

Photochemical Grafting of Acrylated Azo Dyes onto Polymeric Surfaces. VII. Kinetics and Mechanism of Dye-Sensitized Photoinitiation of Some Diacrylates

IGNAZIO RENATO BELLOBONO, ELENA SELLI, and BRUNO MARCANDALLI, *Cattedra di Chimica, Department of Physical Chemistry and Electrochemistry, University of Milan, 20133 Milan, Italy*

Synopsis

Photoinitiated grafting and graft polymerization of liquid mixtures, adsorbed onto polypropylene, polycaprolactam, and poly(ethylene terephthalate) films, containing one of four acryloxy-substituted aromatic diazenes and one of four diacrylate comonomers, in the presence of 1,2-diphenyl-2,2-dimethoxyethanone as photoinitiator, were investigated kinetically at $30 \pm 2^\circ\text{C}$. Irradiation was carried out polychromatically, with impinging photoenergy from 2.1×10^{-8} to 20.5×10^{-8} einstein $\text{s}^{-1} \text{cm}^{-2}$; in some of the runs the ultraviolet radiation was filtered. The ratio R between the molar concentration of photoinitiator and the sum of concentrations of dye and diacrylate varied between 0.005 and 0.095; the ratio M between the molar concentration of dye and diacrylate varied between 0.005 and 0.046. The moles of dye and diacrylate n initially deposited per unit apparent polymeric surface S varied between 2 and $74 \mu\text{mol cm}^{-2}$.

No selective effect was shown by the presence of dyes in the comonomer mixture. The surface density of grafted molecules at the end of the grafting process was not affected by the photoinitiator concentration (for $0.030 < R < 0.095$), by diacrylate or dye concentrations, or by the kind of polymer substrate. This parameter, on the contrary, clearly depended on n/S , and linearly up to $n/S \cong 30 \mu\text{mol cm}^{-2}$. Quantum efficiencies for the two consecutive kinetic processes of grafting and graft polymerization (Φ_1 and Φ_2 , respectively) were evaluated. The dependency of Φ_1 on R , as well as of Φ_2 on n/S , are critically discussed on the basis of the proposed mechanism involving grafting of an oligomeric chain (Φ_1 values up to the order of 10^2) followed by a step-by-step graft polymerization (Φ_2 limiting values of the order of unity). The sensitizing effect of acryloxy-substituted aromatic diazenes on both Φ_1 and Φ_2 is evidenced.

INTRODUCTION

During the course of previous studies,¹⁻⁵ some model azo dyes have been functionalized for photochemical reactivity by introducing an acrylic group in a suitable part of the molecule, sufficiently isolated from the electronic system and the chromophores. With one or more of these dyes, self-sensitized grafting and graft polymerization onto polymeric surfaces have been investigated. The influence of the most relevant parameters that characterize these processes has been examined: (1) the form of contact between the dye and the substrate (crystalline dyes were adsorbed onto the surface by evaporation from volatile solutions^{1,2,4} or, alternatively, the substrate was irradiated while simply immersed in dye solutions^{2,3,5}); (2) monochromatic or polychromatic irradiation; (3) kind of polymer; and (4) dye concentration

(when working in solution) or mass of dye deposited per unit apparent surface (when working with crystalline dyes adsorbed on films or fibers). Self-sensitized grafting of acrylated dyes, however, occurs, in the absence of any added photoinitiator, with very low quantum yields. The effect of 1,2-diphenyl-2,2-dimethoxyethanone as photoinitiator on grafting and graft polymerization of acrylated azo dyes onto polypropylene and polycaprolactam fibers has also been systematically investigated⁶ by polychromatic irradiation. Mean quantum efficiencies for grafting Φ_1 and graft polymerization Φ_2 have been evaluated⁶ as a function of the ratio R between n/S (moles n per unit apparent surface S) of photoinitiator and the corresponding value of dye. Although Φ_2 values were practically unaffected by the presence of photoinitiator, Φ_1 values, on the contrary, were markedly influenced, with an acceleration factor of about 30 when R was of the order of 10. This latter behavior already approaches technologically acceptable levels of photochemical rates, when photografting onto polymers must be used as a practical method for modifying surface properties. It must at any rate be noted that, with increasing amounts of photoinitiator, several drawbacks are met, the most serious of which is a progressive buildup of radical species at $R > 0.1$ and a consequent variation of the reflectance spectrum of the grafted dye on the surface.⁶

In the present report, grafting and graft polymerization of the four acryloxy-substituted aromatic diazenes, previously employed as model molecules, were investigated polychromatically by adding to the system both photoinitiator and other commercial diacrylate monomers. The purpose has been that of obtaining mechanistic informations in a condensed viscous medium and, in the presence of a bifunctional monomer, of investigating the ability of this system to initiate surface grafting with high and technologically interesting quantum yields, as well as of examining the influence of dye sensitization specifically.

