Photochemical Grafting of Acrylated Azo Dyes onto Polymeric Surfaces. V. Grafting of Some Acryloxy-Substituted Aromatic Diazenes as Model Molecules onto Polypropylene, Polycaprolactam, and Poly(ethylene Terephthalate) Films

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Synopsis

Photochemically induced grafting (1) and graft polymerization (2) from N,N-dimethylformamide solutions of four acryloxy-substituted aromatic diazenes, chosen as model molecules of acryloxy azo dyes, were investigated kinetically at 25°C onto polypropylene, polycaprolactam, and poly-(ethylene terephthalate) films, by polychromatic irradiations. Quantum efficiencies at zero concentration of dyes and lifetimes of excited states for processes (1) and (2) were evaluated from experimental data by Stern–Volmer plots. The surface density of grafted molecules at the end of process (1) was not affected by the concentration of dyes in solution, but varied sensibly with the chemical nature of polymers and dyes. The relevant parameters are discussed on the basis of the proposed mechanism.

INTRODUCTION

Photochemically induced grafting and graft polymerization of 4-(N-ethyl,N-2-acryloxyethyl)amino-4'-nitro-azobenzene, chosen as model molecule of an acrylated azo dye, brought into contact in its crystalline state with polyamide and polypropylene fibers[1,2] as well as with cellulose[3] by evaporation of solvent from monomer solutions, had been investigated kinetically by polychromatic[1,3] or monochromatic[2] irradiation in previous works. Some experiments had also been effected in n-hexane solution of the monomer dye.[2] Systematic kinetic measurements of grafting and graft polymerization were then carried out[4] from N,N-dimethylformamide solutions of four acryloxy-substituted aromatic diazenes onto polypropylene fibers by monochromatic irradiation at various wavelengths. The influence of dye concentration could thus be investigated and quantum efficiencies at zero concentration of dyes, as well as lifetimes of both grafting and graft polymerization processes, evaluated by means of Stern–Volmer plots. The marked influence of wavelength and the constancy of the relatively long lifetimes, for each dye, at the various wavelengths investigated[2,4] allowed a fairly detailed photochemical analysis of the processes, consistent with reactive triplet intermediates of the dyes formed from the states populated by light absorption.

In the present report, grafting and graft polymerization of the model molecules from N,N-dimethylformamide solutions onto some polymer films were inves-

tigated polychromatically, with the purpose of obtaining more information about some features of the process,[1] such as the influence of the chemical nature of the substrate on the rate of grafting, the effect of dye and substrate on the density of grafted molecules, as well as the effect of dye concentration on this surface density of molecules.

EXPERIMENTAL

Materials

Polycaprolactam bioriented commercial films 0.060 mm thick (BX, Snia Viscosa) were purified by Soxhlet extraction with 50% v/v cyclohexane–ethanol. Poly(ethylene terephthalate) (WSL, Snia Viscosa) and polypropylene (Shell) films, 1 cm in diameter and approximately 0.20 mm thick, were prepared by placing 50 mg polymer, completely free from additives, in a continuously evacuated, nitrogen-purged die and compressing to about 15 tons/cm^2 for 5 min in a Perkin–Elmer hydraulic press. Films prepared in this way were opaque.

3-Methyl-4-acryloxy-4'-phenylazoazobenzene[4] (I), 4-(N-methyl-N-2-acryloxyethyl)amino-2',6'-dichloro-4'-nitroazobenzene[4] (II), 2-[2'-methyl-4'-(N-ethyl-N-2-acryloxyethyl)aminophenylazo]-5-nitrothiazole[4] (III), and 4-(N-ethyl-N-2-acryloxyethyl)amino-4'-nitroazobenzene[1] (IV) were prepared and purified as described previously.

