

Photochemical Grafting of Acrylated Azo Dyes onto Polymeric Surfaces. I. Grafting of 4-(*N*-Ethyl, *N*-2-Acryloxyethyl) Amino, 4'-Nitro, Azobenzene onto Polyamide and Polypropylene Fibers

I. R. BELLOBONO, F. TOLUSSO, and E. SELLI, *Cattedra di Chimica, Facoltà di Scienze, Università di Milano, 20133 Milan, Italy*, S. CALGARI and A. BERLIN, *Centro Sperimentale "F. Marinotti," Snia Viscosa, 20031 Cesano Maderno, Milan, Italy*

Synopsis

Photochemically induced grafting and graft polymerization of 4-(*N*-ethyl, *N*-2-acryloxyethyl) amino, 4'-nitro, azobenzene(I), brought into contact with polyamide and polypropylene fibers by evaporation of solvent from toluene solutions, has been investigated kinetically at 45° C. Two constant-rate periods were observed. The first one was interpreted on the basis of an autosensitized grafting mechanism of monomeric or oligomeric species of (I), photochemically initiated by hydrogen abstraction from the polymer surface. This first step occurred at a rate dependent on the chemical nature of the substrate being faster for polyamide than for polypropylene by a factor of about 1.25; it was followed by a brief induction period, after which a transient autoacceleration led to a second constant rate process, independent of the substrate. This latter step was explained as an auto-sensitized photochemically induced graft polymerization of (I) on the first grafted layer.

INTRODUCTION

Chemical or physical modification of the surface properties of polymeric materials is undoubtedly a fascinating field for research as well as a practical way to improve their values. Surface and not bulk properties determine the most relevant aspects of the behavior in many technologically important fields, such as dyeing, printing, adhesion, and so on. Their influence, which is already so decisive in films and molded materials, becomes of the uttermost importance in fibers. A great amount of research has been published in this area, particularly in the last decade.¹⁻³ Among the physical methods of modification, however, the photografting technique has not been the subject of much attention. Photografting onto polymers blended with photosensitizers has been first studied by G. Oster et al.^{4,5} Hydrophilic polymers, such as cellulose and its derivatives, which are susceptible to radical attack, can be grafted photochemically using dyes,^{6,7} with or without other sensitizers.^{8,9} Polyolefins, too, which had been reported previously as inert⁷ toward the photochemical grafting, have been more recently grafted by this technique. The modification of the polypropylene film surface by the photochemical graft polymerization of acrylamide from its solution in the presence of sensitizers,¹⁰ for instance, has been shown to be initiated through hydrogen abstraction from the polymer surface by the triplet excited state of the sensitizer.

The present work has been undertaken with the purpose of investigating the

possibility of grafting a dye onto polymeric fibers by means of photochemical initiation. 4-(*N*-ethyl, *N*-2-acryloxyethyl) amino, 4'-nitro, azobenzene was selected as the model compound for this study, both in view of the fact that photochemistry of the parent molecule, 4-diethylamino, 4'-nitro, azobenzene has been extensively investigated,¹¹⁻¹⁵ and because of the peculiar photochemical behavior of compounds which have a carbonyl group and a double bond capable of twisting in an excited state, and which have been recently reported to undergo photochemical reactions through abnormally long-lived upper excited states.¹⁶⁻¹⁸

In this article, photochemical grafting and graft polymerization of 4-(*N*-ethyl, *N*-2-acryloxyethyl) amino, 4-nitro, azobenzene(I) on polyamide and polypropylene fibers was carried out with a view to investigating kinetically the extent and rate of grafting and polymerization, in the absence of any added sensitizer.

EXPERIMENTAL

Materials

Polyamide (nylon 6 Lilion 60/18, Snia Viscosa) and polypropylene (Meraklon 160/22, Montedison) fibers were used in the form of a ribbon obtained from a woven fabric. The ribbons were purified through a mild cleaning treatment with sulfonated lauryl alcohol (5 g/liter) for 30 min at 60° C, thoroughly rinsed with water, dried at room temperature, and finally Soxhlet extracted with 50% v/v cyclohexane-ethanol.

