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Processes amplifying the effects of light on polymer layers

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Contents

I.	Introduction	35
II.	The influence of spin – orbit and hyperfine interactions on the efficiency and mode of the photochemical reaction	36
III.	Processes amplifying the latent image	39
IV.	Photochemical etching of bismuth films	47

Abstract. Processes bringing about amplification of the primary photoeffect in polymer layers through complex formation, autocatalysis, autosensitisation, and acid catalysis are discussed and their practical applications are considered. Attention is concentrated on highly sensitive photoresists for the photolithographic process used in advanced technologies. The bibliography includes 114 references.

I. Introduction

The problem of the amplification of the primary photoeffects on polymer systems is of cardinal importance because it is based on fundamental phenomena such as spectral and chemical sensitisation, complex formation, and electronic excitation energy and charge transfer. Furthermore, the use of amplification processes makes it possible to create highly sensitive polymer layers for the optical recording of information and highly sensitive photoresists and electronic resists and also to achieve directed far-reaching modification of polymer layers.

Systems in which the amplification processes occur with participation of components present in the polymer layers and do not require additional treatment of these layers in liquid or gaseous media, in contrast to, for example, well known photographic materials with chemical or physical development of the latent image in developer solutions, are considered below. The amplification coefficient of the primary photoeffect is equal to the ratio η_{ef}/η_0, where η_0 is the quantum yield of the formation (consumption) of the products of the primary action of light and η_{ef} is the effective quantum yield measured after the amplification of the primary effect.

These systems can be used in fields such as highly sensitive optical recording of information, detection of weak optical signals, photomodification of spectral and physicochemical properties of polymer layers, and selective photosynthesis of a series of chemical compounds in polymer matrices.

In the present communication, attention is concentrated on processes involving the amplification of the primary photoeffects in polymer layers in order to create on their basis highly sensitive photoresists for use in photolithography. In the first stage of the photolithographic process, photochemical reactions in polymer layers result in a change in the physicochemical properties of the exposed sections such as solubility, thermal stability, light transmittance, etc. On subsequent heating, treatment in solvents, or plasmachemical etching, the exposed (positive) or unexposed (negative) sections are fully removed from the support. The next stage of the photolithographic process is the treatment of the support (a plate made of silicon, a metal, or another material) through apertures obtained in the polymer layer (resistor) by etching or in some other way.[1–3] We emphasise that photolithography based on the use of photoresists has in fact made it possible to achieve a qualitative major advance in electronics—the introduction of the manufacture of integrated circuits.

The high sensitivity of polymer compositions to the action of light, X-rays, and electron irradiation is ensured by the electron donor – acceptor (EDA) interactions, the formation of aggregates from chromophoric groups, as well as autocatalytic,[4] chemical,[5,6] and optical[4,7] processes amplifying the primary photoeffects. In the systems considered below, catalysts are formed directly during the photochemical reaction or in the reaction of photoproduct with a compound introduced additionally—a chemical sensitiser. The mechanism of the optical amplification in the resist-free photoetching of metallic films by halogen-containing radicals, formed and deposited on these films of polymeric EDA compositions as a result of the dissociative addition of an electron to the halogen-containing acceptor, is also discussed.

A photoinitiated autocatalytic free-radical process is characteristic of the well known class of photoresists based on aromatic azides.[8] In order to create highly sensitive photoresists for use in microelectronics, detailed studies have been made in recent years, in connection with the manufacture and copying of optical [compact] discs, of the photoinitiated cross-linking of polyfunctional oligomeric acrylates in which $10^4 - 10^5$ cross-links arise as a result of a single photochemical act.[9]

The primary chemical stage of the photoprocess in polymeric EDA systems is electron transfer from the donor (D) to the acceptor (A). Compounds which dissociate into free radicals when acted upon by light, for example, ketones [R – C(O) – R'], are used as photoinitiators of the cross-linking of acrylates. This results in the formation of radical-ion pairs $[D^{\cdot+}...A^{\cdot-}]$ or radical pairs $[\dot{R}-\dot{C}(O)...\dot{R}']$. The spin – orbit and hyperfine interactions of the unpaired electrons determine the efficiency and mode of the subsequent reactions. Examples of reactions in which magnetic interactions exert an appreciable influence on the characteristics of the photoprocess are examined below.

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II. The influence of spin–orbit and hyperfine interactions on the efficiency and mode of the photochemical reaction

The efficiency and mode of the photochemical reaction depend on the multiplicity of the radical-ion or radical pair formed as a result of the action of light. Indeed, the reverse electron transfer or recombination of radicals are allowed only for the singlet orientation of the radical-ion spins in the geminal pair $[D^{\cdot+}...A^{\cdot-}]$ or the radicals in the pair $[R-\dot{X}...\dot{R}']$ respectively:

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad D+A \rightleftharpoons D\cdot A \\ D\cdot A \xrightarrow{h\nu} {}^1(D\cdot A)_1 \longrightarrow {}^1[D^{\cdot+}\ldots A^{\cdot-}] \longrightarrow [D\ldots A] \\ \qquad\qquad\quad \downarrow \qquad\qquad \rightleftarrows \\ \qquad\qquad\quad {}^3(D\cdot A)_1 \longrightarrow {}^3[D^{\cdot+}\ldots A^{\cdot-}] \longrightarrow (D^{\cdot+} + A^{\cdot-}) \end{array} \tag{1}$$

$$\begin{array}{l} R-X-R' \xrightarrow{h\nu} {}^1[R-X-R']_1 \longrightarrow {}^1[R-\dot{X}\ldots\dot{R}'] \longrightarrow R-X-R' \\ \qquad\qquad\quad \downarrow \qquad\qquad \rightleftarrows \\ \qquad\qquad\quad {}^3[R-X-R']_1 \longrightarrow {}^3[R-\dot{X}\ldots\dot{R}'] \xrightarrow{RH} R-XH+ \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad +R-R'. \end{array}$$

The spin forbiddenness of these reactions in triplet pairs increases the probability of the liberation of radical-ions from the pair and is also responsible for the preferential interaction of radicals with the compounds (RH) present in the composition. For this reason, the quantum yield of the free radical-ions or the mode of the photochemical reaction depend on the rate of intersystem crossing in the pair (i.e. on the rate of change of the spin of the unpaired electron in one of the radicals as a consequence of either spin–orbit interaction (SOI)[10] or hyperfine interaction (HFI)[11]. These interactions ensure an admixture of the singlet (triplet) configuration in the triplet (singlet) state of the pair:

$$\varphi^T[D^{\cdot+}\ldots A^{\cdot-}] = \varphi^3[D^{\cdot+}\ldots A^{\cdot-}] + \alpha\varphi^1[D^{\cdot+}\ldots A^{\cdot-}],$$

or

$$\varphi^S[D^{\cdot+}\ldots A^{\cdot-}] = \varphi^1[D^{\cdot+}\ldots A^{\cdot-}] + \alpha\varphi^3[D^{\cdot+}\ldots A^{\cdot-}].$$

The probability of intersystem crossing in the radical-ion pair is determined by the contribution of the singlet (triplet) state α^2, where

$$\alpha = \frac{1}{{}^1E - {}^3E}\int \varphi^1[D^{\cdot+}\ldots A^{\cdot-}]H_n\varphi^3[D^{\cdot+}\ldots A^{\cdot-}]. \tag{2}$$

Here ${}^1E-{}^3E$ is the distance between the the energy levels of the 'pure' S and T states in the radical-ion pair and $H_n = H_{SOI}$ and H_{HFI}, where H_{SOI} and H_{HFI} are the operators of the spin–orbit and hyperfine interactions respectively:

$$H_{SOI} = \sum_i \xi_i\rho_i\bar{l}_i\bar{S}_i\ ,$$

$$H_{HFI} = \sum_i a_i\bar{S}_i\bar{I}_i\ ,$$

where ξ_i is the SOI constant for the ith atom, $\bar{l}_i$ is the azimuthal quantum number of the atom, $\bar{\rho}_i$ and $\bar{S}_i$ are the density and spin of the unpaired electron on the ith atom, a_i is the HFI constant, and I_i is the spin of the ith nucleus. According to Buchachenko et al.,[11]

$${}^1E - {}^3E = 2J_0\exp[-(R-R_0)],$$

where $J_0\exp(-R_0) \simeq 1.5$ eV is the energy of the exchange interaction between the radical-ions separated by the van der Waals distance R_0. R is the distance between the radical-ions in the pair (Å).

It follows from Eqn. (2) that intersystem crossing occurs for distances between the radical-ions such that the following relation holds:

$${}^1E - {}^3E \leq \int \varphi^1[D^{\cdot+}\ldots A^{\cdot-}]H_n\varphi^3[D^{\cdot+}\ldots A^{\cdot-}].$$

Thus for SOI and HFI, intersystem crossing takes place with the greatest probability under the following conditions:

$$\begin{aligned} 2J_0\exp[-(R-R_0)] &\simeq \sum_i \xi_i\rho_i\ , \\ 2J_0\exp[-(R-R_0)] &\simeq \sum_i \alpha_i\ . \end{aligned} \tag{3}$$

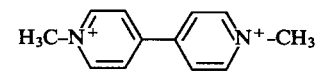
In polymeric media, where the separation of the radical-ion components may be difficult, the probability of the S → T or T → S conversion increases with increase in ξ_i and α_i.

1. Spin–orbit interaction

The spin–orbit interaction constant ξ_i increases with increase in the charge on the nucleus (Z_i) with which the unpaired electron interacts:

$$\xi_i = \sum_i \frac{Z_i^4}{n_i^3}\ ,$$

where n_i is the principal quantum number of the ith atom. In liquid-phase donor–acceptor–sensitiser systems, where the donor is an amine (Am), the acceptor is Methyl Viologen (MV^{2+})



and the sensitisers are the organometallic complexes $M(L)_3^{2+}[M^{2+} = Ru^{2+}, Os^{2+}$; L = bipyridyl (bipy) or other ligands], electron transfer takes place with participation of the triplet-excited sensitiser. The equilibrium reduction potential of MV^{2+} is $E_{1/2}(MV^+/MV^{2+}) = -0.44$ V relative to the potential of the normal hydrogen electrode (n.h.e.).[12] Depending on the oxidation potential of the donor $E_{1/2}(Am/Am^{\cdot+})$, two types of electron transfer are possible. In one of them, the primary reaction is

$$\begin{array}{l} Am + {}^3[M(L)_3^{2+}]_1 \longrightarrow {}^3[Am^{\cdot+}\ldots M(L)_3^{1+}] \longrightarrow \\ \qquad\qquad\qquad\qquad \longrightarrow Am^{\cdot+} + M(L)_3^{1+}, \end{array} \tag{4}$$

while the second reaction is

$$M(L)_3^{1+} + MV^{2+} \longrightarrow M(L)_3^{2+} + M^{\cdot+}. \tag{5}$$

In the other type of electron transfer, the primary reaction is

$${}^3[M(L)_3^{2+}]_1 + MV^{2+} \longrightarrow {}^3[M(L)_3^{3+}\ldots MV^{\cdot+}] \longrightarrow M(L)_3^{3+} + MV^{\cdot+} \tag{6}$$

while the second reaction is

$$M(L)_3^{3+} + Am \longrightarrow M(L)_3^{2+} + Am^{\cdot+}. \tag{7}$$

The free energies of reactions (4)–(7) can be calculated from the following formulae respectively:

$$\Delta G(4) = eE_{1/2}\left(\frac{Am}{Am^{\cdot+}}\right) - eE_{1/2}\left(\frac{M(L)_3^{1+}}{{}^3[M(L)_3^{2+}]_1}\right),$$

$$\Delta G(5) = eE_{1/2}\left(\frac{M(L)_3^{1+}}{M(L)_3^{2+}}\right) - eE_{1/2}\left(\frac{MV^{\cdot+}}{MV^{2+}}\right),$$

$$\Delta G(6) = eE_{1/2}\left(\frac{{}^3[M(L)_3^{2+}]_1}{M(L)_3^{3+}}\right) - eE_{1/2}\left(\frac{MV^{\cdot+}}{MV^{2+}}\right),$$

$$\Delta G(7) = eE_{1/2}\left(\frac{Am}{Am^{\cdot+}}\right) - eE_{1/2}\left(\frac{M(L)_3^{2+}}{M(L)_3^{3+}}\right).$$