I

II

III

IV
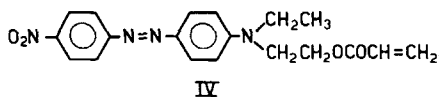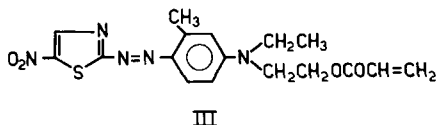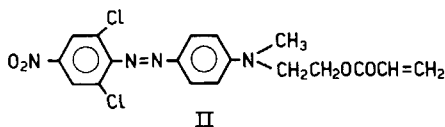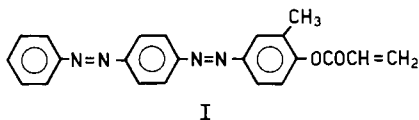
Spectrograde N,N-dimethylformamide (DMF) as solvent for dyes I–IV was used without further purification.

Apparatus and Grafting Procedure

Kinetic investigations of the grafting processes were carried out at various dye concentrations with 1.0×3.0 cm^2 or 1.0 cm-diameter film specimens immersed in 7.8×10^{-7}–$6.5 \times 10^{-5}M$ solutions of acrylated dyes I–IV in DMF. Irradiations were effected with a 500-W high-pressure mercury arc lamp (Italquartz). This latter, fitted with a reflector of semielliptical cross section, was placed in a suitable housing inside a glovebox, and oxygen was excluded by a stream of purified nitrogen (oxygen content < 0.3 ppm). Nitrogen bubbling was also used to deoxygenate solvent when preparing DMF solutions of acrylated dyes.

The film specimen was held on one of the parallel faces of a spectrophotometric quartz cell, immersed in the DMF solution of dye, and irradiated through the solution. The reaction system was thermostatted at 25°C during irradiation. No dark reaction was observed at this temperature for the exposure times used. The distance of the irradiated samples from the lamp could be regulated in such a way as to have an overall impinging photoenergy of 80 ± 2.5, 54 ± 1.8, or 35 ± 1.1 mW/cm^2. Potassium ferrioxalate was used for actinometry according to the method of Hatchard and Parker.[5] Quantum yields were always corrected for unabsorbed energy.

Graft yields as a function of time were obtained as the ratio between grafted dye and that initially present in DMF solution. The former was calculated on the basis of decrease of concentration of the dye in DMF solution, as obtained by spectrophotometric analysis. In some of the runs, it was verified that the graft yields obtained this way were substantially coincident with those obtained by reflectance analysis of the grafted films, within the range of experimental uncertainty.

RESULTS AND DISCUSSION

Grafting and graft polymerization of acrylated azo dyes I–IV from 7.8×10^{-7}–$6.5 \times 10^{-5}M$ DMF solutions onto polypropylene, polycaprolactam, and poly(ethylene terephthalate) films were investigated kinetically at 25°C by polychromatic irradiation at 80, 54, and 35 mW/cm^2. The kinetic behavior of the systems under consideration was qualitatively similar to that which was observed,[1] in the absence of any solvent, when polyamide and polypropylene ribbons were irradiated under a thin layer of acrylated dye IV brought into intimate contact with the substrate in the solid state. Kinetic curves such as those illustrated in Figures 2 and 3 of Ref. 1 were obtained. An initial constant-rate process (grafting) with quantum yield Φ_1 dependent on the nature of the polymer film, as well as on dye concentration, was observed. This was followed by a brief induction period, the duration of which generally increased with increasing concentration of dye in DMF solution, and was slightly longer for polypropylene than for polycaprolactam films and fairly shorter for polyester films. Finally, a second constant-rate process (graft polymerization) was observed, with quantum yield Φ_2; this was practically independent of the nature of the polymer but markedly influenced by dye concentration.

In the preceding experiments,[1,2,4] the two constant-rate periods could be interpreted by the photochemical rate equation

$$\frac{1}{S}\frac{dn}{dt} = \Phi I \tag{1}$$

where S (cm^2) is the apparent surface of the polymer film, n is the number of moles of dye present in the solution at time t (s), Φ (mol/einstein) is the mean polychromatic quantum yield of the pertinent process, and I is the radiation intensity effectively absorbed by the sample (einstein/s·cm^2). Within each constant-rate period, the left-hand side of eq. (1), at the various values of impinging radiation flux, could be evaluated by linear regression analysis of the experimental data. Quantum yields $(\Phi)_{1,2}$, where the suffixes refer to the grafting (1) or graft polymerization (2) processes at dye concentration c (mol/L), could thus be evaluated.

