Adiabatic Photopolymerization of Acrylamide*

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Synopsis

Although the adiabatic polymerization of acrylamide using photoinitiation was first described over 30 years ago, it still offers convenient opportunities for innovation. In the present work, the effect of EDTA (ethylenediaminetetraacetic acid, tetrasodium salt) as a reducing agent with two photosensitizers is described. With riboflavin-5'-phosphate sodium, the rate of polymerization rises with the ⅓ power of the EDTA concentration. With a new photosensitizer, 4-benzoyl-*N,N,N*-trimethylbenzenemethanaminium chloride, the rate rises with the ½ power of the EDTA concentration. Adiabatic temperature rise is used as the measure of conversion in the early stages of polymerization.

INTRODUCTION

Photopolymerization of acrylamide in water can produce a high molecular weight polymer very rapidly.[1-4] Many years ago, Oster et al.[1] showed that riboflavin has some distinct advantages as an initiator. Oxygen does not have to be removed from the system. In fact, some oxygen is necessary for initiation to proceed. Visible light is almost as effective as ultraviolet. Over the years, acrylamide gels for chromatographic separations have been prepared using acrylamide–riboflavin with the addition of methylene bisacrylamide as a crosslinking agent. The phosphate derivative of riboflavin (Fig. 1) is more popular than the unsubstituted riboflavin because it is more soluble in water.

At monomer concentrations of 4–7 mol/L (30–50% by weight), the reaction proceeds almost adiabatically and the temperature rise can be used to follow conversion.[1,2,5] An extensive analysis of the kinetics is difficult because the Trommsdorff effect becomes apparent rather early on. However, the initial temperature rise rate gives a reasonable correlation in many cases. The ease with which multiple samples can be run simultaneously and rapidly has made this photopolymerization a convenient example for a teaching laboratory exercise.[5]

We have observed that various lots of acrylamide obtained from diverse sources do not always give consistent results. The response to changes in monomer and riboflavin concentrations is of the same power dependence, but the absolute value of polymerization rate differs from lot to lot. On the other hand, when EDTA (ethylene diamine tetraacetic acid, sodium salt) is added to the monomer solution, the induction period is decreased, and the rate differences from lot to lot seem to be diminished. The EDTA probably

* Presented at the 14th Northeast Regional Meeting of the American Chemical Society at Fairfield University, Fairfield, CT, June 10–13, 1984.

Journal of Applied Polymer Science, Vol. 30, 1629–1637 (1985)
 CCC 0021-8995/85/041629-09$04.00

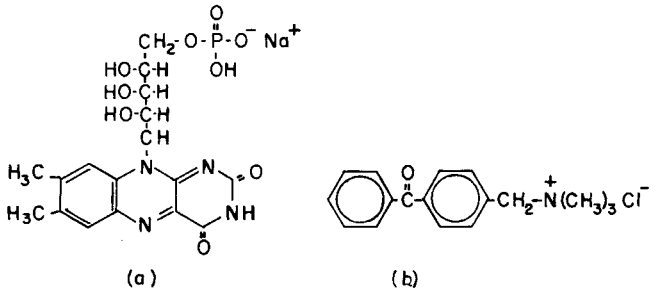

Fig. 1. Photoinitiators: (a) riboflavin-5'-phosphate ester, monosodium (dihydrate), FW = 376 for riboflavin (ester dihydrate is equivalent to 70% active riboflavin); (b) 4-benzoyl-*N,N,N*-trimethylbenzenemethanaminium chloride (Quantacure BTC), FW = 289.8.

acts as a reducing agent since so many dye-sensitized systems seem to require a reducing agent.[1-4]

In the work reported here, the effect of EDTA on photopolymerization was studied. Also, a parallel study was conducted with a new photoinitiator, 4-benzoyl-*N,N,N*-trimethylbenzenemethanaminum chloride (Quantacure BTC) (Fig. 1). This second initiator, abbreviated as BTC, has been disclosed along with other analogous water-soluble benzil and benzophenone derivatives.[6] A similar initiator has been used to polymerize butyl acrylate.[7]

EXPERIMENTAL

Acrylamide (Eastman Kodak) generally was used as received although recrystallization from chloroform did give a slightly lower rate of polymerization as mentioned later. The EDTA salt (Aldrich), riboflavin phosphate (Hoffman-LaRoche), and BTC (Aceto) were used as received.

