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Photopolymerization Studies. III. Thermal Sensitization and Desensitization Effects[1]

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ABSTRACT: Heating and pH effects on the dark storage are studied for photopolymerizable solutions of barium acrylate in water. Methylene Blue and sodium *p*-toluene- or benzenesulfinate are used as photopolymerization-initiating agents. When solutions of pH 6 are heated, the photosensitivity initially increases and then gradually decreases until desensitization is complete. The sensitization process is partly due to a decrease in sulfinate quenching of the excited dye, but a decrease of oxygen inhibition due to its reaction with monomer appears to be the major factor. The desensitization is due to the ionic dark addition of the elements of *p*-toluenesulfinic acid to monomer double bond, forming a sulfone which is unreactive with the excited state of the dye. Photopolymerization rates measured as a function of prior heating are used to make a kinetic analysis of the dark reactions. Desensitization occurs faster at lower pH because the ionic addition is much faster with acrylic acid than with the acrylate ion. Desensitization is slower at higher pH due to absence of acrylic acid, and due to an equilibrium of sulfinate ion and sulfone at high hydroxide ion concentrations. Long storage times are possible at high pH; however, the photopolymerization efficiency is also decreased in the high pH range.

We have already described[2,3] a direct imaging system based on photopolymerization of acrylic monomer solutions containing a phenothiazine dye and a salt of an arylsulfinic acid. Polymerization is initiated by transient free radicals resulting from the redox reaction between the dye-triplet state and the sulfinate ion.[4] The photopolymer image is due either to the light-scattering properties of polymer or to refractive index differences within the partially polymerized film. Applications for rapid-access, large-screen display devices[5] and holographic recording have been demonstrated.[5-8]

This paper describes the sensitizing and desensitizing effects obtained by heating photopolymerizable aqueous compositions of barium acrylate, Methylene Blue, and sodium *p*-toluene- or benzenesulfinate. A kinetic analysis is made on the thermal dark desensitization reaction. Comparisons are made with other studies[9] in which the rate constants (k in eq 1) for the ionic addition of sulfinate ions to acrylic monomers were measured by techniques not involving polymerization.

$$\mathrm{RSO_2^-} + \mathrm{CH_2{=}CHY} + \mathrm{H_2O} \underset{k'}{\overset{k}{\rightleftharpoons}} \mathrm{RSO_2CH_2CH_2Y} + \mathrm{OH^-} \quad (1)$$

The effects of low pH and high pH on the room-temperature stability and photosensitivity of these photopolymerizable solutions are also described. The reverse reaction of eq 1 (k' direction) is followed at high pH by analysis of the benzenesulfinate ions produced from the reaction of hydroxide ions with 3-(benzenesulfonyl)propionate ions.

Experimental Section

Materials. Barium acrylate solutions were prepared by neutralizing aqueous solutions of acrylic acid with an equivalent amount of barium hydroxide. The pH was adjusted with excess acrylic acid, and the solutions were treated with activated carbon and filtered. The concentrations were determined by atomic absorption spectroscopy or by heating measured volumes of solution to dryness; the results of the two methods agreed within 2%. Concentrations of sulfinate solutions were determined by a potentiometric titration with standard sodium nitrite solution,[10] which indicated that the commercial sodium *p*-toluenesulfinate and sodium benzenesulfinate were better than 97% pure. Photosensitive solutions were prepared by mixing aqueous solutions of barium acrylate, Methylene Blue, and the sodium salt of either *p*-toluenesulfinic or benzenesulfinic acid. The compositions of these solutions are summarized in Table I.

When basic barium acrylate solutions were prepared, we noted that often they spontaneously consumed hydroxide ion and gradually became less basic. This is attributable to the presence of β-acryloyloxypropionic acid as an impurity in the glacial acrylic acid.[11] This ester "dimer" undergoes hydrolysis in base, consuming $\mathrm{OH^-}$. We found that after barium acrylate solutions were allowed to stand for about 1 week with an excess of base they would remain nearly constant at a given pH in the 9-12 range.

3-(Benzenesulfonyl)propionic acid was synthesized by the reaction of sodium benzenesulfinate with methyl acrylate in aqueous methanol and hydrolysis of the resulting methyl 3-(benzenesulfonyl)propionate in 6 *N* hydrochloric acid. The melting point was 124° (lit. mp 125-126°,[12] 125.5-127°[13]).

Photopolymerization Rate Measurements. Photopolymerization was followed optically, since the polymer that is formed scatters light. It has been shown[2] that, at least in the region of low monomer conversion, the apparent optical density of a light-scattering photopolymer film is proportional to the amount of polymer formed. The sample of photosensitive composition was held between two glass slides separated by a peripheral plastic shim 0.15 mm thick. For expt 1 and 2 unfiltered light from a 500-W tungsten filament projection lamp was used to induce polymerization, and the light transmitted by the sample was attenuated with neutral density filters and detected with an RCA 931A phototube. For the remaining experiments the polymerization was followed by passing through the polymerizing spot an analyzing light beam having a low intensity and a wavelength that was in-

Table I
Compositions of Photosensitive Solutions and Light Sources Used for Photopolymerization

Expt No.	[Barium Acrylate], M	Initial [Sulfinate], $\times 10^2$, M^a	[Methylene Blue], $\times 10^4$, M	Initial pH	Light Source^b	Light Intensity (mW/cm^2)^c	Pertinent Tables and Figures
1	1.25	2.0 T	2.0	5.92	W	6.25	II, 7, 8, 9
2	1.25	2.0 T	2.0	Varied	W	6.25	2
3	2.23	1.0 T	2.3	6.7	He–Ne		III
4	1.98 (+0.46)^d	3.6 B	9.1	8.05	Xe	0.42	4
5	1.91	0.899 B	5.0	Varied	Xe	0.34	5
6	1.90	0.85^e B	5.5	7.0	Xe	0.34	V
7	1.88	^{f} B	4.9	7.0	Xe	0.34	VI, 1, 6

[a] T = sodium *p*-toluenesulfinate; B = sodium benzenesulfinate. [b] W = 500-W tungsten filament lamp, unfiltered; He–Ne = 3-mW helium–neon laser (632.8 nm); Xe = 300-W xenon arc lamp, filtered through 5 cm of water in a Pyrex cell and a 667-nm interference filter. [c] Measured with an Eppley thermopile. [d] 1.98 M barium acrylate plus 0.46 M strontium acrylate. [e] Or less, due to prior reaction with monomer. [f] Concentrations in test solutions determined by comparison with standard solutions in which the sulfinate concentration was varied.

