

SYNTHESIS AND PHOTOCHROMISM OF ACRYLIC ESTER COPOLYMERS BEARING PENDANT VIOLOGEN GROUPS

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ABSTRACT

A series of acrylic ester copolymers with viologen group as pendant were synthesized through the reaction of MMA-EBA (Ethenyl bromoacetate) copolymer with 4-(4'-pyridyl)-N-alkyl (or arylalkyl) pyridiniums. These viologen copolymers can exchange their anion with NH_4PF_6 in methanol to improve their solubility in organic solvents such as DMF and acetone. Compared with the corresponding low molecular viologens, these viologen copolymers have relatively lower color development rate under UV light and fade faster in air due to less affinity to photo-reductant and deficiency of association between their cation radicals. Their photofatigue resistant ability is also slightly better than that of low molecular viologens.

INTRODUCTION

Various viologen polymers have been synthesized either by polymerizing monomers containing viologen unit or by the Menshutkin reaction of 4,4'-bipyridine with dihaloalkanes or dihaloarylalkanes, but most of them are soluble in water^[1-3]. In this paper the synthesis of some acrylic ester copolymer derivatives with pendant viologen groups in their side chains by macromolecular reaction was described. These viologen polymers are water-insoluble and can be easily dispersed in oil-based methacrylate copolymer. This makes viologen more convenient as practicable photochromic material. The photochromic behavior of these viologen copolymers was also compared with the corresponding low molecular viologens.

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EXPERIMENTAL

Material

Ethenyl bromoacetate was prepared in our laboratory^[4]. 4,4'-Bipyridine was purchased from Tokyo TCI Company. Other reagents are all of C.P. grade from domestic market.

Measurement

Infrared (IR) was recorded on a Shimadzu 430 spectrophotometer. Molecular weight was measured by OX-08 VPO. Elemental analyses were determined by a Heraeus CHN-RAPID Elemental Analyzer.

Synthesis

Copolymer of ethenyl bromoacetate (EBA) and methyl methacrylate (MMA) **1**:

To a solution of ethenyl bromoacetate (10g, 0.06mol) in 4-methyl-2-pentanone (3g) at 85°C under stirring in N₂, a solution of BPO (0.09g) and MMA (10g, 0.01mol) in 4-methyl-2-pentanone (10g) was added dropwise within 2h. The system was then heated at 95° ~100°C for 3h, and finally at 100°C for 30 min. The reaction mixture was added dropwise into a large amount of ethyl ether. After standing for 3h the precipitated white polymer was filtered out in a 50% yield. $\overline{M}_n$ of polymer was 4036. Elemental analyses found: Br, 11.51%.

1-Methyl-4-(4'-pyridyl)-pyridinium iodide **2a**:

Methyl iodide and 4,4'-dipyridine were mixed and stirred for 24h at room temperature in ethyl acetate. The resulting orange powder was separated in a 84% yield with satisfactory elemental analyses.

1-Propyl-4-(4'-pyridyl)-pyridinium bromide **2b**:

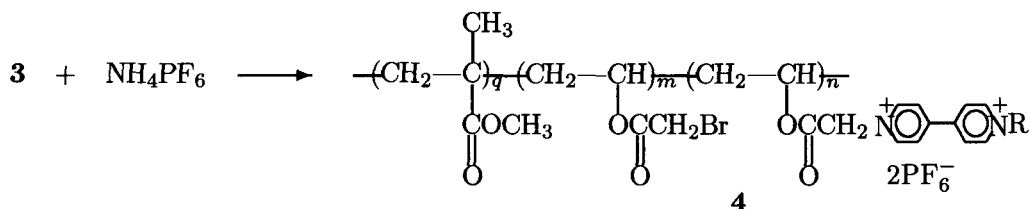
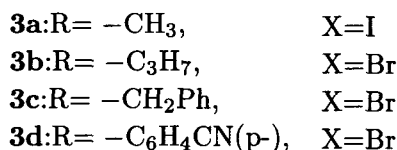
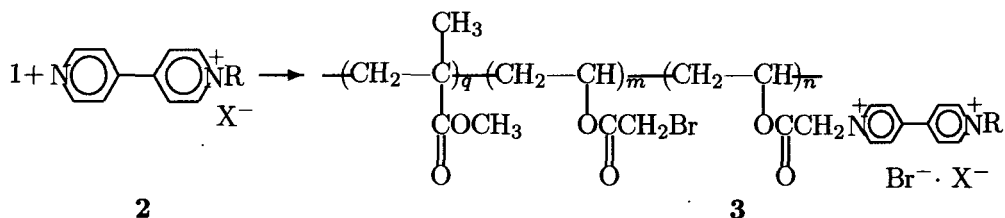
1-Bromopropane and 4,4'-dipyridine were mixed together and refluxed in anhydrous acetonitrile for 24h. The resulting yellow crystal powder was filtered in a 24% yield.