We shall consider as an example a system where the sensitiser is a bipyridyl complex of ruthenium. The corresponding reduction and oxidation potentials of the triplet-excited ruthenium complex $^3[Ru(bipy)_3^{2+}]_1$ are

$$E_{1/2}\left(\frac{Ru(bipy)_3^{1+}}{^3[Ru(bipy)_3^{2+}]_1}\right) = E_{1/2}\left(\frac{Ru(bipy)_3^{1+}}{Ru(bipy)_3^{2+}}\right) + \frac{E(^3[Ru(bipy)_3^{2+}]_1)}{e} = -1.27 + 2.1 = 0.83 \text{ V (n.h.e.)} \quad (8a)$$

and

$$E_{1/2}\left(\frac{^3[Ru(bipy)_3^{2+}]_1}{Ru(bipy)_3^{3+}}\right) = E_{1/2}\left(\frac{Ru(bipy)_3^{2+}}{Ru(bipy)_3^{3+}}\right) - \frac{E(^3[Ru(bipy)_3^{2+}]_1)}{e} = 1.27 - 2.1 = -0.83 \text{ V (n.h.e.)}; \quad (8b)$$

$E_{1/2}[Ru(bipy)_3^{1+}/Ru(bipy)_3^{2+}]$ and $E_{1/2}[Ru(bipy)_3^{2+}/Ru(bipy)_3^{3+}]$ are the equilibrium reduction and oxidation potentials of $Ru(bipy)_3^{2+}$ in the ground state respectively and $E(^3[Ru(bipy)_3^{2+}]_1)$ is the distance from the ground to the excited triplet level of the sensitiser.

Reactions (4) and (5) are more favourable on energy grounds only in the case where one uses as the donors compounds with equilibrium oxidation potentials $E_{1/2}(D/D^{\cdot+}) < 0.83$ (n.h.e.) [see Eqn. (8a)] for which the free energies $\Delta G(4)$ and $\Delta G(5)$ are negative. The aromatic amines tetramethyl-*p*-phenylenediamine [$E_{1/2}(Am/Am^{\cdot+}) = 0.16$ V], diphenyl-*p*-phenylenediamine (0.36 V), tetramethylbenzidine (0.49 V), phenothiazine (0.53 V), β-naphthylamine (0.64 V),[13] as well as anthracene, 9-methylanthracene, and 9-bromoanthracene are classified as donors of this kind.[12] If compounds such as ethylenediaminetetraacetic acid (EDTA) or triethanolamine (TEOA), having $E_{1/2}(D/D^{\cdot+}) = 1.0$ or 0.9 V (n.h.e.), are used as the donors, then reaction (4) has a positive free energy: $\Delta G(4) = +0.16$ and $+0.06$ eV respectively. In this case, reactions (6) and (7) are energetically more favourable, because in both of them ΔG is negative [see Eqn. (8b)]:

$$\Delta G(6) = -0.83 - eE_{1/2}\left(\frac{MV^{\cdot+}}{MV^{2+}}\right) = -0.83 + 0.44 = -0.39 \text{ eV}$$

and

$$\Delta G(7) = eE_{1/2}\left(\frac{D}{D^{\cdot+}}\right) - 1.27 = \begin{cases} 1.0 - 1.27 = -0.27 \text{ eV (for EDTA)}, \\ 0.9 - 1.27 = -0.37 \text{ eV (for TEOA)}. \end{cases}$$

The quantum yield of the free radical-cations $D^{\cdot+}$, which avoided recombination in pairs, depends on a number of factors: the reaction pathway and the chemical structures of the sensitiser and donor. A number of systems can be quoted as examples.

(1) In systems comprising the donors Am sensitising $M(L)_3^{2+}$ (where $M^{2+} = Ru^{2+}$ or Os^{2+}) and the acceptor MV^{2+}, the quantum yield reaches 1, if the primary reaction (4) takes place, and is 0.2 ± 0.07 for the primary reaction (6).[12,13] According to the concepts developed, such decrease in the quantum yield is caused by the increase in the probability of the T → S intersystem crossing in the radical-ion pair and hence by the increase in the rate of the reverse reaction in the transition from the $^3[Am^{\cdot+}...M(L)_3^{1+}]$ pairs [see reaction (4)], where the electron transferred from Am to the metal complex is concentrated on the ligands and the spin–orbit interaction constant does not exceed $\xi = 76$ cm^{-1}, to the $^3[M(L)_3^{3+}...MV^{\cdot+}]$ pairs. In the latter case, the unpaired electron interacts with the orbitals of the central heavy atom, which has a spin–orbit constant $\xi = 1100-1350$ cm^{-1} (Ru^{2+}) or 3000 cm^{-1} (Os^{2+}).[14]

(2) The T → S intersystem crossing in the radical-ion pairs is responsible for the low quantum yield (~0.01) of the free radical-cations $MV^{\cdot+}$ and $D^{\cdot+}$ in systems containing a set of xanthen dyes, incorporating heavy iodine atoms ($\xi = 5060$ cm^{-1}) as sensitiser.[15,16]

(3) The quantum yield of the free radical-cations $D^{\cdot+}$ and $MV^{\cdot+}$ in reactions (4) and (5) is reduced from 1 to 0.74 when donors such as anthracene or 9-methylanthracene are replaced by 9-bromoanthracene and to 0.3 on subsequent addition of CH_3I to the solvent (a mixture of CH_3CN and CH_2Cl_2).[12] The authors explained this decrease by the effect of the heavy bromine ($\xi = 2640$ cm^{-1}) and iodine ($\xi = 5060$ cm^{-1}) atoms.

(4) In systems containing EDTA or TEOA as donors, Methyl Viologen as the acceptor, and Ru^{2+}, Os^{2+}, and Cu^+ complexes or the set of xanthen dyes as sensitisers,[15,16] an increase in the quantum yield of the radical-ion $D^{\cdot+}$ (which avoided recombination within the pairs) by a factor of 3–80 was attained by introducing species such as the anthracene-9-carboxylate anion (AA^-) or 9-methyl-anthracene.[12,15–17] These species are effective acceptors of the triplet energy of the photoexcited sensitiser and participate in the excited triplet state in the subsequent redox reactions (6) and (7) with formation of the triplet pairs $^3[AA^{\cdot}...MV^{\cdot+}]$, which do not contain heavy atoms.

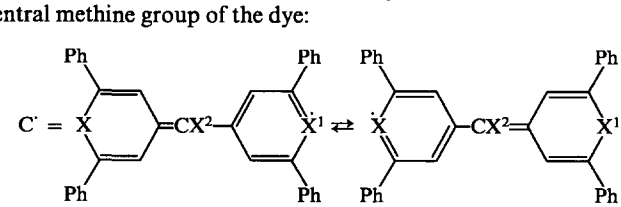
(5) In the photosensitive EDA composition consisting of a poly(vinyl ethylal) (PVE) matrix, in which are dissolved diphenylbenzylamine (DPBA) [$E_{1/2}(DPBA/DPBA^{\cdot+}) = 0.98$ V relative to the saturated calomel electrode (s.c.e.) or 0.74 V (n.h.e.)] as the donor and di(tribromomethyl) sulphone (DTBMS) as the acceptor, the dye (S^+)-sensitised formation of the coloured product (CP^+) takes place in accordance with the reaction[18]

$$S^+ \xrightarrow{h\nu, S\to T} {}^3(S^+)_1 \xrightarrow{DPBA} {}^3(DPBA^{\cdot+}...S^{\cdot-})_1 \longrightarrow$$

$$\longrightarrow {}^3[DPBA^{\cdot+}...S^{\cdot}] \xrightarrow{DTBMS} S^+ + {}^3[DPBA^{\cdot+}...DTBMS^{\cdot-}] \longrightarrow$$

$$\longrightarrow CP^+Br^- + HR \text{ (or } CP^+R^- + HBr). \quad (9)$$

Here Cp^+Br^- = *N*,*N*-diphenyl(phenylmethyleneiminium) bromide $(C_6H_5)_2N^+=CH-C_6H_5Br^-$ with $\lambda_{max} = 665$ and $HR = H[CBr_2=S(O_2)-CBr_3]$.[19] In the case of the dyes listed in Table 1, the pair $^3[DPBA^{\cdot+}...S^{\cdot}]$ is formed during reaction (9), the unpaired electron in the radical $S^{\cdot}$ being concentrated on the X^1 and X atoms. The decrease in the quantum yield in the formation of CP^+ via reaction (19) on passing from oxygen- to sulphur-containing dyes, indicated in Table 1, was explained[20] by the corresponding increase in the rate of the reverse reaction owing to the acceleration of T → S intersystem crossing in the pair $^3[DPBA^{\cdot+}...S^{\cdot}]$ with increase in the spin–orbit interaction constant from 113–130 cm^{-1} for the O atom to 382 cm^{-1} for the S atom. The unpaired electron interacts weakly under these conditions with a H atom or the heavy bromine atom in the central methine group of the dye:



2. Hyperfine interaction

Those S → T and T → S transitions in which the overall magnetic quantum number M_z of the electronic-nuclear system does not change become allowed as a result of hyperfine interaction:

$$M_z = M_s(1) + M_s(2) + \sum_i m_i(1) + \sum_k m_k(2),$$

Table 1. Equilibrium redox potentials $E_{1/2}$(Ox) and $E_{1/2}$(Red) (measured relative to the saturated calomel electrode) and the maxima positions in the optical spectra (λ_{max}) of the sensitising dyes (S^+), the quantum yield η_0 of *N,N*-diphenyl(phenylmethyleneiminium) bromide [formed by reaction (9)] in the composition consisting of PVE, DPBA, DTBMS, and S^+.

Dye (S^+)	$E_{1/2}$(Ox)/ V	$E_{1/2}$(Red)/ V	λ_{max}/ nm	η_0
2,2',6,6'-Tetraphenylpyrylomethinecyanine-perchlorate (X = X¹ = O, X² = H)	1.2 *	–0.65 *	571	0.12
2,2',6,6'-Tetraphenylthiopyrylo-methinecyanine perchlorate (X = O, X¹ = S, X² = H)	1.15 *	–0.55 *	596	0.02
2,2',6,6'-Tetraphenylpyrylobromo-methinecyanine perchlorate (X = X¹ = O, X² = Br)	1.7	~0	620	0.09
2,2',6,6'-Tetraphenyldithiopyrylo-methinecyanine perchlorate (X = X¹ = S, X² = H)	1.08 *	–0.46 *	630	0.00

* The redox potentials of the dyes were taken from Mikheeva et al.[21]

where $M_s(1)$ and $M_s(2)$ are the magnetic quantum numbers of the unpaired electrons 1 and 2 in the pair, and $m_i(1)$ and $m_k(2)$ are the magnetic quantum numbers of the nuclei over which the electron densities of the unpaired electrons 1 and 2 extend.