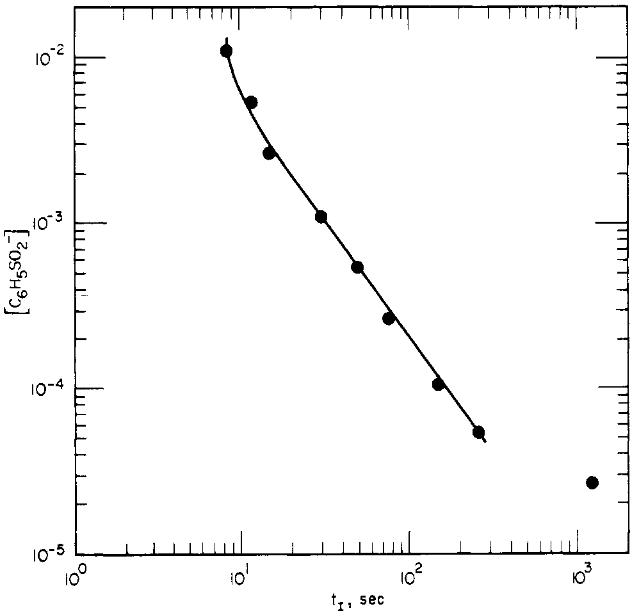

Figure 1. Effect of benzenesulfinate ion concentration on the induction period (expt 7).

effective in inducing polymerization. In expt 3 this beam was passed through a 486-nm interference filter; in expt 4-7 an attenuated 515-nm pulsed argon ion laser beam was used. In each case the intensity of the transmitted analyzing light was detected with a photodiode and recorded as a function of time. The light sources and intensities used to effect polymerization are indicated in Table I.

Thermal Sensitization and Desensitization (Expt 1 and 2). The effects of heating were determined by placing the filled sample cells in a preheated oven with circulated air for measured periods of time. When a thermocouple was inserted into a sample cell filled with water and the cell was heated under the same conditions, the heating period required for the water to reach the oven temperature was 3.0, 3.0, and 2.5 min at 80, 65, and 45°, respectively. Data from expt 1 (pH 5.92) were obtained by photopolymerization immediately after removal from the oven. Since polymerization generally required only a few seconds, cooling effects were considered to be negligible. Samples in expt 2 (other pH's) were allowed to cool to room temperature prior to exposure.

Oxygen Inhibition (Expt 3). Oxygen was removed by purging the photosensitive solution in the dark for 15 min with purified nitrogen. Purging was carried out by passing the gas upward through the solution in a syringe barrel, and the purged sample cell was then filled by reversing the gas flow.

Storage Life Tests (Expt 4). The samples were stored in the dark in tightly sealed brown screw-cap bottles.

Effect of pH on Photopolymerization Sensitivity (Expt 5). The monomer was first adjusted to a pH of 12 with 1 M sodium hydroxide and allowed to stand in a closed container for 24 hr, filtered, and then combined with the sulfinate and dye. Portions were readjusted to the desired pH by adding 1 M hydrochloric acid from a syringe microburet.

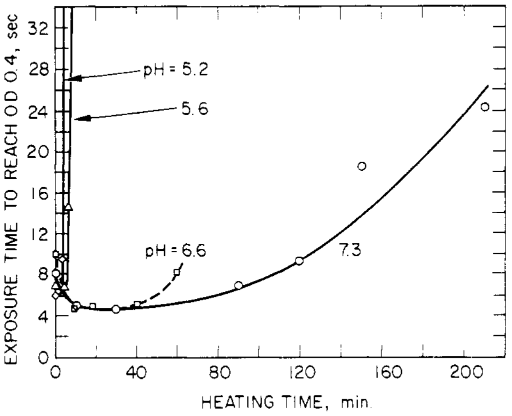

Figure 2. Effect of pH on thermal desensitization at 80°, shown by exposure time required for room-temperature photopolymerization after heating (expt 2).

The photopolymerization sensitivities were determined by measuring the induction period (t_I) and the rate of change in the transmission (m) at the 50% level. The functions t_I and $-1/m$ varied in a similar manner.

Effect of Base on Sulfinate Ion Addition (Expt 6). The monomer was first treated with excess base to reduce dimer impurities. Solutions that were 2.09 M in barium acrylate and 9.36×10^{-3} M in sodium benzenesulfinate were stored in glass serum bottles with rubber stoppers through which samples were withdrawn by syringe. The photosensitive solutions described in Table I were obtained by adjusting the pH to 7.0 with 1 N HCl and adding dye solution just prior to photopolymerization.

Elimination of Benzenesulfinic Acid from 3-(Benzenesulfonyl)propionate Ion (Expt 7). The elimination reaction was followed at 25° in a stoppered serum bottle using a 5.0×10^{-2} M aqueous solution of sodium 3-(benzenesulfonyl)propionate at a pH of 12.5. Samples were withdrawn periodically with a syringe and combined with barium acrylate solution. The pH was then adjusted to 7.0, dye solution was added, and portions were photopolymerized at 667 nm. The concentration of benzenesulfinate ion was estimated from the induction period using the plot shown in Figure 1, which was obtained by similarly photopolymerizing solutions having known benzenesulfinate ion concentrations.

Spectrophotometric analyses for both sulfone and sulfinate were carried out on samples after more than 5 months of storing the sulfone in base, by measuring the 264-nm peak and 268-nm valley absorbances with a Cary 14R on samples diluted 1:100. Calculations were made from values of the pure materials: sulfinate, $\epsilon_{264} = 9.06 \times 10^2$, $\epsilon_{268} = 8.3 \times 10^2$ and sulfone, $\epsilon_{264} = 1.11 \times 10^3$, $\epsilon_{268} = 6.16 \times 10^2$. The acrylate concentrations in these solutions were measured indirectly from the total consumption of bromine[14] (which reacted quantitatively with both sulfinate and acrylate) and then subtracting the independently measured sulfinate concentration.

Fluorescence Measurements. Relative fluorescence intensities

Table II
Effect of Heating on Sensitivity and Polymerization Rate (Expt 1)

Temp (°C)	t_H[a] (min)	t_I[b] (sec)	Exposure Time (sec) to Achieve OD of 0.1	0.2	0.4	0.6	0.8	1.0
23	0	8.2	12.8	14.8	18.1	21.5	25.1	29.6
45	2.5	5.3	8.6	10.2	13.2	16.8	20.1	23.8
	5.0	4.6	7.3	8.9	11.5	14.7	19.0	22.1
	10.0	4.3	6.9	8.4	11.2	13.6	16.7	20.4
	20.0	3.6	6.6	8.1	10.8	13.3	17.0	21.8
	30.0	3.3	5.5	6.8	8.7	11.0	13.0	15.6
	40.0	2.5	4.7	5.7	7.8	9.7	11.8	
	50.0	2.0	4.2	5.4	7.7	10.0	12.8	16.0
	80.0	0.4	2.0	3.7	6.0	9.6	12.2	16.2
	120.0	0.5	3.8	6.0	7.5	11.4	16.0	28.4
	150.0	0.6	7.0	10.2	17.8	28.0	37.0	48.0
	190.0	1.0	8.8	13.6	28.4	42.8	64.8	96.8
65	3.0	1.8	3.8	5.2	7.6	10.1	14.5	17.3
	5.0	1.0	3.4	4.7	6.9	9.4	12.6	16.0
	7.5	0.6	3.0	4.4	6.7	9.6	13.0	17.6
	11.0	0.5	2.6	3.9	6.2	8.8	11.8	16.0
	20.0	0.4	2.6	4.0	6.3	9.4	12.8	18.0
	35.0	0.5	3.3	5.1	8.4	11.9	16.5	22.4
	45.0	0.5	3.3	5.2	8.4	12.0	16.3	22.4
	60.0	0.4	4.1	6.8	13.6	19.2	27.4	
	75.0	0.5	8.6	15.2	29.0	51.0	84.0	
	90.0	2.4	48.8	149.2				
	3.0	1.6	3.2	4.3	6.0	7.7	9.8	11.8
80	3.5	0.5	2.6	3.8	5.8	8.0	10.7	13.6
	4.0	0.5	2.2	3.9	5.9	8.3	11.0	14.4
	5.5	0.6	4.3	6.2	9.6	14.8	20.0	31.0
	7.0	0.6	4.6	6.6	10.2	15.0	22.0	35.4
	10.0	0.8	4.8	8.0	13.3	19.6	28.4	40.0
	15.0	1.0	7.6	11.2	18.4	27.0	39.6	56.8
	20.0	1.8	18.0	28.2	52.4	87.0	160.0	
	30.0	10.5	120.4	501.8	>1400.0			