A total of eight "black light" lamps are arranged in a square box (Fig. 2). The lamps (General Electric F15T8/BLB) have a peak intensity at 354 nm and fit in common 15-W fluorescent lamp fixtures. There is no particular

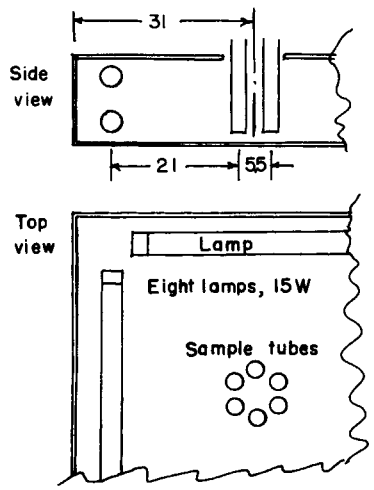

Fig. 2. Photopolymerization apparatus containing eight lamps and six sample tubes. Dimensions shown are in centimeters. Interior of box is lined with aluminum sheet.

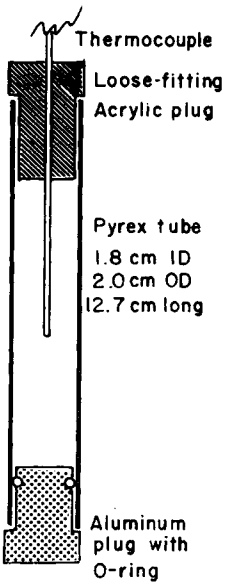

Fig. 3. Polymerization tube.

hazard to the eyes with these lamps, but caution is always advisable. The monomer solutions (16 mL each) are contained in Pyrex tubes cut from standard tubing (Fig. 3). The use of the aluminum plugs with rubber O-rings simplifies removal of the polymer at the end of the experiment. In each tube, a stainless-steel sheathed thermocouple is centered. In the case of the BTC-initiated samples, nitrogen or helium is bubbled through the solution for 5 min before irradiation begins. The typical pattern for polymerization is indicated in Figure 4 along with the method of analysis. Both the induction period θ_i and the rate of temperature rise, $(dT/d\theta)^*$, arbitrarily measured at 35°C, are important and reproducible for riboflavin-initiated polymerization. All polymerizations were started at approximately 25°C. The induction period is an indicator of the rate of initiation during the time when some competitive reaction is favored over propagation. It is often assumed that dissolved oxygen is responsible for the induction period. However, removal of all oxygen keeps the polymerization with riboflavin from

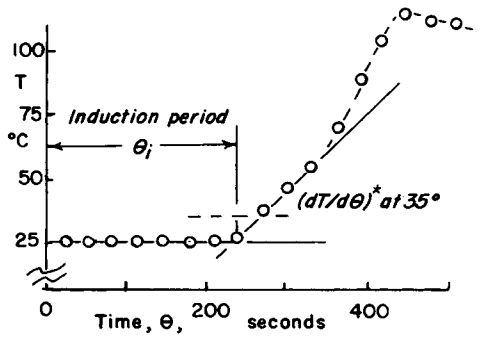

Fig. 4. Typical quasi-adiabatic exotherm for acrylamide polymerization with photosensitizer and EDTA. The linear behavior in the initial stage is not uncommon.

occurring. On the other hand, the induction period when BTC is the initiator can be reduced to a few seconds if the solution is thoroughly sparged with nitrogen and a small amount of EDTA is present.

RESULTS AND DISCUSSION

Riboflavin Initiation

The effects of EDTA are a decrease in the induction period θ_i and an increase in polymerization rate (Fig. 5). In the absence of EDTA, rather large fluctuations have often been noted, especially in θ_i. The dependence of the same two performance variables on riboflavin concentration is very similar (Fig. 6). This suggests that the EDTA does not act by suppressing or activating some minor metallic constituent such as iron or copper, but in the same manner as the reducing agents in other redox couples. EDTA will inactivate the copper ions added to commercially available monomer solutions as inhibitors. Manufacturers recommend addition of EDTA as one method of dealing with inhibitors.[8,9] However, even small amounts of EDTA cause the usual redox couples to become inactive. Presulfate–metabisulfite[10] and hydrogen peroxide–hydroxyl amine[11] are two such systems. Both of these systems are strongly accelerated by iron salts but only operate in the absence of EDTA.