We shall consider how hyperfine interaction affects the rate of recombination of the components of the triplet pair in relation to dibenzyl ketone (DBK).[11] This influence is manifested by the photochemical enrichment of dibenzyl ketone in the ^{13}C isotope. The process is due to the fact that dibenzyl ketone dissociates in the excited triplet state into radicals, which form the radical pair $^3[R-\dot{C}(O)...\dot{R}]$, where $\dot{R} = \dot{C}H_2C_6H_5$. The triplet pairs decompose preferentially with formation of the dibenzyl ketone cleavage product if they contain the ^{12}C isotope in the $R-\dot{C}(O)$ group, but recombine with reformation of the initial ketone if the group contains the ^{13}C isotope. The effect is caused by the fact that, in contrast to the ^{12}C isotope, the ^{13}C isotope (the natural abundance of which is 1.1%) has a magnetic moment ($I = 1/2$) and the T → S transitions become allowed as a consequence of the hyperfine interaction:

$$-\overset{O}{\overset{\|}{C}}\cdot\uparrow(m_i = -1/2)\ldots R\cdot\uparrow \xrightarrow{T_{+1}\to S} -\overset{O}{\overset{\|}{C}}\cdot\downarrow(m_i = +1/2)\ldots R\cdot\uparrow$$

$$-\overset{O}{\overset{\|}{C}}\cdot\downarrow(m_i = +1/2)\ldots R\cdot\downarrow \xrightarrow{T_{-1}\to S} -\overset{O}{\overset{\|}{C}}\cdot\uparrow(m_i = -1/2)\ldots R\cdot\downarrow$$

$$-\overset{O}{\overset{\|}{C}}\cdot^-(m_i = \pm 1/2)\ldots R\cdot^- \xrightarrow{T_0\to S} -\overset{O}{\overset{\|}{C}}\cdot\downarrow(m_i = \pm 1/2)\ldots R\cdot\uparrow\ .$$

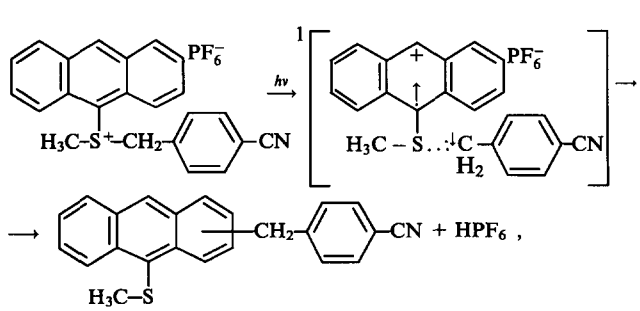
This permits the recombination of the radical pair. (The direction of the electron spin is indicated in the above formulae by arrows.)

In the general case the probability of the T → S transitions is determined by the sum of the hyperfine interaction constants:[11]

$$a^2 = \left[\sum_i a_i^2(1) + \sum_k a_k^2(2)\right] t\ ,$$

where t is the hyperfine interaction time.

In order to devise photoresists whose operation is based on acid photocatalysis, a large number of onium salts, such as arenediazonium salts ($ArN_2^+\ MX_n^-$), aryliodonium salts ($Ar_2I^+\ MX_n^-$), arylsulphonium salts ($Ar_3S^+\ MX_n^-$), and arylammonium salts, arylphosphonium salts, and arylarsonium salts ($Ar_4M'^+\ MX_n^-$; M' = N, P, and As respectively) were synthesised; $MX_n^- = PF_6^-$, AsF_6^-, BF_4^-, etc. On photoexcitation of the onium salt, the spectral sensitiser, or the charge-transfer complex between the additional organic donor (RH) and acceptor (onium salt), a reaction accompanied by the appearance of a Lewis (MX_{n-1}) or Brønsted (HMX_n) acid takes place. The acids induce the degradation of the chains or the cross-linking of the polyesters. The mode of such photochemical reactions is determined by the hyperfine interaction,[22,23] because S → T intersystem crossing in the singlet radical pair formed in the primary step competes with the reaction between the radicals. Thus the photolysis of sulphonium, arsonium, and phosphonium salts proceeds in different ways,[22] which is associated with the increase in the hyperfine interaction constant on passing from sulphonium [$a(^{32}S) = 0$ Oe] to arsonium [$a(^{75}As) = 4.65$ Oe], and further to phosphonium [$a(^{31}P) = 306$ Oe]. Whereas the products of the photolysis of sulphonium salts are formed as a result of an intramolecular rearrangement via the singlet state of the pair,[22,23] the photolysis of arsonium salts takes place both via the singlet and triplet states of the pair,[22] while the ammonium and phosphonium salts are photolysed solely via the triplet state, because in this case S → T intersystem crossing predominates and results in the formation of a triplet radical pair. In this case, the intramolecular rearrangement becomes spin-forbidden and the formation of HMX_n requires the involvement of a molecule of the solvent. For example, in the case of the salt 9-anthrylmethyl-*p*-cyano-benzylsulphonium hexafluorophosphate the photoexcitation of the 9-anthryl chromophore entails charge transfer from the sulphonium fragment and subsequent rearrangement within the pair[23]



whereas in arsonium salts the following reactions takes place.

$$(C_6H_5)_3As^+ - CH_2 - C_6H_4 - CN \xrightarrow{h\nu}$$

$$\begin{cases} \rightarrow\ ^1[(C_6H_5)_3As^{\cdot+}\ldots\dot{C}H_2C_6H_4 - CN\ \ MX_n^-] \\ \qquad \downarrow \\ \qquad (C_6H_5)_2As - C_6H_4 - CH_2 - C_6H_4CN + HMX_n\ , \\ \rightarrow\ ^3[(C_6H_5)_3As^{\cdot+}\ldots\dot{C}H_2C_6H_4 - CN\ \ MX_n^-] \\ \qquad \downarrow H_2O \\ \qquad (C_6H_5)_3AsO + (CH_3 - C_6H_4CN) + HMX_n\ . \end{cases} \qquad (10)$$

A high rate of S → T intersystem crossing is to be expected in the radical pairs of iodonium salts via both spin–orbit and hyperfine interaction mechanisms as well as the predominance of reaction (10), because high spin–orbit and hyperfine interaction constants are characteristic of the iodine atom.

III. Processes amplifying the latent image

1. Highly sensitive photoresists based on [2 + 2] photoaddition

In the familiar photoresists consisting of poly(vinyl cinnamates) (PVCI) and related compounds $-CH_2-CHR-$, the chromophore R incorporates the $-CH=CH-$ group, which is responsible for the photoinduced cross-linking of the polymer chain via the [2 + 2] photocycloaddition mechanism:[2]

$$2(-CH=CH-) \xrightarrow{h\nu} \begin{matrix} -CH-CH- \\ | \quad | \\ -CH-CH- \end{matrix} \quad (11)$$

As a result of this reaction, the exposed polymer film is not removed from the support throughout the period of the dissolution of the unexposed sections in organic solvents.

[2 + 2] Photocycloaddition involving PVCI proceeds via the excited singlet and triplet states of the chromophores R when the latter are themselves photoexcited. The process proceeds with a much higher efficiency under the conditions of triplet energy transfer to R from the photoexcited spectral sensitiser. For a random relative distribution of the chromophores in neighbouring PVCI chains ($R = -OCO-C=CH-C_6H_5$), the quantum yield of the cyclobutane rings formed via reaction (11) is $\eta_0 \simeq 0.045$ and the exposure corresponding to the onset of gel formation is $H_g \simeq 700$ mJ cm^{-2}. In order to increase the photosensitivity of photoresists, much attention has been devoted in recent years to the synthesis of new polymers with an increased triplet energy migration distance[24] and also the synthesis of compounds in which the cinnamoyl groups form aggregates.[7,25,26]

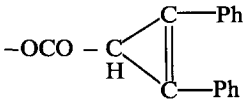
The lifetimes of the triplet excitation (τ), the quantum yield of the cyclobutane ring (η_0), and the photosensitivities $S = 1/H_g$ (estimated relative to S for PVCI) have been compared[24] for PVCI and the polymers **1–3**

$$(-CHR-CH_2-)_{0.9}-(-CHOH-CH_2-)_{0.1};$$

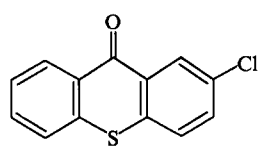
1–3

1: R = $-OCO-CH=CH-C_6H_4-COOC_2H_5$;

2: R = $-OCO-CH=CH-C_{10}H_8$

3: R = 

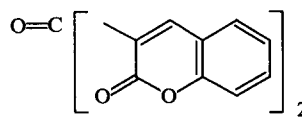
in the presence of 2-chlorothioxanthene-9-one **4**



(E_T = 65 kcal mol^{-1})

4

or 3,3′-carbonylbiscoumarin **5**



(E_T = 56.2 kcal mol^{-1})

5

as the sensitiser (Table 2). The table shows that, on passing from PVCI to the polymer **3**, the lifetime of the triplet excitation increases by more than four orders of magnitude. This is responsible for the increase in S by a factor of 17.5, i.e. a decrease in H_g to 40 mJ cm^{-2}.

In order to obtain intermolecularly bound chromophoric groups, poly(vinyl cinnamates) $-CH_2-CH(RX)-$ were synthesised with chromophoric groups (RX) containing a fragment X with electron-donating (PVCI–D) or electron-accepting (PVCI–A) properties:[25,26]

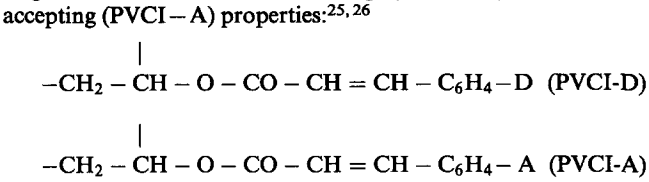
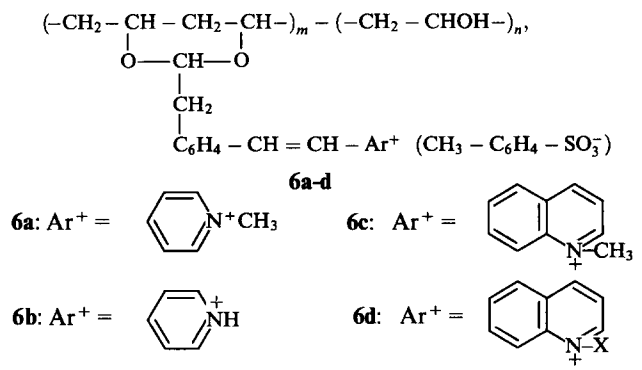


Table 3 presents the quantum yields of the overall consumption of the double bonds (η') and the intermolecular cross-links (η'') and the values of H_g for different combinations of PVCI-D and PVCI-A in the absence of a sensitiser and on photoexcitation of 3,3-carbonylbiscoumarin as the sensitiser.[25,26] Table 3 shows that the relative efficiency of the gel formation, which can be estimated from the ratio η''/η', increases with enhancement of the donor–acceptor interaction from 0.18 for pure PVCI to 0.82 for the PVCI–OCH_3/PVCI–Cl (50 : 50) pairs. As a consequence of this, on passing from the homopolymer PVCI to the equimolar mixture of polymers PVCI–OCH_3/PVCI–Cl, there is also a decrease in H_g from 700 to 152 and 62 mJ cm^{-2} in the non-sensitised and sensitised systems respectively.