EXPERIMENTAL

Materials

Polycaprolactam bioriented commercial films 0.060 mm thick (BX, Tec-nopolimeri) were purified by Soxhlet extraction with 50% v/v cyclohexane-ethanol. Poly(ethylene terephthalate) and polypropylene films, 1 cm in diameter and approximately 0.20 mm thick, were prepared as described previously.⁵

3-Methyl-4-acryloxy-4'-phenylazoazobenzene³ (I), 4-(*N*-methyl-*N*-2-acryloxyethyl)amino-2',6'-dichloro-4'-nitroazobenzene³ (II), 2-[2'-methyl-4'-(*N*-ethyl-*N*-2-acryloxyethyl)aminophenylazo]-5-nitrothiazole³ (III), and 4-(*N*-ethyl-*N*-2-acryloxyethyl)amino-4'-nitroazobenzene¹ (IV) were prepared and purified as indicated in preceding papers. Structural formulas and spectroscopic data of acryloxy-substituted aromatic diazenes I-IV are reported in previous works of this series.^{3,5,6}

1,4-Butanediol diacrylate (V) and 1,6-hexanediol diacrylate (VI) (Union Chimique Belge), as well as diethyleneglycol diacrylate (VII), tetraethyleneglycol diacrylate (VIII) (Sartomer), and 1,2-diphenyl-2,2-dimethoxyethan-

one (IX) (Fratelli Lamberti), were commercial products. They were used as received without further treatment or purification.

Reagent-grade acetone was purified by sodium hydroxide and potassium permanganate following the literature method⁷ and successively anhydri-fied by refluxing and rectification over sodium under a nitrogen stream.

Apparatus and Grafting Kinetics

A solution in anhydrous acetone (0.037–0.100 mL) containing 0.0021–0.0650 M of dyes I–IV, 0.042–2.15 M of comonomers V–VIII, and photo-initiator IX in a ratio R of its molar concentration with respect to the sum of molar concentrations of dye and diacrylate comonomers varying between 0.005 and 0.095, was uniformly deposited by a standard procedure making use of a microsyringe dispenser on $1.00 \times 3.00 \text{ cm}^2$ or 1.0-cm diameter film specimens previously weighed, and the solvent was evaporated at room temperature in the dark in a desiccator under vacuum. Irradiations were effected with a 2000-W high-pressure mercury arc lamp (Hanovia). This latter, fitted with a reflector of semielliptical cross section, was placed in a suitable housing, where the distance from the irradiated samples could be regulated in such a way as to have an overall impinging photoenergy from $(2.1 \pm 0.2) \times 10^{-8}$ to $(20.5 \pm 0.8) \times 10^{-8}$ einstein $\text{s}^{-1} \text{ cm}^{-2}$. Potassium ferrioxalate was used for actinometry according to the method of Hatchard and Parker.⁸ In some of the runs, the ultraviolet portion of the irradiating lamp was eliminated by a filter, removing 99% of the impinging energy at wavelengths shorter than 390 nm, where absorption by photoinitiator IX began to occur. Quantum yields were always corrected for unabsorbed energy.

The system was placed inside a cooled glove box, and oxygen was excluded by a stream of purified nitrogen (oxygen content < 0.3 ppm). The temperature of the reaction system increased to about 30°C during irradiation. No dark reaction was observed at this temperature for the exposure times used. After the desired irradiation time, the sample was Soxhlet extracted with acetone, which was able to remove efficiently nonreacted monomers and ungrafted homo- and copolymers.

Graft yields as a function of time were obtained by two kinds of analysis: (1) the ratio between grafted dye and that initially present on the surface was obtained by adsorption spectrophotometry of the acetone solution after Soxhlet extraction (a Varian DMS-90 Plus spectrophotometer was employed); (2) the weight of extracted specimen, by difference with respect to the initial one (both measured after prior desiccation under vacuum followed by 24 h conditioning of the sample at 20°C and 60% relative humidity), allowed us to calculate overall graft yields.