While the dependence of rate on both EDTA and riboflavin is to the 1/3 power, there are limits. In the case of riboflavin, increasing concentration much above 30 μmol/L does not increase the rate. Apparently, the light absorption becomes localized at the wall so that nonuniform polymerization takes place. At EDTA concentrations below 0.10 mg/g of monomer, the rate is seen to be less reproducible. The induction period also changes in its exponential dependence at low concentrations perhaps reaching a value of -1 as opposed to the $-1/3$ at higher concentrations.

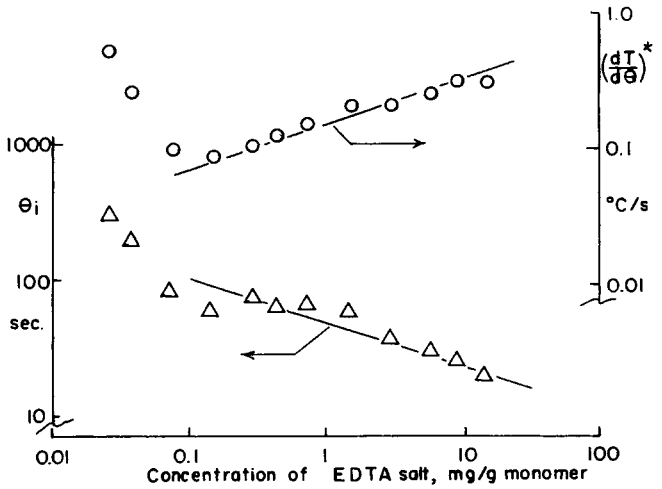

Fig. 5. Effect of EDTA on induction period, θ_i, and rate of polymerization, $(dT/d\theta_i)^*$. All runs started at 25°C with 6.0 mol/L acrylamide and 19 μmol/L riboflavin.

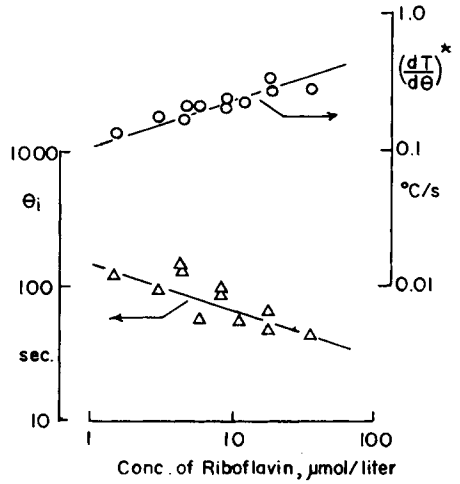

Fig. 6. Effect of riboflavin phosphate concentration on induction period, θ_i, and rate of polymerization, $(dT/d\theta)^*$. Slopes shown are $-1/3$ and $+1/3$, respectively. Runs started at 25°C with 6.0 mol/L acrylamide and 7.0 mg EDTA/g acrylamide.

The dependence of rate on monomer concentration is similar to that found by previous workers.[1,2] The rate appears to depend on the initial monomer concentration to about the third power (Fig. 7). Since EDTA was used in constant ratio to monomer in these experiments, the actual rate dependence on monomer alone at constant total EDTA concentration would be to a power of about $2\frac{2}{3}$. The rationalization for the high power dependence on monomer concentration given by Delzenne et al.[2] is that acrylamide reacts with the initiator in two stages and that a cage reaction is important in giving some radical recombination.

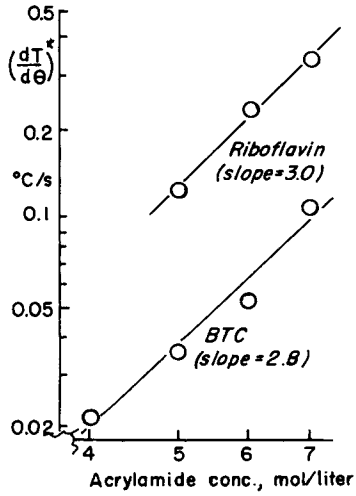

Fig. 7. Effect of initial monomer concentration on rate of polymerization, $(dT/d\theta)^*$. Runs started at 25°C with 19 μmol/L of riboflavin phosphate and 7 mg EDTA/g acrylamide or 1.0 mmol/L BTC and 1.5 mg EDTA/g acrylamide.

