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Photoinitiated Polymerization of Methyl Methacrylate Using Q-Sized ZnO Colloids

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The polymerization of methyl methacrylate has been shown to occur readily using Q-sized ZnO semiconductors as photoinitiators. We have examined the effects of solvent, monomer concentration, initiator concentration, light intensity, and semiconductor particle size upon the reaction rates. The reaction pathway appears to be via anionic initiation, followed by free-radical propagation steps. The holes formed upon illumination are scavenged by the solvent. Increasing the concentration of the photoinitiator increased polymer yield until a saturation value was achieved. The rate of polymerization rapidly increased with increasing monomer concentration, due to the Trommsdorf effect. The rate of polymerization was found to depend upon the square root of the incident light intensity, as predicted from simple kinetic theory. Quantum yields of polymerization decreased as particle size decreased, due to either increased surface defects or enhanced rates of competing electron-hole recombination. Under the same experimental conditions, no polymerization occurred with bulk-size ZnO particles as photoinitiators; thus Q-sized ZnO particles were more efficient photoinitiators of polymerization.

Introduction

Previous research efforts in semiconductor photoassisted polymerization have demonstrated that semiconductors can be used as initiators for radical polymerization reactions.¹⁻⁴ For example Markham and Kuriacose¹ reported on the photopolymerization of methyl methacrylate in the presence of aqueous suspensions of ZnO, while Bard et al.² used a platinized TiO₂ powder to initiate the photopolymerization of methyl methacrylate. In more recent studies Funt and Tan,³ have demonstrated the polymerization of methyl methacrylate and styrene on solid TiO₂ electrodes, and Kamat and Todesco^{4,5} were able to polymerize 1-vinylpyrene on n-type GaAs electrodes and in suspensions of CdS, CdSe, or Fe₂O₃ powders. Although these studies clearly demonstrated the capability of semiconductors to photoinitiate polymerization, the photoefficiencies were limited by the use of solid electrodes or powders with a low surface area and a high degree of light scattering.

Some of these limitations may be overcome by the use of Q-sized semiconductor particles as photoinitiators. The synthesis and characterization of ultrasmall semiconductor particles has been a subject of much interest in recent years.^{6,7} These small particles, which typically have diameters between 1 and 10 nm, fall into the region of transition between molecular and bulk

semiconductor properties. They exhibit shifts of the absorption onset (i.e., bandgap) from the UV for small agglomeration numbers to the visible or near-IR region for the bulk material. These shifts are consistent with quantum mechanical calculations that suggest that the energy of the first excited state of the exciton increases as the particle size decreases, thus leading to a blue shift in the absorption spectrum.⁸ Because of the small particle diameters, colloidal dispersions of Q-sized semiconductors exhibit negligible light scattering. In addition, Q-sized colloids have relatively high surface-area-to-volume ratios and therefore act as better catalysts for surface-controlled reactions. The increasing bandgap energy with decreasing particle size also provides the ability to influence reactivity by controlling the particle size distribution. Fox⁹ has shown that the photoelectrochemical oxidation of the radical cation of diphenylethylene resulted in different reaction products than those obtained by electrochemical oxidation on a metal electrode.

With these studies in mind, we have investigated the polymerization of methyl methacrylate using Q-sized ZnO as a photoinitiator. In our study we have examined the effects of solvent, monomer concentration, light intensity, initiator concentration, and semiconductor particle size upon the rates and quantum yields of polymerization.

Experimental Section

Chemicals and solvents were reagent grade and were used without any further purification. This included the methyl methacrylate (Aldrich), which contained 10 ppm of hydroquinone monomethyl ether inhibitor that was not removed. Quantum-sized

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ZnO was synthesized according to the methods of Bahnemann et al.¹⁰ 1 mmol of zinc acetate was dissolved with stirring at 50 °C into 80–90 mL of isopropyl alcohol. After the dissolution the resulting solution was diluted to 920 mL and the temperature lowered to 0 °C. Then 80 mL of 0.02 M NaOH was added at 0 °C with vigorous stirring. The ZnO colloids were stored up to three months at 4 °C (i.e., in isopropyl alcohol) with only a small decrease in absorption intensity. The colloids were stabilized by pH-dependent electrostatic repulsion; no chemical stabilizers were added.

The ZnO colloids were characterized by absorption, fluorescence, and transmission electron microscopy. UV/vis absorption spectra were measured with a Shimadzu MPS-2000 spectrometer and/or a Hewlett-Packard 8451A diode array spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF 540 spectrophotometer. The resulting absorption bands and edges gave an estimate of particle diameter according to the method of Brus.⁶ Exact particle size ranges were obtained using a Philips EM 430 transmission electron microscope at 300 kV. Analysis by energy-dispersion X-ray techniques were also performed using a EDAX 9900 analyzer and detector. Samples for TEM were prepared by placing 10 μ L of the colloidal suspension on to a substrate consisting of a copper mesh covered with a carbon film. After 30 s, the excess liquid was drawn off with a piece of filter paper.

The photolysis apparatus consisted of an Osram XBO 450W xenon lamp in a Muller LX 1450-2 lamp housing or a Kratos 450-W xenon lamp. Appropriate bandpass filters were employed to limit the heating of the sample and to select proper irradiation wavelengths. A fan was also employed to cool the sample during irradiation, and a water filter was used to absorb most of the infrared light. Actinometry was performed using Aberchrome 540 according to the method of Heller and Langan.¹¹ Typical light intensities during photolysis were 1.0×10^{-4} einsteins $L^{-1} min^{-1}$.

