

INITIATION OF FREE RADICAL POLYMERIZATION BY HETEROGENEOUS PHOTOCATALYSIS AT SEMICONDUCTOR POWDERS

The generation of free radicals employed as initiators for polymerization can be accomplished by thermal decomposition (e.g., of peroxides), electrochemically, or by homogeneous photochemical processes (e.g., photofragmentation reactions) (1). Because photoinitiated radical chain polymerization is easy to apply and control, it is of considerable current interest in such processes as photochemical curing, and in the application of photoactive relief printing plates and photoresistive materials (2). With most homogeneous photopolymerizations, the sensitizer, which must be capable of absorbing the light, produces compounds which are incorporated into the polymer (3). We have recently described the photocatalytic decomposition of various saturated carboxylic acids at semiconductor powders, such as platinized n-TiO₂ (the photo-Kolbe reaction) (4), and the postulated free radical intermediates in the process were confirmed by electron spin resonance detection of spin-trapped products (5). We were thus encouraged to attempt the application of such heterogeneous photocatalytic processes to the initiation of polymerization. We report here the successful application of such techniques to the polymerization of γ -methyl-methacrylate (MMA) with several initiating compounds.

The results of the experiments are summarized in Table I. A typical experiment (No. 1) was carried out as follows: In a Pyrex cell connected to a gas volumetric system, a mixture containing 100 mg of reduced and partially platinized n-type TiO₂ powder (anatase) (6),* 18 ml of glacial acetic acid (HOAc, Fisher), and 3.6 ml of freshly distilled MMA was irradiated[†] while stirring at 40°C. A slow evolution of gas accompanied by a visible increase in viscosity was observed. After 4 hr the irradiation was stopped, the evolved gas mixture (12 ml) was analyzed by mass spectrometry, while the suspension was further treated as follows. First the semiconductor powder was separated by ultracentrifugation (2300 rpm, 30 min). The supernatant liquid was then slowly added to 500 ml of distilled water with immediate precipitation of a white solid. This solid was filtered off, resuspended in 200 ml of water, refiltered, washed twice with 200 ml of water, and finally dried for 24 hr at ambient temperature. The 9.6 g of white solid thus collected still contained ca. 50% by weight of solvent. The polymer was analyzed by gel permeation chromatography (GPC) to obtain \bar{M}_w and \bar{M}_n . The gas mixture, analyzed by mass spectrometry, was predominantly CO₂, with only minor amounts of CH₄ and

*TiO₂ powders were sieved to a particle size 125-250 μ m (grain size ca. 0.2 μ m), reduced in a hydrogen atmosphere at 600°C for 7-12 hr, and photoplatinized to produce 1-5% Pt by weight on final powders.

[†]The light output of a 2500-W Xe lamp (operated at 1600 W) was focused on a flat window on the Pyrex vessel to illuminate an area of about 5 cm².

TABLE I

Summary of Experiments on Heterogeneous Photocatalytic Polymerization

Exp. No.	Solution ^a	Catalyst ^b	Irradiation Conditions	CO ₂ (mg ² BaCO ₃)	Polymer yield (mg)	Polymer Distribution		
						\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
1	HOAc (18 ml) MMA (3.6 ml)	Yes	4 h, 40° (no filter)		5,000	Bimodal Distribution 145K 35K 4.2		
2	as No. 1	Yes	3.5 h, 35° (420 nm filter)		0			
3	AN (22 ml) HClO ₄ (1 ml) MMA (3 ml)	None	1 h, 70° (no filter)		100-200			
4	HOAc (18 ml) MMA (3.6 ml)	None	3.7 h, 38° (no filter)			105K	57.6K	1.8
5	AN (14 ml) NaHG (4 g) MMA (3 ml)	Yes	3.5 h, 30° (no filter)	12	950	350K	100K	3.5
6	AN (13 ml) NaHG (1 g) MMA (3 ml)	Yes	2.5 h, 40° (no filter)		350	104K	50.2K	2.1
7	AN (13 ml) NaHG (1 g) MMA (3 ml)	Yes	4 h, 40° (380 nm filter)	3-4	475	95.5K	27.2K	3.5
8	as No. 6	Yes	3.7 h, 40° (no filter)		380	48K	11.2K	4.3
9	AN (13 ml) HClO ₄ (1.2 ml) NaHG (4 g) MMA (1 ml)	Yes	4 h, 38° (380 nm filter)	6.5	* 20			
10	AN (13 ml) HClO ₄ (0.7 ml) NaHG (2 g) MMA (1 ml)	Yes	3.8 h, 23° (320 nm filter)	7.5		18K	3.0K	6.0
11	AN (11 ml) HClO ₄ (0.5 ml) H ₂ O (3 ml) NaHG (2 g) MMA (2 ml)	Yes ^c	2.5 - 5 h (330 nm filter)		0			
12	AN (13 ml) HClO ₄ (0.7 ml) NaHG (4 g) MMA (4 ml)	None	4 h, 30° (330 nm)	6	142			

