Photochemistry of Polymeric Systems. VI. Photocrosslinking of Basic Polymers and Copolymers: Dyeing

GASTON M'BON, COLETTE ROUCOUX, A. LABLACHE-COMBIER,
and C. LOUCHEUX, LA CNRS 351, *Laboratoires de Chimie
Macromoléculaire et de Chimie Organique Physique, Associés à l'ENSCL,
Université des Sciences et Techniques de Lille,
59655 Villeneuve d'Ascq Cedex, France*

Synopsis

Poly(N-vinylamine) (PVAm) and methylmethacrylate/dimethylaminoethylmethacrylate copolymers (MMA/DMAEMA) were prepared and then substituted by cinnamic or cinnamylidene photosensitive groups. The photosensitivity of these materials was determined using the so-called photoresist test in various experimental conditions. A comparison was made between MMA/DMAEMA and methylmethacrylate/4-vinylpyridine (MMA/4VP) photosensitized copolymers. The best results were obtained with MMA/DMAEMA on textile support. A photosensitization study was carried out by adding some compounds such as thioxanthone (10% in bulk). It showed that the multiplicity factor can be 10 with MMA/DMAEMA copolymers and even up to 64 for photosensitive PVAm. The addition of anionic dyes on the polymers emphasized that a better fixation occurred for aliphatic amines than for pyridinic ones.

INTRODUCTION

In a previous paper we have described the photocrosslinking of polymers and copolymers bearing pendant cyanocinnamylidene–pyridinium groups.[2] After irradiation the reticulated polymers and copolymers were able to fix acidic dyes on their free pyridine units. But the binding of such dyes on the pyridine units is weak, and the dyes were eliminated when the material was washed with a slightly basic water. The aim of the present paper is to know whether such dyes will or will not be linked more strongly on the polymeric material if the pyridine units are replaced by a more basic moiety. In this purpose we synthesized some copolymers of methymethacrylate and dimethylaminoethylmethacrylate, along with homopolyvinylamine. We bound to them photosensitive cinnamic or cinnamilidene chromophores. We report here the results of the photosensitivity studies of these polymers and the preliminary results on the fixation of dyes on the photoreticulated materials. A comparison was made with the corresponding properties of a methylmethacrylate-4-vinylpyridine copolymer substituted by cinnamylidene groups.

EXPERIMENTAL

Photosensitive Groups

The synthesis of the photosensitive molecules to be bound on the polymeric chain of vinylpyridine or dimethylaminoethylmethacrylate–methylmethacrylate

CCC 0021-8995/84/020651-10$04.00

copolymers have been already described.[2] They are

$$Br-(CH_2)_2-O-\overset{\overset{\displaystyle \|}{O}}{C}-CH=CH-CH=CH-\phi$$

$$Br-(CH_2)_2-\overset{\overset{\displaystyle \|}{O}}{C}-\overset{\overset{\displaystyle |}{CN}}{C}=CH-CH=CH-\phi$$

Bromoethylcinnamylidene acetic acid ester E_1
Bromoethylcyanocinnamylidene acetic acid ester E_2

Polyvinylamine was functionalized by the acid chloride of either cinnamylidene acetic acid (CAACl), cyanocinnamylidene acetic acid (CCAACl), or cinnamic acid (CACl). These compounds were synthesized from the corresponding acid in the usual way.[2]

Monomers

4-Vinylpyridine (4VP), methylmethacrylate (MMA), and dimethylaminoethylmethacrylate (DMAEMA) were Merck compounds. They were used after distillation by standard procedures. N-vinyl-acetamide was synthesized by pyrolysis of bisacetamide according to Dawson's procedure.[3]