The highly sensitive water-soluble photoresists



6a-d

6a: Ar^+ = **6c**: Ar^+ =

6b: Ar^+ = **6d**: Ar^+ =

whose operation is based on [2 + 2] photocycloaddition, have been proposed.[27,28] The capacity of these photoresists to form aggregates is responsible for their high sensitivity even at a low concentration of chromophoric groups:

Polymer	(m/n)/%	H_g/ mJ cm^{-2}
6a	2.2	~12
6b	2.5	~10

It has been shown in relation to the polymer **6c** [27,28] that the deprotonation of the quinoline group by treatment in an organic solvent containing amines, i.e. its transformation from an electron-accepting into an electron-donating group, leads to a 100-fold increase in H_g and also to a shift of the long-wavelength optical absorption maximum from 420 nm to 360 nm. It was therefore suggested that a polymer with a low sensitivity be employed and that it be sensitised directly before exposure by treatment in acid-containing solvents. The photosensitivity obtained under these conditions depends on the nature of

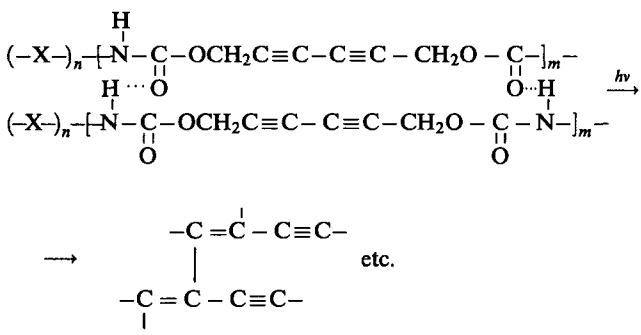
Table 2. The lifetimes of the triplet excitation (τ), the quantum yield in the formation of the cyclobutane ring (η_0), and the photosensitivity ($S = 1/H_g$) relative to S for PVCI) of PVCI and the polymers **1–3**.[24]

Polymer	τ/ μs	η_0	S/ cm^2 mJ^{-1}
PVCI	0.01	0.045	1
1	6.9	0.073	2.5
2	10	0.12	3.3
3	360	0.53	17.5

the acid[28] and increases in the sequence corresponding to the ratios HCl : HPO_3 : $HClO_4$: H_2SO_4 : p-$CH_3C_6H_4SO_3H$ = = 1 : 21 : 71 : 100 : 101.

The intermolecular interactions in the linear polyesters $-CO-C(CN)=CH-CH=CHC_6H_4CH=C(CN)-CO-O-[(-CH_2-)_2-O-]_3-$ in the ground state ensure their high photosensitivity[29] with H_g = 1.6 mJ m^{-2}.

It has been suggested[30,31] that the hydrogen bonds in the block-copolymers of diacetylene with polyurethanes, polyesters, and polyamides are responsible for the formation of stacks of chains containing diacetylene fragments. Light at the wavelength corresponding to the absorption bands of diacetylene ($\leqslant$400 nm) initiates the chain reaction involving the cross-linking of neighbouring acetylene groups with formation of a branched system of conjugate bonds. This reaction proceeds effectively when an exposed film is heated (80 °C, 10 min):



The highest sensitivity (H_g = 0.5 mJ cm^{-2} when the content of diacetylene groups is 30 wt%) is shown by copolymers based on aliphatic polyurethanes, which is associated with the flexibility of the chains promoting the formation of stacks of rigid diacetylene fragments and also with the absence of groups which absorb light in the same region as the diacetylene chromophore.

2. Autocatalysis

A typical example of compositions in which the catalyst is formed as a result of a photochemical reaction directly from the photosensitive components is the system incorporating a polymer matrix and an electron donor [$(C_5H_5)_2Fe$] and acceptor (CBr_4) dissolved in it. The donor–acceptor complex $(C_5H_5)_2Fe \cdot CBr_4$, the optical absorption maximum of which is in the range 370–400 nm, is responsible for the photosensitivity of the composition. Photoexcitation of the complex leads to its dissociative decomposition:[5,32,33]

$$(C_5H_5)_2Fe \cdot CBr_4 \xrightarrow{h\nu}$$

$$\longrightarrow (C_5H_5)_2Fe^+ \ldots Br^- \ldots \dot{C}Br_3 \text{ (or } Br^{\cdot} \ldots CBr_3^-) \longrightarrow$$

$$\longrightarrow [Fe^{3+}Br_4]^- + \text{products} \qquad (12)$$

with formation of the ferrocenium cation $(C_5H_5)_2Fe^+$, which is converted by interaction with the free radical $\dot{C}Br_3$ into the tetrabromoferrate(III) anion $[Fe^{3+}Br_4]^-$ with characteristic optical absorption bands at λ_{max} = 397 and 472 nm, which are responsible for the brown colour.

It has been noted[34] that heating of the exposed layer at 70–100 °C ensures the development of the latent image. It has been established[5,34,35] that the key factor in this process is the formation of trivalent iron which enters into the thermal reaction[36]

$$Fe^{3+} + (C_5H_5)_2Fe \longrightarrow Fe^{2+} + (C_5H_5)_2Fe^+.$$

This is followed by charge transfer:

$$Fe^{2+} + CBr_4 \longrightarrow Fe^{3+} + Br^- \ldots CBr_3^{\cdot} \text{ (or } Br^{\cdot} \ldots CBr_3^-).$$

Thus the Fe^{3+}/Fe^{2+} pair, arising as a result of illumination, catalyses the thermal electron transfer between the donor and acceptor components. The overall process can be formulated as follows:

$$(C_5H_5)_2Fe + CBr_4 \xrightarrow{Fe^{3+}/Fe^{2+}}$$

$$\longrightarrow (C_5H_5)_2Fe^+ + Br^- \ldots CBr_3^{\cdot} \text{ (or } Br^{\cdot} \ldots CBr_3^-). \qquad (13)$$

The thermal stages of the photochemical reaction (12) are then repeated.

The factors limiting the amplification coefficient as a consequence of the parallel occurrence of the photoinitiated autocatalytic reaction (13) and the dark thermal electron transfer in the complex $(C_5H_5)_2Fe \cdot A$, where A = CBr_4 or halo-derivatives of organic compounds of different structure, have been analysed.[37] It was established that the principal stages of the autocatalytic process (13) include diffusion-controlled reactions, so that the decisive factors are the size of the acceptor and the segmental mobility of the polymer chains at elevated temperatures. The primary quantum yield of the coloured product [formed via reaction (12)] is η_0 = 0.05–0.1 regardless of the nature of the acceptor. It has been shown that, when a polystyrene matrix is used, the highest

Table 3. The influence of the donor–acceptor interaction on the principal characteristics of PVCI-based photoresists.

Polymer	η'	η''	H_g/ mJ cm^{-1}
	Without sensitiser, λ = 300 nm		
PCVI	0.28	0.05	700
PVCI–CO–OCH_3/ PVCI–Cl	0.28	0.03	~1160
PVCI–CH_3/ PVCI	0.245	0.085	410
PVCI/PVCI–Cl	0.1265	0.1	350
PVCI–OCH_3/ PVCI	0.32	0.13	270
PVCI–CH_3/ PVCI–CO–OCH_3	0.27	0.125	280
PVCI–OCH_3/ PVCI–Cl			
100 : 0	–	0.06	–
50 : 50	0.28	0.23	152
0 : 100	–	0.02	–
	6 wt% of sensitiser, λ = 400 nm		
PVCI–OCH_3/PVCI–Cl			
100 : 0	–	0.08	–
50 : 50	–	0.58	62
0 : 100	–	0.02	–

amplification coefficient (~6000) is attained in the case of CBr_4. When CBr_4 is replaced by $O_2N-C_6H_4-SO_2-CBr_3$, the amplification coefficient is reduced to 450.

Compositions containing, in addition to the ferrocene donor, also aromatic amines (Am), namely diphenylamine (DPA), DPBA, and dibenzylaniline (DBA), have been investigated.[38-41] It was established that the photoexcitation of the complex $(C_5H_5)_2Fe \cdot CBr_4$ and subsequent heating of the composition to 60–100 °C results in the autocatalytic accumulation not only of the ferrocene decomposition products but also of the triphenylmethane dye (TPM D) derived from the aromatic amine, the dye being responsible for the absorption at λ_{max} = 605 nm. It has been suggested[40,41] that the charge transfer

$$(C_5H_5)_2Fe^+ + Am \longrightarrow (C_5H_5)_2Fe + Am^{\cdot+} \qquad (14)$$

and subsequent thermal reactions of the radical cation $Am^{\cdot+}$ and of $Br^-...CBr_3^{\cdot}$, i.e.

$$Am^{\cdot+}...Br^- \ ...CBr_3^{\cdot} \xrightarrow[HBr]{2Am}$$

$$\longrightarrow R^1R^2N^+ = C_6H_4 = C(C_6H_4NR^1R^2)_2Br^- \qquad (15)$$

(TPM D)

take place.

Under the conditions of the photoexcitation of the complex $(C_5H_5)_2Fe \cdot CBr_4$ in the presence of amines it was established[38] that DPA inhibits the autocatalytic accumulation of $[Fe^{3+}Br_4]^-$ to a much greater extent than do DPBA and DBA. It is most likely that the inhibition is due to the charge-transfer process (14), the rate of which is determined by the nature of the aromatic amine. Indeed, the ionisation potentials of ferrocene (I_D = 6.88 eV[42]), DPA (7.2 eV[43]), DPBA (~7.5 eV[20]), and DBA (7.55 eV[20]) correspond to the following free energies of activation for reaction (14): ΔG_1 = 7.2–6.88 = 0.32 eV for DPA, ΔG_2 = = 7.5–6.88 = 0.62 eV for DBA. Hence it follows that the rate constants for reaction (14) with participation of the tertiary amines DPBA and DBA are smaller by the factor $\exp[(\Delta G_2 - \Delta G_1)/kT]$, i.e. by approximately five orders of magnitude, than in the case of DPA. However, it has been established experimentally that the rate of formation of the coloured products from the tertiary amines DPBA and DBA is the same as the rate measured for the secondary amine DPA. It is most likely that the coloured products derived from the tertiary amines DPBA and DBA and the secondary amine DPA are formed via different pathways.

It is known that the photoexcitation of complexes between DPA and CBr_4 involves electron transfer from the donor to the acceptor component with formation of the radical-ions $CBr_3^{\cdot}...Br^-$ and $DPA^{\cdot+}$ and the products of their interaction:[44]

$$DPA^{\cdot+} + CBr_3^{\cdot} \ ...(Br^-) \longrightarrow p\text{-DPA} - CBr_3 + HBr.$$

It has been suggested[45,46] that the free radical chain process

$$\begin{array}{l} DPA + \dot{C}Br_3 \ (Br^{\cdot}) \longrightarrow DPA^{\cdot} + CHBr_3 \ (HBr) \\ \quad\uparrow\qquad\qquad\qquad\qquad\qquad\quad\downarrow \\ DPA^{\cdot} + CBr_4 \longrightarrow p\text{-DPA}-CBr_3 + Br^{\cdot} \end{array} \qquad (16)$$

takes place and leads to the amplification of the latent image. The interaction of DPA–CBr_3 with DPA ensures the formation of the triphenylmethane dye.

The interaction of tertiary amines with $\dot{C}Br_3$ radicals involves the abstraction of a hydrogen atom from the α-position relative to the nitrogen atom:[47]

$$C_6H_5(R)N - CH_2 - C_6H_5 + CBr_3^{\cdot} \longrightarrow$$

$$\longrightarrow C_6H_5(R)N - \dot{C}H - C_6H_5 + HCBr_3 . \qquad (17)$$

The α-radicals $R_2N-\dot{C}H-R$ exhibit powerful electron-donating properties and transfer an electron to the acceptor in dark reactions.[46,49] On this basis, one may postulate the occurrence of a chain process involving the formation of the coloured products CP^+Br^- [see Eqn. (9)]:

$$C_6H_5(R)N - \dot{C}H - C_6H_5 + CBr_4 \longrightarrow$$

$$\longrightarrow C_6H_5(R)N^+ = CH - C_6H_5 \ Br^- ...\dot{C}Br_3 \qquad (18)$$

and its subsequent accumulation via reactions (17) and (18). On heating, the product CP^+Br^- reacts with the amine and other components of the layer with formation of compounds of the type of triphenylmethane dyes.[19,50,51]

Molecular oxygen lowers the rate of autocatalytic accumulation of the coloured species $[Fe^{3+}Br_4]^-$ due to its consumption via the reaction

$$Fe^{3+} \xrightarrow{O_2} Fe_2O_3 + Fe(OH)_3 \ , \text{etc.}$$

It has been shown[40,41] that the autocatalytic amplification of the latent image occurs also at room temperature when the content of molecular oxygen has been reduced appreciably in the polymeric photosensitive layer by placing it between two protecting films of poly(vinyl alcohol) (PVA). It is known[52,53] that PVA prevents the penetration of O_2 from the atmosphere and also adsorbs the oxygen dissolved in the polymer layer. The autocatalytic formation of coloured products ceases completely when the upper protective PVA film is removed from the photosensitive layer. The high amplification coefficients (~10^4 in the absence of oxygen), characteristic of these compositions, are responsible for their maximum photosensitivity (~0.01 $lx^{-1}\ s^{-1}$) among non-silver photographic systems.

