Summary

tert-Butyl peresters based on aromatic hydrocarbon and aryl ketone chromophores with lowest lying π–π^* transitions have been synthesized and tested as photoinitiators in radical processes. The systems designed are of varying efficacy, with the nonketonic systems serving as better initiators with higher concentrations of aromatic monomers such as styrene.

Acknowledgment. This work has been supported by the National Science Foundation, DMR 8103100. We are most grateful for this support. The authors also acknowledge many helpful discussions with Professor Satyendra Gupta.

Registry No. **1**, 88475-85-8; **2**, 88475-86-9; **3**, 88475-87-0; **4**, 88475-88-1; **5**, 88475-89-2; 4-(bromomethyl)benzoyl chloride, 52780-16-2; pyrene, 129-00-0; 4-carbomethoxybenzoyl chloride, 7377-26-6; 4-[(1-pyrenyl)carbonyl]benzoic acid, methyl ester, 88475-90-5; 4-[(1-pyrenyl)carbonyl]benzoic acid, 88475-91-6; pyrene-1-carboxylic acid, 19694-02-1; 4-carboxyfluorenone, 6223-83-2; anthracene-9-carboxylic acid, 723-62-6; styrene, 100-42-5; polystyrene, 9003-53-6; MMA, 80-62-6; poly(MMA), 9011-14-7.

References and Notes

(1) I. I. Abu-Abdoun, L. Thijs, and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(2) L. Thijs, S. N. Gupta, and D. C. Neckers, *J. Org. Chem.*, **44**, 4123 (1979).
(3) I. Gupta, S. Gupta, and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 147 (1982).
(4) F. C. De Schryver in "Reactivity, Mechanism and Structure in Polymer Chemistry", Chapter 14, A. D. Jenkins and A. Ledwith, Eds., Wiley, New York, 1974.
(5) D. L. Tuleen and B. A. Hess, *J. Chem. Educ.*, **40**, 476 (1971).
(6) L. Thijs and D. C. Neckers, unpublished results.
(7) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", Macmillan, New York, 1964.
(8) C. Buchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).
(9) S. Gupta, I. Gupta, and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 103 (1981).
(10) D. O. Cowen and W. Schmiegel, *J. Am. Chem. Soc.*, **94**, 6779 (1972).
(11) S. Tazuke and F. Banba, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2463 (1976).
(12) F. C. De Schryver, *Pure Appl. Chem.*, **34**, 213 (1973).

Photolysis of Poly(acrylic acid) Containing an Aryl Ketone Chromophore

Yves Merle,*,[†] Liliane Merle-Aubry,[†] and James E. Guillet

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.
Received March 4, 1983

ABSTRACT: The synthesis of a copolymer of phenyl isopropenyl ketone and acrylic acid gives a water-soluble photodegradable polyelectrolyte. The ultraviolet spectra are different in dioxane and water solutions. The quantum yields ϕ of the Norrish type II photoreaction at 313 nm are determined in dioxane and in water solution at different degrees of ionization and ionic strengths, where the polyelectrolyte is in a more or less expanded random coil or in a stretched conformation. The value of ϕ is 0.13 in dioxane solution and 0.07 in water solutions, in spite of the different conformations. This behavior is explained by identical local conformation of the dyad acid–ketone, which differs from the overall conformation of the macromolecule.

The photochemistry of polymeric carboxylic acids has been studied mainly on poly(methacrylic acid) at a wavelength of 254 nm[1-3] in aqueous solution. The first step of the photochemical reaction is a carboxylic group abstraction followed by a scission of the chain.[1] The quantum yields of chain scission seem dependent both on the pH and on the tacticity.[2,3]

The photochemistry of poly(acrylic acid) (PAA) has not been investigated at short wavelengths, but poly(alkyl acrylates)[4,5] and poly(naphthyl acrylates)[6] underwent simultaneous photolysis and cross-linking, probably due to the recombination of radicals formed by tertiary hydrogen abstraction.[6]

The introduction in the polymer chain of a ketone chromophore can induce photolysis at wavelengths where the remainder of the polymer does not absorb. The Norrish type II reaction is responsible for the chain scission.