RESULTS AND DISCUSSION

Photochemical grafting and graft polymerization of viscous liquid mixtures adsorbed onto polycaprolactam, polypropylene, and poly(ethylene terephthalate) films containing one of the acrylated dyes I–IV and one of the comonomers V–VIII, in the presence of photoinitiator IX, were investigated kinetically at $30 \pm 2^\circ\text{C}$. Irradiation was carried out polychromatically over the whole lamp spectrum or over its visible and near-infrared portion alone,

with impinging photoenergy from $(2.1 \pm 0.2) \times 10^{-8}$ to $(20.5 \pm 0.8) \times 10^{-8}$ einstein $\text{s}^{-1} \text{cm}^{-2}$. The ratio R between the molar concentration of photoinitiator IX in the acrylic monomer mixture and the sum of concentrations of dye and diacrylate monomer was varied between 0.005 and 0.095. The ratio M between the molar concentrations of dyes I–IV and diacrylate comonomers V–VIII was varied between 0.005 and 0.046, with an overall n/S value (moles of dye and diacrylate monomer, n , initially deposited per unit apparent surface S) from 2.0 to $74 \mu\text{mol cm}^{-2}$.

One typical graft yield curve is shown in Fig. 1. The kinetic behavior of all systems under consideration was qualitatively similar to that observed in previous studies^{1–6}; quantitative differences, however, were noted in the present investigation. As Fig. 1 illustrates, an initial constant rate process (grafting) took place, which was the only process observed for $n/S \lesssim 30 \mu\text{mol cm}^{-2}$. With $n/S \gtrsim 30 \mu\text{mol cm}^{-2}$, a very brief induction period followed, which sometimes could not even be remarked experimentally, and finally, a second constant rate process (graft polymerization) was evidenced, up to high graft yields, which was nearly quantitative with respect to the amounts of acrylated monomers present.

Quantum yields $\Phi_{1,2}$ of grafting and graft polymerization were calculated from kinetic curves following the method described in preceding papers.^{1–6}

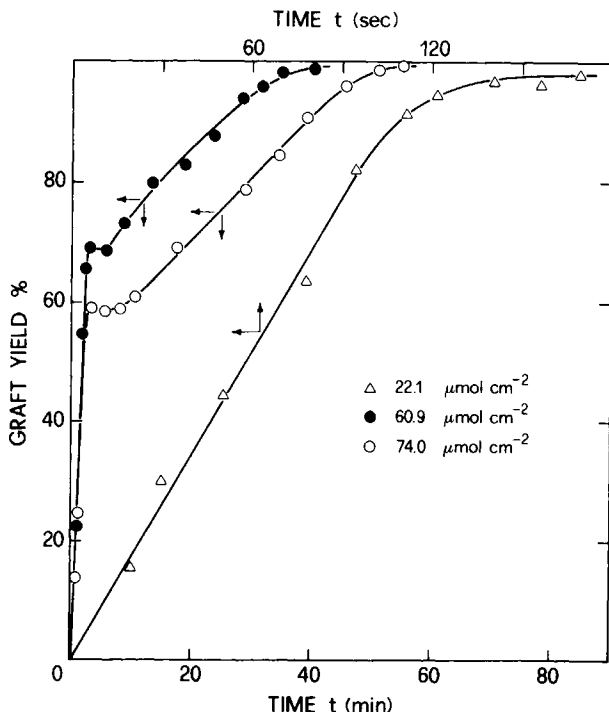


Fig. 1. Some examples of the influence of n/S ($\mu\text{mol cm}^{-2}$), overall moles n of comonomers deposited per unit apparent surface S of polypropylene film, on percentage graft yield as a function of irradiation time t , for 1,6-hexanediol diacrylate (VI) and dye IV, with M (molar ratio between photoinitiator IX and comonomers) = 0.042, at constant irradiation flux (whole lamp spectrum) of $(18.2 \pm 0.7) \times 10^{-8}$ einstein $\text{s}^{-1} \text{cm}^{-2}$.

The surface density of grafted molecules at the end of the first constant rate period is an important parameter in the interpretation of graft yield kinetic curves⁶; in Fig. 2 data relative to different experimental systems are reported as percentage graft yield at the end of the first constant rate period and plotted as a function of initial n/S values. The following facts could be easily observed.

1. For n/S initial values $\leq 30 \mu\text{mol cm}^{-2}$, a graft yield $\geq 95\%$ was reached by grafting; this is the reason that the second constant rate process was not noticed in these cases (see Fig. 1).