Recrystallization of the monomer from chloroform, at least in one instance, did not change the qualitative effects of concentration. The θ_i was not changed at all, but the rate was uniformly decreased by a factor of 1.3. This suggests the removal by recrystallization of some accelerating species. With this in mind, copper, a common contaminant, was added. However, copper in the range of 1–10 g/g acrylamide had no discernible effect on θ_i or $(dT/d\theta)^*$ at EDTA concentrations of 0.15 or 1.5 mg/g acrylamide.

The molecular weights produced are quite high and increase, as one might expect, as the initiator concentration is decreased (Fig. 8). Molecular size is most conveniently measured by dilute solution viscosity. The use of a salt solution ($1N$ $NaNO_3$) diminishes the complication arising from partial hydrolysis. A partially ionic polyacrylamide shows typical reduction in viscosity with salt addition so that a "normal" Huggins equation can be used to extrapolate data to an intrinsic viscosity $[\eta]$ according to

$$\eta_{sp}/c = [\eta] + k'[\eta]_c^2$$

where the specific viscosity η_{sp} is the ratio of the difference between solution and solvent viscosity to the solvent viscosity, c is the concentration (g/dL), and k' is a constant. For high molecular weight polymers in $1N$ $NaNO_3$ at 30°C, we have found $k' = 0.5$ is a reasonably reproducible number. Actual concentrations of 0.05–0.2 g/dL were used in the present work. In the absence of salt, dilute solution viscosities often are as much as 100 times greater and are not represented by the Huggins equation.

The change in molecular size is consistent with the pattern of rate dependence on initiator concentration. The power of -0.4 for dependence of intrinsic viscosity on riboflavin concentration translates to a power dependence of about -0.5 when intrinsic viscosity is converted to molecular weight by one of the several Mark–Houwink equations recommended in the literature.[12] In a way, this consistency is rather surprising because much

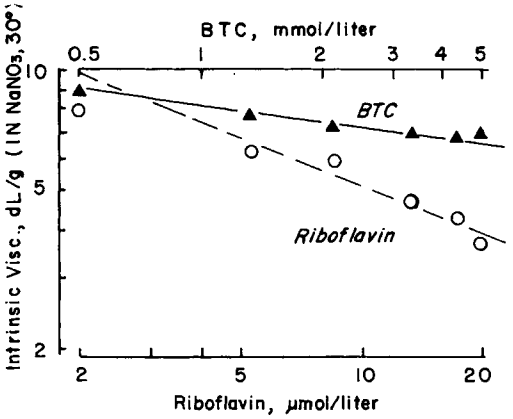

Fig. 8. Intrinsic viscosity decreases with riboflavin concentration to the 0.4 power and with the BTC concentration to the 0.15 power. For both initiators, the monomer concentration is 6 mol/L and EDTA level is 7 mg/g monomer.

of the high molecular weight polymer is probably produced during the Trommsdorff period in which the termination rate is diminished by the high viscosity of the system.

BTC Initiation

When BTC is used as the photoinitiator, the system has to be sparged with nitrogen as has been noted before. Induction periods are not reported here since they are virtually eliminated. The dependence of rate on BTC and EDTA concentrations is to the one-half power for each (Figs. 9 and 10). The dependence on monomer concentration is very similar to the riboflavin case, about the 2.8 power (Fig. 7).

The salient feature of initiation by BTC is the necessity for EDTA in order to get a reasonable rate. Also, without EDTA, long induction periods may be encountered, even with nitrogen sparging. At an EDTA level of 0.10 mg/g acrylamide, the rate is almost the same as with no EDTA (Fig. 9) but the induction period is negligible.

Thus it would appear possible to get approximately the same rate of polymerization using either BTC or riboflavin with the difference that the needed concentration of BTC is 100 to 1000 times as large. The general features are the same. The induction periods with riboflavin are an inconvenience, but they can be correlated and predicted. The absence of the sparging step is a redeeming feature.

When it comes to examining the molecular size obtained with each initiator, a more clear-cut differentiation is possible (Fig. 8). The intrinsic viscosity is higher when BTC is used at concentrations giving comparable rates to those with riboflavin. Also, the intrinsic viscosity decreases only with the -0.15 power of BTC whereas the falloff with riboflavin is to the -0.4 power. A permissible surmise perhaps is that the riboflavin–oxygen product acts as a chain terminator whereas BTC or its degradation product is a less potent terminator.

