

PHOTOCHEMICAL IMAGING PROCESSES FOR THE FORMATION OF METALLIC PATTERNS ON POLYMERS[†]

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Summary

A homogeneous polymer for photometallization containing anthraquinonyl (AQ) and hydroxyalkyl groups was studied, where some of the hydroxyalkyl groups are complexed with copper carboxylate. On irradiation AQ is excited to an $n \rightarrow \pi^*$ type of triplet state and subsequently reacts with a hydroxyalkyl group to form the semiquinone radical and the hydroxyalkyl radical. Almost all semiquinone radicals disproportionate to AQ and AQH₂. Copper ions are reduced to catalytic nuclei by AQH₂ as well as by hydroxyalkyl radicals. Hydroxyalkyl radicals that are not consumed for reduction recombine to form a cross-linked polymer.

1. Introduction

Today, imaging processes are a most important area in industrial photochemistry [1]. It is no exaggeration to state that microelectronics (the third technological revolution) would not have been possible without the progress in photochemistry. Photochemical imaging processes with photopolymers are the basis of the mass production of electronic components. In this paper a special field of imaging science, the creation of metallic patterns, is discussed.

Print and etch processes are still the standard procedure for producing metallic patterns (Fig. 1(a)). The base material, a copper foil laminated on an insulator, is coated with a photoresist layer and exposed through a negative. The exposed parts of the photoresist are rendered insoluble by photo-cross-linking reactions and remain after development in a suitable solvent. The uncovered copper parts are etched, the resist is removed and a conducting pattern similar to a printed circuit board results.

In contrast with this procedure are photometallization processes (Fig. 1(b)). Here a pattern consisting of metal nuclei or metal clusters is

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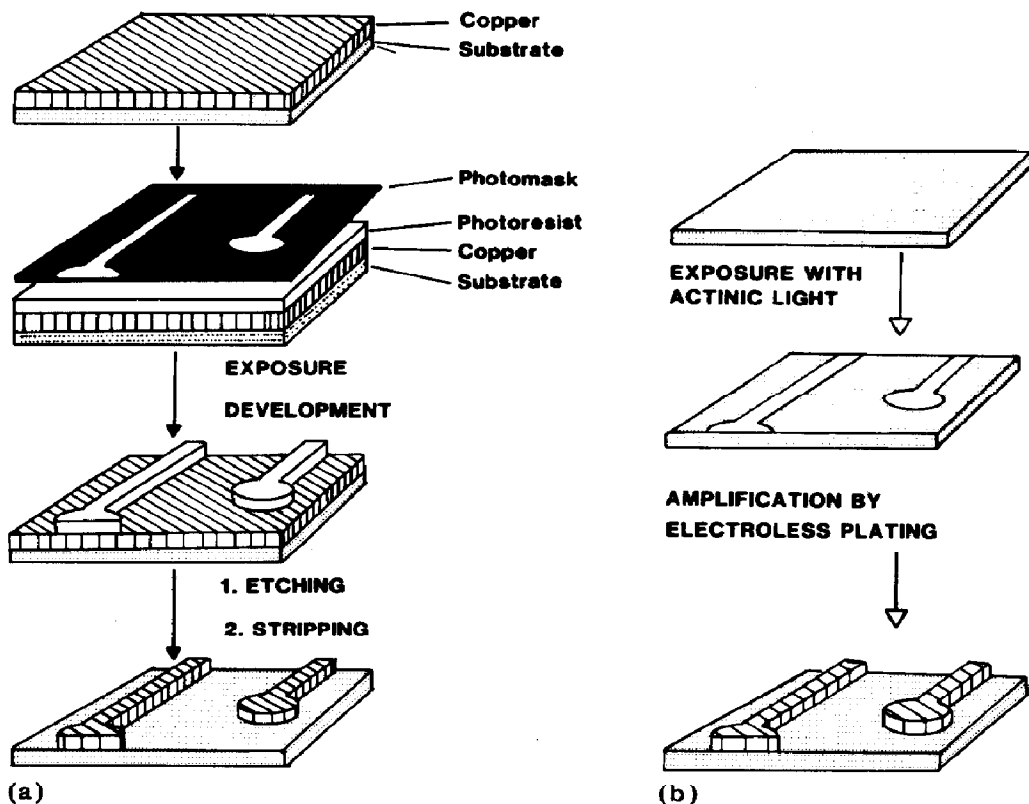


Fig. 1. Schematic representation of (a) a print and etch process and (b) photometallization.