From the sets of kinetic experiments carried out at the various concentrations of the acrylated dyes I–IV, the effect of concentration quenching could then be allowed for by means of the Stern–Volmer[6] equation:

$$\frac{1}{(\Phi)_{1,2}} = \frac{1}{(\Phi_0)_{1,2}} (1 + k_q \tau c) \qquad (2)$$

where $(\Phi_0)_{1,2}$ is the quantum yield extrapolated to zero concentration; k_q is the quenching rate constant, which was assumed to be equal to the diffusion controlled rate constant in DMF[4]; and τ is the lifetime of excited states. Equation (2) accounted for experimental quantum yields as a function of dye concentration quite satisfactorily, as can be seen from Figures 1 and 2, where all $(\Phi)_{1,2}$ values for the acrylated dyes I–IV, relatively to the three polymer films investigated, are shown in the form of Stern–Volmer plots.

The $(\Phi_0)_1$ and τ_1 as well as the $(\Phi_0)_2$ and τ_2 values obtained by linear regression analysis from eq. (2) applied to experimental data are reported in Table I. It may be easily observed that lifetimes τ_1 and τ_2 of excited states are independent

Fig. 1. Stern–Volmer plots, eq. (2), relative to experimental quantum yields for grafting (Φ_1) and graft polymerization (Φ_2) of acrylated dyes I and II onto polypropylene (●), polycaprolactam (○), and poly(ethylene terephthalate) (△) films from DMF solutions at 25°C.
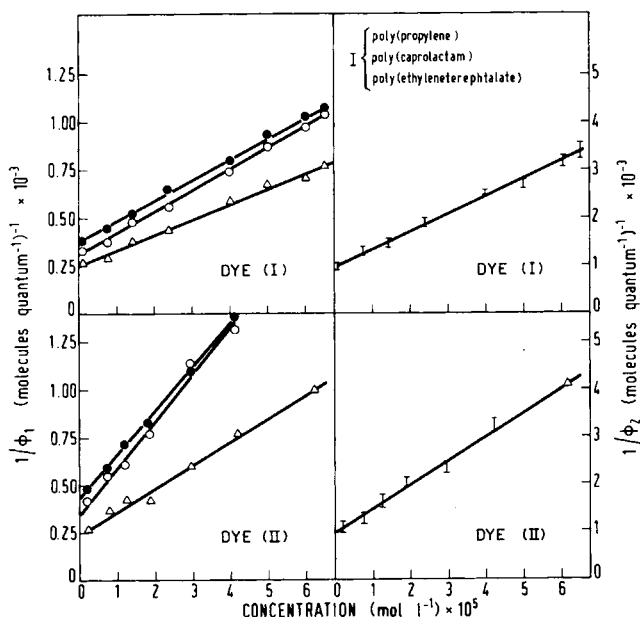
Fig. 2. Stern–Volmer plots, eq. (2), relative to experimental quantum yields for grafting (Φ_1) and graft polymerization (Φ_2) of acrylated dyes III and IV onto polypropylene (●), polycaprolactam (○), and poly(ethylene terephthalate) (△) films from DMF solutions at 25°C.
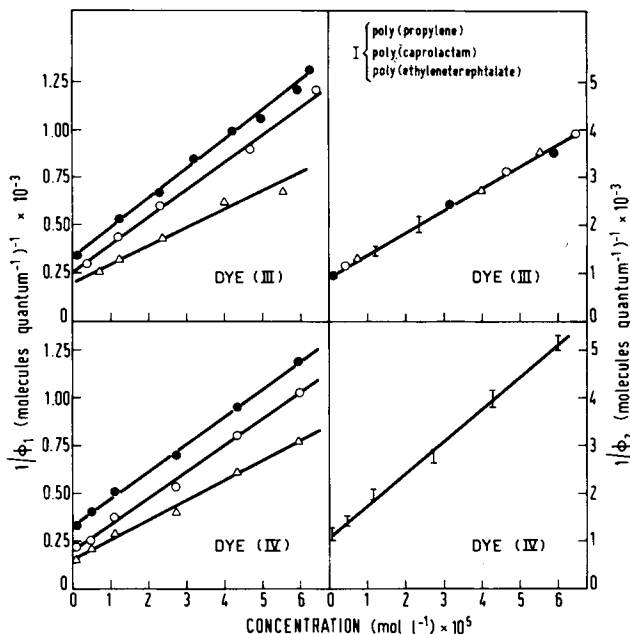
on the polymer substrate and substantially coincide, within the limits of experimental uncertainty, for the two processes of grafting and graft polymerization, varying only with the molecular structure of the investigated dyes. Quantum