Amerik and Guillet have reported the photolysis of a methyl methacrylate–methyl vinyl ketone copolymer at 313 nm,[7] and similar studies have been made with styrene–phenyl vinyl ketone copolymers.[8] In both cases, a low ketone content (2.3 mol %) in the copolymer was sufficient to induce extensive photodegradation. The photolysis of such copolymers makes possible the investigation of the mechanism of main-chain scission in polymeric ketones,[9] which has been the subject of a great number of papers.

Nevertheless, the problem of the dependence of the quantum yield of the chain scission process on polymer configuration is not yet clear. Tanaka and Otsu[10] found greater quantum yields for atactic poly(*tert*-butyl vinyl ketone) than for the isotactic configuration. However, Kilp et al. found no difference in the quantum yield of main-chain scission between isotactic and atactic poly(phenyl vinyl ketones).[11] This was explained on the basis of identical local conformations of the biradical intermediate.

Determination of Quantum Yields of Main-Chain Scission

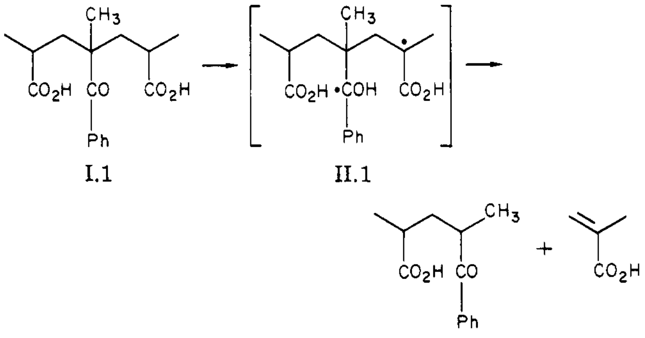
In polyelectrolytes, changes in chain conformation can be easily obtained without changing the solvent or the temperature since the conformation of a polyelectrolyte is dependent both on the pH and on the ionic strength. A polyelectrolyte such as PAA, which is a weak flexible polyacid, is in a Θ condition in dioxane at 30 °C,[12] in a

---

[†] Permanent address: Laboratoire de Chimie Macromoléculaire, ERA 471, Faculté des Sciences de Rouen, 76130 Mont-Saint-Aignan, France.

slightly expanded random coil in NaBr (0.1 M) aqueous solution,[13] and in an expanded state in pure water.

Copolymers of acrylic acid with less than 2% vinyl ketone can be used to study the influence of chain conformation on the quantum yield of the main-chain scission, because these copolymers have the same solubility in water as PAA and the hydrodynamic properties should be similar. Phenyl isopropenyl ketone (PIPK) was chosen as the ketone comonomer for two reasons: first, this is an aryl ketone which is known to give exclusively the Norrish type II photoelimination and second, this monomer does not homopolymerize by a radical mechanism, thus eliminating the possibility of PIPK dyads. In this case the Norrish type II photoelimination should occur only between a PIPK monomeric unit and an acrylic acid unit following the scheme



I.1 II.1 III.1

Irradiation light of λ 313 nm was chosen because at this wavelength the homopoly(acrylic acid) is nonabsorbant (which might lead to cross-linking), and the ketone chromophore is sufficiently absorbant ($\epsilon_{313} = 130$ L mol^{-1} cm^{-1}) to obtain efficient photolysis.

The photodegradation was followed by automatic viscometry measurements of copolymer viscosity in solution. The intrinsic viscosity $[\eta]$ was calculated from the reduced viscosity data by using the Solomon–Ciutta relation,[14] which allows the determination of intrinsic viscosity by the "single-point method".

$$[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{1/2}/c$$

where η_{sp} is the specific viscosity, η_{rel} the relative viscosity ($\eta_{rel} = \eta_{sp} + 1$), and c the concentration of the solution in g mL^{-1}.