The ZnO colloids were used as synthesized with the exception of a series of experiments in which the solvent effects were examined. In these latter experiments, samples of colloid in isopropyl alcohol were evaporated in a rotoevaporator to yield thin films of ZnO which were immediately resuspended into the alternate solvents.

The colloid, monomer, and solvent were measured volumetrically into a 3-dram glass vial with a magnetic stir bar on the bottom. The vial was capped with a rubber stopper. Samples were degassed for 25 min with argon prior to irradiation to reduce the induction period caused by oxygen inhibition. After irradiation, samples were filtered and washed with water, 4 N HCl, and extra solvent. The acid treatment dissolved the semiconductor colloid and effectively removed it from the polymer. The polymeric products were dissolved in chloroform and washed several times with water and HCl before rotoevaporation to remove the chloroform. This procedure provided the cleanest product as shown by FTIR spectra.

Molecular weights of the polymers were determined by gel permeation chromatography. Samples were dissolved in tetrahydrofuran and injected into the GPC system (i.e., a Waters 410 differential refractometer and two linear Ultrastaygel columns). Identity of the polymers was confirmed by Fourier transform IR spectroscopy (FTIR) using a Perkin-Elmer Model 1600 FTIR and by differential scanning calorimetry using a Perkin-Elmer Model 4 DSC.

Results and Discussion

Preparation and Characterization of Q-Sized Semiconductor Colloids. Absorption spectra of 1 mM ZnO in isopropyl alcohol at different stages of growth are shown in Figure 1. Shown in Figure 2 is the fit of the absorption onset to the equation for a direct bandgap semiconductor.¹² As the colloid ages, the absorption onset shifts to longer wavelengths. This size-dependent shift is called the quantum-size effect. The total wavelength shift is about 50 nm. The bulk-phase ZnO bandgap energy is 3.3 eV.¹³ The average diameter of the aged colloids from our syntheses is 50 Å as determined by TEM. Assuming spherical particles and

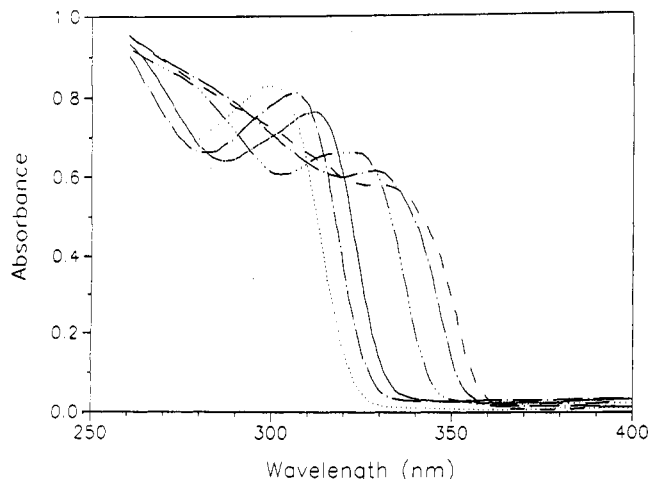


Figure 1. Absorption spectra of 1 mM ZnO in isopropyl alcohol at different stages of particle growth.

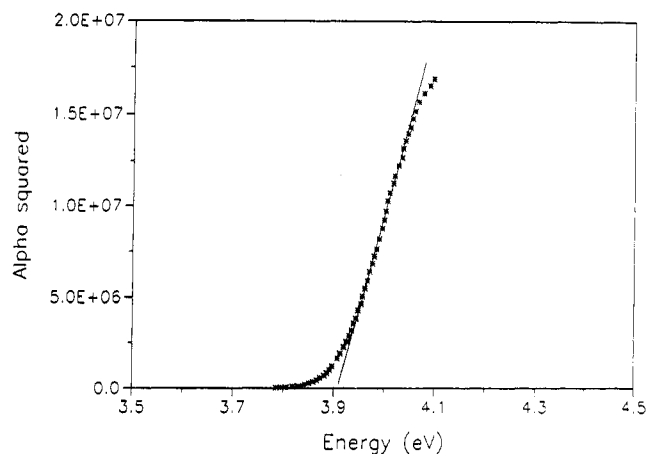


Figure 2. Fit of absorption edge of ZnO to equation for a direct transition.

a density of 5.610 g cm^{-3} , this diameter corresponds to an approximate agglomeration number of 2700 ZnO monomers/particle. Electron diffraction of the aged colloid reveals a moderately diffuse ring pattern characteristic of hexagonal wurtzite structure. Spanhel and Anderson¹⁴ also recently observed ZnO crystallites of hexagonal character.

Polymerization Reactions Using Q-Sized Semiconductor Colloids. In all polymerization experiments, blank samples consisting of only the monomer and solvent were used to check the extent of homogeneous polymerization. The appropriate excitation wavelengths and intensities were selected by using combinations of bandpass and neutral density filters in order to keep the self-polymerization less than 15% of the total yield. Irradiation of the colloid without monomer (and also in cases with monomer where no visible polymerization occurs) resulted in eventual precipitation of the semiconductor particles. Each of the solvents used was a nonsolvent for the polymer, so as the polymerization occurred, a milky white color followed by visible precipitate was observed. The time required to produce precipitated polymer was named the apparent induction period. The length of the apparent induction period depended upon the amount of oxygen and inhibitors and the light intensity. In the presence of oxygen, the induction period was more than 1 h for methyl methacrylate and ZnO. Upon degassing with argon, the induction period decreased to less than 10 min. After irradiation, dark periods of up to 24 h increased the yield of polymer.