2. No influence of photoinitiator concentration in the range of R values between 0.030 and 0.095 could be detected.

3. No effect appeared to be brought about on this parameter either by the difference between the various diacrylate monomers V–VIII or by that between these latter and acrylated dyes I–IV.

4. No influence by the polymer substrate on these values could be determined outside the experimental uncertainty.

The influence of photoinitiator, expressed as R ratio, on said parameter, for $R \leq 0.030$, is illustrated in Fig. 3 at various initial n/S values: a plateau was reached at $R \approx 0.030$ and maintained up to the highest value of R investigated in this work.

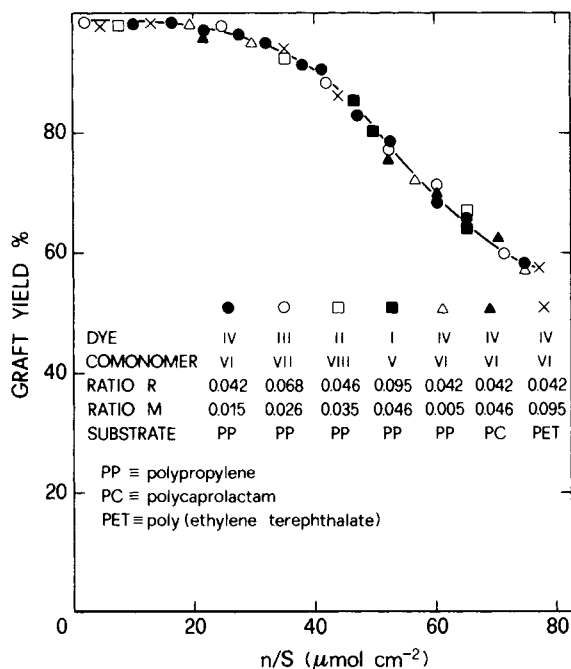


Fig. 2. Some examples of percentage graft yield, measured at the end of the first constant rate period, as a function of n/S ($\mu\text{mol cm}^{-2}$), overall moles of comonomers deposited per unit apparent surface, onto various polymer films for dyes I–IV and diacrylates V–VIII at various values of R (ratio between molar concentrations of photoinitiator IX and comonomers) and of M (ratio between molar concentration of dye and that of diacrylate monomer) and various values of irradiating flux (whole lamp spectrum) ranging between 2.1×10^{-8} and 20.5×10^{-8} einstein $\text{s}^{-1} \text{cm}^{-2}$.

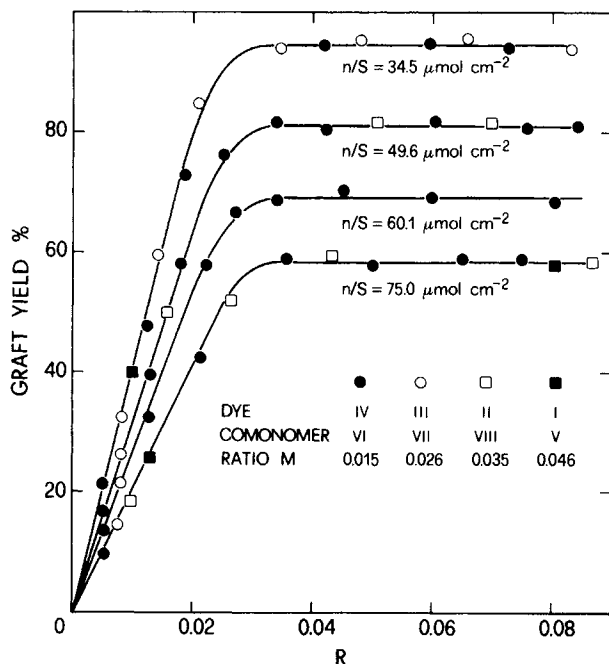


Fig. 3. Some examples of the influence of R , the ratio between the molar concentration of photoinitiator IX and that of overall comonomers, on percentage graft yield, measured at the end of the first constant rate period, onto polypropylene, at various initial n/S values. Irradiation flux (whole lamp spectrum): 20.5×10^{-8} einstein $s^{-1} cm^{-2}$.

The surface density of grafted molecules at the end of the first constant rate period, expressed as grafted moles per unit apparent surface, is reported in Fig. 4 as a function of n/S values in four different experimental conditions. The dependency is fairly linear and corresponds to a nearly quantitative graft yield with respect to the amounts of monomer present up to initial n/S values of about $30 \mu mol cm^{-2}$, after which a smooth curvature follows. In the same figure, the graph relative to the same kind of plot for dye IV alone, without any photoinitiator or comonomer, taken from a previous paper,¹ is reported as a dotted line. Quantitative differences between self-sensitized photografting of dye alone and the effects brought about by photoinitiator and diacrylate comonomer may be easily pointed out.