[a] t_H = time in oven. [b] t_I = induction period.

(F_R) were obtained at 680 nm from room-temperature solutions, using an Aminco-Keirs fluorimeter with an RCA 7102 photomultiplier cooled to −80°. Photopolymerization was avoided by not removing oxygen and by minimizing the excitation exposures.

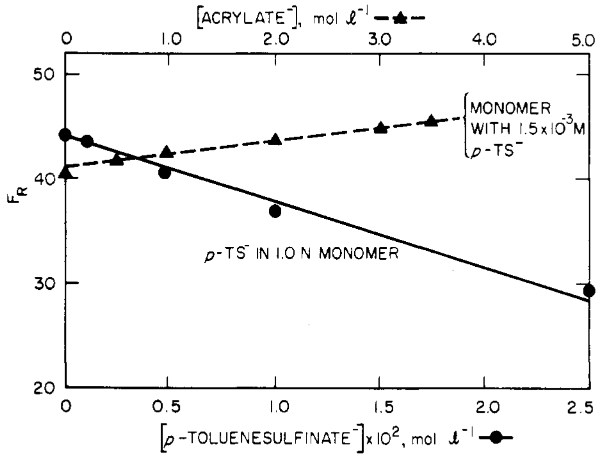

Figure 3. Effect of sulfinate ion quenching on the relative fluorescence intensity (F_R) of 8 × 10^{-6} M Methylene Blue in barium acrylate, pH 7.

Results

Studies in Lower pH Range. The thermal stability of these photopolymerizable solutions decreases markedly at pH's low enough to give an appreciable amount of acrylic acid in equilibrium with the barium acrylate. Figure 2 shows that the heating time required to deactivate the samples was greatly decreased below pH 6. If a composition with a sufficiently low pH is used, desensitization can be accomplished in seconds. For example, one solution with a pH of 4.6 was desensitized by immersing it for only 15 sec in a water bath at 85°.

The results of heating a photopolymerizable composition initially at pH 5.92 are presented in Table II. In brief, the sensitivity to light increased at first and then decreased. Complete desensitization occurred on continued heating.

Quenching of the excited singlet state of the dye by the sulfinate ion offers a partial explanation for the sensitization effect. Previous studies[4] with 1 M acrylamide solutions showed that the quenching of the dye singlet increased at sodium p-toluenesulfinate concentrations above 10^{-3} M, and that the photopolymerization rate decreased as a result. A similar effect occurs in pH 7 barium acrylate, as indicated in Figure 3 by the decreased fluorescence of the dye at higher sulfinate ion concentrations. The Stern-Volmer quenching equation (eq 2) gives a good

$$(F_R^0 - F_R)/F_R = K_Q[\mathrm{RSO_2}^-] \qquad (2)$$

correlation of the solid line data in Figure 3. It gives a quenching constant (K_Q) of 20 for p-toluenesulfinate, which is higher than the K_Q of 16 reported in acrylamide. The dashed line in Figure 3 shows that more fluorescence and less quenching occurs as the barium acrylate concentrations is increased; however, the effect is considerably smaller than was found for acrylamide.[4] Thus, at room temperature probably about 20-25% quenching of the excited singlet state of Methylene Blue would be expected from the 2 × 10^{-2} M p-toluenesulfinate ion initially present in the 2.5 N acrylate solutions studied in Table I.

Sensitization could be achieved by a reaction that would consume the oxygen present in the photosensitive solution. The inhibiting effect of oxygen is illustrated by the data in Table III. In all cases a short induction period elapsed before polymerization could be observed. Typical-

Table III
Effect of Nitrogen Purging on Sensitivity (Expt 3)

	t_I[a] (sec)	Exposure Time (sec) to Achieve OD of 0.1	0.2	0.4	0.6	0.8	1.0
Not purged	1.43	2.80	3.40	5.36	7.97	11.17	15.15
Purged	0.21	0.84	1.18	1.83	2.55	3.36	4.21

[a] t_I = induction period.

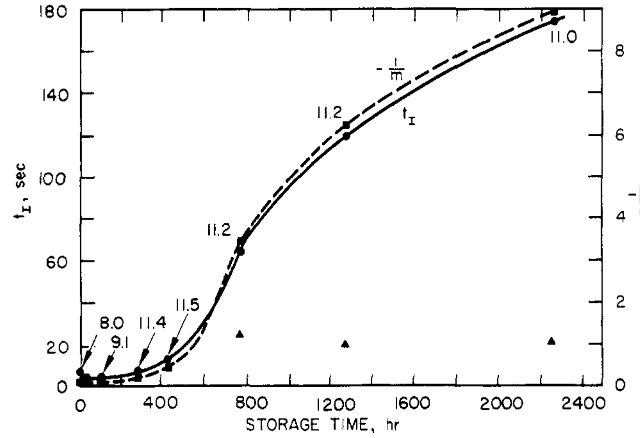

Figure 4. Effect of dark storage at 23° on a photopolymerizable barium, strontium acrylate solution initially at pH 8.05. Photopolymerizations on the curves were at the pH indicated. Other points (▲) show the t_I after readjusting to pH 7 (expt 4).

ly, when oxygen was removed from the solution by purging with nitrogen and then prevented from redissolving, the induction period was reduced by 80–90%. Moreover, the rate of polymerization after the end of the induction period was also increased. The fact that the induction period was not completely eliminated was expected, since the monomer undoubtedly retained some of the inhibitors present originally in the acrylic acid.

Oxidation of the sulfinate ion was at first suspected as a reaction by which the oxygen was consumed. However, the rate of sulfinate ion disappearance from a stirred aqueous solution in contact with air indicated that such a reaction takes place at a rate too slow to account for sensitization. Data in Table IV show that less than 10% of the sulfinate was lost in 48 hr at 80°, and it is not certain that even this quantity involved any consumption of oxygen.