Polymers and Copolymers

Copolymers of MMA with 4VP, DMAEMA, and homo(N-polyvinylacetamide) were obtained by conventional solution radical polymerization using α,α'-azobisisobutyronitrile as the inhibitor. The solvents used were isopropanol for the polymerization of vinylacetamide and benzene for all copolymers of methylmethacrylate. All samples were polymerized at 60°C in vacuum degassed and sealed tubes. All polymeric materials were recovered by precipitation in a convenient non solvent (acetone for PVAm, petroleum ether for MMA/4VP copolymers, and diethylether for MMA/DMAEMA copolymers). Poly(vinylamine hydrochloride) was obtained by acid hydrolysis of poly(N-vinylacetamide).[3] A precipitate of polyvinylamine (PVAm) was formed by neutralization by NaOH 8N of an aqueous solution of its hydrochloride. After filtration PVAm was dried under vacuum at 100°C for 1 h. As for PVAm previously synthesized by other workers,[4] our sample contained some residue after combustion (9% in our case). The specific viscosities η_{sp} were determined for 1 g/100 mL solutions. In the case of MMA copolymers the solvent was a $0.01M$ LiCl solution in methanol and for PVAm, a $0.1M$ NaCl solution in water. Unfortunately, in the absence of any viscosity law, these values cannot be used to give the values of the molecular weights.

Quaternization Reactions of Copolymers: Functionalization of PVAm. All quaternization reactions of the MMA copolymers were performed in tetramethylenesulfone (TMS) for compounds E_1 and E_2 as previously reported.[2]

A typical experience was conducted as follows: the copolymer was dissolved in TMS (2 g for 100 mL) at 50°C during 6 h under nitrogen flow. Then, the ester was added (1.1 mol ester for 1 mol of base) and the stirred solution was allowed to react at 70°C during 70 h. The crude quaternized material was washed many times with the precipitant (dry diethylether). A further purification by dissolution and precipitation was necessary.

The functionalization of PVAm by an acid chloride was performed in methanol in the presence of pyridine. A typical experience was conducted as follows: PVAm was dissolved at room temperature in methanol distilled on Mg/I_2 complex and dried molecular sieve (1 g in 10 mL) at room temperature. Pyridine (1 mol for 1 mol of acid chloride) was added, and then an acetone solution of acid chloride (1 mol of acid chloride for 1 mol of PVAm) was dropped under stirring. After the complete addition of the acid chloride the reaction mixture was stirred at room temperature during 1 h. Then the modified materials were precipitated (PVAm–CAACl in diethyl ether and PVAm–CACl in acetone) filtered off and dried under vacuum at 50°C.

Analytic Characterization

Spectroscopic Characterization. Spectroscopic characterization of esters, acid chlorides, and polymeric materials was performed by recording IR spectra (Perkin-Elmer 257 or Beckman IR 18 Spectrometers), UV spectra (from Beckman DBG Spectrometer), and NMR proton spectra (from Brucker WP 80 Spectrometer).

Determination of Basic Groups of the Copolymers. The pyridinyl groups of MMA/4VP copolymer were determined using the Tamikado conductimetric method already described.[5] The tertiary amine groups of MMA/DMAEMA copolymers were determined by $HClO_4$ titration in acetonitrile (titration made in the Centre de Recherches sur les Macromolécules, Strasbourg).

Determination of the Quaternized Groups. The determination of pyridinium groups in E_1- or F_2-quaternized MMA/4VP copolymers was done by potentiometric titration of Br^- ions as previously described.[2]

However, for MMA/DMAEMA-quaternized copolymers, the determination of free pyridine groups was made in acetonitrile by $HClO_4$ titration in the presence of CH_3CO_2Hg.

Determination of the Percent of Functionalized PVAm. In the case of modified PVAm–CACl and PVAm–CAACl polymers, the percent of free base was titrated in glacial acetic acid by $HClO_4$. The reactions of PVAm with cinnamic or cinnamylidene acid chloride are nearly stoichiometric.

Irradiation Methods; Determination of Illumination Photoresist Test

The preparation of thin films, their irradiation, the determination of the energy received by a given sample, and the bismuth photoresist test used for the determination of the insolubilization of the photoirradiated films are described in detail in Ref. 5.

The photosensitivity S was defined as[6]

$$S = K/E = K/It$$

where E is the energy needed to insolubilize 1 cm^2 of the film, I is the illumination, and t is the time needed for insolubilization. The constant K is arbitrarily taken, as $K = 1$. This photosensitivity is defined for a given type of irradiation source.