created by a photoredox reaction and subsequently amplified to a metallic pattern by electroless plating [2, 3]. Although many chemical possibilities exist to reduce a metal salt to the metal by actinic light with photoredox or photodecomposition reactions, the state-of-the-art processes are all based on a 50-year-old imaging reaction discovered by Koegel [4] (see also refs. 5 and 6) (Fig. 2). It involves an aqueous solution of copper(II) carboxylate, sorbitol and anthraquinonedisulphonic acid disodium salt. On irradiation the anthraquinonyl (AQ) is reduced to AQH₂ (the alcohol provides the hydrogen); subsequently copper ions are reduced to copper(0) and the AQ molecules may take part in the next photoredox cycle. In the amplification step these metal nuclei serve as catalytic sites for the electroless plating reaction. An electroless plating bath is a thermodynamically unstable, but kinetically stable, mixture of the metal salt and its reducing agent, stabilized by complexing agents. Metal deposition takes place only when catalytic sites such as metal clusters or the metal surface are present. To achieve practically useful conducting patterns on a substrate, the substrate surface has to be rendered porous and hydrophilic to be wetted by the aqueous photoredox solution. On irradiation copper nuclei are formed inside the cavities and on

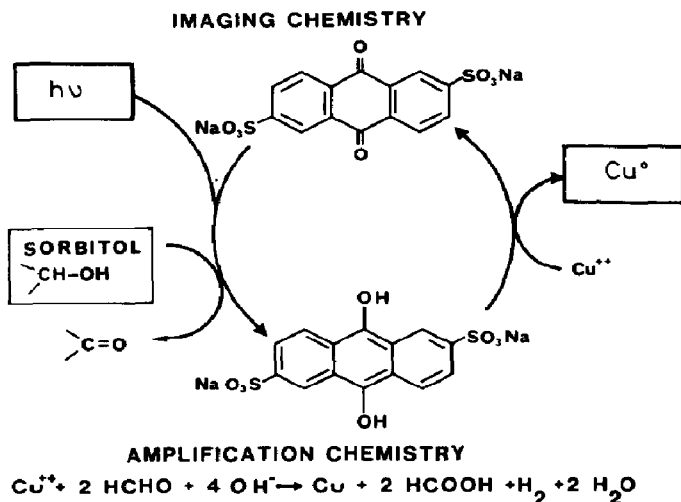


Fig. 2. Scheme of a photometallization system.

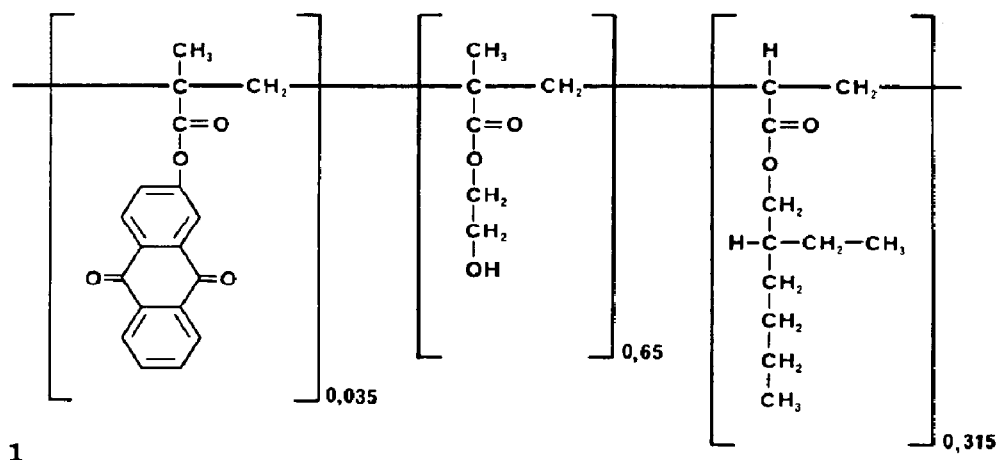
the surface. The remaining photoredox solution on the unexposed parts has to be removed by washing or fixation procedures without the copper nuclei being affected. Adhesion of the metal pattern is accomplished by physical interpenetration of the metal in the cavities.

The fascinating aspects of this chemistry are the high number of amplification steps per photochemically created catalytic site and the possibility of yielding electrically conducting patterns that may be useful for electronic applications. However, to fulfil the requirements of good adhesion as well as good resolution with photosystems of low molecular weight, heterogeneous multicomponent systems consisting of at least two components, a special surface and a photoredox solution, must be chosen.