Tests on PAA, made in dioxane and in 0.1 M NaBr aqueous solution, show that the error between the intrinsic viscosity obtained by extrapolation at zero concentration and the data obtained with the Solomon–Ciutta relation was negligible.

The viscosity-average molecular weight $\bar{M}_v$ was then calculated with the Mark–Houwink–Sakurada relationship:

$$[\eta] = K\bar{M}_v^{a} \tag{1}$$

Values of K and a are those given by Noda, Tsuge, and Nagasawa for PAA in solution of 0.1 M sodium bromide.[13]

The extent of main-chain scission can be calculated with the equation

$$S = (W/\bar{M}_n^{0})[(\bar{M}_n^{0}/\bar{M}_n^{t}) - 1] \tag{2}$$

where S is the number of chain breaks, W is the weight of the irradiated copolymer (in grams), and $\bar{M}_n^{0}$ and $\bar{M}_n^{t}$ are the initial and final number-average molecular weights after irradiation time t. Nemzek and Guillet[15] have shown that eq 2 can be approximated by

$$S = \{W[\Gamma(a + 2)]/\bar{M}_v^{0}\}^{1/a}[(\bar{M}_v^{0}/\bar{M}_v^{t}) - 1] \tag{3}$$

where Γ is the gamma function.

If the initial number-average molecular weight is known, eq 3 can be approximated by

$$S = (W/\bar{M}_n^{0})[(\bar{M}_v^{0}/\bar{M}_v^{t}) - 1] \tag{4}$$

The number-average molecular weight can be measured by GPC using the poly(methyl acrylate-*co*-isopropenyl ketone) copolymer obtained after methylation of the carboxylic functions of the original polymer.

In pure water solution, where the reduced viscosity increases strongly when the concentration approaches zero due to the polyelectrolyte effect, the Solomon–Ciutta relationship is no longer applicable. In this case, the reduced viscosity η_{red} can be expressed by the Fuoss relationship:[16]

$$\eta_{red} = [\eta]/(1 + Bc^{1/2}) \tag{5}$$

where B is a constant that depends on the molecular weight[17,18] and c is the concentration in g mL^{-1}.

Equation 5 can be written in the form

$$[\eta] = (\eta_{sp}/c)(1 + Bc^{1/2}) \tag{6}$$

where η_{sp} is the specific viscosity.

The initial slope of the specific viscosity did not change with irradiation, so B is essentially constant, and at constant concentration c we have

$$[\eta]^{0}/[\eta]^{t} = \eta_{sp}^{0}/\eta_{sp}^{t} \tag{7}$$

where $[\eta]^{0}$, η_{sp}^{0}, $[\eta]^{t}$, and η_{sp}^{t} are, respectively, the intrinsic and specific viscosities at the initial state and after an irradiation time t.

Then, from eq 1, 4, and 7, the number of chain breaks is given by

$$S = (W/\bar{M}_n^{0})[(\eta_{sp}^{0}/\eta_{sp}^{t})^{1/a} - 1] \tag{8}$$

The value of a reported by Kay and Treloar[19] was 1.35 for PAA at a degree of neutralization $\alpha = 0.5$, but using the data of intrinsic viscosities given by these authors for molecular weights between 19 000 and 49 000, one finds by using the least-squares method $a = 1.44$, the value used in this work.

For all experiments, the quantum yield ϕ is obtained by

$$\phi = S/It$$

where I is the light absorbed (in einsteins s^{-1}) by the polymer solution and t is irradiation time.

Experimental Section

Copolymer Synthesis. Phenyl isopropenyl ketone was prepared by the procedure of Burckhalter and Fuson.[20] Copolymerization was carried out by mixing 6.55% PIPK with 93.4% freshly distilled acrylic acid and 0.05% azobisisobutyronitrile (in molar fraction) in toluene solution (70 wt %) and heating for 8 h at 70 °C, after being degassed under vacuum. In these conditions, the conversion is about 20%. The copolymer, which precipitates during the copolymerization, is purified by dissolution in isopropyl alcohol and precipitation with anhydrous ethyl ether. This process was repeated three times. The white polymer so obtained was stored in the dark.