The photosensitivity measured according to the "bismuth photoresist test" is called S_b. Similarly, photoresist tests were also made on thin polymeric films laid out directly on the transparent polyester support (without bismuth), as

M'BON ET AL.

TABLE I
Polymerization Conditions and Specific Viscosity: Homopolymer, PVAm; Copolymers, MMA/
4VP and MMA/DMAEMA

Sample	Formula	AIBN (mol/L)	Solvent	Time (h)	Precipitant	Conversion (%)	η_{sp} (mL/g)
P	PVAm	3.66×10^{-2}	Isopropanol	1	Acetone	22	0.26
C_I	MMA–4VP	1.22×10^{-2}	Benzene	15	Petroleum ether	70	1.15
C_{II}	MMA–DMAEMA	1.22×10^{-2}	Benzene	24	Diethylether	83	0.68
C_{III}	MMA–DMAEMA	1.35×10^{-2}	Benzene	24	Diethylether	74	0.30
C_{IV}	MMA–DMAEMA	1.51×10^{-3}	Benzene	24	Diethylether	87.5	0.49

previously described.[2] The photoreticulated spots were then visualized by soaking the film in a solution of dye (color index: Acid Red No. 57, for example). The corresponding photosensitivity is called S_t. Moreover, a "textile photoresist test" was used in which the polymeric photosensitive film was laid out on a Tergal® stuff polyester support. The visualization was made by dyeing as in the precedent case. The corresponding photosensitivity is called S_T.

The photosensitivity $S_{\lambda_{max}}$ was determined using the bismuth photoresist test after a Hanovia L 5430 1 KW Xenon Source and a GM 250 Schoeffel Monochromator. The wavelength range of the monochromator was centered on the wavelength λ_{max} of the maximum optical density of the polymeric photosensitive material: $\Delta\lambda = \lambda_{max} \pm 10$ nm.

RESULTS AND DISCUSSION

Polymeric Materials. The conditions of obtaining crude polymers, their specific viscosity, and the determination of their composition are given in Tables I and II. In Table III are the conditions of functionalization of the various copolymers and of PVAm, along with the molar fraction f_E of photosensitive groups on the resulting polymeric material. We were not able to synthesize a soluble polymer neither by quaternization of copolymer C_{IV} with E_2 whatever the quaternization reaction time was, nor by reaction of PVAm with the acid chloride CCAACl.

The UV spectra of the functionalized polymers are nearly the same as those of the corresponding polymers formed by quaternization of MMA–4VP copolymers already described.[2] The IR spectra are, *mutatis mutandis*, the same.[2]

TABLE II
Composition of MMA–4VP and MMA–DMAEMA Copolymers[a]

Polymer	F_{4VP}	F_{MMA}	F_{DMAEMA}	f_{4VP}	f_{MMA}	f_{DMAEMA}
C_I	0.16	0.84		0.22	0.78	
C_{II}		0.75	0.25		0.75	0.25
C_{III}		0.50	0.50		0.50	0.50
C_{IV}		0.25	0.75		0.25	0.75

[a] F refers to the molar fraction in the feeding mixture; f to the molar fraction in the copolymer.

<div align="center">TABLE III</div>
<div align="center">Functionalization of Polymers by Photosensitive Molecules</div>

Sample	Composition	Weight (g) of the photosensible molecule added for 1 g of the nonfunction-alized starting polymer	Reaction temp (°C)	Reaction time (h)	f_E[a]	λ_{max} (nm)
$C_{I,1}$	MMA/4VP–E_2 78/22	1.5	70	24	13.70	355 ($CHCl_3$)
$C_{I,2}$	MMA/4VPQ–E_1 78/22	1.5	50	24	18	315 ($CHCl_3$)
$C_{II,1}$	MMA/DMAEMA–E_2 75/25	1.5	70	24	21.24	355 ($CHCl_3$)
$C_{II,2}$	MMA/DMAEMA–E_1 75/25	1.5	50	24	20.78	315 ($CHCl_3$)
C_{III}	MMA/DMAEMA–E_2 50/50	3.0	70	24	36.23	355 ($CHCl_3$)
C_{IV}	MMA/DMAEMA–E_2 25/75	3.0	70	6	G[b]	
P_1	PVAm–CCAACl	1.0	0–20	1	i[c]	
P_2	PVAm–CAACl	0.45	0–20	1	18.23	310 (CH_3OH)
P_3	PVAm–CAACl	0.55	0–20	1	23.14	310 (CH_3OH)
P_4	PVAm–CACl	1.83	20	1	23.50	277 (CH_3OH)
P_5	PVAm–CACl	2.57	20	1	32.41	277 (CH_3OH)