Studies in Upper pH Range. As the pH of these polymerizable solutions is increased above pH 7, their thermal stability continues to increase, although not as dramatically as the effect in the low pH range. When unbuffered solutions of barium acrylate at pH 7–10 are mixed with benzenesulfinate, the pH gradually increases (due to the reaction indicated by eq 1) and fairly long-term photosensitivity is observed, as illustrated in Figure 4. After 600-hr storage, there was also some change in the color of this solution, probably due to hydroxide ion attack on Methylene Blue.[15] A partial loss in photopolymerization sensitivity results directly from an increase in pH even before any thermal desensitization occurs. This is shown in Figure 5, in which two indicators of sensitivity are plotted as a function of pH. It is not surprising that the photosensitivity varies in this manner, since the redox potential of the dye is reported[16] to be a function of the pH. The ▲ points in Figure 4 show that after long periods of storage much of the photosensitivity of this solution was regained by simply adjusting the pH down to 7.

The effect of pH on the desensitization due to the ionic addition reaction (eq 1) was separated from other effects on the dye by allowing benzenesulfinate ions to react with barium acrylate in the absence of dye, and then readjusting to pH 7 and adding dye just prior to photopolymerization. The results are shown in Table V, where five solutions of sodium benzenesulfinate and barium acrylate (previously base treated) were stored at 25° with initial pH's ranging from 7.3 to 10.0. After about 12 hr, they had all increased slightly in pH and showed improved photopolymerization sensitivity at pH 7. After 30 days the pH's were all 10.8–11.0. When adjusted to pH 7 and combined with dye, the resulting solutions exhibited considerable photosensitivity, the induction periods having increased only up to 15 sec as compared to their minimum induction times of 7.5–9.5 sec. The benzenesulfinate concentration in the test solutions can be estimated from the curve in Figure 1, in which nearly the same monomer and dye concentrations were used. The 15-sec induction period corresponds to a benzenesulfinate concentration of about 2.7×10^{-3} *M* in the test solution, or about 3×10^{-3} *M* in the 1-month old storage solutions. Thus, nearly one-third of the initial sulfinate apparently remained in these solutions as their basicity rose to pH 11.

Because of these results we looked for the reversibility indicated by k' in eq 1. Evidence for the formation of sulfinate from sulfone was obtained from solutions of 3-(benzenesulfonyl)propionate in sodium hydroxide. The results are shown in Figure 6 and Table VI. The sulfinate concentrations in Figure 6 were obtained by periodically withdrawing samples, combining them with monomer, adjusting to pH 7, adding dye, and measuring the photopolymerization rate. The sample was initially inactive, but it began to change within a few hours and after 20 days at 25° the analysis showed 0.014 *M* benzenesulfinate in the sample (Figure 6) or 28% conversion of the sulfone to the sulfinate. This sample and two other samples were examined after more than 5-months storage, and the results are tabulated in Table VI. Spectrophotometric analysis was used as well as the above photopolymerization method. The spectral method showed the following 5-month conversions to the sulfinate ion: 42% from 0.1 *M* sulfone placed in pH 12.5, 77% from 0.05 *M* sulfone placed in pH 12.5, and 5.3% from 0.05 *M* sulfone placed in pH 11.

Table IV
Disappearance of *p*-Toluenesulfinate Ion in Stirred Aqueous Solutions at 80–85° in Contact with Air

Initial pH[a]	5.00	6.20	7.50
Concentration[b] prior to heating (mol/l.)	0.00970	0.00970	0.00970
Concentration[b] after heating for 3 hr (mol/l.)	0.00973	0.00973	0.00975
Concentration[b] after heating for 48 hr (mol/l.)	0.00876		0.00906
pH after heating for 48 hr	3.99		4.32

[a] pH adjusted with concentrated hydrochloric acid or concentrated sodium hydroxide solution. [b] Concentrations determined by titration with 0.1 *N* sodium nitrite solution.[10]

Table V
Effect of Base on Sulfinate Ionic Addition to Monomer (Expt 6)

Storage pH (of Monomer and Sulfinate)			Photopolymerization at pH 7 after Storage: Induction Time (t_I), sec			Rate of Polymerization ($-1/m$)		
0 hr	12 hr	725 hr	0 hr	12 hr	725 hr	0 hr	12 hr	725 hr
7.3	7.6		8.5	7.5	15.0	4.7	5.1	3.5
8.0	8.0	10.8	8.5	8.0	15.0	5.0	5.1	3.6
8.5	8.8	11.0	9.5	8.0	15.0	5.6	4.8	3.5
8.6	8.6	11.0	(16)	9.5	15.0	4.4	5.3	3.1
10.0	10.2	10.8	12.5	9.5	15.0	4.2	5.1	3.5

Table VI
Sulfinate Formed in Aged Solutions of Sulfone in Base (Expt 7)

Initial Conditions: [Sulfone][a]	pH	Aging Period: Months	Aged Conditions: pH	$[RSO_2^-]$[b]	[Acrylate][e]
0.1	>12.5	5.5	11.60	0.044[c] 0.042[d]	0.027 0.029
0.05	>12.5	5.0	11.62	0.044[c] 0.038[d]	0.015 0.021
0.05	11.0	5.0	9.30	0.00055[c] 0.0026[d]	

[a] (Benzenesulfonyl)propionic acid in NaOH. [b] Benzenesulfinate ions. [c] Analyzed by photopolymerization. [d] Analyzed by ultraviolet spectrum. [e] Analyzed by difference between total bromine analysis and the sulfinate analysis.

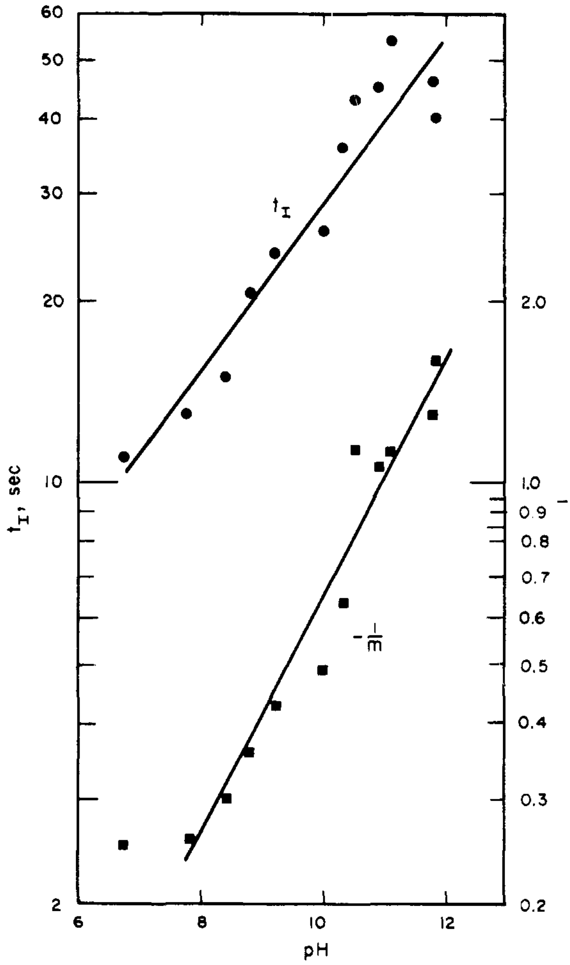

Figure 5. Effect of pH on photopolymerization sensitivity (expt 5).