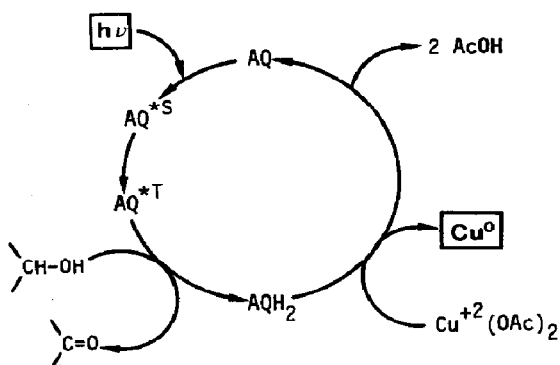
A totally new concept in photometallization is to tailor a homogeneous system of high molecular weight where the surface is the photosystem itself [7]. Homogeneous systems are formed with polymers carrying the components of the photoredox system as pendent functional groups. Anthraquinones together with alcohols are certainly a good choice for a photoredox system, as the molar extinction coefficient is sufficiently low, the quantum yield of the photoreaction may equal unity and the alcohol groups provide hydrophilicity which is necessary for the amplification step.

2. Results and discussion

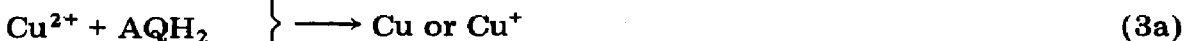
In the following we shall focus on the photochemistry of a homogeneous poly(methacrylate) model system with pendent AQ and hydroxyalkyl groups:



This polymer is synthesized by radical polymerization of the corresponding methacrylate esters leading to a material with a weight average molecular weight of 120 000 daltons and a glass transition temperature of 43 °C. The photochemistry of the polymer system is schematically depicted in the following cycle:



The cycle can be described by the following reactions:



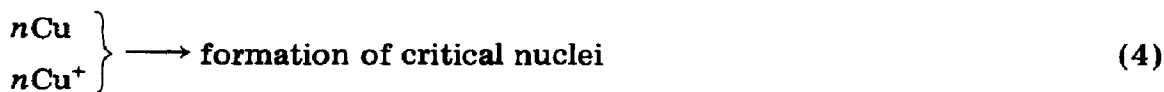
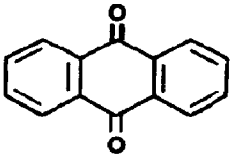
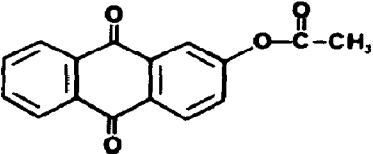
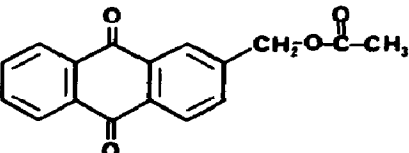
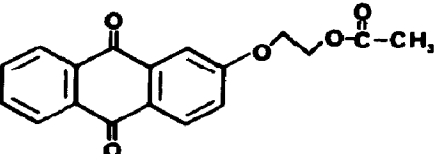
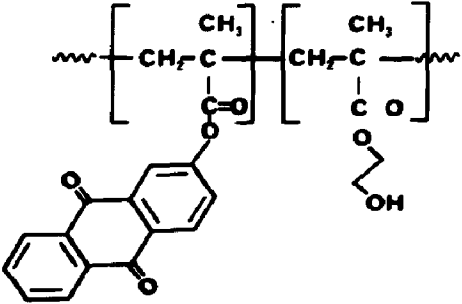


TABLE 1
Photophysical data for anthraquinonyl derivatives

	UV-visible absorption ^a			Phosphorescence ^b Φ		
	λ_{max}	ϵ_{max}	$\epsilon(366)$	E_{T} (kcal mol ⁻¹)	τ (ms)	
	322	5400	310	63.3	3.3	> 0.5
	322	4500	300	63.4	4	> 0.5
	322	4900	400	62.9	4	> 0.5
	327	3800	2500	56.1	200	< 0.1
	322	—	—	66	4	—

The quantum yields were measured according to ref. 11.

^a In methanol.

^b At 77 K in 2-methyltetrahydrofuran.