The ketone content was determined to be 1.82 mol % by comparison of the copolymer absorbance in dioxane solution at 241 nm with that of homopoly(phenyl isopropenyl ketone) in the same solvent ($\epsilon_{241} = 8500$ L mol^{-1} cm^{-1}).

The poly(PIPK) was obtained by ionic polymerization using either *n*-butyllithium[21] or diethylzinc[22] as initiator.

Gel Permeation Chromatography. The copolymer was first methylated with diazomethane prepared according to a nonhazardous method[23] in ethyl ether solution. The GPC of poly(methyl acrylate-*co*-PIPK) was then carried out in benzene solution with a Waters Type ALC-GPC-501 with 100–500-Å Porogel columns.

Photolysis Studies. The photolysis was carried out at 313 nm under nitrogen in a quartz cell coupled with an automatic

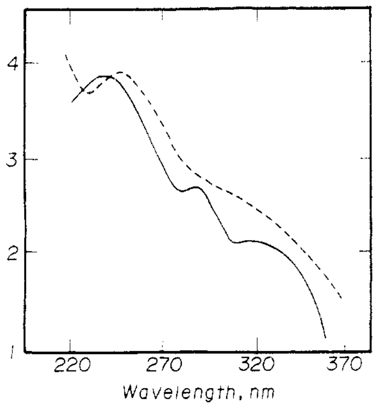


Figure 1. UV spectra of poly(phenyl isopropenyl ketone-*co*-acrylic acid) in (—) dioxane and (---) water.

Table I
Molar Absorptivities ε and Wavelengths of Poly(PIPK-AA) in Dioxane and Water Solution

solvent	band	wavelength, nm	ε, L mol^{-1} cm^{-1}
dioxane	^1L_A	241	8500
	^1L_B	288	500
	n-π*	317	130
		313	130
water	^1L_A + ^1L_B	247	8500
	n-π*	315 (shoulder)	360
		313	370

viscometer.[24] Viscosity measurements were made after preset intervals of irradiation. The incident light intensity at 313 nm was monitored by potassium ferrioxalate actinometry[25] and was 1.66×10^{-8} einstein s^{-1}. The light absorbed was calculated from the optical density of the solution in the cell at 313 nm.

Results and Discussion

Ultraviolet Absorption Spectra. The UV spectrum of the copolymer was determined in water solution at different degrees of ionization and in dioxane solution. There is no significant difference in water solution, but in dioxane strong differences appear. In dioxane, the ^1L_A and the ^1L_B bands (according to Platt's nomenclature[26]) are well defined, but in water these same bands are broadened and unresolved, and the n–π* band at 315 nm appears only as a shoulder. The maximum of the ^1L_A band is shifted to the red (from 241 to 247 nm), presenting a slight bathochromic effect (Figure 1), which has an effect on the absorption of the incident light at 313 nm. In dioxane solution, the molar absorptivity (ε = 130 L mol^{-1} cm^{-1}) is mainly due to the n–π* transition. In water, the molar absorptivity is stronger (ε = 370 L mol^{-1} cm^{-1}) and an important fraction is due also to the ^1L_B band.

Table I shows the wavelengths of maxima and the molar absorptivity of the copolymer in the two solutions. The spectra are shown in Figure 1.

The wavelength effects for different solvents, as described above, are similar to those observed with alkyl ketones such as acetone and are related to the hydrogen-bonding ability of the solvents.[27]

Gel Permeation Chromatography. In order to use eq 4, the number-average molecular weight $\bar{M}_n$ of the copolymer must be known.

The GPC of poly(phenyl isopropenyl ketone-*co*-acrylic acid) (poly(PIPK–AA)) not possible in dioxane solution at room temperature, probably because of the formation of aggregates, since the solution was below the Θ temperature.

Methylation of the carboxylic functions of the copolymer makes possible the GPC of the new copolymer obtained (PIPK–methyl acrylate) in benzene solution.