Discussion

Sensitization Reactions. The data in Table II show that the induction period initially decreased until a minimum induction period of 0.5 ± 0.1 sec was reached. This decrease in induction period was more than a simple temperature effect. At each temperature the decrease in induction period continued beyond the time (2.5-3.0 min) required to raise the temperature of the solution to the temperature of the oven. Furthermore, the minimum induction period was achieved more rapidly as the temperature was raised and the minimum induction period was essentially the same regardless of the temperature to which the solution was heated. As discussed below, continued heating caused complete desensitization due to the disappearance of sulfinate ions by ionic addition to the olefin as indicated in eq 1. The sensitization effect (decreased t_I and faster polymerization) was maximum only after an appreciable period of heating at each temperature, during which the initial *p*-toluenesulfinate concentration (0.02 *M*) would be substantially reduced by reaction with the monomer. Estimates from the deactivation kinetics below indicate that only about 10-30% of the initial sulfinate was present at the minimum t_I.

One factor consistent with these observations is that some quenching of the excited singlet state of the dye occurs at higher sulfinate concentrations, as shown by the fluorescence quenching in Figure 3. We have shown[4] that the photoexcited singlet state (eq 3) can be deactivated by sulfinate quenching (eq 4) without any net reaction. This quenching reduces the formation of the dye triplet (eq 5), which is the reactive species needed for the initiation of polymerization:

$$D^+ + h\nu \xrightarrow{I_a} {}^1D^+ \quad (3)$$

$${}^1D^+ + RSO_2^- \xrightarrow{k_q'} D^+ + RSO_2^- \quad (4)$$

$${}^1D^+ \xrightarrow{\phi} {}^3D^+ \quad (5)$$

The quenching constant (K_Q = 20) found here in 1 *N* barium acrylate corresponds to 28% quenching of ${}^1D^+$ by 0.02 *M* *p*-toluenesulfinate ion. The room-temperature quenching would be less in 2.5 *N* barium acrylate (Figure 3), but at temperatures 45-80° the quenching could be accentuated because of decreased solution viscosity. From these observations and our earlier studies in acrylamide,[4] it seems

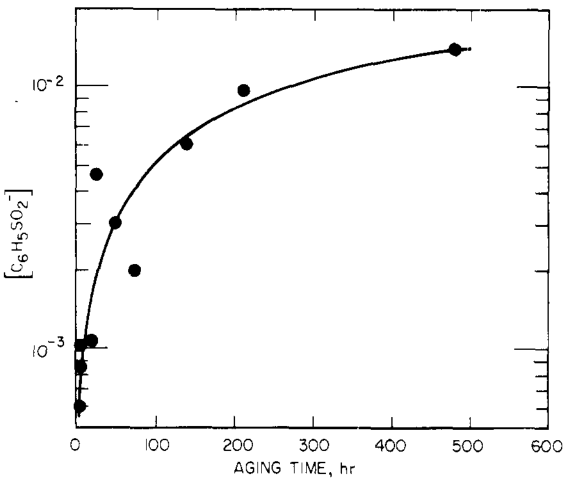

Figure 6. Apparent benzenesulfinate ion concentration in a solution initially 0.05 *M* in sodium 3-(benzenesulfonyl)propionate and pH 12.5 sodium hydroxide (expt 7).

likely that a decrease of 50–70% in the initial 0.02 *M* sulfinate ion concentration might be necessary to reach maximum photopolymerization sensitivities at the higher temperatures. Thus the decrease in sulfinate ion concentration due to ionic addition would at first decrease the dye quenching and this probably accounts for part of the observed sensitization effect.

However, the sensitization effect in Table I is quite large and must involve some other effect, such as the removal of oxygen as an inhibitor. Although photochemically induced redox initiation of polymerization has been investigated extensively, there has been no general agreement on the role of oxygen. Some investigators[17-23] reported that oxygen was at least an important if not an essential component of the initiating system. However, we and others[24-26] have found it to behave primarily as an inhibitor, as indicated in Table III.

Heating increases the rate of polymerization after the end of the induction period. This is shown by the smaller values of ($t_{OD} - t_I$) in Figure 7. The solid lines show the effect of heating for the minimum time required to raise the solution to the oven temperature. The fastest polymerization rates were obtained after heating long enough to reach the minimum t_I. This is illustrated by the dashed lines in Figure 7, which are approximately independent of temperature. The effects of sensitization by heating are similar to those of nitrogen purging in that both a decreased induction period and increased polymerization rates are obtained. This suggests that heating causes the removal of oxygen as an inhibitor. The results in Table IV indicate that oxygen does not react rapidly enough with *p*-toluenesulfinate to be a significant factor. It appears most likely that in the heated solutions the oxygen is consumed by a reaction with the monomer, although we do not know the mechanism of this reaction.

Desensitization Reactions. As heating is continued, there is a time beyond which photopolymerization is markedly retarded and the induction period is increased. After a sufficiently long heating time the composition becomes insensitive to visible light. This type of desensitization was first observed in systems which employed acrylamide and methylenebisacrylamide as the monomers. Storage of the dye and the sodium *p*-toluenesulfinate as a single solution followed by combination with monomer just prior to exposure did not affect the sensitivity; neither did storage of a combined dye and monomer solution with the sulfinate added just prior to exposure. Storage of combined monomer and sulfinate solution or of combined monomer, sulfinate, and dye solution caused the activity to be diminished, however. This behavior revealed that the inactivation was the result of a reaction between the monomer and the *p*-toluenesulfinate. An elevation in pH was noted when an aqueous solution of acrylamide and sodium *p*-toluenesulfinate was allowed to stand. Periodic titration with dilute acid to restore the pH to its original value yielded a curve describing the rate of the base-releasing reaction. As this reaction approached completion, desensitization of photopolymerization activity occurred.

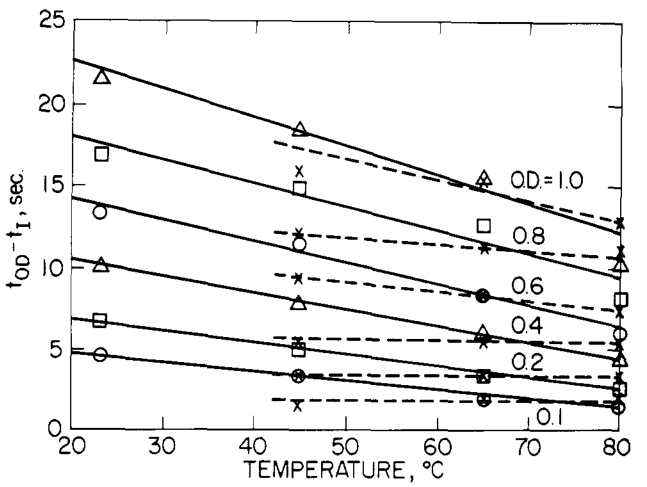

Figure 7. The effect of temperature on polymerization rate, shown by exposure time after induction period to reach a given optical density. Solid lines (open points), immediately after reaching indicated temperature; broken lines (X points), after samples first reached the minimum t_I (0.5 sec) at indicated temperature (expt 1).