1-Benzyl-4-(4'-pyridyl)-pyridinium bromide **2c**:

Benzyl bromide and 4,4'-dipyridine were mixed and refluxed in ethyl acetate for 6h. The resulting pale yellow powder was filtered in a 85% yield.

1-(4-Cyanophenyl)-4-(4'-pyridyl)-pyridinium bromide **2d**

2,4-Dinitrobromobenzene and 4,4'-dipyridine were mixed and refluxed in ethyl acetate for 10h. 1-(2,4-Dinitrophenyl)-4-(4'-dipyridyl)-pyridinium was separated in a 54% yield. This product and excessive 4-cyanoaniline were stirred in DMF at 120°C for 10h with pyridine as catalyst and the resulting yellow crystal powder was obtained in a 39% yield.

Table 1 Some structure data of viologen copolymers **3**

Viologen copolymer		Elemental analyses		Conversion of reacting	Polymer structure		
No.	alkyl	Br %	N %	group%	<i>m</i>	<i>n</i>	<i>q</i>
3a	—CH ₃	—	1.55	83.0	1	4.8	30.8
3b	—C ₃ H ₇	13.82	1.87	63.1	2.1	3.7	30.8
3c	—CH ₂ Ph	11.87	1.05	33.8	3.8	2.0	30.8
3d	—PhCN	12.44	2.53	63.2	2.1	3.7	30.8

When the added molar ratio of monomer EBA and MMA was 1:1.5, the molar ratio of two components in the resulting copolymer **1** deduced from its elemental analysis was found only 1:5.3 because the polymerization rate of EBA was much slower than that of MMA. The molecular weight of copolymer **1** was 4037, and its structure can be expressed as $p = 5.8$, $q = 30.8$. Copolymer **1** was reacted with 1-alkyl(aryl)-4-(4'-pyridyl) pyridinium haloid **2** to give viologen copolymer **3** containing pendant viologen groups. Since the copolymers are water insoluble, it is possible to purify **3** by washing the powder with water to remove the excess **2**. Elemental analysis data of these products demonstrated that only 40 ~ 83% of bromine in copolymer **1** had reacted with 1-alkyl(aryl)-4-(4'-pyridyl) halide even after they were refluxed in anhydrous acetonitrile for 20h, although bromine at α -position of carbonyl group is moderate-active in Menshutkin reaction. The reaction conversion of bromine in this macromolecular Menshutkin reaction and the composition data of viologen

copolymers **3** from elemental analysis were given in Table 1.

In order to improve the solubility of viologen copolymers in organic solvents and oil-based polymers, the methanol solution of **3** were added dropwise into methanol solution of NH_4PF_6 to precipitate new viologen copolymers **4**. According to their IR spectra, the ion exchange has been achieved easily and completely. The solubility of viologen copolymer **4** in DMF and acetone are much better than that of **3**.

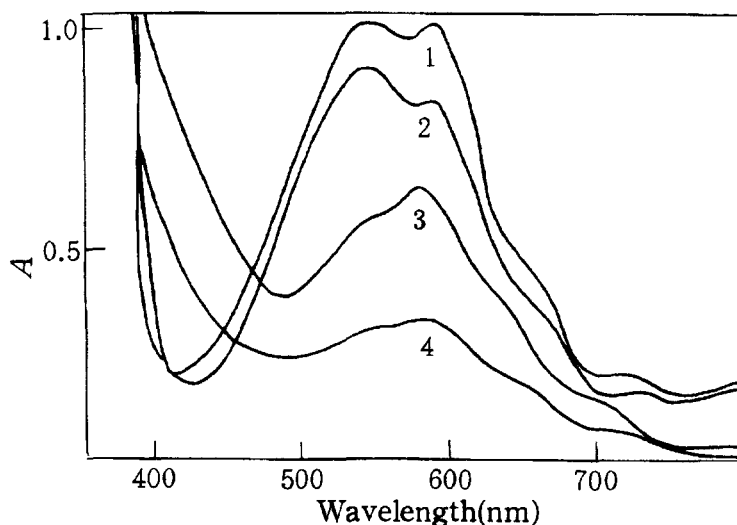


Fig. 1 UV-VIS Spectra of viologen copolymers and corresponding low molecular viologens under UV-irradiation for 4 min