[a] f_E refers to the molar fraction of the photosensitive group in the polymer.
[b] There is formation of an insoluble gel.
[c] The polymer formed is an insoluble powder.   There is no gel formation.

Photosensitivity. Table IV collects the photosensitivities of polymers. All samples were irradiated with a high pressure mercury source (Philips SP 500).

The difference of photosensitivity of copolymer C_{III} as compared with copolymer $C_{II,1}$ is partially due to the fact that polymer C_{III} swells more than copolymer $C_{II,1}$ during its development with the chloroform–methanol mixture, and perhaps to the fact that in copolymer C_{III}, which has a higher content of photosensitive E_2 units than polymer $C_{II,1}$ (36.2 vs. 21.2), the probability of intrachain photobinding is higher.

For photosensitized PVAm some expected results are obtained: (i) for a given photosensitive group, the photosensitivity increases with the percent bound; (ii) the photosensitivity is better for cinnamylidene units (CAACl) than for

TABLE IV
Photosensitivity of the Different Soluble Functionalized Polymers[a]

Sample	Formula	Development solvent	S_b (cm²·J⁻¹)	S/f_E = R	S_t (cm²·J⁻¹)	S_T (cm²·J⁻¹)
Commercial products	KPR (KODAK) + sensitizer	Ethylene glycol acetate	10	20	—	—
	P.E. 4125 (KODAK) + sensitizer	butylphthalate	25	50	—	—
$C_{I,1}$	MMA/4VP–E₂ 78/22/13.7	CHCl₃	6.85	50	35.71	157.85
$C_{I,2}$	MMA/4VP/El 78/22/18	CHCl₃–CH₃OH– toluene (1:1:2)	0.45		8.77	28.99
$C_{II,1}$	MMA/DMAEMA–E₂ 75/25/21.24	CHCl₃–CH₃OH (1:1)	6.85	32	17.86	76.92
$C_{II,2}$	MMA/DMAEMA–E₁ 75/25/20.78	CHCl₃–CH₃OH (1:1)	6.85	33	17.54	57.97
C_{III}	MMA/DMAEMA–E₂ 50/50/36.23	CHCl₃–CH₃OH (1:1)	0.16	44	8.77	153.85
P_2	PVAm–CAACl (18.23 %)	CH₃OH	0.011	0.06	0.055	0.48
P_3	PVAm–CAACl (23.14%)	CH₃OH	0.046	0.2	0.17	1.07
P_4	PVAm–CACl (23.50%)	CH₃OH	0.007	0.03	0.050	0.33
P_5	PVAm–CACl (32.41%)	CH₃OH	0.021	0.065	0.11	0.38

[a] Irradiations with Philips SP 500 source: S_b = photosensitivity on bismuth plated polyester transparent support, S_t = photosensitivity on polyester transparent support, S_T = photosensitivity on polyester textile support, $R = S/f_E$ is the photosensitivity rapported to a photosensitive unit of the polymeric material, and f_E is the molar fraction of the photosensitive group in the polymer.

cinnamic ones (CACl). This difference is a direct function of the molar extrinction coefficients of the chromophores:

$$\epsilon_{277} = 20{,}000 \text{ L/mol·cm in ethanol for CACl}$$

$$\epsilon_{310} = 40{,}500 \text{ L/mol·cm in isopropanol for CAACl}$$

The photosensitivities of photosensitized PVAm are 2 orders of magnitude lower than for MMA–4VP- or MMA–DMAEMA-photosensitive polymers described in this paper. The high sensitivity of the latter is due to the fact that they contain quaternized amines.[2,8]

One observes that $S_b < S_t < S_T$. This is due to differences of adhesion of the polymeric material on the support. In the case of S_b the adhesion forces deal with the polymer/Bi system since for S_t and S_T they deal with the polymer/polyester support system. The experimental result $S_T > S_t$ is easy to explain: in S_t determination the support is glossy since for S_T it is rough (textile).