Exposure to laser radiation at 441 or 488 nm, acting in the region corresponding to absorption by the complex $(C_5H_5)_2Fe \cdot CBr_4$, and subsequent heating at 70–90 °C results in the formation of ester bonds in the copolymer of vinyl acetate and crotonic acid $[-CH_2-C(COOH)H-]_n-[-CH_2-C(OCOCH_3)H-]_m$ containing $(C_5H_5)_2Fe$ and CBr_4, which leads to an appreciable decrease in the solubility of the polymer composition in aqueous alkaline solution.[54] It has been shown[54,55] that the divalent iron formed via reactions (12) and (13) catalyses the processes:

$$Fe(II) + (-CH_2 - \underset{\underset{O-COCH_3}{|}}{CH}-) \longrightarrow -CH_2 - \underset{\underset{O^-...\dot{C}OCH_3}{|}}{CH} - + Fe(III) \xrightarrow{H_2O}$$

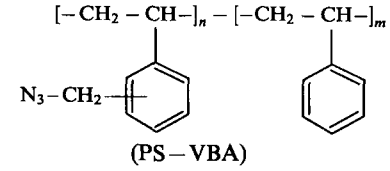
$$\longrightarrow -CH_2 - \underset{\underset{OH}{|}}{CH} - + CH_3COOH + Fe(II)$$

and further

$$-CH_2 - \underset{\underset{COOH}{|}}{CH}- + -CH_2-\underset{\underset{OH}{|}}{CH}- \longrightarrow \underset{\underset{HC-CO-O-CH}{|}}{H_2C} \qquad \underset{\underset{}{|}}{CH_2} + H_2O.$$

After the exposed film has been placed in a 2.5% aqueous solution of $(CH_3)_4NOH$ for 5 min, the non-exposed sections are fully dissolved, while the thickness of the sections which receives an exposure $H_g \geqslant 10$ mJ cm^{-2} (λ = 488 nm) remains unchanged.

Photoinitiated autocatalytic decomposition is characteristic also of aromatic azides, a very familiar class of photoresists. The branched chain decomposition has been investigated in relation to low-molecular-weight azides[8,56-59] as well as layers made up the styrene–vinylbenzyl azide (PS–VBA) copolymer:[60-62]



(PS–VBA)

The chain mechanism of the decomposition of phenyl azide in liquid media has been established:[8,56]

(a) chain initiation

$$C_6H_5-N_3 \xrightarrow{\lambda=254\ nm} C_6H_5-N: + N_2,$$

(b) chain propagation

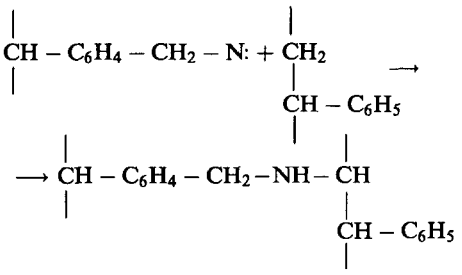
$$C_6H_5-N: + C_6H_5-N_3 \longrightarrow 2C_6H_5-N: + N_2,$$

(c) chain termination

$$C_6H_5-N: + C_6H_5-N_3 \longrightarrow C_6H_5-N=N-C_6H_5+N_2,$$

$$2C_6H_5-N: \longrightarrow C_6H_5-N=N-C_6H_5.$$

The initial quantum yield of $C_6H_5-N:$, measured either in diluted (to 10^{-4} M) solutions at room temperature or in organic glasses frozen at 77 K, is ~0.58. At high $C_6H_5-N_3$ concentrations (~0.08–0.72 M) at room temperature, the amplification coefficient reaches 10^3-10^4.[8] The efficiency of the chain decomposition of PS–VBA layers increases under the conditions of the photoexcitation of additional triplet energy donors (thioxanthone, anthracene, and their derivatives).[60,61] The azide-containing compositions are negative photoresists, their reduced solubility in organic media being caused by the cross-linking of the



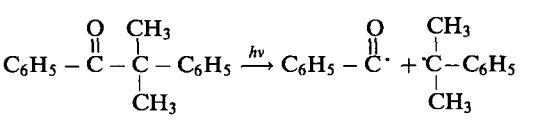
polymer chains with participation of the nitrene formed under the inluence of light:

In compositions comprising PS–VBA (m/n = 14.9%) and 2,4-diisopentylthioxanthone (sensitiser), the onset of gel formation corresponds to the exposure H_g = 45 mJ cm^{-2}.[62]

3. Photochemically induced cross-linking of polyfunctional acrylates

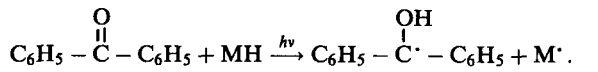
In recent years, much attention has been devoted to the photoinitiated cross-linking of polyfunctional oligomeric acrylates (compounds containing two and more $-O-CO-CH=CH_2$ groups). Studies on this subject have been recently discussed in detail in review publications[63–66] and only compositions proposed as highly sensitive photoresists for use in micro-electronics, in the manufacture and copying of compact discs,[9,67–69] and also in the manufacture of microencapsulated photographic material[70] will therefore be considered below.

Diacrylates of aliphatic polyurethanes, the diacrylates of polyepoxybisphenol A, and the triacrylate of trimethylpropane [trimethylpropanetriol?] have been used as polyfunctional acrylates. The photoinitiators (I) were ketones of different structure: dimethylphenylacetophenone, isobutyl ether of benzoin or benzophenone, phenanthrenequinone, etc. Depending on the structure of the initiator, either direct photodissociation



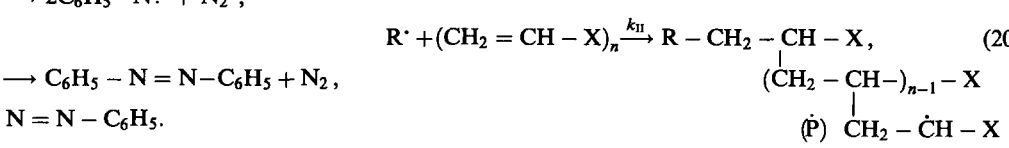
(19)

or (in the presence of added MH) a photoredox process with the transfer of an electron and a proton)



(19a)

Free radicals formed in sections (19) and (19a) give rise to polymerisation



(20)

and chain termination

$$P^{\cdot} + P^{\cdot} \xrightarrow{k_0} 2P, \quad (21)$$

$$P^{\cdot} + R^{\cdot} \longrightarrow PR. \quad (21a)$$

The influence of hyperfine interaction on the rate of recombination of radicals in the pair formed via reactions (19) and (19a) was discussed above (see sub-section II.2).

The quantum yield of radicals formed by reactions (19) and (19a) is ~0.1 both in dilute liquid solutions and in viscous media.[67] The chain termination corresponds to the second-order reaction (21) in the polymerisation of monofunctional acrylates in any condensed media. The chain termination in the polymerisation of monomers in microcapsules has been shown to be a first-order process,[70] where the consumption of radicals mainly as a result of their preferential reaction with the walls of the capsule predominates. The first-order process of destruction of the radical $\dot{P}$ has also been observed on exposure to intense pulsed laser radiation.[9] On the basis of the analysis of the kinetics of photopolymerisation with the use of photoinitiators of different kinds, it has been suggested[77] that, in the photoredox reaction (19a), the radicals formed serve simultaneously as initiators and inhibitors of polymerisation and are responsible for the first order of the consumption of $\dot{P}$ via reaction (21a).

The polymerisation of a polyfunctional molecule involves simultaneously several groups and the polymer network is formed already in the early stages of the reactions. The mutual approach of the radicals grafted to the network is sterically hindered. In the case of the diacrylate of polyepoxybisphenol A, the kinetic chain of reaction (20) included 10^4-10^5 links,[9,69] which is the reason for the high photosensitivity of the system[9] corresponding to $H_g \simeq 3$ mJ cm^{-2}. Molecular oxygen greatly reduces the rate of polymerisation and the length of the kinetic chain when low-intensity light sources are used.[69]

4. Chemical amplification of the latent image

Nowadays much attention is devoted to photoresists whose action is based on the photochemical formation of acids and subsequent occurrence of chain processes (chemical amplification) involving the polymerisation of vinyl monomers or epoxides,[6,7,72–74] cationic polycondensation and cross-linking of polymer chains (for example novolac resin and hexamethoxymethylenemelamine),[75,76] and cationic depolymerisation [degradation of poly(phthalic aldehyde) to gaseous products].[77–79] The creation of photoresists based on polymers with protecting groups, which are abstracted by a photochemically generated acid, thus altering the polarity and hence the solubility of the polymers, has found wide application.[80–84] Specific photoresist systems of this type have been discussed in detail in recent years in the review literature[6,7,55] and only fundamental questions referring to chemical amplification will therefore be considered below.

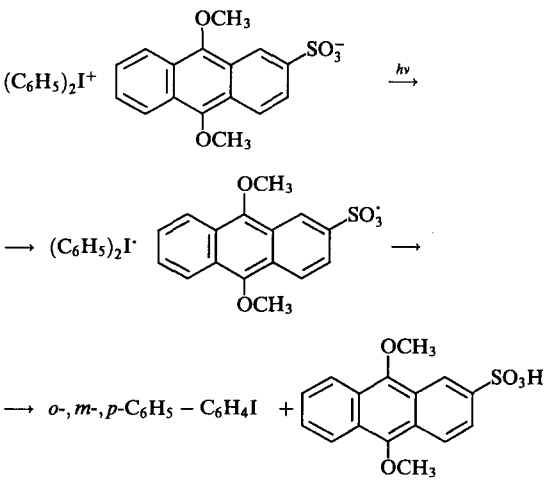
As stated above (see sub-section II.2), acids are generated photochemically from onium salts via reaction (10). Iodonium

Table 4. The free energies $^{S}\Delta G$ and $^{T}\Delta G$ of electron transfer from singlet-excited and triplet-excited dye respectively to the onium salt.