The reaction that occurs is the Michael-type addition of the sulfinate to the acrylic double bond, as indicated in eq 1. We have made detailed studies[9] of this reaction with various benzenesulfinate and acrylic structures. Periodic titrations of the base formed were used to determine the rate constant for the reaction of *p*-toluenesulfinate with 1.0 *N* barium acrylate ($k_B = 2.6 \times 10^{-5}$ l. mol^{-1} sec^{-1} at 25°), and a spectrophotometric technique was used to determine its reaction rate with dilute acrylic acid ($k_A = 9.1 \times 10^{-4}$ l. mol^{-1} sec^{-1} at 25°). In general, the rate of photopolymerization desensitization is related to the rate of sulfinate ion disappearance given by

$$-\mathrm{d}[S]/\mathrm{d}t = k_A[S][M_A] + k_B[S][M_B] \qquad (6)$$

in which [S] is the concentration of *p*-toluenesulfinate ion, $[M_A]$ is the concentration of acrylic acid, $[M_B]$ is the concentration of acrylate ion, and k_A and k_B are the rate constants for desensitization by addition to the free acid and the acrylate ion, respectively. The above values indicate that $k_A = 35k_B$ at 25°. Since acrylic acid has a pK = 4.25, the desensitization of barium acrylate in the low pH range becomes increasingly dominated by the fast ionic addition to the acrylic acid present in equilibrium as the pH is lowered below 6. This accounts for the very rapid deactivation of photosensitivity observed at pH 4.6. On the other hand, as the pH is increased above 6 the ionic addition to the acrylate ion becomes the dominant factor in desensitization.

Kinetic Analysis of Thermal Desensitization. We have previously analyzed the mechanism of photopolymer initiation and have shown evidence of dye triplet reaction with sulfinate ions to produce the free radicals that initiate polymerization.[4]

The reactions governing the early stages of photopolymerization can be approximated as follows, with the accompanying expressions for their reaction velocities

$$^3D^+ + RSO_2^- \rightarrow D\cdot + RSO_2\cdot \qquad k_c[^3D^+][S] \qquad (7)$$

$$^3D^+ \rightarrow D^+ \qquad [^3D^+]\tau^{-1} \qquad (8)$$

$$^3D^+ + RSO_2^- \rightarrow D^+ + RSO_2^- \qquad k_q[^3D^+][S] \qquad (9)$$

$$D\cdot + RSO_2\cdot \longrightarrow D^+ + RSO_2^- \qquad k_r[D\cdot][S\cdot] \qquad (10)$$

$$2D\cdot + H_2O \rightarrow D^+ + DH + OH^- \qquad k_d[D\cdot]^2 \qquad (11)$$

$$RSO_2\cdot + N \rightarrow RSO_2N\cdot D\cdot \text{ (inactive)} \qquad k_n[S\cdot][N] \qquad (12)$$

$$RSO_2\cdot + M \longrightarrow RSO_2M\cdot \qquad k_p[S\cdot][M] \qquad (13)$$

$$RSO_2(M)_x\cdot + M \rightarrow RSO_2(M)_{x+1}\cdot \qquad k_p[R\cdot][M] \qquad (14)$$

$$2RSO_2(M)_x\cdot \rightarrow [RSO_2(M)_x]_2 \qquad k_t[R\cdot]^2 \qquad (15)$$

$$RSO_2(M)_x\cdot + D\cdot \longrightarrow RSO_2(M)_xD \qquad k_{t'}[R\cdot][D\cdot] \qquad (16)$$

$$RSO_2(M)_x\cdot + D^+ \longrightarrow RSO_2(M)_xD\cdot^+ \qquad k_a[R\cdot][D] \qquad (17)$$

When the sulfinate concentration is low enough to avoid quenching of the dye's excited singlet state (eq 4), then its triplet state ($^3D^+$) photostationary state concentration can be derived from eq 3, 5, 7, 8, and 9 to give

$$[^3D^+] = I_a\phi/\{\tau^{-1} + (k_c + k_q)[S]\} \qquad (18)$$

where I_a = intensity absorbed, ϕ = intersystem crossing efficiency, and τ = triplet lifetime. The initial reactions of the free radicals are mainly with the inhibitor (N); however, as the induction period ends, $[N] \rightarrow 0$ and the free-radical concentration, $[R\cdot]$, builds up while polymerization is initiated. Consequently, after the induction period we can assume photostationary state concentrations of $RSO_2\cdot$, $D\cdot$, and $R\cdot$ are established, where $R\cdot$ is taken to indicate all active polymer radicals. (The radical formed by eq 17 is assumed to be an active radical for purposes of this analysis, although we do not know about its subsequent reactions.) We can further assume that at high monomer concentrations $RSO_2\cdot$ is almost entirely captured by monomer, so that eq 10 can be neglected. It follows that

$$k_c[^3D^+][S] - k_p[S\cdot][M] = 0 \qquad (19)$$

$$k_c[^3D^+][S] - 2k_d[D\cdot]^2 - k_{t'}[R\cdot][D\cdot] = 0 \qquad (20)$$

$$k_p[S\cdot][M] - 2k_t[R\cdot]^2 - k_{t'}[R\cdot][D\cdot] = 0 \qquad (21)$$

Equations 19 to 21 can be combined with eq 18 and rearranged to give eq 22, in which $\beta = 2k_t + k_{t'}(k_t/k_d)^{1/2}$

$$[R\cdot] = \left(\frac{k_c[^3D^+][S\cdot]}{\beta}\right)^{1/2} = \left[\frac{k_c[S]}{\beta}\left(\frac{I_a\phi}{\tau^{-1} + (k_c + k_q)[S]}\right)\right]^{1/2} \qquad (22)$$

The rate of polymerization, P, is given by

$$P = -\,d[M]/dt \simeq k_p[R\cdot][M] = k_p[M]\left[\frac{k_c[S]}{\beta}\left(\frac{I_a\phi}{\tau^{-1} + (k_c + k_q)[S]}\right)\right]^{1/2} \qquad (23)$$

An approximate measure of the polymerization rate can be obtained by letting $P = -\Delta[M]/\Delta t$ and using the reciprocal of the exposure time after the induction period to achieve an optical density of 0.1 as a measure of $-\Delta[M]/\Delta t$ in the initial stages. The data are plotted in Figure 8.

