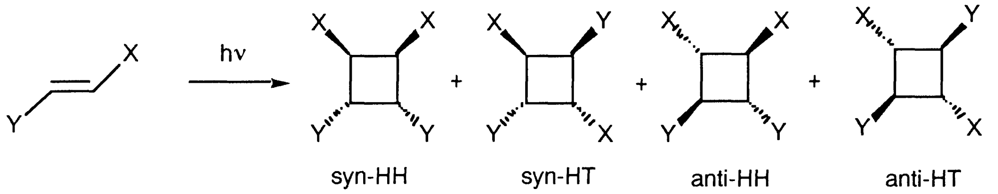
4-(*N,N*-Dimethylamino)stilbazolium ion dispersed in thin films of poly(styrenesulfonates) (PSS) or copolymer of poly(ethylene and maleates) (PEcoMA) was shown to be aligned by electric field poling on the basis of the resulting photodimerization giving the *syn*-head-to-head dimers.

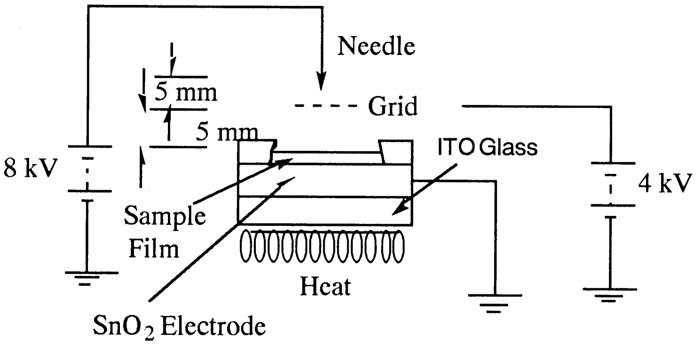
Organic materials show potential for utilization in non-linear optical devices.1) Some compounds with high microscopic polarizability, β, crystallize in a centrosymmetric fashion, thus cancelling these tensols to give zero or negligible bulk polarizability χ. A number of devices have been tried thus far in order to overcome this difficulty by aligning suitable chromophores in a non-centrosymmetric array.2 - 4) Among them, the most convenient and inexpensive is a poled polymer film technique.3) The technique lies in assembling organic dyes with large second-order nonlinear optical susceptibilities in polymer glasses and poling them with an electric filed. *N,N*-Dimethylaminostilbazolium ions and their analogs (stz+) are good candidates on account of their quite high β values and were reported to successfully exhibit second harmonic generations (SHG) incorporated in Langmuir-Blodgett fims. However, no attempt has been reported to align stz+ ions by electric field poling in polymer films.

Previously, irradiation of stz+ ions, organized in heterogeneous fields such as micelles and inorganic interlayers, was found to result in a photodimerization reflecting their molecular orientation.5) That is, the stereochemistry of resulting photodimers (Eq. 1) depends on the molecular alignment. The present communication discloses a study on photocyclodimerization of stz+ ions organized by an intense electric filed in ionic polymer glasses.

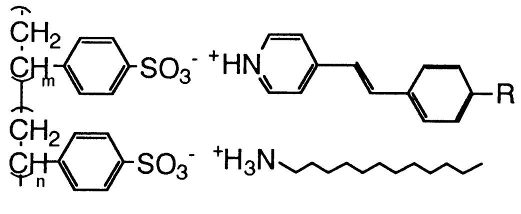


(1)