The photosensitivities S_b, S_t and S_T of Table IV refer to all the light emitted by the Philips SP 500 medium pressure mercury lamp. Only a small amount of it is actually absorbed by the polymer.

In three cases (cf. Table V) we measured the $S_{\lambda_{max}}$ photosensitivity corresponding to the maximum absorption of the polymer.

The $S_{\lambda_{max}}$ are obviously higher than the S_b, S_t, or S_T photosensitivities. It is in the case of polymer P_3 (PVAm–CAACl 23.14%) that the increase is the highest.

TABLE V
Photosensitivity $S_{\lambda\text{max}}$ at the Maximum Absorption

Sample	Formula	Wavelength $(\lambda_{\text{max}} \pm \Delta\lambda/2)$ (nm)	Photosensitivity $S_{\lambda\text{max}}$ $(\text{cm}^2\cdot\text{J}^{-1})$
$C_{II,1}$	MMA/DMAEMA–E_1 75/25/21.24	355 ± 10	9.17
$C_{II,2}$	MMA/DMAEMA–E_1 75/25/20.78	310 ± 10	13.89
P_3	PVAm–CAACl (23.14%)	310 ± 10	4.17

Influence of Sensitizers.   We have already noticed[2] that since the addition of benzophenone (10% in weight to a polymer solution) slightly increases the photosensitivity of the films of such polymers, usual commercial photosensitizers decrease it.   Williams already described such phenomenon for styrylpyridinium-substituted vinyl polymers.[8]

We found a similar behavior of usual photosensitizers toward polymer $C_{II,1}$ (cf. Table VI); moreover, the addition of benzophenone decreases also the photosensitivity.   On the other hand, we noticed that compounds, such as anthrone, benzanthrone, erythrosine, thioxanthone, and xanthone added in 10% in bulk, strongly increases, in most cases, the photosensitivity of the polymer studied (cf. Table VII).

Photosensitive copolymer $C_{I,1}$ containing 10% in bulk of thioxanthone is more than three times more sensitive than the commercial PF 4125 Kodak polymer, which is also photosensitized.

The mechanism of this photosensitization was not studied.   It seems not to be related with the triplet energy E_T of the photosensitizer: E_T of erythrosine is 42 kcal/mol, whereas that of the other photosensitizers is higher than 60 (Michler's ketone, 60 kcal/mol; thioxanthone 65.6 kcal/mol; benzophenone 69 kcal/mol; anthrone, benzanthrone 72 kcal/mol; xanthone 74.2 kcal/mol.[9]

The increase of the photosensitivity (R) of the nonquaternized PVAm–CCAACl or PVAm–CAACl photosensitive polymers by these photosensitizers is much higher than is the increase of the photosensitivity of the quaternized polymer.

Spectroscopic Studies—Reaction Rate.   The variation of the UV or IR spectra of an irradiated photosensitive film studied as a function of irradiation

TABLE VI
Influence of the Addition of 10% in Bulk of Photosensitizers on the Photosensitivity of
Copolymer $C_{II,1}$ (MMA/DMAEMA–E_2) (75/25/21.24)

Photosensitizer	None	Benzophenone	Michler's ketone	Kodak BN[b]	Tartrazine
$S_b{}^a$ $(\text{cm}^2\cdot\text{J}^{-1})$	6.85	3.05	0.87	1.02	3.05

[a] Bismuth test, Philips SP 500 Source-I = 0.164 w/cm^2, development solvent $CH_3OH/CHCl_3$ = 1/1.

[b] Kodak BN: N-methyl-2-benzoyl-p-naphthatiazoline.