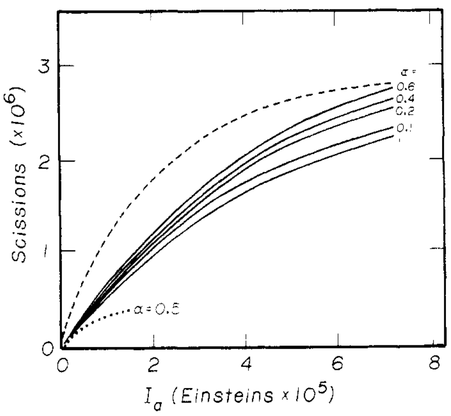


Figure 2. Scission of poly(phenyl isopropenyl ketone-*co*-acrylic acid) vs. intensity in (---) dioxane at 30 °C, (—) 0.1 N NaBr at 25 °C, and (···) water. α = degree of neutralization of acrylic acid.

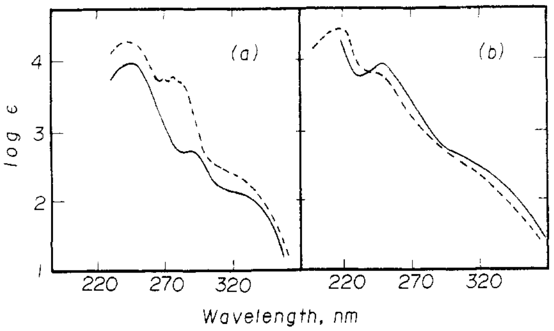


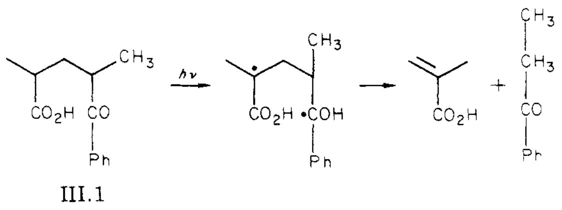
Figure 3. UV spectra of poly(phenyl isopropenyl ketone-*co*-acrylic acid) (—) before and (---) after irradiation at 313 nm: (a) in dioxane solution, *t* = 280 min; (b) in 0.1 N NaBr, *t* = 590 min, α = 0.5.

The number-average molecular weight $\bar{M}_n$ and the polydispersity index (PI) are calculated by using values of *K* and *a* for poly(methyl acrylate) in benzene,[28] applying the universal calibration method.[29]

The results of these calculations for the methylated copolymer are $\bar{M}_n$ = 47 000 and PI = 2.6. This gives for the original copolymer (PIPK–AA) $\bar{M}_n$ = 39 000 and the same polydispersity index.

Photodegradation Results. Irradiation at 313 nm was carried out for periods of up to 9 h, first in dioxane at 30 °C, where PAA is at a Θ condition,[12] then in 0.1 N NaBr aqueous solution at successive degrees of ionization (α = 0.103, 0.2, 0.4, 0.6, and 1) after neutralization by NaOH, where the copolymer is an increasingly expanded random coil, and lastly in pure water at α = 0.5, where the copolymer is in an expanded conformation.

Figure 2 shows the kinetics of photolysis for all the experiments. The number of main-chain scissions is expressed as a function of the light absorbed. The shape of the curves may be due to the variation of the polydispersity index, which tends toward 2 when the photodegradation advances, as shown by Nemzek and Guillet,[15] or to the photoreaction of Norrish type II on the reaction product III which gives a scission which does not modify the molecular weight, according to the following scheme.



III.1

Table II
Expansion Coefficients ξ_η^3 and Main-Chain Scission Quantum Yields ϕ_s of Poly(PIPK-AA) at Various Degrees of Ionization α

solvent	temp, °C	α	$K \times 10^4$	a	ξ_η^3	ϕ_s
dioxane	30	0	8.5	0.5^a	1	0.13
0.1 N NaBr	25	0.103	2.07	0.679^b	1.41	0.078
	25	0.2	1.61	0.743^b	2.02	0.073
	25	0.4	1.93	0.771^b	2.84	0.070
	25	0.6	2.35	0.768^b	3.07	0.067
	25	1	3.12	0.755^b	2.92	0.062
water	25	0.5	0.0203	1.44^c		0.071

[a] Reference 12. [b] Reference 13. [c] Reference 19.