4-(*N*-ethyl, *N*-2-acryloxyethyl)amino, 4'-nitro, azobenzene(I) was prepared in 85% yield by acrylation of 4-(*N*-ethyl, *N*-2-hydroxyethyl) amino, 4'-nitro, azobenzene(II). The latter (C.I. disperse red 1:commercial product "scarlatto microsetile B" by Acna, Italy) was purified by Soxhlet extraction with anhydrous acetone, followed by column chromatography on silica gel, elution with 50% v/v benzene-ethyl acetate (by TLC monitoring of the collected fractions) and finally by repeated crystallizations from methanol-benzene. A mixture of 4 g of purified (II) and 4 g of acryloyl chloride, dissolved in 400-ml acetone, was cooled to -5° C, and 77.5 ml 1*N* NaOH were added with vigorous stirring over a 1-hr period, while maintaining a temperature slightly below 0° C. After dilution with water, precipitated (I) was extracted with ethyl ether. Purification of the ethereal solution was carried on by column chromatography on silica gel and elution with 50% v/v benzene-ethyl acetate: mp 103° C. The pure compound showed the band of C=O stretching at 1730 cm⁻¹ in KBr pellet. The electronic spectrum showed a broad band at 440 nm in *n*-hexane (molar absorptivity 12,000M⁻¹ cm⁻¹) and in the near UV region a maximum at 280 nm (molar absorptivity 4740M⁻¹ cm⁻¹) in this same solvent. NMR spectrum was obtained with a Varian A-100 spectrometer at 100M cps in 5% w/v CDCl₃ solution containing tetramethylsilane as an internal standard, at the operating temperature of the instrument (about 35° C). It showed triplets at 1.30 (three protons of —CH₃ in *N*-ethyl group) and 4.43 (two protons of —CH₂ adjacent to acryloxy group), as well as multiplets at 3.45-3.88 (four protons of the two —CH₂ groups attached to amino nitrogen), at 5.80-6.57 (three protons of —CH=CH₂— in the acryloxy group), and at 6.80-8.45 (eight protons of the two aromatic rings) (chemical shifts are quoted as δ, ppm, downfield from tetramethylsilane).

ANAL. Calc for $C_9H_{20}N_4O_4$: C, 61.94%; H, 5.47%; N, 15.2%. Found: C, 61.66%; H, 5.41%; N, 14.95%.

Graft Polymerization

Two milliliters of 0.04–0.14*M* solutions of (I) in toluene were uniformly deposited by a standard procedure making use of a microsyringe dispenser on 5.00×10.00 cm² of ribbon, and the solvent evaporated at room temperature. Irradiations were then carried out with a 500-W high-pressure mercury arc lamp (Italquartz). This was placed in suitable housing at a distance of about 21 cm from the irradiated samples in such a way as to have an overall impinging photoenergy of 90 ± 5 mW cm⁻². No particular care was generally devoted to excluding oxygen during experiments, except in some of the runs, to check its influence. The temperature of the reaction system increased to about 45°C during irradiation. No dark reaction was observed at this temperature for exposure times used. After the desired irradiation time, the sample was Soxhlet extracted with acetone, and acetone solution of (I), thus obtained, analyzed spectrophotometrically. The graft or graft polymerization yield was calculated as the ratio between unextracted (I) and that initially deposited on the ribbon. The grafted surface, which was very resistant to the solvent, was also examined by reflectance spectroscopy and optical microscopy, in order to check the chemical and physical form of the grafted dye.