Dye	$\Delta G(22)$	ΔG/eV			
		$C_6H_5N_2^+$ BF_4^- [0.3 V][a]	$(C_6H_5)_2I^+$ BF_4^- [−0.16 V][a]	$(C_6H_5)_3S^+$ BF_4^- [−1.06 V][a]	$Bz(C_6H_5)_3P^+$ BF_4^- [−1.83 V][a]
Xanthone					
$E_{1/2}(Ox) = 1.41$ V					
$^1E_{00} = 3.41$ eV	$^{S}\Delta G$	−1.91	−1.45	−0.55	0.22
$^3E_{00} = 3.2$ eV	$^{T}\Delta G$	−1.7	−1.24	−0.35	0.43
Thioxanthone					
$E_{1/2}(Ox) = 1.67$ V					
$^1E_{00} = 3.14$ eV	$^{S}\Delta G$	−1.77	−1.31	−0.41	0.36
$^3E_{00} = 2.8$ eV	$^{T}\Delta G$	−1.43	−0.97	−0.07	0.7
Acridone					
$E_{1/2}(Ox) = 1.5$ V					
$^1E_{00} = 2.5$ eV	$^{S}\Delta G$	−1.75	−1.29	−0.39	0.38
$^3E_{00} = 2.6$ eV	$^{T}\Delta G$	−1.4	−0.94	−0.04	0.73
10-Methylacridone					
$E_{1/2}(Ox) = 1.46$ V					
$^1E_{00} = 2.92$ eV	$^{S}\Delta G$	−1.76	−1.3	−0.4	0.37
$^3E_{00} = 2.6$ eV	$^{T}\Delta G$	−1.44	−0.98	−0.08	0.69

[a] Equilibrium potentials of the reduction the ionium salts are shown in brackets.

salts have been synthesised in which the photosensitivity is due to the optical absorption of the counteranion.[85] The acid is formed as a result of the electron phototransfer via the reaction



The decomposition of ionium salts under the conditions of the photoexcitation of organic sensitisers (dyes or aromatic hydrocarbons ArH) has been investigated in detail.[86–90] Electron transfer takes place via a stage involving the formation of an exciplex, for example, we have for a diphenyliodonium salt

$$\mathrm{ArH} \xrightarrow{h\nu} {}^{1,3}(\mathrm{ArH})_1 \xrightarrow{(C_6H_5)_2I^+X^-} {}^{1,3}(\mathrm{ArH})_1\cdot(C_6H_5)_2I^+X^- \longrightarrow$$

$$\longrightarrow {}^{1,3}[\mathrm{ArH}^{\cdot+}\ldots(C_6H_5)_2I^{\cdot}\,X^-] \longrightarrow$$

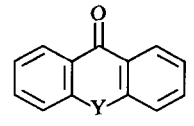
$$\longrightarrow \mathrm{Ar}-C_6H_5 + C_6H_5I + \mathrm{HX}. \qquad (22)$$

It has been established experimentally that for onium salts the reaction proceeds effectively only when the free energy change on electron transfer is $\Delta G(22) \leqslant -0.43$ eV:[86–89]

$$\Delta G(22) = e\left[E_{1/2}\left(\frac{^{1,3}(\mathrm{ArH})_1}{\mathrm{ArH}^{\cdot+}}\right) - E_{1/2}\left(\frac{\mathrm{On}^{\cdot}\mathrm{X}^-}{\mathrm{On}^+\mathrm{X}^-}\right)\right]\mathrm{eV}\ ,$$

where $E_{1/2}[^{1,3}(\mathrm{ArH})_1/\mathrm{ArH}^{\cdot+}] = E_{1/2}(\mathrm{ArH}/\mathrm{ArH}^{\cdot+}) - {}^{1,3}E_{00}$ and $E_{1/2}(\mathrm{ArH}/\mathrm{ArH}^{\cdot+})$ are equilibrium potentials of the oxidation of the sensitiser in the excited singlet and triplet ground states respectively [via the reactions $^{1,3}(\mathrm{ArH})_1 \rightleftarrows \mathrm{ArH}^{\cdot+} + e$ and $\mathrm{ArH} \rightleftarrows \mathrm{ArH}^{\cdot+} + e$], $^{1,3}E_{00}$ is the distance from the ground to the reactive singlet or triplet level of the sensitiser, and $E_{1/2}(\mathrm{On}^{\cdot}\mathrm{X}^-/\mathrm{On}^+\mathrm{X}^-)$ are the equilibrium potentials of the reduction of the onium salts by the reaction $\mathrm{On}^{\cdot}\mathrm{X}^- = \mathrm{On}^+\mathrm{X}^- + e$ (listed in brackets in Table 4).

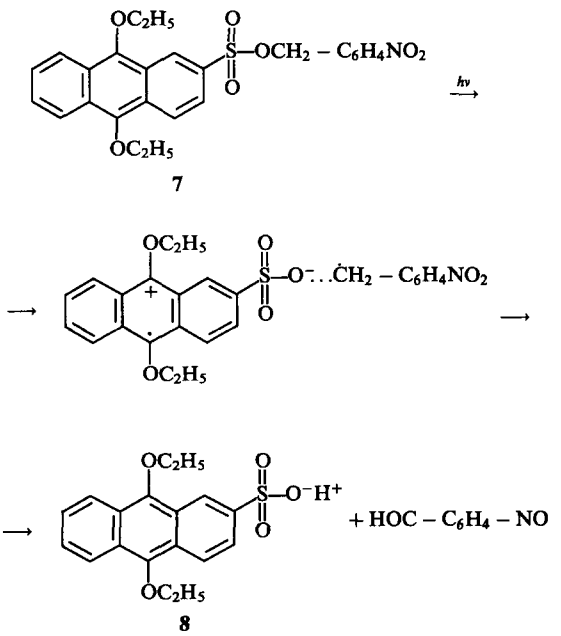
Table 4 also includes the values of ΔG_{22} ($^{S}\Delta G$ and $^{T}\Delta G$, the free energies of electron transfer to the onium salt from the acridine dye in the excited singlet and triplet states respectively).[87,89]



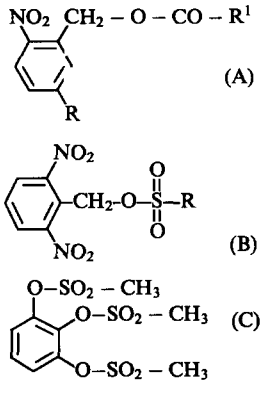
Y = O	xanthone
S	thioxanthone
NH	acridone
NCH_3	10-methylacridone

It follows from the tabulated data that the diazonium and iodonium salts can be sensitised by any of the dyes considered in the excited singlet or triplet state. The effective electron phototransfer to the sulphonium salt is possible only from the singlet-excited xanthone. As a rule, the sensitisers used for sulphonium salts are aromatic hydrocarbons, for example, perylene (Pe),[87,91] the equilibrium oxidation potential of which in the excited singlet state is $E_{1/2}(^1\mathrm{Pe}_1/\mathrm{Pe}^{\cdot+}) = -1.86$ V, since $E_{1/2}(^1\mathrm{Pe}_1/\mathrm{Pe}^{\cdot+}) = 1$ V and $^1E_{00} = 2.86$ eV. Owing to the high reduction potentials, it has not been possible to sensitise phosphonium and ammonium salts.

Special interest attaches to organic acid-forming compounds such as *p*-nitrobenzyl 9,10-diethoxyanthracene-2-sulphonate **7**,[91–93] in which dissociative intramolecular electron transfer takes place under the influence of light (250–300 nm) with the subsequent formation of the strong 9,10-diethoxyanthracene-2-sulphonic acid **8**:



Esters having the structures (A),[94] (B),[80,84,95] and (C),[81,96] also belong to the acid-forming class:



where R = H, NO_2; $R^1 = CH_3$, C_2H_5;

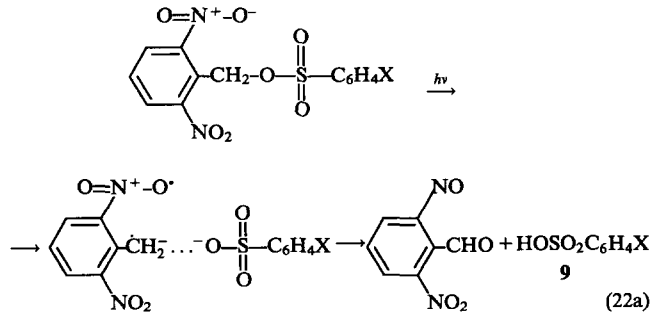
(A)

where R = CH_3, *p*-C_6H_4–CH_3, C_6H_5, *p*-C_6H_4–NO_2 etc.

(B)

(C)

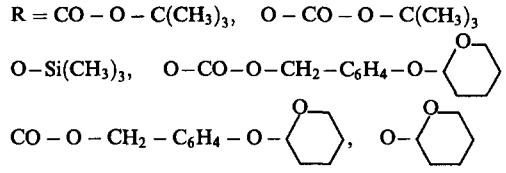
Acids are formed from these esters as a result of the dissociative intramolecular electron phototransfer, for example by the reaction



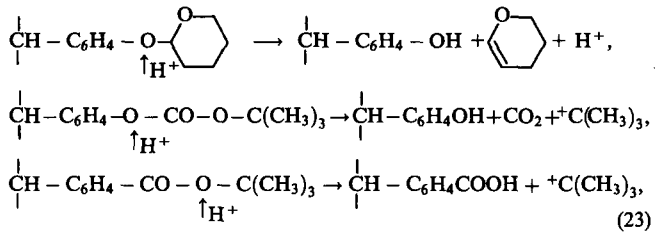
(22a)

The quantum yield of the acid **9** diminishes when the electron-donating substituent X is replaced by an electron-accepting one and its values are 0.16 (X = CH_3), 0.14 (X = H), and 0.1 (X = NO_2).

Photochemically generated acids deblock polymers which contain protecting groups[6,7,82,84,91,96,97] such as $-C(p\text{-}C_6H_4R)H-CH_2-$, $-C(p\text{-}C_6H_4R)(CH_3)-CH_2-$, and $-C(p\text{-}C_6H_4R)H-CH_2-)_2-SO_2-$, where



i.e. they transform them in accordance with the schemes presented below[6,82,93,96,97] into polymers which readily dissolve in 1–2% aqueous solution of $(CH_3)_4NOH$:



(23)

$$^{+}C(CH_3)_3 \rightarrow CH_2=C(CH_3)_2 + H^{+},$$

$$^{+}C(CH_3)_3 + {}^{-}O-SO_2-C_6H_4X \rightarrow (CH_3)_3C-O-SO_2-C_6H_4X.$$

It has been shown[93] that the probability of chain termination decreases when the electron-donating groups X in the acid **9** are replaced by electron-accepting groups which withdraw the negative charge from the oxygen atom in the direction of the phenyl fragment. As a result, following the replacement of CH_3 by NO_2, the chain length, i.e. the chemical amplification coefficient (holding at 120 °C for 4 min), increases from 200 to 800.

Processes based on the inhibition of the dissolution of the novolak resin $[-C_6H_2(OH)(CH_3)-CH_2-]_n$ following the addition to the solvent of compounds with protecting groups have been widely investigated in recent years.[7] As an example, one may quote the composition of the novolak resin, the acid-forming ester, and an inhibitor—bisphenol A with *tert*-butoxycarbonyl groups.[81] As a result of the formation of acids on photoexcitation of the acid-forming ester, the inhibitor is transformed into bisphenol A via the reaction

$$(CH_3)_3COC(O)OC_6H_4C(CH_3)_2C_6H_4OC(O)OC(CH_3)_3 \xrightarrow{2H^+}$$
$$\longrightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + 2CO_2 + 2CH_2=C(CH_3)_2.$$

It has been shown[81] that the initial quantum yield of the acid is 0.205 and the kinetic length of this chain, i.e. the amplification coefficient, is 76–123.

The working exposures in photoresists with chemical amplification are in the range H = 2–10 mJ cm^{-2}.

5. Chemical sensitisation of photosensitive systems

Chemical sensitisation is understood as the increase in the effectiveness of the chemical amplification by the introduction of an additional compound—a chemical sensitiser.

The mechanisms of the chemical sensitisation have been examined[55,98–100] as a function of the nature of the donor in photoresists based on charge-transfer complexes. Systems consisting of a poly(vinyl ethylal) matrix containing DTBS as the acceptor and tertiary amines—diphenylbenzylamine and triphenylamine (TPA)—as the donor have been investigated.