Another cause of the curvature is the formation of absorbant unreactive compounds which occur in the experiment in dioxane solution, as shown in Figure 3, where the UV spectrum of the irradiated solution is compared with that of the initial spectrum. In this case the fine vibrational structure, which could be the ^1L_B band of phenol, appears at 270 nm, suggesting an important Norrish type I reaction, with the phenyl radical reacting with the hydroxyl group of the carboxylic function (Figure 3a).

This phenol band does not appear in the spectrum of the polymer irradiated in 0.1 N NaBr aqueous solution, where a decrease of the optical density is observed after 590 min of irradiation (Figure 3b).

The quantum yields determined from the initial slope of the curves of Figure 2 are shown in Table II. The values of K and a used are also given. When the conformation of the PAA is a more or less expanded random coil, the cube of the viscometric expansion coefficient ξ_η^3 related to its unperturbed dimensions at the considered degree of ionization is given by

$$\xi_\eta^3 = [\eta]/[\eta]_\Theta \tag{9}$$

$$[\eta]_\Theta = K_\Theta M^{0.5} \tag{10}$$

where $[\eta]_\Theta$ is the theoretical intrinsic viscosity at the unperturbed dimensions, calculated from eq 10, and K_Θ is the Mark–Houwink constant at Θ conditions, taken from data of Noda et al.[13]

The quantum yields are lower than those of poly(phenyl vinyl ketone)[11] and poly(phenyl isopropenyl ketone-*co*-styrene).[9] The main result is the independence of the quantum yield ϕ_s with regard to the conformation of the copolymer in water solution. In all of these experiments, the value of ϕ_s was approximately 0.07.

In dioxane solution, the value of ϕ is approximately twice that in water, i.e., 0.13. In this case, the absorption at 313 nm is mainly due to the n–π^* transition, leading to the n–π^* triplet state which generates the biradical (II). In water solution we suggest that the absorption at 313 nm is not only due to the n–π^* transition but also to the ^1L_B transition, leading to the π–π^* state, which is known to show substantially reduced reactivity in intramolecular γ-hydrogen abstraction.[30] This could more than compensate for the enhancement of the quantum yield by hydrogen-bonding solvents, which are known to retard reverse hydrogen transfer in the solvated biradical (II),[31] especially since the phenyl ketone group is hydrophobic and is not solvated by water.

The independence of the quantum yield with the conformation of the polymer in aqueous solution is analogous to the results of Kilp et al. in studies of isotactic and atactic poly(phenyl vinyl ketone).[11] In this study it was shown that the quantum yield of chain scission was the same for the two polymers. It was proposed that the biradical has identical local conformation, for both isotactic and atactic dyads, as is probably the case in poly(PIPK–AA). The hydrophobic interactions between the phenyl ketone group and the neighboring acrylic moiety where the γ-hydrogen abstraction occurs are probably greater than the hydrophilic interactions. The electrostatic repulsion of charges, which controls the expansion coefficient and the conformation of the macromolecule, apparently does not affect the relative reactivity.

In other words, ϕ_s is dependent on the local conformation of the ketone–acrylic acid dyad, which controls the stability of the biradical (II), but is not dependent on the overall conformation, which is modified by the degree of ionization of the polyacid and the ionic strength of the aqueous solution. However, the change of solvent to dioxane, which modifies the polymer–solvent interactions and the local conformations, does cause a substantial increase in the quantum yield.

Conclusions

The quantum yield of main-chain scission of poly(PIPK–AA) by the Norrish type II photoreaction is independent of the overall conformation of the polymer in aqueous solution. This behavior is probably due to the independence of the local conformation of the dyad PIPK–AA to the overall conformation of the copolymer, resulting in identical local conformations in aqueous solution for the biradical intermediate (III).

The lack of any effect on the quantum yields with the chain expansion points out that there is no change in local conformation, even with quite large changes in coil dimensions.