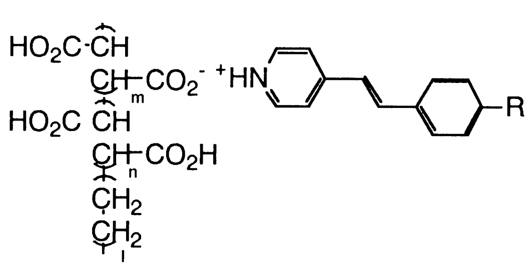
Thin film samples were prepared by casting an aqueous ethanolic solution of stilbazolium poly(styrenesulfonates) (**1a** and **2a**) on ITO galss plates (40 mm x 40 mm) heated by a hot plate at around 60 - 80 °C; **1a** and **2a** had been obtained by mixing the stilbazoles (20 mg / 10 ml in ethanol) with appropriate amounts of aq. 65 mM poly(styrenesulfonic acid) (PSSH),6) The resulting films, pale yellow (λmax 334 nm for **1a**) or red (λmax 470 nm for **2a**), were of 10 - 50 μm thickness and were somewhat fragile. Neutralization of the remaining protons of **1a** and **2a** by laurylamine remarkably improved the fragility of films. But, laurylammonium ion is flexible in structure and akin to stz+ ions in size to cause homogeneous mixing with stz+. Thus, it is suspected that additon of laurylamine may suppress an interaction of an excited stz+ with neighboring stz+ in the films to lower an efficiency of the photocyclodimerization.



Scheme 1. A schematic drawing for high electric field poling.



1a, R = H; **2a**, R = N(CH$_3$)$_2$



2b, R = N(CH$_3$)$_2$, m+n : l = 64 : 36

A strong excimer fluorescence was observed at *ca.* 500 nm on irradiating a film of **1a** by 350 ± 2 nm light; its intensity was decreased but the monomer fluorescence at 430 nm was increased by adding an excess amount of laurylamine. Then, monomer to excimer fluorescence ratios (Im / Ic) were examined against the content of stz+ ions. Figure 1 shows that the monomer fluorescence disappears at stz+ ions in content of more than 10%. This indicates that an effective interaction leading to the photodimerization is possible at least more than 10% coverage of PSSH anionic sites by stz+.

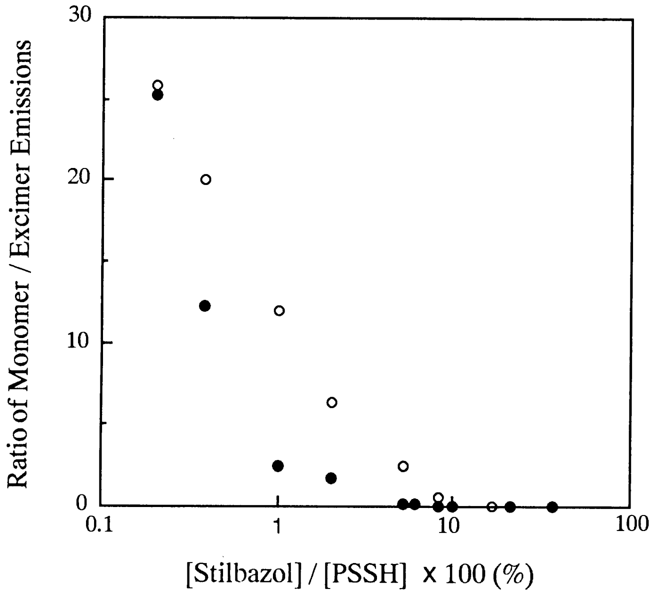


Fig. 1. Plots of monomer to excimer fluorescence ratios of **1a** (Im / Ie) against % content of stilbazol in PSSH with (○ ;[laurylamine] + [stilbazol] = [PSSH]) and without laurylamine (●).

As an alternative anionic polymer, copolymer of poly(ethylene and maleate) (PEcoMA, Aldrich)[7] was studied. Thin films (**2b**) of up to 8.2% of 4-(*N,N*-dimethylamino)stilbazolium ions based on carboxylic protons of copolymer of PEcoMA were found to be transparent and suitable for the poling and irradiation procedures.