^aAbbreviations: HOAc, acetic acid; MMA, γ -methyl methacrylate; AN, acetonitrile; NaHG, sodium γ -hydroxybutyrate.

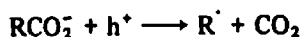
^b100 mg of photocatalyst (Pt/TiO₂) (6).

^c100 mg of reduced anatase, unplatnized.

H₂. (In an experiment in which the CO₂ was trapped as BaCO₃, the CO₂ evolved accounted for ca. 90% of the volume of all gaseous reaction products.) These results indicate efficient trapping of the photogenerated radicals (e.g., CH₃·) by the MMA monomer, since in the absence of olefin under these conditions, CO₂ accounts for only ca. 50% of the evolved gases. The bimodal distribution found in the resulting polymer in this experiment can be ascribed to partial homogeneous photopolymerization following light absorption by MMA as well as via the heterogeneous photocatalytic path in the full output of the xenon lamp (see Nos. 3 and 4). Light absorption by the MMA occurs

at wavelengths below about 305 nm, and irradiation of the solutions through filters with a cutoff below 330 and 380 nm (which also cuts off appreciably the amount of light absorbed by the TiO_2) decreased the polymerization by direct absorption by MMA. Polymerization of MMA was also initiated with the sodium salt of γ -hydroxybutyric acid (NaHB) (in a HClO_4 -acetonitrile solution adjusted to pH 6-7 with Na_2CO_3) under similar conditions. An increase in the ratio of the NaHB to MMA produced polymer of lower molecular weight (compare Nos. 7 and 10). Irradiation of mixtures through a 420-nm filter, which removes essentially all light absorption by TiO_2 (No. 2), or experiments with unplatized TiO_2 (No. 11) yielded no polymer. Coating of the TiO_2 particles with polymer was not observed and the weight of the TiO_2 after irradiation (after recovery and drying) was essentially the same ($\pm 3\%$) as the amount of photocatalyst added.

While detailed studies of the mechanism of heterogeneous photopolymerization have not yet been carried out, the results of past experiments with TiO_2 powders and electrodes (4-7) suggest a mechanism in which free radicals produced at the TiO_2 surface by reaction with photogenerated holes (h^+) serve as initiators:



Polymerization of MMA by radicals produced electrolytically via the Kolbe reaction has been described previously (8). The results also suggest the applicability of other irreversibly oxidizable materials as radical initiator precursors. Indeed preliminary experiments have demonstrated that 12-hydroxystearic acid and ammonia can also initiate polymerization of MMA.

These initial studies demonstrate the feasibility of heterogeneous photoinitiated polymerization and suggest several advantages of this method: (1) flexibility in choice of initiator material and resulting end groups in the polymer; (2) control of the initiation rate, polymer molecular weight, and molecular weight distribution by controlling intensity of illumination; (3) control of sequence distributions in copolymers; (4) use of thermally and light-stable initiators; (5) flexibility in choice of photocatalyst material and possible use of smaller-band-gap materials or dye sensitization for initiation with light of longer wavelengths. Direct applications to the design of photoresistive materials and in the coating as semiconductors also appear possible.

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