2.1. *The anthraquinonyl triplet state*

Reaction (1) leads to an excited triplet state. From the literature it is evident that the electronic nature of this state depends on the type of substituents at the AQ skeleton and that only $n \rightarrow \pi^*$ -type excited triplet states give high quantum yields of photoreduction [8 - 10]. We therefore studied the triplet state and the quantum yield of some model compounds to choose a suitable type of functional group to link the AQ chromophore to the polymer chain (Table 1). The quantum yield of the photoreduction of copper(II) acetate in methanol solution was measured by the method given by Kuwana [11]. A fixed amount of AQ derivative and copper acetate were irradiated until the solution showed the fluorescence of the 9,10-dihydroxyanthracene which appears when all the copper ions have been consumed. As is evident from the short triplet lifetime (typically 4 ms) and the quantum yield of copper formation (greater than 0.5), the AQ derivatives exhibiting $n \rightarrow \pi^*$ -type triplet states such as the unsubstituted AQ, the 2-acetate and the 2-methyl derivatives show good reducing properties, whereas an ether-type substitution causes a bathochromic shift of the chromophore and induces a $\pi \rightarrow \pi^*$ excitation of long lifetime and of low reactivity for reduction. Hence, from considerations of the electronic nature of the excited state it is clearly a good choice to select 2-anthraquinonyl methacrylate as the chromophore unit of a polymer.

2.2. *Anthraquinonyl photoreduction products*

According to eqns. (2) and (2a) the dihydroxyanthracene as well as the semiquinone radical are possible reaction products. For the photochemistry of the low molecular weight AQ in solution it is generally accepted that the dihydroxyanthracene is formed by disproportionation of two semiquinone radicals. The quantum yield for the reaction varies around unity in neutral or acidic media. Figure 3 shows the UV-visible spectra of an AQ-containing solid polymer film after various irradiation times as well as the spectrum of 9,10-dihydroxyanthracene produced by the chemical reduction of AQ. It is evident that the product of the photoreduction in the solid film is the dihydroxyanthracene. It is formed with a quantum yield of 0.05 in the solid film and with a quantum yield of 0.15 in solution. The maximum conversion in the film is 25% - 30% of the AQ units. This value is certainly due to the high steric demands for the formation of the photoproducts because (a) the excited AQ triplet and a hydroxyalkyl group need to be sterically close for hydride transfer and (b) two semiquinone radicals should be close enough for disproportionation. In solution the photoreduction occurs almost quantitatively.

It might be supposed that not all radicals formed in a solid film have the chance to be in a favourable position for disproportionation. Surprisingly, no semiquinone radicals can be detected in the UV-visible spectrum as is evident by the lack of absorption in the 700 - 900 nm region [12].

The evolution of radicals in the solid film may be monitored by electron spin resonance spectroscopy. Figure 4 shows the spectrum of a solid

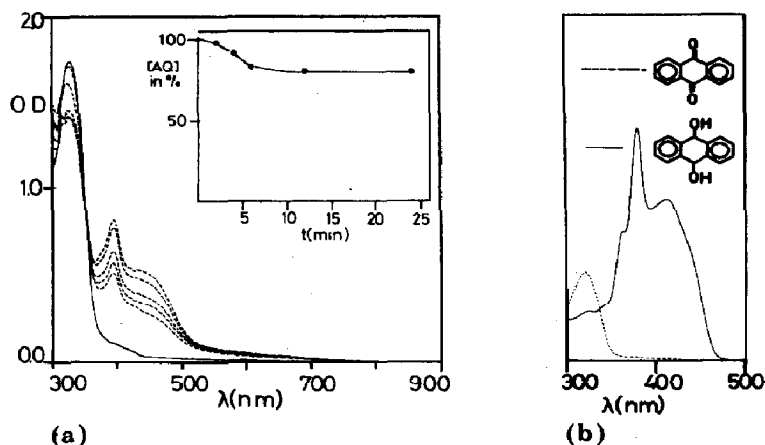


Fig. 3. UV-visible spectra of (a) a solid polymer film after exposures of 2, 4, 6, 12 and 24 min (340 nm; 25 °C; $I = 2 \text{ mW cm}^{-2}$) and (b) chemically reduced 9,10-anthraquinone.