The poly(methyl methacrylate) product was characterized by differential scanning calorimetry, FTIR, and gas-phase chromatography (GPC). The differential scanning calorimetry (DSC) analysis gave a glass transition temperature and a melting temperature of 90 and 205 °C, respectively, which compares favorably with the literature values of 115 and 200 °C for pre-

TABLE I: GPC Analysis of Polymer Products

exptl conditions	$10^{-3}M_w$	$10^{-3}M_n$	PDI
(A) Effect of Initiator Concentration upon GPC Results ([MMA] = 2.34 M, Isopropyl Alcohol)			
0.25 mM ZnO	1209	914	1.3
	137	62	2.2
0.4 mM ZnO	1320	1093	1.2
	162	74	2.2
0.55 mM ZnO	1413	1255	1.1
	191	76	2.5
0.75 mM ZnO	1080	868	1.2
	99	51	2.0
(B) Effect of Monomer Concentration upon GPC Results ([ZnO] = 0.25 mM, Isopropyl Alcohol)			
1.40 M MMA	298	77	3.8
1.87 M MMA	361	96	3.8
2.34 M MMA	1209	914	1.3
	137	62	2.2
3.74 M MMA	308	139	2.2
4.68 M MMA	431	268	1.6
(C) Effect of Irradiation Time upon GPC Results ([ZnO] = 0.25 mM, [MMA] = 2.34 M, Isopropyl Alcohol)			
7 min	245	115	2.1
14 min	275	137	2.0
26 min	484	164	3.0
47 min	463	137	3.4
61 min	351	68	5.2
90 min	452	115	3.9
106 min	585	164	3.6
(D) Effect of Solvent upon GPC Results ([ZnO] = 0.25 mM, [MMA] = 2.34 M)			
isopropyl alcohol	1467	1234	1.2
	228	109	2.1
ethanol	1654	1060	1.6
	153	94	1.6
methanol	2084	1249	1.7
	76	54	1.4

dominantly syndiotactic PMMA.¹⁵ Isotactic PMMA exhibits a lower glass transition temperature and melting temperature of 45 and 160 °C, respectively. The FTIR spectra accurately reproduce the earlier published spectra of syndiotactic PMMA.¹⁶ Syndiotactic PMMA is observed in free radical chain mechanisms while isotactic PMMA is produced by anionic chain mechanisms. The polymer was found to be free of residual monomer as indicated by the absence of an IR band at 1600 cm⁻¹. No evidence of incorporation of solvent radicals into the polymer was observed vide infra. The weight-averaged molecular weights varied from 50 000 to 2 000 000 depending upon experimental conditions (Table I). The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) are given by the following equations:

$$M_w = \frac{\sum N_i(M_i)^2}{\sum N_i M_i} = \frac{\sum A_i M_i}{\sum A_i} \quad M_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum A_i}{\sum (A_i/M_i)} \quad (1)$$

where M_i = molecular weight, N_i = number of molecules having molecular weight M_i , and A_i = the area of slice data corresponding to molecular weight M_i . Some of the polymers obtained exhibited bimodal GPC spectra and thus have two entries in Table I. The polydispersity indexes (i.e., the ratio of the weight-average molecular weight to the number-average molecular weight) ranged from 1.2 to 5, which is also typical of chain mechanisms. Note that the workup procedure for the polymer product includes a possible bias toward the high molecular weight species since they are more likely to precipitate from the fluid medium.

Apparent Induction Periods. Since the net induction period is reproducible for a given set of experimental conditions, it is probably not due to impurities in the solvent or to oxygen-degassing procedures. We propose the induction period is a combination of two factors: the time required to destroy the inhibitor and the time required to produce a concentration of precipitated polymer sufficient to be visible to the naked eye. The effects of solvent,

semiconductor concentration, monomer concentration, and light intensity upon the apparent induction period were examined.

The induction period increased as the solvent was changed from isopropyl alcohol to ethanol to methanol. This is an increase with increasing dielectric strength of solvent. Watanabe and Honda observed a similar effect with ZnO in alcoholic solvents;¹⁷ the quantum yield of reduction of methyl viologen decreased as the solvent was changed from ethanol to methanol to water. They suggest the different quantum yields reflect different rates of photocatalytic oxidation of the solvent. Henglein et al.¹⁸ detected the products of the oxidation of alcoholic solvents using Q-sized ZnS and found the same order of efficiency of hole scavenging. The mechanism of removal of the hydroquinone monomethyl ether inhibitor is unknown, since no reaction intermediates were isolated. We propose that the inhibitor is oxidized to produce a di- or trihydroxybenzene, which is known to act as an inhibitor only in the presence of oxygen.¹⁹ The observed trend in induction periods is inconsistent with a competition for holes between the inhibitor and the solvent unless the solvent with the higher dielectric strength binds more strongly to the ZnO surface. Alternatively, the solvent could act as a "hole shuttle", effectively trapping the holes and preventing electron-hole recombination, followed by a slower reaction to remove the inhibitor.

Increasing the concentration of methyl methacrylate shortened the induction period up to a certain concentration, and then higher concentrations lengthened it again. Increasing the concentration of ZnO decreased the induction period. The effect can be explained as follows: with a constant monomer concentration, as the ZnO concentration was increased, the rate of inhibitor destruction increased because more photons are absorbed and the rate of polymerization was faster because the rate of initiation increases as the ZnO concentration increases. The net effect is that the induction period is shortened. With a constant ZnO concentration at very low concentrations of MMA (i.e., low inhibitor concentrations), the time required to destroy the inhibitor is less, but the rate of polymerization is also less because of the lower monomer concentration. Of these two opposing effects, the slower rate of polymerization predominates and the induction period is lengthened. Increasing the concentration of MMA increases the rate of polymerization more than the counter effect of increasing inhibitor and the induction period shortens. When the concentration of MMA is relatively high, the ratio of the concentration of inhibitor to ZnO is high, and then the rate of inhibitor destruction becomes a major factor that outweighs the increased rate of polymerization. For a given time period, if the inhibitor is not totally degraded no polymer forms and the expected rate of polymerization is irrelevant. With degassed 0.25 mM ZnO and 4.68 mM MMA no initiation is seen in 1 h.