(1) Propyl viologen; (2) Methyl viologen; (3) **4a**; (4) **4b**

Photochromism of the viologen copolymers

The visible spectra of the viologen copolymers **3a** and **3b** in the mixture of polyvinylpyrrolidone (PVP) and MMA-HEMA (methyl methacrylate and hydroxyethyl methacrylate) copolymer matrix (showed in Fig.1) are quite different from that of the corresponding low molecular viologens after irradiation by UV-light. There are two absorption peaks in the visible spectra of low molecular viologens but there is only one peak in viologen copolymers. It is well known that the absorption peak of viologen radical cation usually appears at 602nm and its shoulder peak at higher wavelength belongs to its associated form^[5]. The phenomenon that there is scarcely shoulder peak in the spectra of viologen copolymer indicates that viologen units in the copolymers are not aggregated due to their fixation to the copolymer chains in small ratio and separation by many spacers. Table 2 summarized color developing rate of the viologen copolymers and corresponding low molecular viologens embedded in polymer matrix. It can be seen from this table that photosensitivity of the

viologen copolymers is much lower than that of low molecular viologens under the same condition. This may be attributed to the fixation of viologen units to low polar principal chain of copolymer which makes them less affinity to photo-reductant PVP with high polarity.

Table 2 Photochromism of viologen copolymers **4** and corresponding low molecular viologens (absorbance at 602nm)

Viologens	Irradiation time (s)			
	60	120	180	240
4a	0.030	0.070	0.120	0.190
Methyl viologen	0.195	0.327	0.340	0.425
4b	0.165	0.309	0.397	0.573
Propyl viologen	0.423	0.719	0.810	0.963
4c	0.437	0.598	—	—
Benzyl viologen	0.476	0.663	—	—

Study on fading behavior of viologen copolymers in air shows that their fading rates conform to the pseudo-first order dynamic rule. The apparent rate constants were shown in Table 3.

Table 3 Apparent fading rate constants of viologen copolymers **4** and the corresponding low molecular viologens (15°C, R.H. 70%)

Viologen copolymers	$K(s^{-1})$	Low molecular viologens	$K(s^{-1})$
4a	3.07×10^{-3}	Methyl viologen	4.05×10^{-4}
4b	1.28×10^{-3}	Propyl viologen	2.54×10^{-4}
4c	1.14×10^{-3}	Benzyl viologen	5.40×10^{-4}
4d	1.66×10^{-3}		

Table 4 Comparison of photofatigue of low molecular viologens and viologen copolymers **4** with corresponding low molecular viologens

Viologen	A_n/A_1									
	Number of irradiation									
	1	2	3	4	5	6	7	8	9	10
4a	1.00	0.984	0.965	0.953	0.937	0.922	0.875	0.844	0.800	0.781
Methylviologen	1.00	0.993	0.900	0.870	0.800	0.680	0.644	0.600	0.574	0.561
4b	1.00	0.983	0.887	0.816	0.707	0.691	0.660	0.630	0.600	0.588
Propylviologen	1.00	0.986	—	0.840	0.800	0.569	0.638	0.600	0.570	0.560
4c	1.00	0.987	0.960	0.876	0.792	0.739	0.672	0.627	0.594	0.538
Benzylviologen	1.00	0.891	0.807	0.695	—	0.633	0.550	0.544	0.444	0.433

It can be also recognized from this table that fading rates of viologen copolymers in polymer matrix are much faster than that of the corresponding low molecular

viologens. The deficiency of association between their cation radicals may be the major reason^[6].

Photofatigue resistant ability of this kind of viologen copolymer draws our much attention and is measured by the method similar to semi-flash number^[7]. It is clear from the results tabulated in Table 4 that all these viologen copolymers are more durable than the corresponding low molecular viologens although they become photofatigued after several irradiation and fading cycles. This may suggest that viologen cation radicals can be stabilized by fixing themselves on polymer chain to reduce further reduction of viologen cation radical and other reactions which cause the photofatigue of viologen.

CONCLUSIONS

New copolymers of types **3** and **4** bearing pendant viologen groups were synthesized through macromolecular reaction. These viologen copolymers have lower color development and faster fading rates in air than the corresponding low molecular viologens due to polymer effect and deficiency of association between cation radicals of these viologens. Furthermore, their photofatigue resistant ability is also better than that of the corresponding low molecular viologens. This may be explained by that cation radical of these viologens can be stabilized by fixing themselves on polymer chain.

Keywords:

Viologen copolymer; Photochromism; Fading rate; Fatigue resistance

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