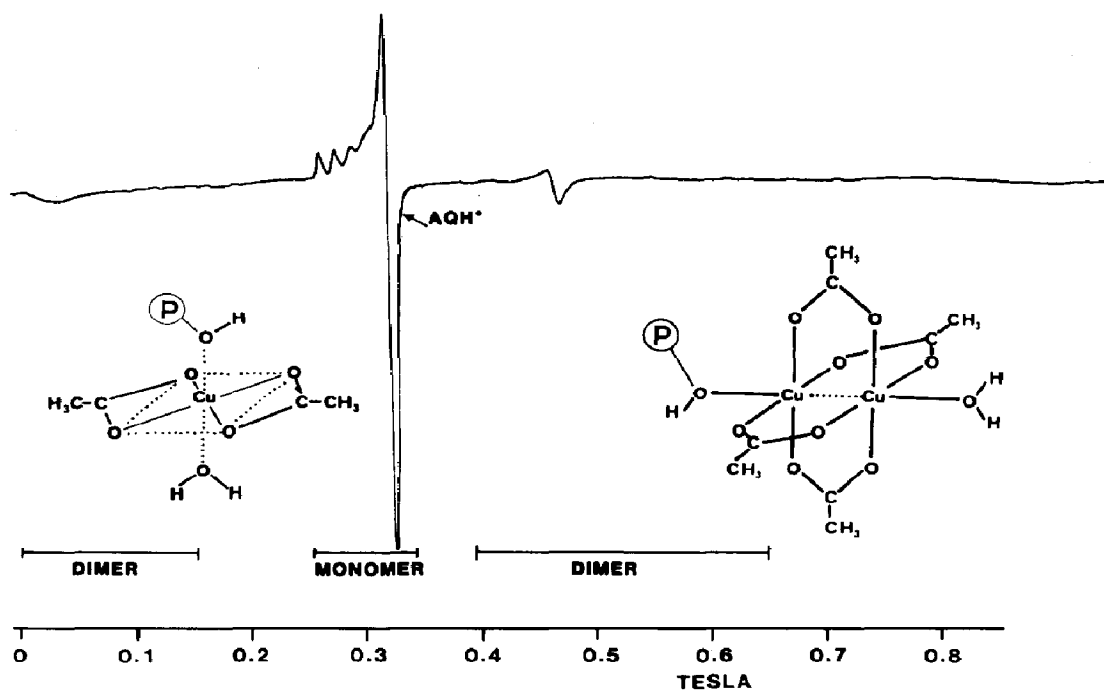


Fig. 4. Electron spin resonance spectrum of a solid polymer film containing copper(II) acetate.

film containing copper(II) acetate during irradiation at 365 nm. The signals are due to paramagnetic copper acetate monomer and dimer molecules which are at least partially bound to the polymer backbone by complex formation via the hydroxyalkyl groups. The semiquinone radical signal appears as a weak shoulder at 0.33 T on the monomer peak. On irradiation of a solid polymer film, 25% of the AQ units are consumed; the conversion to semiquinone radicals is found to reach 2 per thousand and after irradiation

a permanent concentration of 0.2 semiquinone radicals per thousand AQ units persists in the film for several days. As copper(II) ions as well as copper(0) clusters are paramagnetic this method should also offer the chance to follow the evolution of copper clusters directly during irradiation. However, signals corresponding to copper(0) which would be expected near 0.5 T could surprisingly not be detected [13]. To ensure that no interference between the copper(II) dimer signals and the expected copper(0) signals occurs, the experiment was repeated with copper nitrate. Here also no copper(0) signals were found.

2.3. Copper(II) ion reduction

As eqns. (3) - (3b) show, there are several possibilities for reducing copper(II) ions in a system containing hydroxyalkyl radicals and various reduced AQ species. Most probably, however, reduction occurs via eqns. (3a) and (3b). The redox potential of both reductants should be sufficiently high. Polymer chemistry gives us a possibility of distinguishing between reduction by the hydroxyalkyl radical and reduction by the quinone derivatives.

The combination of two hydroxyalkyl radicals (formed in the exposed parts of the polymer film) leads to a cross-linked insoluble polymer. The efficiency of photo-cross-linking can be measured sensitometrically by standard procedures for photoresists [14]. If copper(II) is reduced to copper(0) predominantly by the hydroxyalkyl radical, the photo-cross-linking reaction should be quenched in the presence of copper(II) ions. Figure 5 shows the sensitivity as a function of the exposure energy at different temperatures