Measurement of Surface Properties

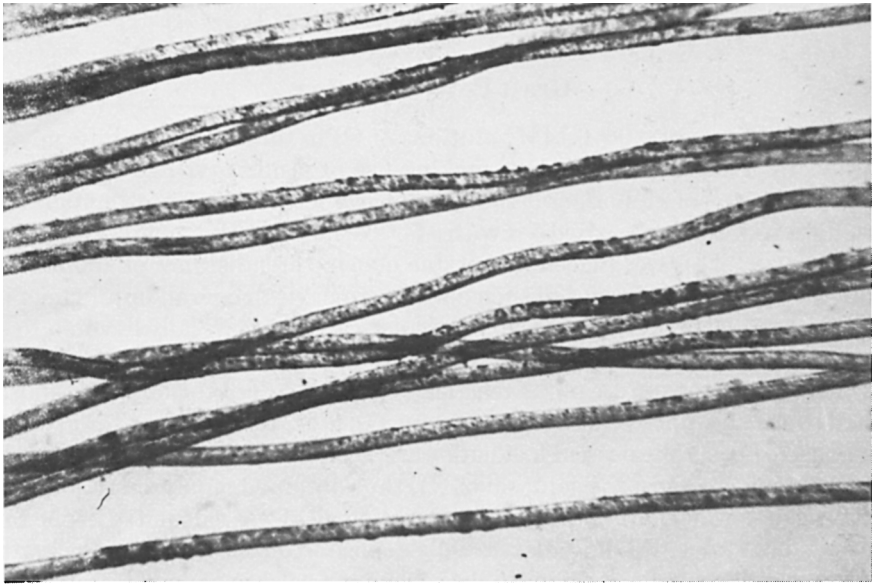
A reflectance spectrophotometer (Zeiss, model PQM 3, equipped with RA 3 accessory modulus) was used for the spectroscopic examination of the grafted dye.

Optical microscopy was carried out in Nujol oil, either directly on single fibers and their bundles isolated from the fabric, or on their sections, with slices obtained by ultramicrotomy.

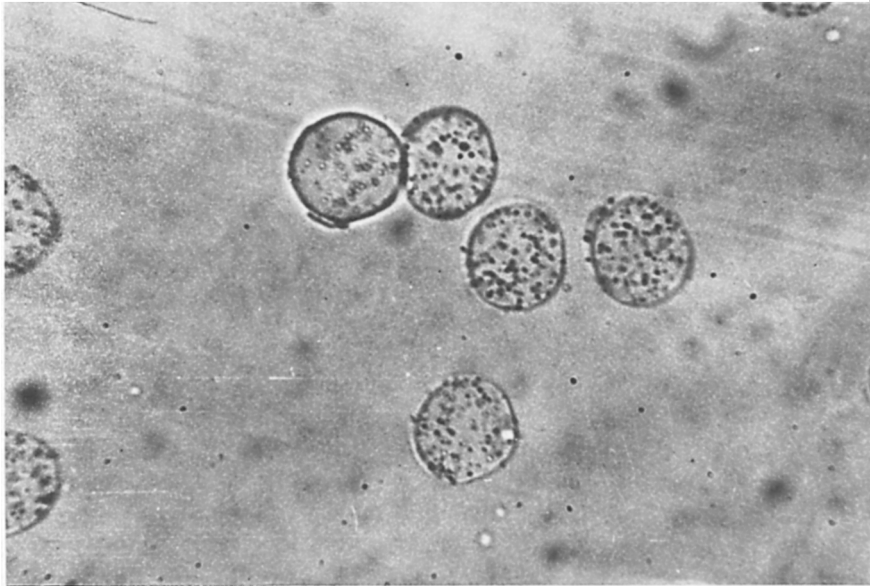
RESULTS AND DISCUSSION

Irradiation of (I) brought into contact in its crystalline form on polyamide and polypropylene fibers was found to bring about a fixation of the dye on these fibers even after extracting the latter several times with acetone, methylethylketone, or methylisobutylketone, which are excellent solvents for both monomer (I) and its polymer. Fixation was not due to thermal polymerization or to an eventual thermally initiated radical grafting, because a series of tests, carried out in the dark and in the same temperature conditions (45°C) reached during the irradiation tests, showed complete recovery of the dye within the experimental range of irradiation times investigated. The dye fixation was thus unequivocally due to grafting of oligomeric or polymeric species of (I) on the polyamide and polypropylene fibers.