TABLE I

Quantum Yields $(\Phi_0)_1$ and $(\Phi_0)_2$ Extrapolated by Stern–Volmer Plots at Zero Concentration in N,N-Dimethylformamide and Lifetimes, τ_1 and τ_2 for Photochemical Grafting (1) and Graft Polymerization (2) Onto Polymer Films by Polychromatic Irradiation at 25°C

Polymer film	$(\Phi_0)_1 \times 10^3$ molecules/ quantum	$\tau_1 \times 10^6$, s	$(\Phi_0)_2 \times 10^3$ molecules/ quantum	$\tau_2 \times 10^6$, s
		Dye I		
Polypropylene	2.6 ± 0.3[a]	4.3 ± 0.4[a]	0.98 ± 0.07[a]	4.1 ± 0.4[a]
Polycaprolactam	3.2 ± 0.3	4.5 ± 0.4	0.94 ± 0.05	4.2 ± 0.5
Poly(ethylene terephthalate)	4.0 ± 0.4	3.9 ± 0.5	0.96 ± 0.08	4.3 ± 0.4
		Dye II		
Polypropylene	2.3 ± 0.3	6.4 ± 0.6	0.95 ± 0.06	6.1 ± 0.5
Polycaprolactam	2.9 ± 0.3	6.3 ± 0.5	0.91 ± 0.08	6.0 ± 0.6
Poly(ethylene terephthalate)	4.2 ± 0.3	6.2 ± 0.6	1.0 ± 0.1	6.5 ± 0.5
		Dye III		
Polypropylene	3.1 ± 0.3	5.8 ± 0.5	1.3 ± 0.1	6.2 ± 0.7
Polycaprolactam	3.9 ± 0.3	6.3 ± 0.7	1.1 ± 0.1	5.9 ± 0.6
Poly(ethylene terephthalate)	5.2 ± 0.4	6.1 ± 0.6	1.2 ± 0.1	6.4 ± 0.7
		Dye IV		
Polypropylene	3.8 ± 0.3	7.3 ± 0.8	0.86 ± 0.04	7.6 ± 0.7
Polycaprolactam	4.9 ± 0.4	8.1 ± 0.9	0.90 ± 0.06	7.7 ± 0.8
Poly(ethylene terephthalate)	6.3 ± 0.5	7.8 ± 0.8	0.93 ± 0.08	7.4 ± 0.6

[a] Uncertainties are probable errors of extrapolated values.

yields of grafting $(\Phi_0)_1$ clearly reflect a slight influence by the dye and polymer structure. As to the first, the presence of strong electron withdrawing groups in the para position with respect to the dialkylamino group and the absence of any steric hindrance are presumably favorable factors for increasing the quantum yield $(\Phi_0)_1$. The small number of model molecules investigated in this study, however, which do not offer the possibility of rationalizing systematically substituent effects, does not offer conclusive evidence from this point of view. The influence of the chemical nature of the polymer seems more soundly confirmed in the order of increasing effect on Φ_1: polypropylene < polycaprolactam < poly(ethylene terephthalate). Quantum yields of graft polymerization $(\Phi_0)_2$, on the contrary, are independent of the nature of the polymer, but probably show a very slight influence of chemical constitution, which only in the acrylated dye III does not appear to be masked by the experimental uncertainty and the low $(\Phi_0)_2$ values. Anyway, due to the isolation of the substituents from the reaction center involved in photochemical reactions, a marked influence of electronic effects in molecules I–IV should not be expected.