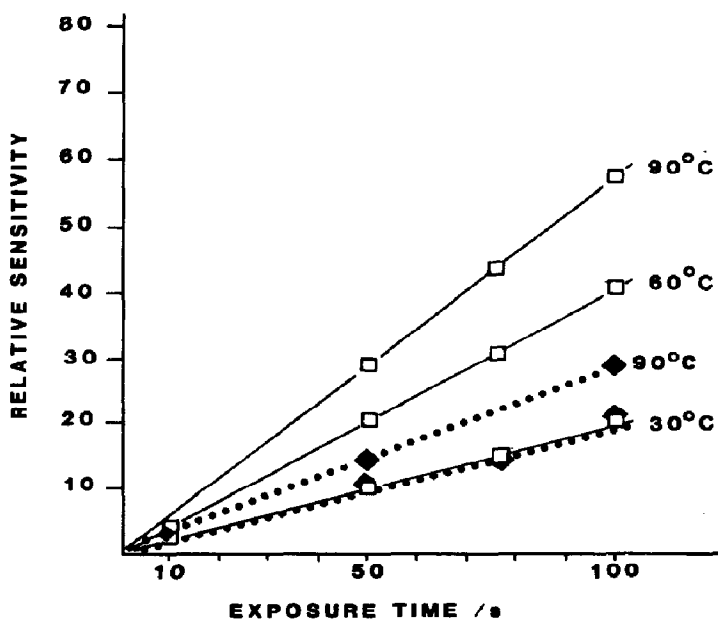


Fig. 5. Relative sensitivity at different exposure times measured with a 21-step tablet with incremental steps of 0.15 optical density [14]: □, pure polymer; ♦, copper(II)-containing polymer.

during irradiation (full lines). The sensitivity increases with increasing temperature owing to increased mobility of the polymer chains. It depends on the free volume inside the polymer [15]. The full lines represent data for the pure polymer films. Polymer films containing copper acetate are represented by the dotted lines. It is evident that at room temperature the cross-linking reaction is not quenched in the presence of copper ions. At elevated temperatures, however, effective quenching occurs. It can therefore be concluded that the production of catalytic nuclei is dependent on the diffusion of the copper ions in the polymers.

2.4. Creation of catalytic nuclei

The electroless plating reaction takes place only in the presence of a catalytic site. The phenomenon of metal deposition in electroless plating may be regarded as analogous with homogeneous nucleation and crystallization from solution. A catalytic nucleus needs to have a certain critical size which depends on the free energy of the plating bath [16]. Nuclei below that size will be dissolved and larger nuclei will be amplified. To estimate the critical size of copper nuclei, copper metal was sputtered onto glass surfaces coated with Formvar in different concentrations, leading to different mean particle sizes from 1.9 to 9.7 nm. Figure 6 shows transmission electron micrographs of these clusters before and after electroless copper plating for 30 s. Only nuclei larger than 1.5 nm are amplified and the smaller nuclei dissolve. From this result it seems quite obvious that the step determining

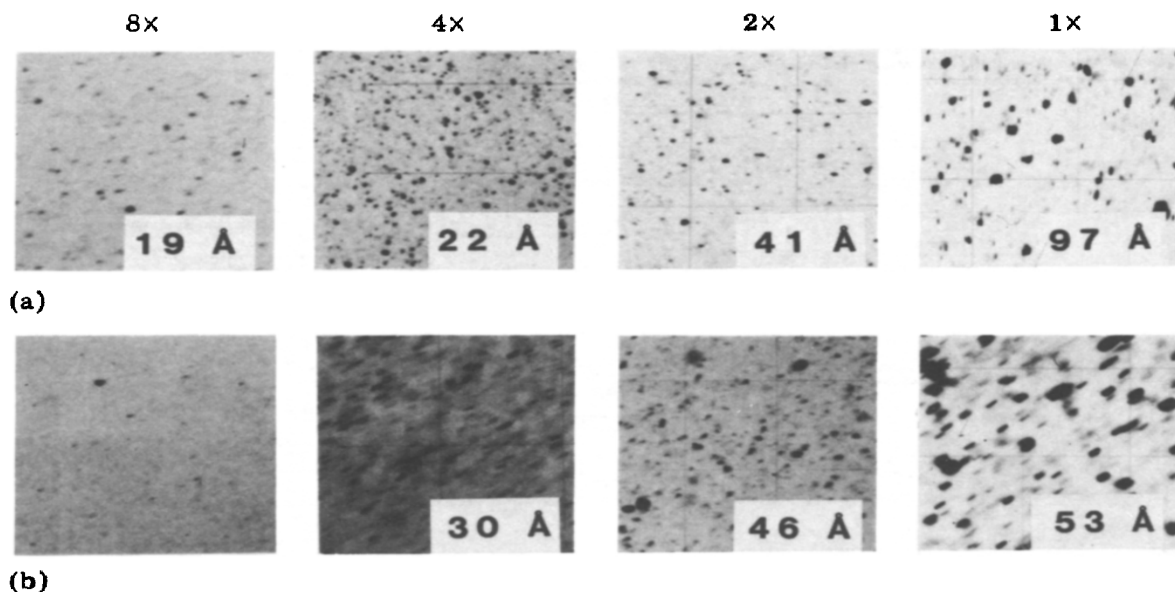


Fig. 6. Transmission electron microscopy of copper clusters sputtered onto Formvar-coated glass (a) before and (b) after 30 s electroless plating with Cuposit Copper Mix 328 Q (SP) from Shipley Corporation, Newton, MA. Numerals above the micrographs refer to distance of the glass plates from the sputtering source.