A microscopic analysis (see Fig. 1) showed that the crystalline dye material, which surrounded the fabric, remained after irradiation permanently bonded onto the polymer surface with a low penetration which did not exceed 10% of the fiber diameter. Reflectance spectroscopy of the photochemically dyed surface indicated that the spectrum was substantially identical to that of the starting



(a)



(b)

Fig. 1. (a) Crystals of 4-(*N*-ethyl, *N*-2-acryloxyethyl) amino, 4'-nitro, azobenzene (I) evaporated on surface of some polyamide fibers (isolated from fabric); magnification 128 \times . (b) Section of some polyamide fibers (isolated from fabric) after 1-hr irradiation (90 mW cm^{-2}) and solvent extraction of ungrafted (I), showing fixation of dye; magnification 800 \times .

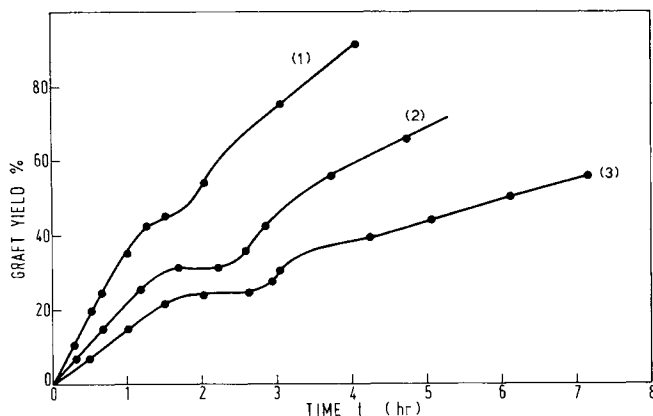


Fig. 2. Influence of n/S , moles of dye deposited per unit surface of polyamide ribbon, on graft yield as function of time, t (hr), energy input 90 mW cm^{-2} : (1) $0.166 \mu\text{mol (I) cm}^{-2}$; (2) $0.334 \mu\text{mol (I) cm}^{-2}$; (3) $0.545 \mu\text{mol (I) cm}^{-2}$.

material (in its trans-azo form); the contribution of an eventually present cis-azo form was very low (not greater than about 5%).

In order to have a deeper insight into the mechanism of this fixation, a kinetic study was carried out to examine the characteristics of photochemical grafting and polymerization.

Kinetics of Photochemically Induced Grafting and Graft Polymerization

Some typical graft-yield curves of (I) onto polyamide and polypropylene fibers are reported in Figures 2 and 3, respectively. A constant-rate kinetics was first observed, followed by an induction period, the duration of which increased with increasing mass of the dye layer deposited into intimate contact on the polymer surface. The induction period that resulted was only slightly greater for polypropylene than for polyamide. A brief autoacceleration period then succeeded, followed by a second constant-rate range up to high graft yield values.

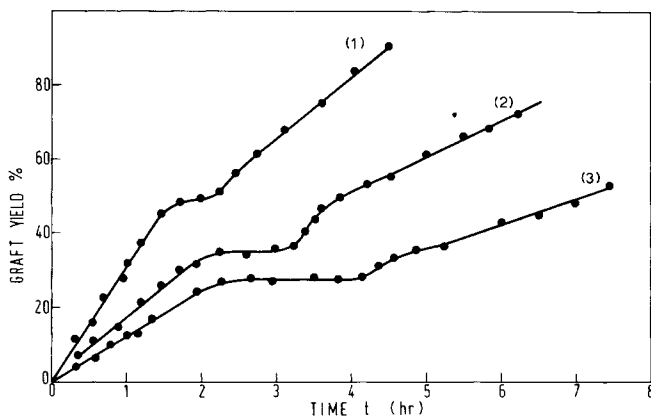


Fig. 3. Influence of n/S , moles of dye deposited per unit surface of polypropylene ribbon, on graft yield as function of time, t (hr), energy input 90 mW cm^{-2} : (1) $0.165 \mu\text{mol (I) cm}^{-2}$; (2) $0.331 \mu\text{mol (I) cm}^{-2}$; (3) $0.553 \mu\text{mol (I) cm}^{-2}$.