Table 1. Effect of Corona Poling on the Photodimerization of **1** and **2** Dispersed in PSSH and PEcoMA Thin Films

Ent.	stz+	Supporting	m : n in	Conv.	Selectivity of Photoproduct (%)			HH
no.	ion	polymer	**1a**, **2a**, or **2b**	(%)	syn-HH	syn-HT	cis	HT
(A) Before poling treatments:								
1	**1a**	PSSH	100 : 0	57[a]	14	70	5	0.20
2	**2a**	PSSH	100 : 0	57	4	12	84	0.33
3	**2a**	PSSH	70 : 30	55	9	7	84	1.3
4	**2a**	PSSH	50 : 50	24	17	21	62	0.81
5	**2b**	PEcoMA	4 : 96[b]	72	3	5	92	0.60
6	**2b**	PEcoMA	8 : 92[b]	71	3	4	93	0.75
(B) After poling treatments:								
7	**1a**	PSSH	100 : 0	65[c]	12	75	<1	0.16
8	**2a**	PSSH	100 : 0	25	12	20	68	0.60
9	**2a**	PSSH	70 : 30	16	25	12	63	2.1
10	**2a**	PSSH	50 : 50	20	25	15	60	1.7
11	**2b**	PEcoMA	4 : 96[b]	42	36	12	52	3.0
12	**2b**	PEcoMA	6 : 94[b]	43	23	5	72	4.6
13	**2b**	PEcoMA	8 : 92[b]	55	18	6	76	3.0

a) Anti-HH dimer was formed (11%). b) The molar ratios of *N,N*-dimethylaminostilbazol to PEcoMA. c) Anti-HH dimer was formed (12%).

Thin films containing the stilbazolium ions were poled by corona charging at 10^5 - 10^6 Vcm^{-1} for 10 min at 117 ± 1 °C,[8] and the same voltage was kept until the films had been cooled down to the room temperature. The schematic drawing for the poling was shown in Scheme 1. The poled films were irradiated for 8 h without a filter by a 150W Xe lamp at room temperature, dissolved in H_2O, and analyzed by HPLC equipped with an ODS column eluting with ethanol : water (270 : 230 ml) including 1ml of conc. ammonium hydroxide. Product distributions were confirmed by NMR analysis of the reaction mixtures in comparison with the authentic samples.[9] The isomeric cyclodimer distributions are summarized in Table 1.

As shown in Table 1, HH to HT ratios of photocyclodimers were increased significantly by the poling treatment in cases of 4-(*N,N*-dimethylamino)stilbazolium ions (**2**) (cf. entry No. 2 and 8, or 6 and 13) while little effect was observed for the unsubstituted one (**1**) (cf. entry No. 1 and 7). That is, the more polar olefins resulted in the higher HH ratios, suggesting their more efficient molecular alignment by an intense electric fields.

It is interesting to note that corona charging of **2b** in PEcoMA copolymer enhances the HH to HT cyclodimer ratios *ca*. 4 - 5 times as much as those without the poling treatments. On the contrary, **2a** in PSSH resulted in a somewhat lower effect, i.e., at most within a factor of 2 (cf. entry No. 2, 3, 4 and 8, 9, 10 of Table 1). The strong acid polymer PSSH forms a polymer salt with stilbazol in a nearly quantitative way, and the molecular movement becomes difficult on account of the highly charged **2a** polymer salt. On the other hand, a weaker acid copolymer PEcoMA interacts more weakly with stz+ ions, and hence the stz+ ions could be reorientated by the poling process.

Finally, a considerable decrease in the photochemical conversion was observed by the poling treatments. This is presumably because the poling procedure made the film surfaces rough to lower the transparency of the films.

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6) Poly(styrenesulfonic acid) (PSSH) was obtained by passing sodium poly(styrenesulfonate) (PS-50, Tosoh, Ltd.) through an acidified cationic exchange resin (Amberlite IR)
7) Monomer ratio of copolymer PEcoMA was estimated by alkalimetry, i.e., PE : MA = 36 : 64.
8) Glass transition temperatures (Tg) of the films were measured by a calorimeter, 107 and 115 °C for PSS and PEcoMA, respectively.
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