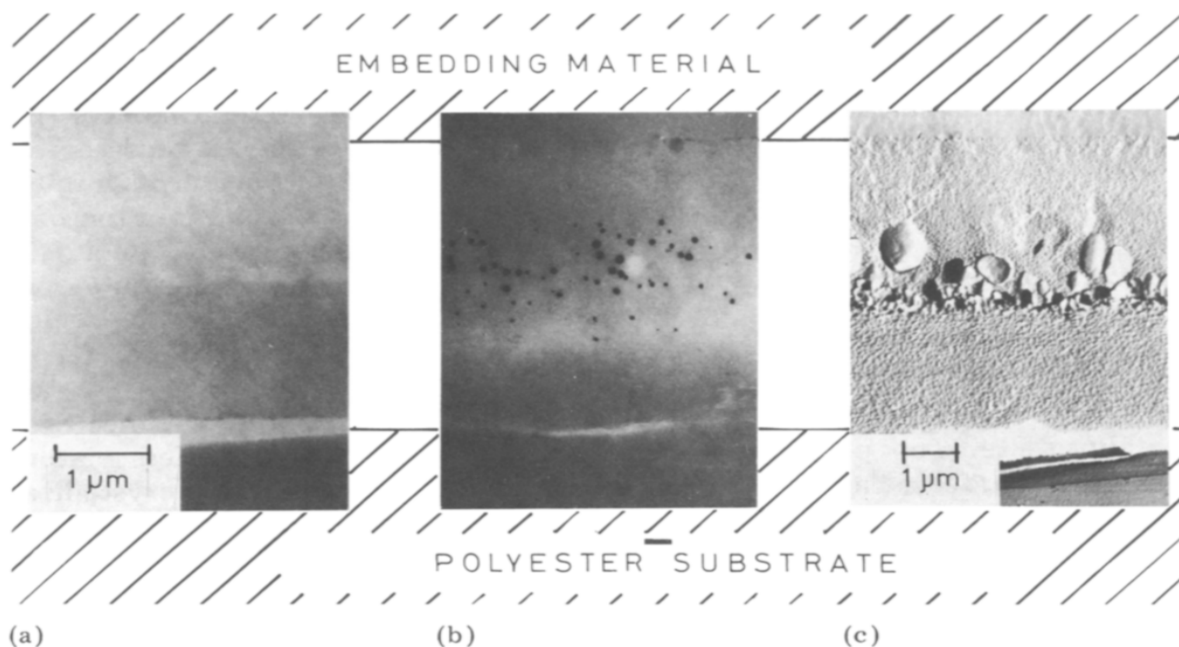


Fig. 7. Cross-sections through irradiated polymer films after different times of electroless copper plating (Cuposit CP 78 from Shipley Corporation): (a) after 30 s; (b) after 180 s; (c) after 300 s. (Sample (c) was etched with HF to enhance the contrast.)