The behavior of the system during the first constant-rate period can be quantitatively interpreted by the photochemical rate eq. (1):

$$\frac{1}{S} \frac{dn}{dt} = \Phi_1 I_o (1 - 10^{-\epsilon n/S}) \quad (1)$$

where S is the apparent surface area (cm^2), n the moles of dye, t the time (sec), Φ_1 the overall quantum yield, I_o the impinging radiation flux (Einstein $\text{sec}^{-1} \text{cm}^{-2}$), and ϵ the molar absorptivity of the dye ($\text{mol}^{-1} \text{cm}^2$). Values of the latter determined experimentally on crystalline (I) have been used in eq. (1). Even if these values do not strongly differ from those calculated, on the basis of the density, from mass of deposited dye and molar absorptivity values in *n*-hexane, they enable us, in any way, to account for the presence of molecular aggregates in the solid state, which have an optical behavior different from that in solution. As the molar absorptivity and the quantum yield are wavelength dependent, integral values along the absorption spectrum of the dye and emission spectrum of the lamp have to be used when polychromatic irradiations are carried out, as in the present study, $I_o (1 - 10^{-\epsilon n/S})$ representing the radiation intensity effectively absorbed by the sample.

In order to calculate the left-hand side of eq. (1) the slope of the graft yield, referring to the first constant-rate period, has to be plotted against reciprocal n/S . In Figure 4 experimental points relative to photochemical grafting onto polyamide and polypropylene are reported. The least-squares treatment of these data gives a specific rate of $(1.77 \pm 0.15) \times 10^{-5}$ and $(1.40 \pm 0.08) \times 10^{-5} \mu\text{mol cm}^{-2} \text{sec}^{-1}$, respectively, for these two polymeric substrates (uncertainties are quoted as probable errors). With these rates, up to 4.5–8.1 molecule/ \AA^2 were photochemically grafted onto the polyamide and 4.9–9.1 molecule/ \AA^2 onto the polypropylene ribbon, at the plateau of the graft yield curve (end of the first constant-rate period).

In Figure 5, the number of grafted molecules of (I) per \AA^2 (apparent surface), at the plateau of the graft yield curve, is plotted against n/S . The graph shows

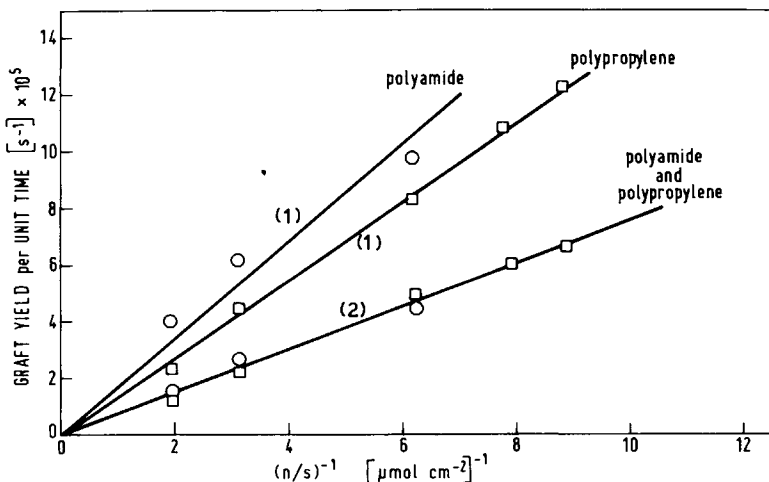


Fig. 4. Graft yields per unit time (sec^{-1}) as function of $(n/S)^{-1}$ ($\mu\text{mol cm}^{-2}$) $^{-1}$ for polyamide and polypropylene ribbon (energy input 90 mW cm^{-2}), relative to first (1) and second (2) constant-rate periods.

a good linearity and may be extrapolated at very low n/S values to give the surface density of molecules resulting from an ideal photochemical grafting of a monolayer dye film. Since the real surface of the ribbons should greatly exceed the apparent one, it is not unrealistic to suppose that this step of the process corresponds to a "monomolecular" layer at very low n/S values of the dye deposit, and to an oligomeric growth of the dye on the photochemically reacting sites of the grafted polymer.