The induction period did not depend strongly upon light intensity. For example, as the light intensity was decreased from 1.9×10^{-4} to 5.0×10^{-4} einsteins L⁻¹ min⁻¹ the induction period was increased slightly from 9 to 14 min. Both the rate of destruction of inhibitor and the rate of polymerization are expected to be slower at lower light intensities.

Yield of Initiating Radicals. Ramsden and Gratzel²⁰ observed rapid reduction of MV²⁺ by semiconductor-initiated electrons in an isopropyl alcoholic TiO₂ system. The quantum yield of MV²⁺/MV⁺ reduction was 100%. This result suggests a method to estimate the quantum yield of initiation in our system. A solution of methyl viologen and Q-sized ZnO was degassed and then irradiated, and the absorption spectrum monitored. As MV²⁺ is reduced in the absence of oxygen ($E^\circ = -440$ mV vs NHE) a concomitant blue color is observed with a two peaks in the absorbance spectrum, $\lambda_{\text{max}} = 398$ nm with an $\epsilon = 41\,100$ M⁻¹ cm⁻¹ and $\lambda_{\text{max}} = 602$ nm with an $\epsilon = 13\,800$ M⁻¹ cm⁻¹ in ethanol.¹⁷ The presence of an effective electron-donating solvent is necessary to scavenge the hole and to prevent recombination. The E° for the oxidation of isopropyl radicals to acetone is +1.8 V; therefore the solvent radicals can also reduce methyl viologen directly. The absorbance spectra showed no evidence for the further reduction of MV⁺ to MV⁰, and the quantum yields calculated from the loss of MV²⁺ absorbance at 260 nm ($\epsilon = 18\,300$ M⁻¹ cm⁻¹) agreed

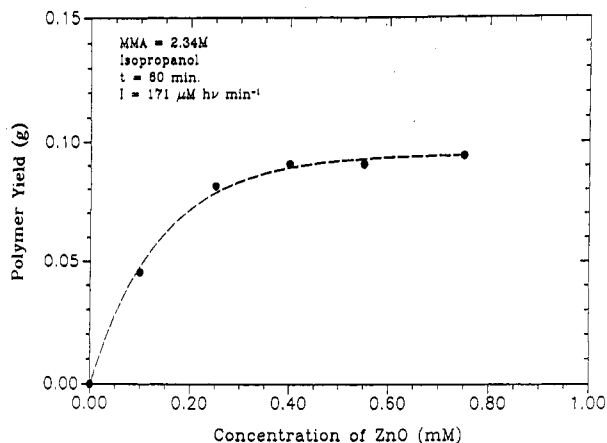


Figure 3. Effect of photoinitiator concentration upon yield of poly(methyl methacrylate).

within 10% to the quantum yields calculated from the rise of MV^+ absorbance at 602 nm. The plot of the concentration of MV^+ versus irradiation time was linear up to 100 s of illumination. The quantum yield of MV^+ formation is given by the equation

$$\Phi = \Delta A / \Delta t \epsilon I_a \quad (2)$$

where $I_a = I_0(1 - 10^{-A})$ is the absorbed photon intensity. Assuming that the quantum yield for the solvent radicals reducing methylviologen is also 100%, then the quantum yield of initiation is 0.097 with the convention that the quantum yield of MV^+ formation is twice the quantum yield of initiation since two radicals are formed per photon absorbed. Analysis of a data recently published by Rabani²¹ for a similar experiment gave a value of 0.167, which is higher due to the lower absorbed light intensity utilized. Nosaka et al.²² demonstrated for Q-sized CdS as the photon density increased, the quantum yield of formation of MV^+ decreased due to faster rate of electron recombination which competes with electron transfer. This value of the quantum yield of initiation is an upper limit.

Effect of Concentration of ZnO. Figure 3 shows the polymer yield as a function of concentration of ZnO. The yield increased as the concentration of ZnO increased until a saturation value was obtained. This saturation effect cannot be attributed to a saturation of surface sites by MMA/inhibitor because this would require a minimum of 6.3×10^6 methyl methacrylate sites per ZnO particle. The effect is also not due to saturation of the colloid absorption because even at the highest concentration not all of the incident photons are absorbed. Likewise an increase in surface-mediated recombination reactions similar to those in a homogeneous solvent cage fails to explain the saturation phenomenon because the increased ZnO concentration results in fewer photon hits per particle. The most likely explanation is that at higher concentrations of ZnO, the primary radicals begin to compete with the monomer for the propagating radicals, and the apparent high molecular weight polymer yield levels off.

Both the weight-averaged molecular weights and the number-averaged molecular weights increased as the concentration of ZnO was increased up to 0.75 mM ZnO. The number-averaged molecular weight divided by the molecular weight of the monomer is proportional to the kinetic chain length, which also equals the ratio of the rate of propagation to the rate of initiation. According to the simple rate equations for initiation and propagation, the kinetic chain length should decrease as the concentration of ZnO increases and the absorbed photon flux increases. The opposite trend is actually observed in this case. For this to occur the rate of polymerization must increase faster than the rate of initiation as the ZnO is increased, and thus either the rate constant of polymerization is a function of ZnO or the initiator efficiency decreases as ZnO increases (i.e., the primary radicals are trapped more efficiently on the surface as the number of ZnO surface sites is increased).