The hydrophobic character of the phenyl ketone group, which has more affinity for the neighboring acrylic unit, ionized or not, than for water, explains this behavior in aqueous solutions.

Possibly a better way to obtain variations of the local conformation which might induce changes in the quantum yields would be to use mixed solvents of different polarities. ϕ_s for the photodegradation in dioxane in this study did show a significant increase over that in water.

Acknowledgment. We thank Dr. H. Garreau from the INSCIR for the GPC measurements. Financial support of this work by the National Research Council of Canada and fellowship support from NATO (to L.M.-A.) are gratefully acknowledged.

Registry No. Poly(PIPK–AA), 88200-47-9; dioxane, 123-91-1; water, 7732-18-5.

References and Notes

(1) Baxendale, J. H.; Thomas, J. K. *Trans. Faraday Soc.* **1958**, *54*, 1515.
(2) Chou, C. H.; Jellinek, H. H. G. *Can. J. Chem.* **1964**, *42*, 522.
(3) Jellinek, H. H. G.; Lipovac, S. N. *J. Macromol. Chem.* **1966**, *1*, 773; *J. Polym. Sci., Part C* **1969**, *22*, 621.
(4) Fox, R. B.; Isaacs, L. G.; Stokes, S.; Kagarise, R. E. *J. Polym. Sci., Part A* **1964**, *2*, 2085.
(5) Morito, K.; Suzuki, S. *J. Appl. Polym. Sci.* **1972**, *16*, 2947.
(6) Merle-Aubry, L.; Holden, D. A.; Merle, Y.; Guillet, J. E. *Macromolecules* **1980**, *13*, 1138.
(7) Amerik, Y.; Guillet, J. E. *Macromolecules* **1971**, *4*, 375.
(8) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212.
(9) Sugita, K.; Kilp, T.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1901.
(10) Tanaka, H.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2613.
(11) Kilp, T.; Guillet, J. E.; Merle-Aubry, L.; Merle, Y. *Macromolecules* **1982**, *15*, 60.
(12) Newman, S.; Krigbaum, W. R.; Langier, C.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 451.
(13) Noda, I.; Tsuge, T.; Nagasawa, M. *J. Phys. Chem.* **1970**, *74*, 710.
(14) Solomon, O. F.; Ciutta, I. Z. *J. Appl. Polym. Sci.* **1962**, *6*, 683.

(15) Nemzek, T. L.; Guillet, J. E. *Macromolecules* **1977**, *10*, 94.
(16) Fuoss, R. M. *J. Polym. Sci.* **1948**, *3*, 603.
(17) Strauss, U. P.; Smith, E. H. *J. Am. Chem. Soc.* **1953**, *75*, 6186.
(18) Liberti, P. A.; Stivala, S. S. *J. Polym. Sci., Part B* **1966**, *4*, 137.
(19) Kay, P. J.; Treloar, F. E. *Makromol. Chem.* **1974**, *175*, 3207.
(20) Burckhalter, J. H.; Fuson, R. C. *J. Am. Chem. Soc.* **1948**, *70*, 4184.
(21) Mulvaney, J. E.; Dillon, J. G.; Laverty, J. L. *J. Polym. Sci., Part A-1* **1968**, *6*, 184.
(22) Merle-Aubry, L.; Merle, Y. *Eur. Polym. J.* **1980**, *16*, 227.
(23) De Baer, J.; Backer, H. J. "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963; Vol. 4, p 250.
(24) Kilp, T.; Houvenaghel-Defoort, B.; Panning, W.; Guillet, J. *Rev. Sci. Instrum.* **1976**, *47*, 1496.
(25) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.
(26) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.
(27) Jaffé, H. H.; Orchin, M. "Theory and Application of Ultraviolet Spectroscopy"; Wiley: New York, 1970.
(28) Brandrup, J.; Immergut, E. M. "Polymer Handbook"; Wiley: New York, 1975.
(29) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1966**, *5*, 753.
(30) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5898.
(31) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; McGrath, J. M.; Schott, H. N.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7506.