The $\Phi_{1,2}$ values obtained from experimental data relative to absorbance analysis of dyes I–IV, following method 1 (see Experimental) resulted in the same ratio as M with respect to values determined on the basis of gravimetric analysis of grafted or graft-polymerized block copolymer (method 2). This confirms that the dyes investigated, at least within the range of M values tested, act as “tracers” for analytic determinations and behave as an ideal system during photografting and copolymerization, without any selective effect of their presence in the comonomer mixture.⁹

No effect of concentration quenching like that observed in dilute solution⁵ could be detected on Φ_1 , probably as a consequence of the low diffusion-controlled rate constant, due to the relatively high viscosity of the photochemically reacting system, as well as by reason of the very high Φ_1 values.

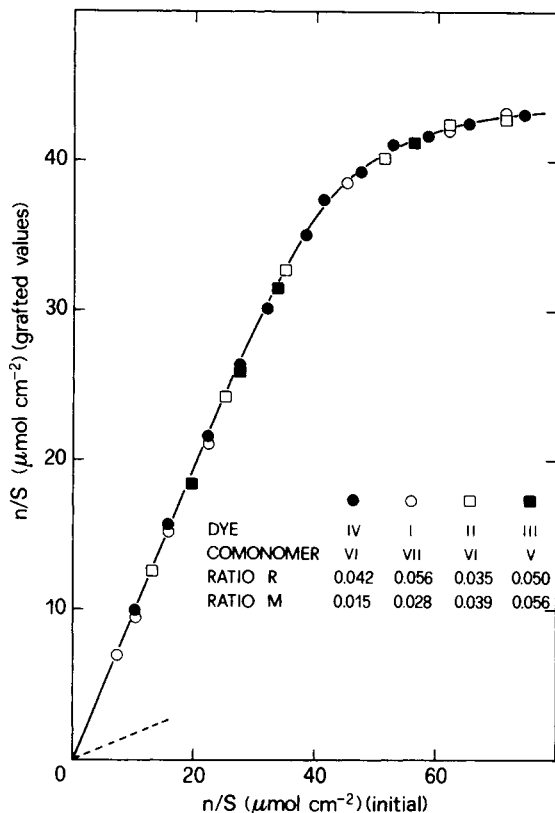


Fig. 4. Some examples of grafted values of n/S , moles per unit apparent surface of polypropylene film, at the end of the first constant rate period, as a function of initial n/S values of overall comonomers deposited onto the polymer surface, at various values of R and M , and irradiation flux (whole lamp spectrum) ranging from 2.1×10^{-8} to 20.5×10^{-8} einstein $s^{-1} cm^{-2}$. For explanation of dotted line see text.

The Φ_1 values were markedly influenced by the concentration of photoinitiator. Linear regression analysis was applied to experimental data, following eq. (1):

$$\Phi_1 = \Phi_1^0 + mR \quad (1)$$

where Φ_1^0 is the quantum yield of block copolymer in the absence of photoinitiator. The ratio between slope m and Φ_1^0 is independent of both the kind of polymer substrate and the molecular structure of both acrylated dyes I–IV and diacrylate monomers V–VIII, provided R values exceed ≈ 0.030 (plateau of plots such as those of Fig. 3). The acceleration factor, expressed as the ratio of m to Φ_1^0 , is $(1.2 \pm 0.2) \times 10^4$; Φ_1^0 values reflect the slight influence of dyes and polymer substrates and coincide within the limits of experimental uncertainty with quantum yields extrapolated to zero concentration by Stern-Volmer plots in N,N -dimethylformamide solution, with the same dyes and substrates.⁵

Comparing Φ_1^0 values measured in the absence of photoinitiator IX and the corresponding Φ_1 , the very marked increase in quantum yields due to photoinitiation is evidenced. For example, for dye IV and 1,6-hexanediol diacrylate as comonomer, with $R = 0.005$, a grafting yield of 72 ± 7 molecules of comonomer per quantum may be reached on poly(ethylene terephthalate) film, corresponding to about this mean number of monomer units in the block copolymer obtained per quantum until the end of the first constant rate period.