Effect of Monomer Concentration. Figure 4 illustrates the dependence of polymer yield on the concentration of methyl

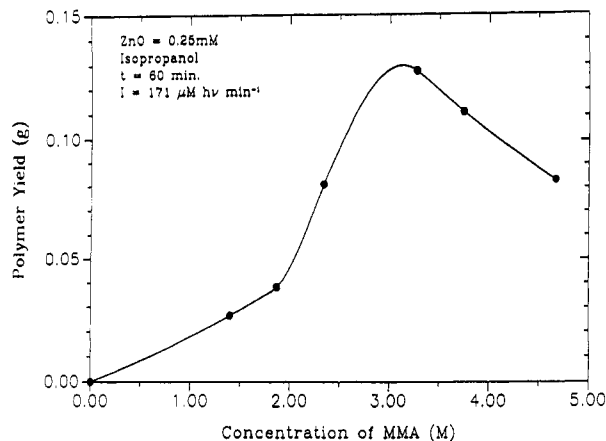


Figure 4. Effect of monomer concentration upon yield of poly(methyl methacrylate).

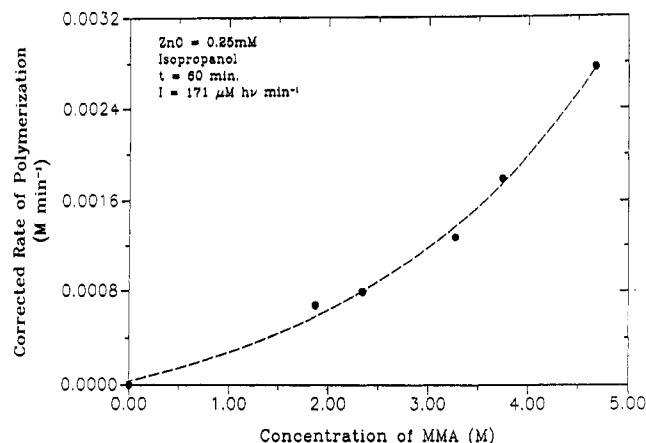


Figure 5. Effect of monomer concentration upon rate of polymerization of methyl methacrylate.

methacrylate. The observed trend is complex. The yield increases initially as [MMA] increases to 3.4 M. It then reaches a maximum, followed by a decrease with increasing monomer concentration. In an ideal system, the rate of polymerization should increase as the monomer concentration increases. However, in the real system the monomer contains an inhibitor which serves to lower the yield at high concentrations. Since the amount of ZnO is constant, longer induction periods occur with increasing inhibitor concentrations. These opposing factors lead to an apparent maximum in the yield vs [MMA] curve. Attempts to subtract the induction period and then to recalculate the yields based on an absolute polymerization time gave an almost exponential increase in yield with concentration of methyl methacrylate. A plot of the corrected rate of polymerization vs the concentration of MMA (Figure 5) is linear for the first three points and then rapidly increases. The rapid increase is most likely due to the Trommsdorf effect.¹⁸ At high percent conversions the viscosity of the solution increases and termination reactions are slowed more than propagation with a net result of an acceleration of the rate of polymerization. This effect has been observed in highly concentrated (i.e. 25–100%) MMA solutions. MMA concentrations were as high as 50% in our experiments, and the acceleration was observed at low conversion (2%). Burnett and Loan (23) have observed in occlusion polymerization the acceleration occurs at much lower percent conversions than in the homogeneous case. In a poor solvent, the growing polymer tends to coil up and precipitate, making termination reactions more difficult to achieve. Propagation occurs inside the precipitated center, where the local concentration of monomer is high. Support for this theory comes from the observation that the yield and molecular weights of polymer increased during postirradiation dark periods, indicating the presence of long-lived radicals.

The kinetic chain length increases as the concentration of MMA increases, as expected since the rate of polymerization increases

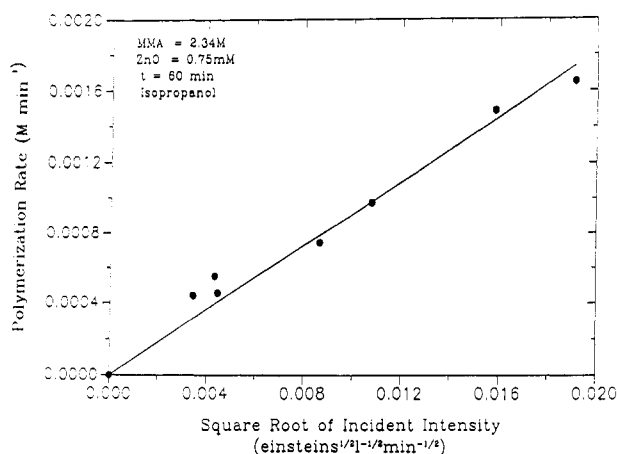
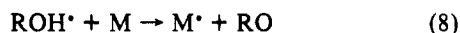
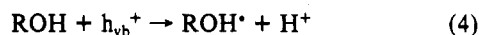
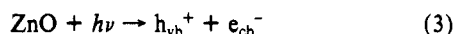


Figure 6. Effect of irradiation intensity upon rate of polymerization of methyl methacrylate.

with increasing MMA and the rate of initiation decreases due to the increasing amount of inhibitor.