Before the addition reaction consumes most of the *p*-toluenesulfinate ion, it is expected to be present in sufficient concentration so that $k_c[S][^3D^+] \gg \tau^{-1}[^3D^+]$. Thus, prior to the onset of thermal desensitization, the initial polymerization rate (P_0) after the inhibitors are gone will be constant for a given light intensity and concentration of dye and monomer, so that eq 23 can be simplified

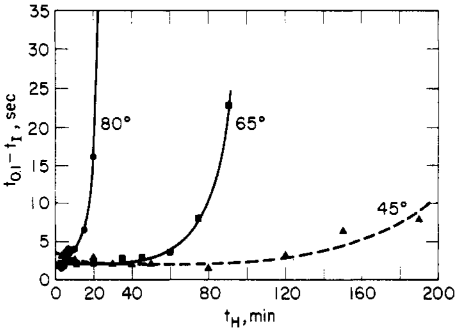

Figure 8. Effect of heating on the initial rate of photopolymerization, shown by exposure time after induction period to reach an optical density of 0.1 (expt 1).

$$P_0 = k_p[M]\left[\frac{k_cI_a\phi}{\beta(k_c + k_q)}\right]^{1/2} \qquad (24)$$

By substituting eq 24 in eq 23 we find that

$$P = P_0\left[\frac{[S]}{\left(\frac{\tau^{-1}}{k_c + k_q}\right) + [S]}\right]^{1/2} \qquad (25)$$

Since $\tau^{-1}/(k_c + k_q)$ is a constant, it can be expressed in terms of a specific initial *p*-toluenesulfinate concentration and a constant of proportionality: $\tau^{-1}/(k_c + k_q) = \alpha[S_0]$. Substituting in eq 25 and rearranging terms, we obtain

$$[S]/[S_0] = \alpha P^2/(P_0^2 - P^2) \qquad (26)$$

From Figure 8 the value of 0.5 sec^{-1} can be obtained for P_0, where $P_0 = (t_{0.1} - t_I)^{-1}$ which is the value after sensitization and before desensitization begins.

The pH change due to eq 1 is small for the solutions in Table II (or Figure 8) because of the presence of acrylate ions. The initial pH of 5.92 can be calculated to change only to 6.13 even after all of the sulfinate ion has reacted *via* eq 1. The pH changes very slightly between its value at P_0 and a slower polymerizing rate P, because about 50–75% of the initial sulfinate is already gone before $P < P_0$. During the desensitization period an average pH of 6.11 is calculated, which corresponds to an approximately constant acrylic acid concentration $[M_A]$ of 3.4×10^{-2} *M*. The acrylate ion concentration $[M_B]$ is constant at 2.45 *M*. Thus $[M_A]$ and $[M_B]$ can be considered as constants in eq 6, and it can be integrated as a pseudo-first-order reaction to give

$$2.3 \log ([S]/[S_0]) = -(k_A[M_A] + k_B[M_B])t_H = k_{app}t_H \qquad (27)$$

Substitution of eq 26 into eq 27 gives

$$\log\left(\frac{P^2}{P_0^2 - P^2}\right) = -\log\alpha - \left(\frac{k_A[M_A] + k_B[M_B]}{2.3}\right)t_H \qquad (28)$$

Plots of eq 28 are shown in Figure 9, where the slopes of the lines give k_{app} values of 5.0×10^{-4}, 2.1×10^{-3}, and 5.8×10^{-3} sec^{-1} at 45, 65, and 80°, respectively. If we assume that the rate constants at higher temperatures have the same ratio[9] as they do at 25°, then $k_A = 35k_B$ and values for k_A and k_B can be calculated from the slopes in Figure 9. These values fit activation energy plots which give E_a = 15.5 kcal/mol. Extrapolation to 25° yields $k_A = 8.5 \times 10^{-4}$ and $k_B = 2.5 \times 10^{-5}$ l. mol^{-1} sec^{-1}, which compare favorably with the values obtained previously[9] (9.1×10^{-4} and 2.6×10^{-5}, respectively). Thus, the rate of thermal desensitization as determined by photopolymerization sensitivity agrees quite well with the rates of

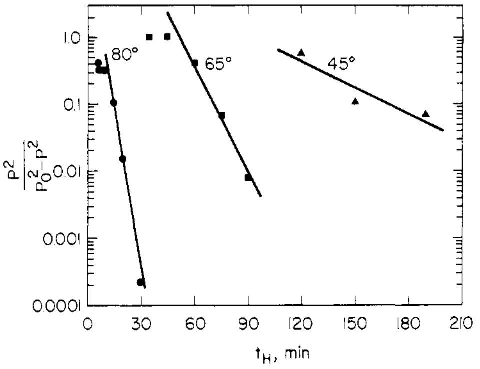

Figure 9. Kinetic plot of the effect of heating time on a function of the initial rate of photopolymerization (expt 1).

ionic addition as determined by titrimetric and spectrophotometric measurements. We calculate that at an average pH of 6 the desensitization would result from about 38% of the *p*-toluenesulfinate ion adding to the free acid and about 62% adding to the acrylate anion.

Stability at High pH. The photopolymerizability of these solutions can be decreased rapidly by heating them at a low pH. On the other hand, prolonged periods of photosensitivity are often desirable and were obtained from solutions at high pH, as shown in Figure 4 and Table V. Raising the initial pH eliminates the ionic addition reaction with the free acrylic acid, which at pH 8 would consume only about 0.4% as much sulfinate as the acrylate anion. Another consequence is that the buffering action of acrylic acid is lost, and the formation of hydroxide ion from the ionic addition of sulfinate to acrylate ions causes the pH to rise substantially. Hydroxide ions react with the sulfone addition product, as shown by our studies of 3-(benzenesulfonyl)propionate in NaOH solutions, where the pH drops and benzenesulfinate ions are formed. These results are shown in Figure 6 as well as by our ultraviolet spectral analysis of the sulfone and sulfinate ions present. This is consistent with the report by Holmberg and Schjånberg[13] that acrylate ions and benzenesulfinate ions are obtained by hydroxide ion reaction with this sulfone, as indicated by the k' reaction in eq 1. The equilibrium constant is expressed by

$$K = k/k' = [\mathrm{RSO_2CH_2CH_2COO^-}][\mathrm{OH^-}]/[\mathrm{RSO_2^-}][\mathrm{CH_2{=}CHCOO^-}] \quad (29)$$

In the aged solutions of sulfone (Table VI) we found somewhat less acrylate ion than sulfinate ion from the hydroxide ion attack. Probably some of the acrylate ions were converted to 3-hydroxypropionate ions by hydroxide ion catalysis.[27,28] Using eq 29 and the concentrations determined for the first two solutions in Table VI, values for the equilibrium constant K were found to be in the range of 0.039–0.19. The 5.5-month old solution had more acrylate present, had the best agreement in the sulfinate analyses, and showed similar amounts of sulfone and sulfinate. Its calculated K was 0.19. If the K were also 0.19 in highly concentrated monomer solutions, then for example a 5 N barium acrylate solution at pH 11 with 0.1 M sulfone would provide an equilibrium concentration of 1×10^{-4} M benzenesulfinate—enough to make the solution photopolymerizable with Methylene Blue. We observed qualitatively that on standing at pH 12 a 4.5 N barium acrylate solution containing dye and 0.1 M 3-(benzenesulfonyl)propionate within 25 min decreased in pH and became slightly photosensitive. Upon adjusting to pH 7 after 6 hr, it was quite readily photopolymerized, indicating a substantial amount of sulfinate had been formed.