Dimethylaminobenzaldehyde (DMABA) was used as the chemical sensitiser. Under the influence of light at the wavelength corresponding to absorption by the complex Am · DTBMS, the latter dissociates into radical-ions with subsequent formation of coloured products and an acid, for example:

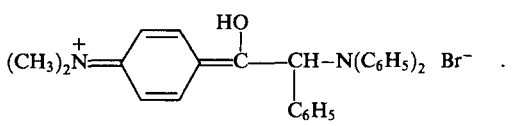
$$\text{DPBA}\cdot\text{DTBMS} \xrightarrow{h\nu} \text{DPBA}^{\cdot+} + \text{Br}^- \ldots \text{R}^\cdot \text{ (or } \text{R}^- \ldots \text{Br}^\cdot) \longrightarrow$$

$$\longrightarrow \text{CP}^+\text{Br}^- + \text{HR} \text{ (or } \text{CP}^+\text{R}^- + \text{HBr}) , \quad (24)$$

$$\text{DPBA}^{\cdot+} = (\text{C}_6\text{H}_5)_2\text{N}^{\cdot+} - \text{CH}_2 - \text{C}_6\text{H}_5,$$

$$\text{R}^\cdot = [\text{CBr}_2 - \text{SO}_2 - \text{CBr}_3]^\cdot .$$

The structures of CP^+Br^- and HR are given in Scheme (9). The quantum yield of CP^+Br^- and hence of the acids HR and HBr is ~0.05. The coloured product reacts with DMABA and forms a compound whose absorption has a maximum at 450 nm:[99,100]



(CP'^+Br^-)

It has been established[98–100] that the main chemical sensitisation reaction involves the protonation of DMABA by the acids HR and HBr, formed by the photochemical reaction (24), and the conversion of part of the keto-form $(CH_3)_2N^+H-C_6H_4-CHO\ R^-$ (and Br^-) into the enolic tautomer $(CH_3)_2N^+=C_6H_4=CHOH\ R^-$, the low oxidation potential of which $E_{1/2}$ = 0.49 V (s.c.e.) is responsible for the thermal electron transfer to DTBMS:

$$(\text{CH}_3)_2\text{N} - \text{C}_6\text{H}_4 - \text{CHO} \xrightarrow{\text{HR}} (\text{CH}_3)_2\text{N}^+\text{H} - \text{C}_6\text{H}_4 - \text{CHO} \rightleftarrows$$

$$\rightleftarrows (\text{CH}_3)_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{CH(OH)R}^- \xrightarrow{\text{DTBMS}}$$

$$\longrightarrow (\text{CH}_3)_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{C}^\cdot\text{OH} \ldots \text{Br}^- \ldots \text{R}^\cdot + \text{HR} . \quad (25)$$

$$(\text{DMABA}^+)$$

As shown in Scheme (25), the electron transfer from the enolic tautomer is followed by the abstraction of a proton, which leads to the formation of the radical-cation $DMABA^{\cdot+}$, the equilibrium reduction potential of which (via the reaction $DMABA \rightleftarrows DMABA^{\cdot-} + e$) is 1.1 (s.c.e.).[101] The mechanisms of the subsequent reactions depend on the ionisation potential of the tertiary amine.

In the case of compositions containing donors with high ionisation potentials $I_D \geqslant 7.3$ eV, such as DPBA (I_D = 7.5 eV) and DMABA itself (I_D = 7.36 eV),[102] new coloured products are formed via the reactions[99]

$$\text{DMABA}^{\cdot+} + \text{Br}^- \ldots \text{R}^\cdot \longrightarrow$$

$$\xrightarrow[-\text{HR}]{\text{DPBA}} (\text{CH}_3)_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{C(OH)HC}(\text{C}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)_2\text{Br}^- \quad (\text{CP}'^+\text{Br}^-)$$

$$\xrightarrow[-\text{HR}]{\text{DMABA}} (\text{CH}_3)_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{C(OH)C(O)C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{Br}^- \quad (\lambda_{max} = 430 \text{ nm})$$

$$\xrightarrow[-\text{HR}]{} (\text{CH}_3)_2\text{N}^+ = \text{C}_6\text{H}_4 = \text{C} = \text{O}\ \text{Br}^- \quad (26)$$

The acid HR (or HBr) formed in addition enters into reaction (25) and ensures the further occurrence of reaction (26). The chemical amplification coefficient in the formation of the product CP'^+Br^- and hence of the acid HR via the upper pathway of reaction (26) is $\eta_{ef}/\eta_0 \simeq 50$.

In layers containing donors with low ionisation potentials, for example TPA (I_D = 6.8 eV),[102] the nature of the coloured product does not change during the chemical amplification process. In contrast to DPBA, a cyclic process takes place in these layers, where the photochemical formation of the acid, i.e.

$$\text{TPA}\cdot\text{DTBMS} \xrightarrow{h\nu} \text{TPA}^{\cdot-} \ldots \text{Br}^- \ldots \text{R}^\cdot$$

$$\text{TPA}^{\cdot+} \ldots \text{Br}^- \ldots \text{R}^\cdot \longrightarrow \begin{cases} \longrightarrow \text{BPDPA} + \text{HR}^\cdot \\ \longrightarrow \text{CP}''^+\text{Br}^- + \text{HR} \end{cases} \quad (27)$$

[BPDPA = 4-bromophenyl(diphenyl)amine] is followed by reaction (25) and charge transfer:

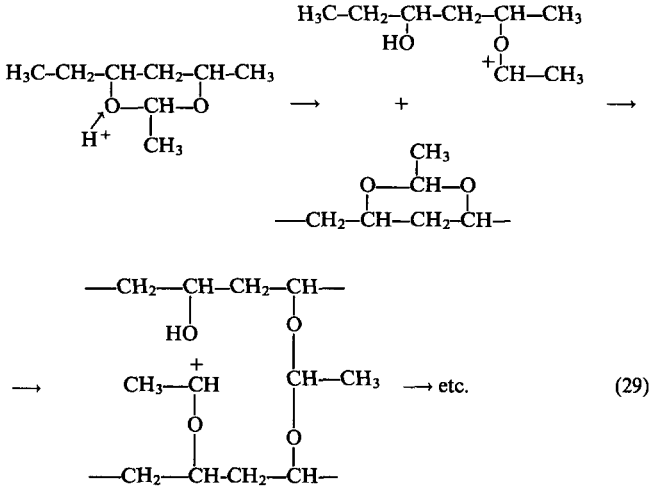
$$\text{TPA} \xrightarrow{\text{DMABA}^+ \ldots \text{Br}^- \ldots \text{R}^\cdot} \text{TPA}^+ \ldots \text{Br}^- \ldots \text{R}^\cdot + \text{DMABA} . \quad (28)$$

where CP''^+Br^- is the coloured product obtained from TPA (with λ_{max} = 610 nm).

The formation of BPDPA as a result of the reaction between $TPA^{\cdot+}$ and Br^- in the presence of the anthracene radical has been established.[103] Reaction (27) is then repeated. The chemical amplification coefficient, determined from the product CP''^+Br^-, reaches ~600.

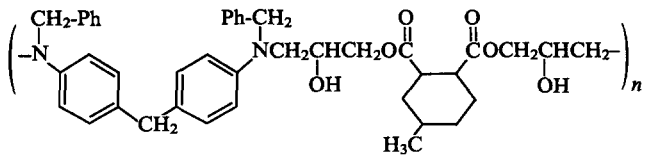
The acid ensures the effective cross-linking of the PVE chains by the reaction[55,97,99]

and a decrease in the solubility of the exposed section of the layer in the developer—a mixture of water and alcohol.



It is seen from the schemes presented above that, under the conditions of the chemical sensitisation of compositions based on tertiary aromatic amines, the photochemical formation of coloured products and the acids HR and HBr [reactions (24) and (27)] is followed by the thermal stages (25), (26), and (28) involving the additional formation of coloured products and the acids HR and HBr, in contrast to the systems based on onium salts and other compounds in which the acid is formed only under the influence of light [see reaction (23)].

Polymers containing electron-donating groups in the main chain, for example polyhydroxyaminoester (PHAE)[104]

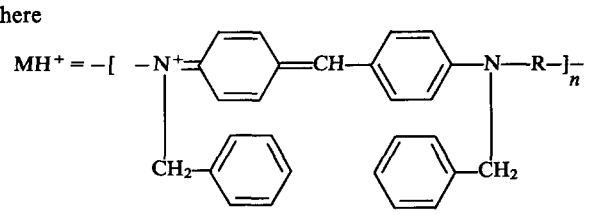


are especially interesting. Polymers of this type are photosemiconductors[105] and, after the addition of halogen-containing acceptors (for example DTBMS) acquire the properties of photoresists. In principle, this makes it possible to use photolithography for the manufacture of microcircuits based on organic photosemiconductors. The photosensitivity is due to the formation of a charge-transfer complex between the donor fragment of the macromolecule and the acceptor. The complex has its intrinsic optical absorption in the visible region (300–550 nm) and its ionic photodissociation leads to the formation of coloured polycationic products of the type of Michler's hydrol (MH^+) (λ_{max} = 630 nm) and the acids HR:

$$PHAE \cdot DTBMS \xrightarrow{h\nu} PHAE^{\cdot+} \ldots Br^- \ldots R^{\cdot} \longrightarrow$$

$$\longrightarrow MH^+Br^- + HR \ , \qquad (30)$$

where



The polyhydroxyaminoester has a low ionisaion potential ($I_D \simeq 7.0$ eV). The addition of DMABA to the layer does not alter the nature of the coloured product but increases its quantum yield from $\eta_0 = 0.12$ to 1.2.[106] Thus, as in the case of TPA, in layers based on PHAE the photochemical formation of the acid via reaction (30) is followed by a cyclic process involving reaction (25), charge transfer with formation of $PHAE^{\cdot+}...Br^-...R^{\cdot}$ [a reaction of type (28)], and the repetition of the thermal stage of reaction (30). The different solubilities of the polycationic products and of the initial PHAE in polar and non-polar solvents are used in development.

In contrast to tertiary amines and PHAE, in compositions containing the secondary amine DPA as the donor, the Mannich reaction between $(CH_3)_2N^+H-C_6H_4-CHO$ and DPA takes place effectively in the presence of DMABA without the participation of DTBMS and with retention of the concentration of the acid formed on photolysis. The quantum yield of the triphenylmethane dye is 0.07 in the primary photochemical reaction. The ratio $\eta_{ef}/\eta_0 \simeq 35$ and 54 after the films have been maintained at 22 °C and 70 °C respectively.[99] The preferential occurrence of the Mannich reaction restricts the involvement of the acid in the cross-linking of the polymer chains via reaction (29).

6. Optical amplification of the latent image

Processes leading to the optical amplification of the latent image in non-silver photographic layers have been frequently discussed in the review literature.[5,20,43,107–110] Optical amplification (autosensitisation) was first established by Fotland.[107] In this process, the entire film carrying the latent image is acted upon by light in the spectral range where only the coloured products of the photochemical reaction [the auto-sensitiser, for example the product CP^+ formed by reactions (9) and (24)] absorbs, while the remaining components of the layer do not. In polymer systems containing donors such as the leuco-form of the triphenylmethane dye (LTD),[107] styryl derivatives,[108] heterocyclic aromatic compounds,[109] and the CBr_4 acceptor, the photoexcited coloured product transmits the energy absorbed to the complex via a triplet–triplet mechanism, ensuring the additional formation of the coloured product via a reaction of type (24). It has been demonstrated for $LTD \cdot CBr_4$ that such transfer is possible by virtue of the low position of the triplet level of the complex.[107] In this complex, the triplet level ($E_T \simeq 1.8$ eV) lies appreciably below the excited singlet level ($E_S \simeq 3.2$ eV) and is close to the triplet level formed as a result of the action of light on the triphenylmethane dye (E_T = 1.7 eV).[107]

In compositions containing benzylanilines (DPBA and DBA) as donors and CBr_4 or DTBMS as acceptors, optical amplification occurs as a result of the transfer of triplet energy to the complex from the two-quantum-excited (with light at $\lambda \geqslant 650$ nm) coloured product CP^+. The subsequent ionic dissociation of the excited triplet complex via reaction (24) is responsible for the additional formation of CP^+ on the exposed sections.[5,110,111] This two-quantum process requires the use of powerful light sources. It has been established[19,97,112] that, when a pyrylium dye (Table 1, 2,2′,6,6′-tetraphenylpyrylomethinecyanine perchlorate) is introduced into the system consisting of PVE, DPBA, and DTBMS, the optical amplification changes from a two-quantum process to a low-energy one-quantum process. It has been shown that the above dye does not quench the fluorescence of the CP^+ but it does quench its phosphorescence. The unfavourable relative positions of the oxidation-reduction potentials of the reacting components are responsible for the low probability of quenching via electron transfer.[19] The coincidence of the upper limit of the spectral range corresponding to the emission of the triplet energy of CP^+ (1.77–1.41 eV) with the position of the triplet level of the pyrylium dye (1.77 eV) ensures that the autosensitisation reaction takes place via the triplet energy transfer mechanism:

$$CP^+ \xrightarrow{h\nu,\ S-T} {}^3(CP^+)_1 + Dy \longrightarrow CP^+ + {}^3(Dy)_1. \qquad (31)$$