Effect of Light Intensity. The effect of light intensity upon the induction period has already been discussed. The plot of the rate of polymerization versus the square root of light intensity shown in Figure 6 is linear. The linear relationship of Figure 5 is predicted by simple theory assuming the mechanism of eqs 3–10.



It should be noted that the anionic initiation of the monomer may not occur directly via the conduction band electrons, since the reduction potential of methyl methacrylate is approximately -1.1 V vs NHE²⁴ and the E_{CB} of bulk ZnO is -0.2 V vs NHE.²⁵ Haase et al.²⁶ have shown that electrons are stored on the surface of ZnO upon UV illumination. They suggest that the stored electrons are either present in traps or in the form of Zn^+ ions, which have a very negative redox potential (< -2 V). Thus, these stored electrons may initiate polymerization. For the purpose of our simple kinetic model, we have written the reaction as a direct. The kinetic expressions for the rate of initiation, propagation and termination of radical chain reactions are given in eqs 11–13.¹⁹ The rate of initiation is given by

$$R_i = Q_i I_0 (1 - 10^{-A}) = Q_i I_a = d[\text{M}^{\cdot}]/dt \quad (11)$$

where Q_i is the quantum yield of initiation, I_0 and I_a are the incident and absorbed light intensity, M^{\cdot} is the initiated monomer, and A is the absorbance of the semiconductor; the rate of propagation is expressed as

$$R_p = k_p [\text{M}^{\cdot}][\text{M}] \quad (12)$$

where k_p is the rate constant of propagation; rate of termination is written

$$R_t = k_t [\text{M}^{\cdot}]^2 \quad (13)$$

where k_t is the rate constant of termination. Under the steady-state approximation the rate of initiation (eq 11) equals the rate of termination (eq 13). Equating these rates allows us to express the steady-state concentration of M^{\cdot} as

$$[\text{M}^{\cdot}] = k_t^{-1/2} (Q_i I_0 (1 - 10^{-A}))^{1/2} \quad (14)$$

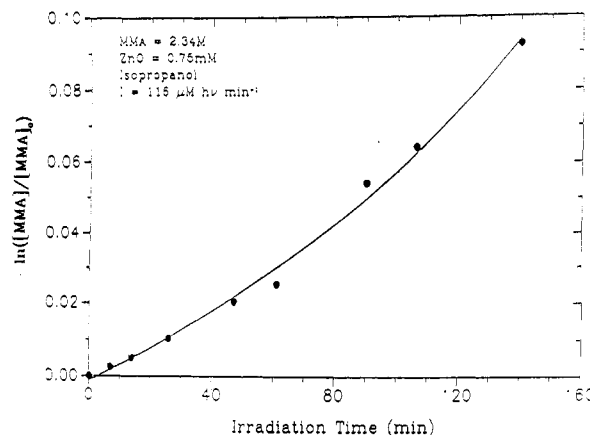


Figure 7. First-order plot of irradiation time versus concentration of methyl methacrylate.

TABLE II: Effect of Solvent upon ZnO-Initiated Polymerization ([MMA] = 2.34 M)

solvent	yield, g	time, min	intensity, $\mu\text{M h}\nu/\text{min}$	Φ_{corr}
acetonitrile	0.0	61	51	0
methanol	0.06	110	53	6.3
ethanol	0.13	107	53	14.9
isopropyl alcohol	0.19	108	52	22.1

Substituting eq 14 into eq 12 gives us an equation for the rate of polymerization as follows:

$$R_p = k_p k_t^{-1/2} [\text{M}] (Q_i I_0 (1 - 10^{-A}))^{1/2} \quad (15)$$

At low percent conversions, the monomer concentration remains essentially constant, so the ratio of the rate constant for propagation to the square root of the rate constant of termination may be calculated from the slope of Figure 6. This yields $k_p/k_t^{-1/2} = 1.23 \times 10^{-1} \text{ M}^{-1/2} \text{ s}^{-1/2}$.

Time Evolution of Yield. In another series of experiments, the polymer yield as a function of irradiation time was examined (Figure 7). A plot of the $\ln[\text{MMA}]/[\text{MMA}]_0$ versus time has two linear regions, indicating a first-order dependence of the rate of polymerization on the concentration of methyl methacrylate at low degrees of conversion. The ratio of the rate constant of propagation to the square root of the rate constant of termination may be calculated from the slope; thus $k_p/k_t^{-1/2} = 1.40 \times 10^{-1} \text{ M}^{-1/2} \text{ s}^{-1/2}$. At higher percent conversions the value is $2.34 \times 10^{-1} \text{ M}^{-1/2} \text{ s}^{-1/2}$. The larger slope at later times is due to the decrease in the rate constant of termination in the occluded polymer. These values may be compared to the value calculated from literature for homogeneous polymerization of $2.5 \times 10^{-2} \text{ M}^{-1/2} \text{ s}^{-1/2}$.¹⁸

GPC analysis of the polymer molecular weights revealed that initially both the weight-averaged and number-averaged molecular weights increased, then after 60 min of irradiation time they decreased. The molecular weight distributions increased in width with increasing irradiation times. Bimodal molecular weight distributions were observed in polymers that were stored in the dark after illumination and prior to workup. In this case, the larger molecular weight peak was much higher than the molecular weight obtained from the polymers with no dark period, while the lower molecular weight peak was slightly lower. This suggests that the polymerization that continues in the dark is subject to very few termination reactions. The polydispersity indexes for low percent conversions and no dark periods were 1.5, which is the theoretical value for termination by recombination. Since the scattering of light increases as polymer precipitates, the kinetic chain length should increase due to the slower rate of initiation. This could be offset by a decreasing rate of propagation due to less monomer and more chain-transfer reactions.