A sensible fraction of these quantum yields (from 14 to 20%) results from dye sensitization: when polychromatic irradiation was effected in the presence of photoinitiator but at wavelengths at which its direct electronic excitation was not possible, a corresponding reduction of Φ_1^0 values is observed and the m/Φ_1^0 value remains constant.

The Φ_2 values, on the contrary, were independent of the relative concentration of IX, as measured by R ratio. They were equally insensitive to the different dyes examined but slightly sensitive to the small differences in chemical structure of diacrylate monomers V–VIII. The more noticeable dependency of Φ_2 on initial overall n/S values of the comonomer mixture results in a good correlation between Φ_2^{-1} and n/S [eq. (2)].

$$\Phi_2^{-1} = a + b \frac{n}{S} \quad (2)$$

The values of b parameter, $(5.3 \pm 0.4) \times 10^3$, $(5.8 \pm 0.5) \times 10^3$, $(4.2 \pm 0.3) \times 10^3$, and $(5.1 \pm 0.4) \times 10^3$ quantum molecule⁻¹ mol⁻¹ cm², for diacrylates V–VIII, respectively, are substantially the same for both dye sensitization and direct photoinitiation by IX. Here again, a not negligible portion of Φ_2 (from 15 to 20%) appears to derive from a dye-sensitized process, as expressed by the relative values of parameter a (0.97 ± 0.09 and 5.9 ± 0.9 quantum molecule⁻¹ for polychromatic irradiation over the whole lamp spectrum and at wavelengths longer than 390 nm, respectively).

CONCLUSIONS

All kinetic parameters measured in the present work qualitatively confirm the reaction scheme previously proposed.^{1,6} Some mechanistic details, however, are further elucidated.

The primary photochemical event presumably consists of a dye-sensitized and/or photoinitiator radical-induced hydrogen abstraction from the reactive sites of the polymer surface. Photochemically produced radical fragments from initiator,¹⁰ moreover, initiate polymerization in the homogeneous phase formed by comonomers.

The grafting mechanism (first constant rate period of Fig. 1), may proceed following two parallel reaction pathways: (1) grafting of a "monomolecular layer" of acrylated monomer and (2) grafting of an oligomolecular layer of block copolymer formed either by photoinitiated or by dye-sensitized copolymerization. In the experimental conditions of the present study, the very high values of Φ_1 yields and their strong dependency on R suggest that the prevailing reaction should be grafting of growing oligomeric chains onto the substrate.

During the second constant rate period the most probable mechanism is a step-by-step polymerization on the first grafted layer. The limiting unitary value of Φ_2 when $n/S \rightarrow 0$ [eq. (2), with $\alpha = 0.97 \pm 0.09$ quantum molecule⁻¹] suggests that the reaction leading to chain termination should be a monomolecular process. Chain propagation by radical transfer, requiring $\Phi_2 > 1$, would not be favored.

Finally, the values of Φ_2 , which are much lower than those of Φ_1 , allow one to detect experimentally a small quenching effect of the Stern-Volmer type, as expressed by eq. (2), which is consistent with lifetimes of intermediate excited states measured in dye solution,^{2,3} if the medium effect is accounted for.

References

1. I. R. Bellobono, F. Tolusso, E. Selli, S. Calgari, and A. Berlin, *J. Appl. Polym. Sci.*, **26**, 619 (1981).
2. E. Selli, I. R. Bellobono, F. Tolusso, and S. Calgari, *Ann. Chim. (Rome)*, **71**, 147 (1981).
3. E. Selli, I. R. Bellobono, S. Calgari, and A. Berlin, *J. Soc. Dyers Colour.*, **97**, 438 (1981).
4. I. R. Bellobono, S. Calgari, M. C. Leonardi, E. Selli, and E. Dubini Paglia, *Angew. Makromol. Chem.*, **100**, 135 (1981).
5. S. Calgari, E. Selli, and I. R. Bellobono, *J. Appl. Polym. Sci.*, **27**, 527 (1982).
6. I. R. Bellobono, S. Calgari, and E. Selli, in *Polymer Additives, Polymer Science and Technology*, Vol. 26, J. E. Kresta, Ed., Plenum Press, New York, 1984, p. 83.
7. J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924).
8. C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).
9. I. R. Bellobono, B. Marcandalli, E. Selli, D. Comi, and L. Righetto, *Polym. Photochem.*, **6**, 339 (1985).
10. A. Borer, R. Kirchmayr, and G. Rist, *Helv. Chim. Acta*, **61**, 305 (1978).