Laser Photolysis Studies of Photoinduced Aggregation in Polymers Containing Spiropyran Units

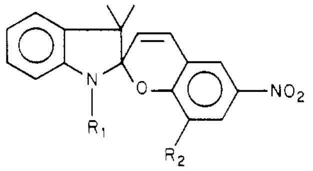
Yehoshua Kalisky and David J. Williams*

Xerox Webster Research Center, Webster, New York 14580. *Received April 14, 1983*

ABSTRACT: The photoinduced processes which lead to isomerization and complexation in polymers and copolymers containing pendant indolinobenzospiropyran groups are investigated by nanosecond transient absorption spectroscopy techniques. The monomer 1-(β-(methacryloxy)ethyl)-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-[2*H*-1]benzopyran] (SP) was copolymerized with methyl methacrylate (MMA) to form copolymers (MMA$_m$-*co*-SP$_n$) and homopolymerized PSP. In solution, the copolymer undergoes a photoinduced ring-opening reaction to form B, the fully isomerized transform via a short-lived nonplanar ring-opened intermediate (X) on the subnanosecond time scale. A second transient (AB) is formed by a bimolecular reaction between the lowest triplet state of SP (^{3}A*) with a ground-state ring (A) on the same chain. Efficient AB formation is observed even in the copolymer which is most dilute in SP (MMA$_{99.9}$-*co*-SP$_{0.1}$). A further red shift occurring at later times is taken to be evidence for higher aggregate formation (AB)$_n$ or (A$_m$B)$_n$. The sterically hindered environment of the homopolymer leads to deactivation of X to the ground state rather than isomerization or complexation is observed. Polar environments produce a similar effect. A detailed mechanism for the observed behavior is proposed.

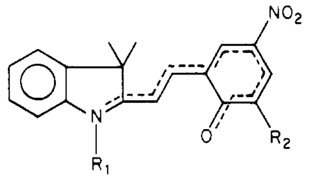
Introduction

In recent years there has been considerable interest in photoresponsive polymers with spirobenzopyran side groups.[1-3] Conformational changes induced in the polymer by photoisomerization of the side groups have been compared to those processes occurring in membranes where photoinduced conformational changes elicit changes in the state of assembly of membranes which control nerve responses and enzymatic activity. There has also been considerable recent activity to understand the process of photoinduced color formation in spirobenzopyran systems such as IA which exhibit spontaneous aggregation of the photoinduced species and lead to "quasi-crystal" formation.[4] When quasi-crystals are formed in an external electric field, they exhibit a polar structure and second-order nonlinear optical effects.[5] Considerable insight into the structure of these aggregates has been gained through spectroscopic and nonlinear optical studies.[6]



IA, R$_1$ = (CH$_2$)$_2$OCO(CH$_3$)C=CH$_2$, R$_2$ = H
IIA, R$_1$ = CH$_3$; R$_2$ = CH$_2$OCO(CH$_3$)C=CH$_2$

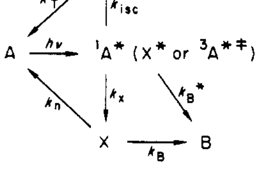
Irie and co-workers[2] have recently reported solvent-dependent photoinduced viscosity changes in copolymers derived from methyl methacrylate and IIA and attributed the effect of solvation of the ring-opened merocyanine form (B) by the methacrylate units of the same polymer chain.



B

Time-resolved absorption spectra following pulsed laser excitation were obtained to help elucidate the nature of the process.

We have recently reported a picosecond and nanosecond time-resolved absorption[7] study on IA in polar and nonpolar solvents. In that study the following mechanism was proposed to account for the primary photoprocesses leading to photocoloration in the picosecond to microsecond time frame:



where A is the parent molecule, X is the nonplanar ciscisoid ring-opened form, B is the planar trans isomer, and AB is a dimer. At long times AB forms higher aggregates

---

* Present address: Research Laboratories, Eastman Kodak Co., Rochester, NY 14650.

0024-9297/84/2217-0292$01.50/0