Whereas the surface density of the "monomolecular" grafted layer (extrapolated values from the graphs of Figure 5 at $n/S \rightarrow 0$), about 2.7 molecule/ \AA^2 for polyamide and 3.8 molecule/ \AA^2 for polypropylene, is dependent on the chemical and physico-chemical nature of the substrate, the oligomeric fraction of the first grafted layer seems to be independent on the substrate, and grows with the initial mass of deposited dye per unit surface at a rate corresponding to about 10 molecule/ \AA^2 .

By eq. (1), a polychromatic quantum efficiency ϕ_I of 3.4×10^{-4} and 2.6×10^{-4} molecule quantum $^{-1}$ can be evaluated for the photochemical grafting of (I) onto polyamide and polypropylene fibers, respectively. These low values are compatible with a hydrogen abstraction mechanism from the polymer backbone—but also from carbonyl and/or hydroxy groups eventually formed by oxidation on the polypropylene surface, as well as from carbonyl, amido, and/or amino groups present in the polyamide polymer—to yield a macroradical capable of initiating grafting.

The intermediate induction period, which follows, is then probably due to a deactivation of this first grafted layer. This deactivation may be partly originated by the radical scavenging action of oxygen. As a matter of fact, oxygen removal in the reacting system somewhat shortens the induction period.

After the induction period, the graft yield versus irradiation time graph rises sharply. This autoacceleration phenomenon could be brought about by the gradual change of the surface properties and by initiation of a graft polymerization, which then proceeds with a nearly constant-rate mechanism. The application to this latter stage of the same treatment illustrated previously for the first constant-rate period (see Fig. 4) yields the straight line of Figure 4, with a

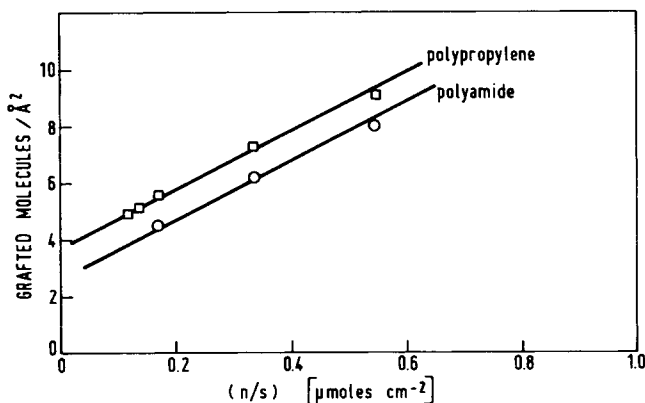
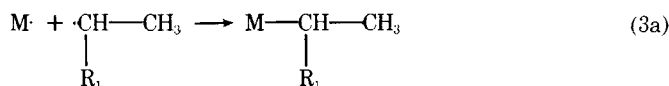
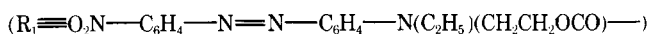
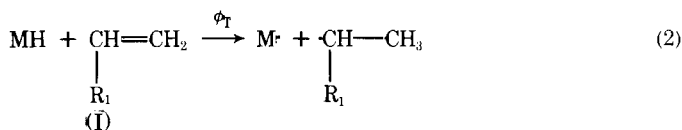


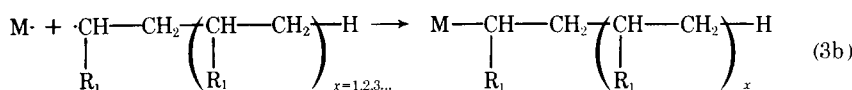
Fig. 5. Grafted molecules of (I) per apparent unit area (\AA^2) at end of first constant-rate period (plateau of the graft yield curve), as function of n/S ($\mu\text{mol cm}^{-2}$) for polyamide and polypropylene ribbon (energy input 90 mW cm^{-2}).

slope of $(7.70 \pm 0.34) \times 10^{-6} \mu\text{mol sec}^{-1} \text{cm}^{-2}$, and a quantum yield $\Phi_{II} = 1.8 \times 10^{-4}$ molecule quantum $^{-1}$. The independence of the rate of graft polymerization on the nature of the substrate is consistent with the fact that the original surface has been modified by the grafted dye; and consequently, this specific rate represents the photochemically induced graft polymerization of (I) on the first grafted layer.