TABLE VII
Influence of the Addition of 10% in Bulk of Photosensitizers on Various Photosensitive Polymers[a]

| Sample | Formula of the polymers | Photosensibility: S_{phot} (cm^2·J^{-1}) R | | | | | |
		Anthrone[b]	Benzanthrone[b]	Erythrosine[b]	Thioxanthone[b]	Xanthone[b]	S
Commercial products	KPR (Kodak) + sensitizer						10
	PE 4125 (Kodak) + sensitizer						25
$C_{I,1}$	MMA/4VP–E$_2$ 78/22/13.7	42.78 6.25	80.24 11.7	21.39 3.12	80.24 11.71	21.39 3.12	6.85
$C_{II,1}$	MMA/DMAEMA–E$_2$ 75/25/21.24			24.39 3.56	24.39 3.56		6.85
$C_{II,2}$	MMA/DMAEMA–E$_1$ 75/25/20.78	25.64 3.74	96.15 14	25.64 3.74	25.64 3.74	25.64 3.56	6.85
P_3	PVAm–CAACl (23.1̄4%)	2.94 64	2.94 64	1.18 25.65	2.94 64	0.98 21.30	0.046
P_5	PVAm–CACl (32.41%)	0.65 31	0.84 40	0.49 23.33	3.57 170	0.98 46.7	0.021

[a] S_b = Sensitivity measured by the "bismuth test"[5]; development solvent CH$_3$OH/CHCl$_3$, 1/1; S_{phot} = sensitivity measured by the "bismuth test" on films containing 10% in bulk of the photosensitizer; I = 0.164 W/cm^2 Philips SP 500 medium pressure mercury lamp λ = 250–800 nm; R = S_{phot}/S.
[b] Photosensitizers.

time allows the determination of the reaction rate τ:

$$\tau \frac{D_{\lambda t} - D_{\lambda 0}}{D_{\lambda 0} - D_{\lambda \infty}} \times 100$$

$D_{\lambda,t}$ being the optical density of the film at the wavelength λ at time t, $D_{\lambda,0}$, at time $t = 0$, and $D_{\lambda,\infty}$, at time $t = \infty$.

Table VIII gives the reaction rate of the photosensitive polymers studied for

TABLE VIII
Reaction Rate of Photosensitive Polymers after 30 s of Irradiation

Sample	Formula	Reaction rate τ[a] (%)
$C_{I,1}$	MMA/4VP–E$_2$ 78/22/13.7	47.55
$C_{II,1}$	MMA/DMAEMA–E$_2$ 75/25/21.24	10.00
$C_{II,2}$	MMA/DMAEMA–E$_1$ 75/25/20.78	61.90
C_{III}	MMA/DMAEMA–E$_2$ 50/50/36.23	29.62
P_2	PVAm–CAACl (18.23 %)	38.71
P_3	PVAm–CAACl (23.14%)	40.56
P_4	PVAm–CACl (23.50%)	43.41
P_5	PVAm–CACl (32.41%)	51.12

[a] τ was determined by irradiation of the photosensitive polymer film (thickness determined for obtaining at λ_{max} an optical density of 1) with a polychromatic light (Philips SP 500 medium pressure mercury lamp, λ = 250–800 nm), I = 0.07 W/cm^2.
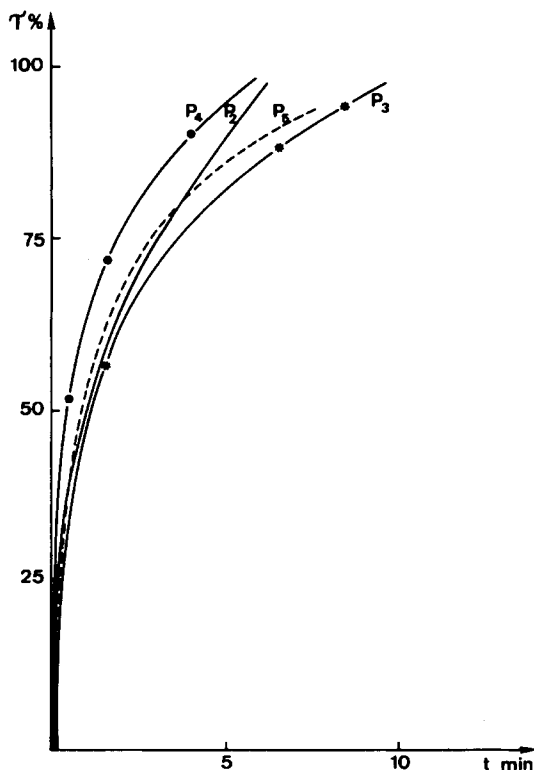
Fig. 1. Variation of τ as a function of irradiation time for the PVAm photosensitive polymers.