The influence of EDTA on molecular size is similar to that for the photoinitiators. There is a difference in that polymerization does occur in the complete absence of EDTA (Table I) albeit in an erratic manner. Polymer-

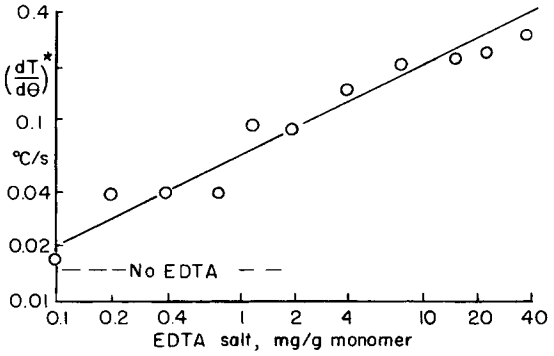

Fig. 9. Rate of polymerization increases with the ½ power of EDTA concentration. Acrylamide concentration was 6.0 mol/L and BTC was 2.5 mmol/L.

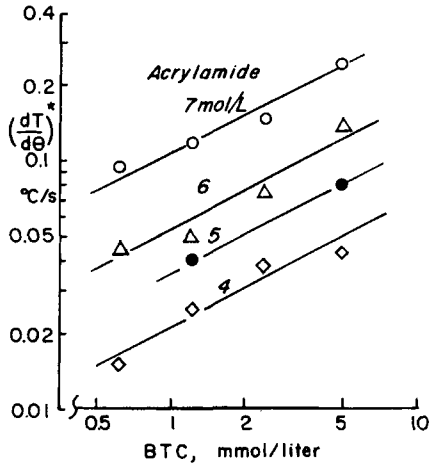

Fig. 10. Dependence of rate of polymerization on BTC concentration at four levels of acrylamide concentration. Slopes drawn are +½. EDTA concentration was 1.5 mg/g acrylamide.

ization does not occur in the absence of a photoinitiator such as riboflavin or BTC. Increased EDTA does lower the intrinsic viscosity. Degradative chain transfer to amines is common enough in free-radical polymerizations to make it seem a reasonable rationalization to invoke at this point.

CONCLUSIONS

The results of our quasiadiabatic polymerizations can be put in the form of an equation for the rate of temperature rise, $(dT/d\theta)^*$ (°C/s) at 35°C. For riboflavin phosphate,

$$(dT/d\theta)^* = 0.2([M]_0/6.0)^{3.0}([I]_0/10)^{1/3}([EDTA]/7.0)^{1/3}$$

where the following ranges apply: $5 < [M]_0 < 7$ (mol/L), $1 < [I]_0 < 20$ [μmol/L (riboflavin)], and $0.1 < [EDTA] < 20$ (mg/g acrylamide). For the photoinitiator BTC,

$$(dT/d\theta)^* = 0.2([M]_0/6.0)^{2.8}([I]_0/2.5)^{1/2}([EDTA]/10)^{1/2}$$

where the ranges are $4 < [M]_0 < 7$ (mol/L), $0.5 < [I]_0 < 5$ [mmol/L (BTC)], and $0.1 < [EDTA] < 40$ (mg/g acrylamide).

TABLE I
Effect of EDTA on Molecular Size[a]

Photoinitiator concentration	EDTA, concentration (mg/g acrylamide)	Intrinsic viscosity (dL/g), 1*N* $NaNO_3$, 30°C
Riboflavin, 19 μmol/L	0	6.5
	1.5	4.5
BTC, 2.5 mmol/L	0	9.5
	1.5	8.0
	15	4.5

[a] Samples polymerized starting at 25°C with 6.0 mol/L monomer.

Both of these photoinitiated systems are capable of producing high molecular weight polyacrylamide with intrinsic viscosities in water of over 6 dL/g. These polymers have many useful applications as flocculants, thickening agents, and drag reducing additives.

The authors thank Hoffmann-La Roche, Inc., for the riboflavin-5'-phosphate and Ward Blenkinsop and Co, Ltd., together with their distributor in the United States, Aceto Chemical Co., Inc. for the Quantacure BTC. We also thank the Eastman Kodak Co. for financial support of this work.

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Received June 11, 1984
Accepted August 30, 1984