Effect of Solvent. The effect of solvent upon the quantum yield of polymerization is shown for ZnO in Table II. The rate of

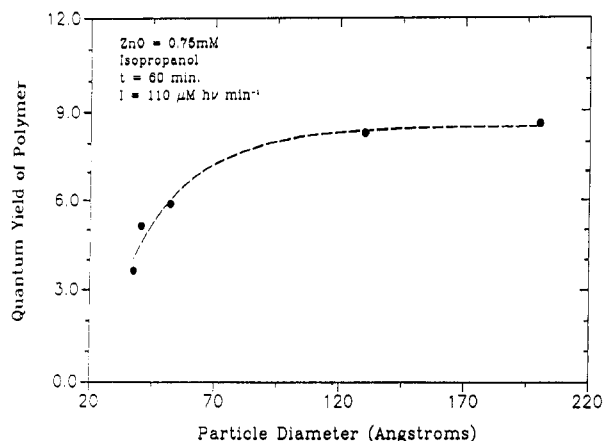


Figure 8. Effect of photoinitiator particle size upon quantum yield of poly(methyl methacrylate).

polymerization for ZnO increases in the order acetonitrile < methanol < ethanol < isopropanol, even when corrected for the differences in induction periods. Since the light intensities were constant, the solvent dependence reflects differences in the rate of polymerization. For ionic chain mechanisms, rates are relatively sensitive to the nature of the solvent (i.e., they are faster in more polar solvents). We observed a lower polymerization rate with an increasing polarity of the solvent. Free-radical chain mechanisms are less sensitive to solvent polarity. The chain-transfer ability of the solvent increases in the same order as the yields. The more the contribution of chain transfer to the reaction, the lower the molecular weights and yield of precipitated polymer. The solvent with the lowest chain-transfer coefficient did produce the highest molecular weights (and the lowest yield), but this could also be due to the effect of shorter net polymerization times since the induction period was longer. The order of increasing yield also follows the trend in increasing hole-scavenging efficiency of the solvent.^{17,18} No polymerization was observed with acetonitrile as a solvent as expected, since it is not an efficient hole scavenger.

Copolymerization of Methyl Methacrylate and Styrene. To provide insight into the mechanism of polymerization, methyl methacrylate and styrene were copolymerized in isopropyl alcohol using Q-sized ZnO as the photoinitiator. The monomer reactivity ratios r_1 and r_2 have been evaluated at different temperatures and with different solvents.^{27,28} r_1 is the ratio of the rate constants for the reaction of an M_1 -type radical with M_1 and M_2 , respectively, while r_2 is the ratio for the reaction of an M_2 -type radical with M_2 and M_1 , respectively. The different r_1 and r_2 values give rise to large differences in the composition of the copolymer depending on the mode of initiation. Methyl methacrylate shows increased reactivity in anionic copolymerization and decreased reactivity in cationic polymerization. The opposite effect is observed for styrene. If an equimolar mixture of methyl methacrylate and styrene is polymerized via a free-radical mechanism, the copolymer is 50% methyl methacrylate and 50% styrene. For the same mixture under an anionic mechanism, the copolymer is almost pure methyl methacrylate. When a 50:50 mixture of methyl methacrylate and styrene were polymerized in isopropyl alcohol, the copolymer product had a percent carbon of 74.9%, which is indicative of the free-radical mechanism.

Particle Size Effect upon Yield. MMA polymerizations were carried out with different size fractions of ZnO colloid. The results are shown in Figure 8. The quantum yields corrected for the absorbance of the colloid increased as the average size of the particle distribution increased. If the reaction were surface-mediated, increasing the total surface area by decreasing the particle size should increase the rate. This was the opposite of what was actually observed, and contradicts the results of Nosaka et al. for Q-sized CdS and MV^{2+} .²² In our case, the small-diameter particles were not annealed to remove the surface site defects, which act as low energy electron traps and decrease the efficiency of electron transfer. In addition, the small-diameter particles may also have inherently faster rates of electron-hole recombination

so that the rate of initiation is less and the yield is lower. This agrees with Warnock and Awschalom,²⁹ who observed shorter exciton lifetimes for CdS as crystallite size decreased in colored glasses. With bulk-size ZnO particles (i.e., 0.1–1.0 mm) no initiation was observed and no polymer was formed. Thus above a critical size range the surface area appears to have a demonstrable effect.

Conclusions

Our results show the polymerization of methyl methacrylate occurs readily using Q-sized ZnO semiconductors as photoinitiators. The reaction pathway appears to involve hole scavenging by the solvent and anionic initiation by the electrons. The experimental results mimic many of the features of free radical homogeneous polymerization reactions; however, the rate constants are found to be higher. Increasing the concentration of the photoinitiator, ZnO, increases the polymer yield until a saturation value is achieved. The rapid increase in polymerization rate with increasing concentration of methyl methacrylate is due to an early onset of the Trommsdorff effect. The primary radicals generated by illumination add to a monomer molecule dissolved in the alcohol phase. With the growth of the polymer chain by propagation some critical chain size is reached at which the oligomers are no longer soluble, and precipitated polymer is observed. Polymerization can continue both inside the precipitated centers and in the bulk alcoholic solvent. Polymerization inside the precipitated centers is subject to a decreased rate of termination and a high local concentration of monomer, resulting in an acceleration of overall polymerization rates. The rate of polymerization depends upon the square root of incident light intensity, as predicted from simple kinetic theory. The quantum yields of polymerization decreased as the particle size decreased, due to either increased surface defects or enhanced rate of competing electron/hole transfer. Under the same experimental conditions no polymerization occurred with bulk-size ZnO particles. Further experiments are needed to determine whether this inability of larger particles to initiate polymerization is an effect of decreased surface area or an effect of lower driving force due to decreased reduction potential of the conduction band electron.