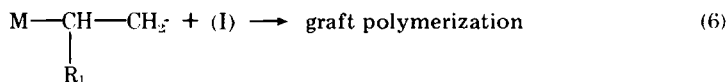
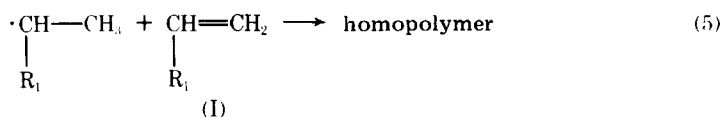
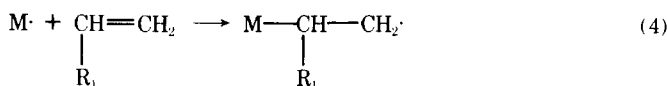
The following general scheme may then be proposed, where MH represents the photochemically reactive sites of the polymer surface. For the first constant-rate period:



(grafting of "monomolecular" layer)

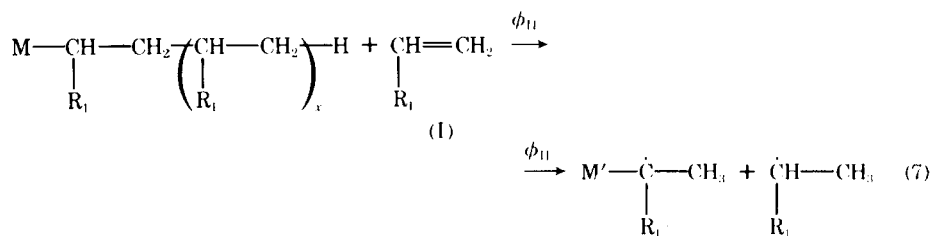


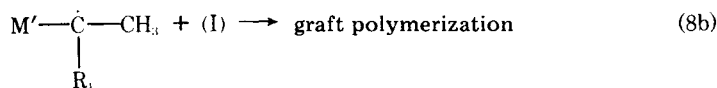
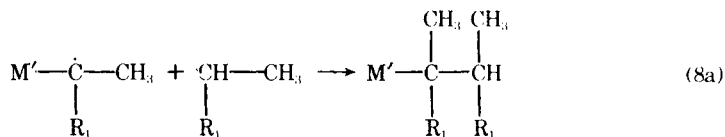
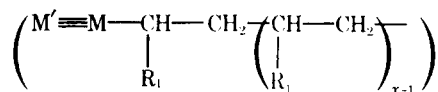
(grafting of an oligomolecular layer)



(partly, at least, inhibited by oxygen).

For the second constant-rate period:





(partly, at least, inhibited by oxygen).

When oxygen was removed from the irradiated system by a stream of nitrogen, the shape of the graft-yield curves versus time did not change dramatically, even if a sensible influence on rates could be observed. On the polypropylene substrate, for instance, the induction plateau was appreciably shortened but not entirely eliminated; the rate of the first constant-rate period was enhanced by a factor of about 1.56, while that of the second constant-rate period was increased by a factor of about 1.85. These facts substantiate the proposed mechanism, even if conclusions about the oxygen influence can only be drawn qualitatively, because oxygen dissolved in the polymer will be more difficult to remove than by a stream of nitrogen, and consequently its effects cannot be completely excluded.

Anyway, during the first constant-rate period (photochemical grafting), eq. (2) should express the stoichiometry of the photochemical rate-determining reaction, for which eq. (1) is valid.