An equilibrium of sulfinate and sulfone in basic acrylate solutions could account for the long-term presence of benzenesulfinate in the solutions described in Table V and Figure 4. However, these solutions maintained a higher sulfinate level than would be expected from the above estimates of K. The 1-month old solutions in Table V rose to a pH of 11 and appeared to contain about 32% of their initial sulfinate concentration. (At a constant pH of 7 the sulfinate would have all reacted in 40 hr.[9]) If these 1-month old barium acrylate solutions were at equilibrium, then K would be only 5×10^{-4}, which is far lower than any of the values calculated above from solutions in which the sulfone was added to sodium hydroxide. The high ionic concentrations in the monomer could alter the activity coefficients of the reactants in eq 1, but the large variations in the estimated K indicate that the reactions may be more complex than the sulfinate–sulfone equilibrium shown by eq 1. In any case, the desensitization of photopolymerizable solutions is retarded in the higher pH range probably because an equilibrium condition is approached. Additional storage stability can be expected by initially using a relatively high concentration of sulfone along with the sulfinate in the photosensitive barium acrylate solutions.

Conclusions

Thermal dark reactions in a photopolymerizable composition of barium acrylate, Methylene Blue, and sodium *p*-toluene- or benzenesulfinate lead to an initial increase in photosensitivity followed by a subsequent decrease. The most important reaction under these conditions is the Michael-type addition of sulfinate to the double bond of monomer. Part of the sensitization can be explained as a decrease in quenching of excited dye as the sulfinate concentration is reduced. This is inadequate to explain the total effect, however, and the major portion of the sensitization appears to be the result of a thermal reaction removing dissolved oxygen, which acts as an inhibitor. Desensitization is caused by the continued loss of sulfinate ion (by ionic addition) after the optimum photocatalytic concentration is obtained. Since the addition to acrylic acid occurs about 35 times as fast as the addition to acrylate ion, the rate of desensitization is strongly dependent on the pH. When the initial quantity of acrylic acid exceeds that of sulfinate ion, the base generated by the addition reaction is neutralized and the desensitization proceeds to completion at a rate consistent with the amounts of acrylic acid and acrylate ion present. When the amount of sulfinate ion exceeds that of acrylic acid, the pH rises sharply as the acid is neutralized. At high pH the reaction of sulfinate and monomer approaches an equilibrium condition, and the composition retains photosensitivity much longer than predicted on the basis of the reaction rates in a neutral solution.

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Microstructure of Poly(2,3-dimethyl-1,3-butadiene) Prepared by Butyllithium in Cyclohexane. 220-MHz Nuclear Magnetic Resonance Study

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ABSTRACT: The 220-MHz nmr spectra of poly(2,3-dimethyl-1,3-butadiene) (PDMB) prepared by butyllithium in cyclohexane are compared to those of free-radical PDMB. By aid of measurements done on *cis*-1,4-and *trans*-1,4-PDMB prepared by Ziegler catalysts, it is shown that not only the overall contents of cis and trans units can be determined but also the distribution of dyads and triads of these structural units. Anionic PDMB presents long sequences of trans units giving rise to a partial crystallization observed by X-ray diffraction.

The microstructure of poly(2,3-dimethyl-1,3-butadiene) (PDMB) prepared by anionic polymerization under various conditions has been extensively studied by Schué[1] about 10 years ago. Using nmr spectroscopy this author has shown that with respect to the concentration of unsaturated side groups in the polymers formed, 2,3-dimethyl-1,3-butadiene (DMB) behaves similarly to butadiene and isoprene. DMB tends to form a polymer rich in 1,2 units in polar systems, such as with lithium in H_4furan or sodium in hydrocarbon solvents and forms a polymer having a high 1,4 content when polymerized with butyllithium or metallic lithium in nonpolar solvent.

More recently, Yuki *et al.*[2] reported essentially the same results and moreover they showed that the 1,2 content of PDMB obtained with *n*-butyllithium in pure H_4furan depends strongly on polymerization temperature, a behavior which contrasts with those of butadiene and isoprene. With regard to PDMB prepared by *n*-butyllithium in pure hydrocarbons, contrary to Schué, these authors were not able to distinguish the cis-1,4 and trans-1,4 isomers using 100-MHz nmr spectroscopy. In a recent study of anionic polymerization of DMB by *sec*-butyllithium in cyclohexane, we were also confronted with this problem.[3] At 100 MHz the resonances of the methyl and methylene protons in trans-1,4 units are barely distinguishable from those of cis-1,4 units. In the present paper the 220-MHz spectra of anionic PDMB are compared to those of free-radical PDMB. By aid of measurements done on *cis*-1,4- and *trans*-1,4-PDMB prepared by Ziegler catalysts, it is shown that not only the overall contents of the cis and trans units can be determined but also the distribution of dyads and triads of these structural units.

Experimental Section

All preparations were carried out in sealed high-vacuum systems. 2,3-Dimethyl-1,3-butadiene of a purity of 99.9% (vapor-phase chromatography) was degassed on the vacuum line, submitted to a partial prepolymerization with *n*-BuLi and distilled in break-seal ampoules. Cyclohexane was distilled over *n*-BuLi before use. *sec*-BuLi was purified by short-path distillation, diluted to a concentration of about 10^{-2} *M* and sealed in fragile bulbs. Anionic PDMB was prepared at 60°. The reaction vessels had been previously purged with *n*-BuLi and washed by distilling solvent from its solution. *cis*- and *trans*-PDMB were prepared at 25° with triethylaluminum–titanium tetrachloride Ziegler catalysts according to the specific methods previously described by Yen.[4] The configurations of these last two samples were confirmed by means of X-ray diffraction according to Yen's data and interpretation. Finally, a free-radical sample was prepared at 60° with 0.01 mol of 2,2′-azobis(2-methylproprionitrile)/mol of monomer.

Powder X-ray diffraction patterns were recorded *in vacuo*, in a flat film Warhus camera using Ni-filtered Cu Kα radiation. Infrared spectra were measured with a Perkin-Elmer 621 spectrometer on either thin film casts or KBr dispersions. Nmr spectra were measured at 100° with a Varian HR-220 spectrometer using chlorobenzene as solvent and tetramethylsilane as internal standard. Sample concentrations were close to 5%. Peaks were resolved by hand on expanded-scale spectra.

Results and Discussion

Contrary to free-radical PDMB, anionic PDMB prepared by butyllithium in pure cyclohexane is a partially crystalline polymer. As shown in Table I, a powder X-ray diffraction pattern of this polymer presents "*d*" spacings identical to those of the trans polymer. On the other hand, as shown in Figure 1, the infrared spectrum of the anionic PDMB is apparently very similar to that of the free-radical PDMB, except for the relative intensities of