Notwithstanding some limitations of the model molecules, their general behavior is completely consistent with the proposed mechanism[1] and particularly with the suggestion that both grafting and graft polymerization proceed exclusively through hydrogen abstraction by upper excited triplet states of the dye,[4] in the former process hydrogen abstraction from the polymer surface, and in the latter predominantly from the first grafted layer.

Further evidence along this line stems from considerations regarding the surface density of grafted molecules at the end of the first constant-rate period of the photochemical treatment. In a previous study[1] of grafting of dye IV from its crystalline phase appropriately deposited on fiber surface, it was found that surface density was growing with the initial mass of dye deposited per unit surface at a rate of about 10 molecules/Å$^2\cdot(\mu$mol/cm^2). This rate of growth, reflecting the oligomeric fraction of the first grafted layer, was independent on the chemical nature of the substrate. The values of surface density extrapolated at $n/S \rightarrow$ 0 were 3.8 and 2.7 molecules/Å^2 (apparent surface) for polypropylene and polyamide, respectively.

Surface densities of grafted molecules from dye solutions at the end of the first (grafting) period experimentally evaluated by kinetic runs in the present work are reported in Table II. Dye concentration seems to have no effect on this molecular coverage of the bare film surface. This marked difference of behavior with respect to grafting from a solid phase may be well explained by considering the "concentration" differences in the two cases. The contribution of oligomers

TABLE II
Grafted Molecules of Acrylated Dyes I–IV per Unit Apparent Area at End of First Constant-Rate Period onto Polymer Films

Polymer film	Grafted dye, molecules/100 Å^2			
	Dye I	Dye II	Dye III	Dye IV
Polypropylene	1.9 ± 0.3[a]	1.8 ± 0.3[a]	2.3 ± 0.5[a]	1.2 ± 0.3[a]
Polycaprolactam	3.1 ± 0.5	3.0 ± 0.4	4.4 ± 0.7	1.8 ± 0.3
Poly(ethylene terephthalate)	4.2 ± 0.6	3.9 ± 0.4	6.0 ± 0.8	2.3 ± 0.3

[a] Uncertainties are standard deviations of experimental values obtained at various concentrations and radiation fluxes tested in kinetic runs.

in the first grafted layer, when grafting is effected from solution, must then be completely negligible, and a truly "monomolecular" layer should be obtained initially on the polymer surface. The low values of surface density reported in Table II, and the very scant grafting probability of an oligomeric chain growing in dilute DMF solution of dye other than in the immediate vicinity of the polymer surface, speak in favor of this interpretation.

Values of first coverage from solutions on films should be comparable with those extrapolated from solid dye on fibers,[1] provided the difference between apparent and real surface areas is accounted for in both cases. A preliminary observation is that extrapolated values at $n/S \rightarrow 0$ on fibers reflect the difference between real and apparent surface of the ribbon specimens, due to the different geometric characteristics (at constant apparent surface) of the polypropylene and polyamide fabrics employed, besides, obviously, the physicochemical characteristics of the two fiber polymers. Consequently, experimental values on fibers represent the sum of these two kinds of effects (geometric and physicochemical). In experiments on films, on the contrary, geometric effects being substantially constant, the initial surface coverage by photochemical grafting should, at least at a first approximation, parallel fairly well the physicochemical properties of the tested polymer materials. For polyamide and polyester polymers it is thus quite reasonable to obtain (see Table II) initial surface coverage values sensibly higher than those for polypropylene, for all dyes examined, even with a susceptibility due to the chemical constitution of the dye molecules. We can therefore conclude that the inversion of this tendency on polyamide and polypropylene fibers[1] was preponderantly due to the different microgeometries of the tested specimens of the woven fabrics.

From these studies, finally, a satisfactorily clear portrait results. On one side, quantum yield measurements by polychromatic or monochromatic irradiation afford detailed information about rate of processes and the relevant parameters which affect them, such as concentration and solvent properties. These kinetic data prove extremely useful both for a mechanistic interpretation of the photochemical process[2,4] and for its practical applications. On the other side, quantitative information about the photochemical initial surface coverage provides an idea of the reactive sites available as well as of the molecular characteristics of the first grafted layer, by some sort of "pseudostationary state" approach to the problem.

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