Next $^3(Dy)_1$ induces the additional formation of CP^+ via reaction (9), as in the direct photoexcitation. Thus the pyrylium dye fulfills two functions in the photosensitive composition: it is a

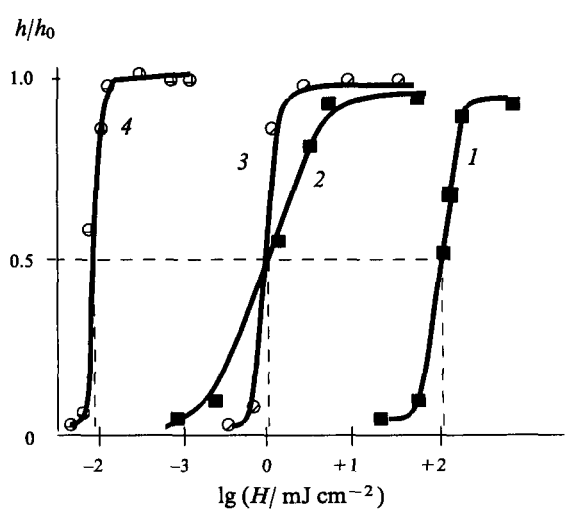


Fig.1 Dependence of the relative height of the relief h/h_0 on the exposure at λ = 576 ± 5 nm: (*1*) and (*3*) without amplification; (*2*) and (*4*) with optical amplification, the energy of the amplifying light being 0.1 J cm^{-2} (λ = 690–720 nm). h is the thickness of the layer retained on the exposed sections after the complete removal of the unexposed sections by dissolution in a mixture of water and alcohol; h_0 is the thickness of the initial layers. Concentrations employed (mol dm^{-3}): [DPA] = [DTBMS] = 0.8; [DMABA] = 0 (curves *1* and *2*) and 0.8 (curves *3* and *4*). The optical density of the dye at λ_{max} is 0.08. After exposure and optical amplification, the layers were maintained for 2.5 min at 100 °C.

Table 5. The photolithographic sensitivities ($H_{0.5}$ and H_{20}) and the photosensitivities ($S_{0.2}$) of layers comprising PHAE and DTBMS.

Optical amplification	$H_{0.5}$/ mJ cm^{-2}	H_{20}/mJ cm^{-2}	$S_{0.2}$/cm^2 J^{-1}
	Layer without DMABA		
Absent	180	180	16.3
Present	–	–	270
	DMABA introduced into layer		
Absent	28	12	163
Present	~0.4	~0.2	2.5×10^4

spectral sensitiser (S^+) in reaction (9) and ensures the formation of CP^+ on photoexcitation with a quantum yield $\eta_0 = 0.12$ (Table 1). Furthermore, it alters the mechanism of the optical amplification of the latent image by entering into reaction (31).

The transformation of the two-quantum process into a one-quantum process in these compositions is also achieved by adding indole. On interaction with the intermediate products of the photochemical reaction (24), the latter forms a new indole-containing coloured compound (ICC, λ_{max} = 550 nm, long-wavelength limit 700 nm), which is an autosensitiser of the oxidation–reduction type and ensures (in the photoexcited state) the occurrence of the one-quantum reaction (9) (in this case S^+ = ICC).[18] It is noteworthy that in compositions based on the DPA donor and the DTBS or CBr_4 acceptor the primary coloured product (λ_{max} = 665 nm) formed on photoexcitation is not an autosensitiser and the optical amplification becomes possible solely by virtue of the addition of indole.[18]

In photoresist systems, optical amplification has been achieved in layers based on charge-transfer complexes between the DPBA or PHAE donor and the DTBMS acceptor.[55,98,99,106] Fig. 1 illustrates the characteristic curves for the photoresists consisting of PVE, DPBA, DTBMS, and the dye 2,2',6,6'-tetraphenylpyrylomethinecyanine perchlorate (Table 1) in the absence or presence of DMABA on photoexcitation of the dye by light at a wavelength of ~576 nm. Fig. 1 shows that, in the absence of DMABA, the exposure giving the relative height of the relief is $h/h_0 = 0.5$, $H_{0.5}$ = 100 mJ cm^{-2}. Optical amplification makes it possible to increase $H_{0.5}$ to ~1 mJ cm^{-2}. Fig. 1 shows that this value of $H_{0.5}$ can be obtained also without optical amplification as a result of the addition of DMABA to the layer. Evidently, under the conditions of chemical and optical amplification of the latent image, a working exposure $H_{0.5}$ = 0.01 mJ cm^{-2} is attained.[98,99] Such low working exposures (high sensitivities) had not been obtained previously.

In layers based on PHAE, Michler's hydrol [formed via reaction (30) on exposure] is an autosensitiser of the oxidation–reduction type and ensures the optical amplification of the latent image [via a reaction of type (9), where $S^+ = MH^+$] on illumination of the entire layer with red light, which acts solely on MH^+, since the remaining components do not absorb in this region. The quantum yield of the additionally formed MH^+ under the conditions of its intrinsic photoexcitation is 0.9×10^{-2} and 0.24 in the absence and with addition of DMABA respectively. Analysis led to the conclusion[106] that in the presence of DMABA optical amplification proceeds in accordance with the mechanism

$$MH^+ \xrightarrow{h\nu,\ S-T} {}^3(MH^+)_1 + DMABA \longrightarrow MH^\cdot + DMABA^{\cdot+},$$

$$MH^\cdot + DTBMS \longrightarrow MH^+ + Br^- \ldots R^\cdot \ (\text{or } R^- \ldots Br^\cdot),$$

which is followed by the charge-transfer process

$$DMABA^{\cdot+} + PHAE \longrightarrow DMABA + PHAE^{\cdot+}$$

and the additional formation of MH^+ as a result of the occurrence of the thermal stages of reaction (30).

Table 5 presents the principal characteristics of the layers based on PHAE and DTBMS, namely $H_{0.5}$ and H_{20}, where H_{20} is the exposure for which the selectivity of the development is $U = t_e/t_u = 20$, where t_e and t_u are the times required for the dissolution of the exposed and unexposed sections, as well as $S_{0.2} = 1/H_{0.2}$, where $H_{0.2}$ is the exposure for which the optical density at the MH^+ absorption maximum (at 630 nm) reaches 0.2. Table 5 shows that the use of chemical and optical amplification of the latent image makes it possible to increase by approximately three orders of magnitude the photosensitivity of the recording layers based on polyhydroxyaminoesters and to obtain $H_{0.5} \simeq 0.4$ and $H_{20} \simeq 0.2$ mJ cm^{-2}, and $S_{0.2} = 2.5 \times \times 10^4$ cm^2 J^{-1}.

IV. Photochemical etching of bismuth films

The processes amplifying the primary effects of light in recording layers and in the photoresists examined above are universal and can be used for the sharp increase of the efficiency of any photochemical processes occurring in polymer systems. As an example, the non-resist photoetching of metallic films with the aid of polymer layers is examined below.

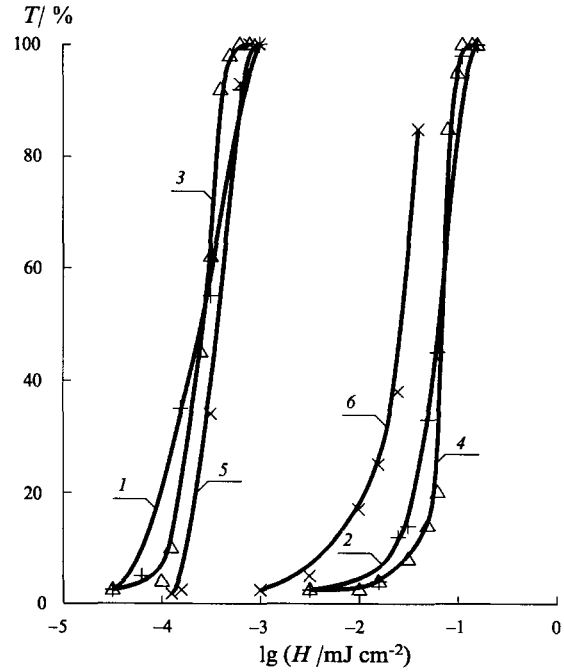


Fig. 2. Dependence of the transmittance of light (T) by a Bi film on the exposure: (*1*), (*3*), (*5*), and (*6*) with optical amplification; (*2*) and (*4*) without amplification; energy of amplifying light 0.06 J cm^{-2}; λ = 650–700 nm. Exposure: λ = 436 nm (curves *1*–*5*) and 633 nm (curve *6*). Composition of the photosensitive layer:
(*1*) and (*2*) PVC–DPA–indole–DTBMS;
(*3*) and (*4*) PVC–DPBA–indole–DTBMS;
(*5*) and (*6*) PVC–DBA–indole–DTBMS.

A new highly sensitive non-resist process for the photoetching of metallic bismuth films has been developed on the basis of polymer compositions incorporating DPBA, DPA, or DBA donors, the DTBMS acceptor, and indole.[113,114] The photosensitive polymer composition was deposited on a bismuth film (film thickness 0.2 μm) sputtered onto a support. It was established that metallic bismuth dissolves in the exposed sections of the polymer layer as a result of a two-stage reaction. In the first stage, bismuth reacts with the radical product Br$^{\cdot}$ (or R$^{\cdot}$) formed on illumination by reaction (24):

$$Bi \xrightarrow{Br^{\cdot}(R^{\cdot})} BiBr_{3-n}R_n ,$$

where $n = 0, 1, 2, 3$. In the second stage, after prolonged storage or on heating to 80–105 °C, the compound $BiBr_{3-n}R_n$ dissolves in the polymer composition as a result of the reaction with the photochemically generated acid HR(HBr). The degree of photoetching was inferred from the transmittance (T) in the range 750–800 nm, where only the metallic film absorbs and the polymer layer does not, or from the transmittance in the range 560–600 nm after the removal of the entire polymer layer by dissolution, for example, in acetone. Fig. 2 illustrates the dependence of the transmittance by the bismuth film on the exposure obtained under conditions with optical amplification of the latent image and without such intensification. Evidently the increase in transmittance from 1.56 to 50% under the influence of light at $\lambda = 436$ nm is attained for exposures $H_{50} \simeq 0.07$ J cm^{-2} in the absence of amplification, but the etching process is characterised by a high photosensitivity: $H_{50} \simeq 3 \times 10^{-4}$ J cm^{-2} for optical amplification of the latent image. For exposure in the region of the long-wavelength absorption limit of the complex DBA · DTBMS at $\lambda = 633$ nm, the photosensitivity is $H_{50} \simeq 2 \times 10^{-2}$ J cm^{-2}, as shown in Fig. 2.

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Thus, a common feature of all the methods of amplifying the primary effects of light is the formation of photoproducts whose physicochemical properties differ significantly from those of the initial components and the accumulation of these photoproducts as a result of the subsequent occurrence of autocatalytic reactions with their participation, the selective action of light on them, etc.

A distinctive property of the systems considered is the fact that only components present in polymer layers participate in the amplification process and there is therefore no need for their additional treatment in liquid or gaseous media.

The fields where these systems are used, determined by the characteristic features of their functioning, are, in particular, the highly sensitive optical recording of information, the detection of weak optical signals, the photomodification of spectroscopic and physicochemical properties of polymer layers, and the selective photosynthesis of a number of chemical compounds in polymer matrices.

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