a 30 s irradiation time, and Figure 1 the variation of τ as a function of irradiation time for the PVAm photosensitive polymers we studied. Similar curves are obtained for the other photosensitive polymers.

Textile Dyeing. The most photosensitive were $C_{I,1}$ (MMA/4VP/E_2, 78/ 22/13.7) and C_{III} (MMA/DMAEMA/E_2, 50/50/36.23). The values of the textile photosensitivity S_T are nearly 156 and 154 cm$^2\cdot$J^{-1}, respectively. The free bases are pyridine for $C_{I,1}$ copolymer and an alkyl tertiary amine for C_{III}. In the case of P_3 the photosensitivity is fairly increased from 1 to 43 cm$^2\cdot$J^{-1} by addition of 10% of thioxanthone in bulk. The free base is an alkyl primary amine in this case. These photosensitivities are high enough to allow the use of these photosensitive polymers as coating protective agents in textile industry. However, the problem of the fixation of dyes is also of interest.

In previous studies,[2] we noticed that if alizaridines are fixed on a polymer such as $C_{I,1}$ and give bright color, the dye is easily removed by water washing. We tried to dye with anionic dyes a Tergal® stuff on the threads of which is fixed by photoreticulation a film of copolymer C_{III} or polymer P_2. Copolymer C_{III} leads to brighter colors than polymer P_2.

Alizarine and neutrichrome dyes have a good solidity to water washing, but have a bad solidity to light (as determined by a "xenon lamp test").

In fact, as expected, polymer containing aliphatic amine groups can be more easily dyed by anionic dyes than are polymers in which the amine is a pyridine group. If the solidity to water washing problem seems to be quite correctly resolved, polymers such as C_{III} or P_2 cannot be used to fix dyes on textiles very

difficult to be dyed such as polypropylene, because of the poor solidity to light of the anionic dyes used.

CONCLUSION

We partially succeeded in our aim. We synthesized polymers of high photo-sensitivity, easily fixable on the threads of a stuff and which fix strongly anionic dyes. We have to resolve the problem of the light solidity of this dye. Another purpose is to synthesize water-soluble photosensitive polymers. Their fixation on a stuff would be industrially much easier if it could be done in a water solution rather than in an organic solution.

References

1. P. Deledalle, A. Lablache-Combier, and C. Loucheux, *J. Appl. Polym. Sci.*, to appear.

2. C. Roucoux, C. Loucheux, and A. Lablache-Combier, *J. Appl. Polym. Sci.*, **26**, 1221 (1981).

3. D. J. Dawson, R. D. Gless, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **98**, 5996 (1976).

4. D. D. Reynolds and W. O. Kenyon, *J. Am. Chem. Soc.*, **69**, 911 (1947); H. Tanaka and R. Senju, *Bull. Chem. Soc. Jpn.*, **49**, 2821 (1976).

5. J. L. Decout, A. Lablache Combier, and C. Loucheux, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2371, 2391 (1980).

6. M. S. Htoo, *Photogr. Sci. Eng.*, **12**, 169 (1968); G. A. Delzenne, *Ind. Chim. Belg.*, **39**, 249 (1974).

7. H. Tanaka, M. Tsuda, and H. Nakanishi, *J. Polym. Sci., Part A-1*, **43**, 1729 (1978); T. Yamaoka, K. Ueno, and T. Tsunoda, *Polymer*, **18**, 81 (1977).

8. J. L. R. Williams, in *Polyelectrolytes*, F. Sélégny, Ed. Reidel, Dordrecht, Holland, 1974, p. 507.

9. *Handbook of Photochemistry*, S. L. Murov, Ed., Marcel Dekker, New York, 1973.