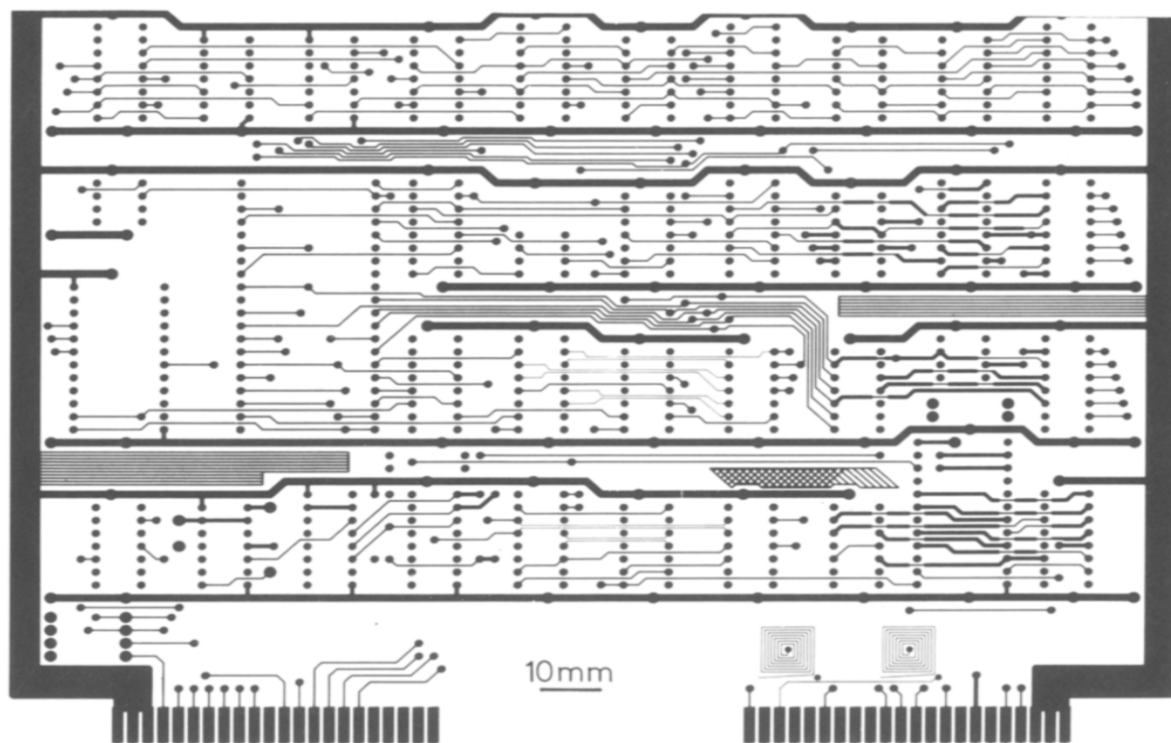


Fig. 8. Printed circuit test pattern on a polyester substrate produced with polymer according to the model system 1 with pendent AQ and hydroxyalkyl groups.

the efficiency of the photoreduction is the formation of copper clusters by a diffusion process.

The amplification of nuclei formed by photoreduction in the solid photopolymer film to a metallic pattern may be monitored by transmission electron microscopy. Figure 7 shows micrographs of cross sections through an irradiated polymer film after electroless plating. The film is homogeneous even after low exposure times to the plating bath. After prolonged exposure, however, crystals start to grow inside the film. They increase in size and grow to the outside in the form of large particles. The surface is finally covered by a uniform copper layer in the exposed parts and adhesion is achieved by the physical interpenetration of the copper layer and the photopolymer. A typical metal image received by this procedure is shown in Fig. 8.

Acknowledgments

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References

- 1 G. A. Delzenne, *Adv. Photochem.*, **11** (1979) 1.
- 2 M. Paunovic, *J. Electrochem. Soc.*, **127** (1980) 441C.
- 3 H. Jonker, C. J. Dippel, H. J. Houtman, C. J. G. F. Janssen and L. K. H. van Beek, *Photogr. Sci. Eng.*, **13** (1969) 1.
- 4 G. Koegel, *U.S. Patent 1,843,822*, 1932.
- 5 A. Schoen, GAF Corporation, *U.S. Patent 2,504,593*, 1950.
- 6 K. Takahashi, K. Ikari, J. Kano, T. Takamura, T. Ueki, T. Yamaoka and T. Tsunoda, *Electrocomponent Sci. Technol.*, **8** (1981) 99.
- 7 J. Finter, Ciba-Geigy AG., *Eur. Patent Appl. 0,080,975*, 1981.
- 8 D. Schulte-Frohlinde and C. von Sonntag, *Z. Phys. Chem. (Frankfurt am Main)*, **44** (1965) 314.
- 9 R. Mitzner, D. Frosch and H. Dorst, *Z. Phys. Chem. (Leipzig)*, **258** (1977) 845.
- 10 H. Mauser, V. Starrock and H.-J. Niemann, *Z. Naturforsch.*, **27b** (1972) 1354.
- 11 T. Kuwana, *Anal. Chem.*, **35** (1963) 1398.
- 12 B. Carlsson, C. Leygraf and G. Hultquist, *J. Photochem.*, **7** (1977) 51.
- 13 R. A. Zhitnov and N. V. Kolesnikov, *Sov. Phys. — Solid State*, **6** (1965) 2645.
- 14 J. Finter, E. Widmer and H. Zweifel, *Angew. Makromol. Chem.*, **128** (1984) 71.
- 15 J. Finter, unpublished data, 1982.
- 16 I. Konstantinov, *J. Photogr. Sci.*, **23** (1975) 1.