The fact that oxygen influences the rate without suppressing the possibility of grafting substantiates the mechanism of autosensitized hydrogen abstraction from the polymer by the dye during the initiation of grafting, until a "monomolecular" layer [eq. (3a)] is formed. In effect, any retardation of the radical reaction (3a) by oxygen may not be decisive, as the radical couple produced by reaction (2) must be sterically close in the solid system irradiated; and consequently, reaction (3a) is fast enough to compete successfully with the radical scavenging action of oxygen. Moreover, the fact that a reasonable value of the number of dye molecules grafted per unit apparent surface up to the plateau of the graft yield curve may be extrapolated from the graph of Figure 5 speaks in favor of a prevailing mechanism represented by eqs. (2) and (3a) for the "monolayer" in this step, with a minor contribution from eqs. (4) and (6). The latter become more important with increasing mass of deposited dye per unit surface, whereby their rate, and consequently the buildup of dye molecules in the grafted layer, is somewhat influenced by the presence of oxygen. The only alternative to eq. (3a) should be represented by the radical reaction (3b) of $M\cdot$ with a growing chain of dye homopolymer, which may lead to an oligomeric grafted layer of dye molecules. Reaction (3b) becomes increasingly important (see Fig. 5) with increasing mass of the deposited dye per unit surface, while it practically coincides with (3a) for experimental n/S values $\lesssim 0.1 \mu\text{mol cm}^{-2}$. The most important mechanism in this first step of the process should thus be the combination of the free radical species, in particular the secondary free-radical species resulting from

the macromolecule, with the dye radical formed by hydrogen abstraction or with its oligomer rapidly grown in the crystal.

The more sensible influence of oxygen during the second constant-rate period supports a prevailing mechanism of graft polymerization on the first grafted layer for this step, stressing the role of eq. (8b) particularly.

References

1. A. Hebeish, S. H. Abdel-Fattah, and M. H. El Rafie, *J. Appl. Polym. Sci.*, **22**, 2253 (1978).
2. A. Hebeish, M. H. El Rafie, A. Waly, and A. Z. Moursi, *J. Appl. Polym. Sci.*, **22**, 1853 (1978).
3. S. E. Shalaby, A. M. Bayzeed, and A. Hebeish, *J. Appl. Polym. Sci.*, **22**, 1359 (1978).
4. G. Oster and O. Shibata, *J. Polym. Sci.*, **26**, 233 (1957).
5. G. Oster, G. K. Oster, and H. Moroson, *J. Polym. Sci.*, **34**, 671 (1959).
6. N. Geacintov, V. Stannett, and E. W. Abrahamson, *Makromol. Chem.*, **36**, 52 (1960).
7. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **3**, 54 (1960).
8. N. P. Davis, J. L. Garnett, and R. G. Urquhart, *J. Polym. Sci., Polym. Symp.*, **55**, 287 (1976).
9. A. H. Reine, and J. C. Arthur, Jr., *Text. Res. J.*, **42**, 155 (1972).
10. S. Tazuke and H. Kimura, *Makromol. Chem.*, **179**, 2603 (1978).
11. G. Irick, Jr., and J. G. Pacifici, *Tetrahedron Lett.*, 1303 (1969).
12. J. C. Pacifici and G. Irick, Jr., *Tetrahedron Lett.*, 2207 (1969).
13. J. C. Pacifici, G. Irick, Jr., and C. G. Anderson, *J. Am. Chem. Soc.*, **91**, 5654 (1969).
14. P. D. Wildes, J. C. Pacifici, G. Irick, Jr., and D. G. Whitten, *J. Am. Chem. Soc.*, **93**, 2004 (1971).
15. H. Rau, *Ber. Bunsenges. Phys. Chem.*, **75**, 1343, 1347 (1971).
16. E. F. Ullman and N. Baumann, *J. Am. Chem. Soc.*, **92**, 5892 (1970).
17. I. R. Bellobono, L. Zanderighi, S. Omarini, B. Marcandalli, and C. Parini, *J. Chem. Soc. Perkin Trans. 2*, 1529 (1975).
18. I. R. Bellobono, E. Dubini Paglia, B. Marcandalli, and M. T. Cataldi, *Gazz. Chim. Ital.*, **109**, 697 (1979).

Received March 4, 1980

Accepted July 9, 1980