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Q-Sized CdS: Synthesis, Characterization, and Efficiency of Photoinitiation of Polymerization of Several Vinyllic Monomers

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Q-sized CdS semiconductors have been synthesized in several nonaqueous solvents without the use of added stabilizers. The effects of solvent viscosity and dielectric strength, concentration of excess cadmium ions, temperature, and stirring upon the colloids' absorption spectra have been examined. In addition, efficiency of photoinitiation of polymerization of several vinyllic monomers has been examined using both bulk and quantum-sized CdS, ZnO, and TiO₂. The Q-sized semiconductors demonstrated significantly higher quantum yields for photopolymerization than their bulk-sized counterparts. A correlation between the reactivity of a monomer toward polymerization and its Alfrey and Price *Q* and *e* values was observed. Hole scavenging by the solvent was necessary for efficient polymerization to occur. A correlation between the semiconductor photoinitiation efficiency, and the reduction potential of its conduction band electrons was also found. On the basis of these observations, a mechanism of an anionic initiation step followed by free radical chain propagation steps has been proposed.

Introduction

The photoelectrochemistry of ultrasmall semiconductor particles has been an area of active research interest in recent years. These ultrasmall particles with diameters ranging between 1 and 10 nm possess properties which fall into the region of transition between the molecular level and the bulk phase. Colloidal suspensions of such Q-sized colloids exhibit shifts of their bandgap absorption onsets from the UV region or small agglomeration numbers to the visible or near-IR region for the corresponding bulk-phase material. The apparent shifts in the bandgap energy have been explained in terms of quantum mechanical calculations which show that the energy of the first excited state of the exciton increases as the particle size decreases. This effect is seen as a blue shift in the absorption spectrum of the transparent colloids. The bandgap shift, ΔE_g , as a function of particle size is given by¹

$$\Delta E_g = \left(\frac{h^2}{8R^2} \frac{1}{\mu} \right) - \frac{1.8e^2}{\epsilon R} \quad (1)$$

where *R* is the radius of the particle, μ is the reduced mass of the exciton (i.e., $\mu^{-1} = m_e^*{}^{-1} + m_h^*{}^{-1}$), m_e^* is the effective mass of the electron, m_h^* is the effective mass of the hole, and ϵ is the dielectric constant of the semiconductor. A wide variety of Q-sized semiconductors have been synthesized; they include ZnO, TiO₂, ZnS, CdS, As₂S₃, FeS₂, PbS, Zn₃P₂, Cd₃P₂, Cd₃As₂, CuCl, AgCl, AgBr, AgI, In₂S₃, CdSe, and ZnSe.²⁻¹⁴ Two generally employed synthetic approaches are controlled precipitation²⁻⁴ or radiolysis.^{15,16} Henglein has provided an extensive review of the various synthetic procedures and general physicochemical properties of Q-sized colloids.¹⁷

Although several different Q-sized semiconductors have been synthesized, the method of obtaining a stable colloid of the desired particle size remains a matter of trial and error. Many of the syntheses to date utilize an added stabilizer such as hexameta-phosphate, poly(acrylic acid), thiosulfate, poly(vinyl acetate), glycerine, or a styrene/maleic anhydride copolymer.^{5,18,19} Very

little is known about the interaction between the colloidal particles and the foreign stabilizers. In addition the reactivity of such stabilizers in semiconductor photoinitiated reactions is generally unknown. Following the examples of Brus et al.⁴ and Gratzel et al.,²⁰ we chose to avoid such complications by synthesizing a variety of nonaqueous colloids without the addition of stabilizers other than the counterions present from the synthesis. To develop further insight into the factors which control particle size and stability, we performed a systematic study of the effect of solvent, temperature, and nature and concentration of counterion upon the colloidal particle growth. CdS was selected for this study.

Illuminated semiconductor suspensions have been shown to be suitable initiators of the polymerization of methyl methacrylate, styrene, and 1-vinylpyrene.²¹⁻²⁶ However, Q-sized semiconductor colloids have not been used previously as photoinitiators. The use of Q-sized semiconductors in heterogeneous photochemical studies has several advantages over suspended powders or solid electrodes. Since the Q-sized particles are extremely small (i.e., the particle diameters (5 nm) are much less than the excitation wavelengths (380 nm)), they exhibit negligible light scattering; thus the accurate determination of quantum yields in heterogeneous photochemistry is possible. Q-sized particles also have high surface area-to-volume ratios, thus enhancing their catalytic activity. These two factors are likely to combine to give high polymerization efficiencies. Another major advantage in the use of Q-sized particles is the increase in effective bandgap energy with decreasing particle size. This property potentially allows for the variation of the redox potential of the valence-band holes and the conduction-band electrons via control of particle growth. A possible disadvantage of using Q-sized particles to initiate polymerization arises in the area of polymer separation and purification; however, in the case of CdS and ZnO, simply changing to a more acidic pH causes the Q-sized particles to dissolve and aids their removal from the polymer.

In this paper we describe our recent investigation of the synthesis of Q-sized CdS in several solvents without added stabilizers. We then examine the polymerization of vinyllic monomers using Q-sized CdS as a photoinitiator. We investigate the effects of solvents, the efficiencies of different semiconductors, and the photopolymerization rates of Q-sized versus bulk particles and determine the reactivity of different monomers toward semiconductor-initiated polymerization.

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