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Studies in the Photopolymerization of Some β-Substituted Ethyl Acrylates

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ABSTRACT

The relative rates of conversion of monomer to polymer were found for the photoinitiated bulk polymerization of various β-substituted ethyl acrylates, $x\text{-}CH_2CH_2OOC\text{–}CH{=}CH_2$. These data were developed for systems in vacuum, with inert flush, with and without inhibitor present. Some plausible suggestions about mechanism are discussed. Data, however, do not permit firm conclusions regarding the mechanism.

INTRODUCTION

Numerous publications have appeared over the last ten years which have reported on the investigation of photopolymerizations of various methacrylate esters. However, only a few studies have appeared in which polymerizations of alkyl acrylates were investigated, where interest was focused on the effects of the alkyl moieties on the polymerization rates. Burnett et al. [1, 2] studied polymerizations of methyl and butyl acrylates, and Melville et al. [3, 4]

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examined structure-reactivity relationships of these two monomers. Burnett observed that in radical-initiated bulk polymerizations of these monomers the increase in the size of the ester group correlated with a diminution in the value of the propagation constant [1, 2]. At the same time, K was markedly reduced when comparing butyl acrylate to methyl acrylate. Recently, Daimon et al. [5, 6] studied radical polymerization of cyclodedecyl acrylate and cyclohexyl acrylate. They concluded that the differences in reactivity could not be interpreted in terms of polar or steric factors of the Taft equation. Also, it is interesting that when Wunderlich [7] investigated radical polymerization of butyl acrylate in two different solvents at three different temperatures, he found that the results did not meet the ideal kinetic model of radical polymerization.

In the present work, relative speeds of achieving final conversions of monomers to polymers were studied in photoinitiated bulk polymerizations of several β-substituted ethyl acrylates. Diethoxyacetophenone was used as the initiator. Reactions were conducted on prepurified monomers, carried out in a vacuum in Pyrex glass tubes in which the atmosphere was repeatedly purged with an inert gas and then evacuated to remove all oxygen. The irradiation was conducted after final evacuation. The above reactions were also carried out on some monomers in the presence of 400 ppm of an inhibitor, hydroquinone monomethyl ether, and also in a third instance in the presence of this inhibitor, but with nitrogen merely swept over the surface of the monomers.

RESULTS AND DISCUSSION

Osborn and Sanders [7] studied the use of diethoxyacetophenone as a photoinitiator in polymerizations of acrylic esters. They demonstrated high quantum efficiency for the initiating reaction and expressed the opinion that irradiation of this ketone does not result in an α-cleavage as does irradiation of benzil dialkyl ketals. Instead, they suggested that a Norrish Type II photochemical process takes place. It is difficult to conclude whether or not the irradiation of diethoxyacetophenone would include a cyclic intermediate. A six-membered intermediate which is postulated for ketones with γ-hydrogen is not possible. In any event, the primary radical came from diethoxyacetophenone because all irradiations were carried out in Pyrex glass containers which block out all radiation capable of affecting the monomers directly. This statement is based on the ultraviolet absorption spectra of all the monomers which demonstrated that light was absorbed by them well below 300 nm.

Table 1 and Fig. 1 present the results of irradiating freshly distilled β-substituted bromoethyl acrylate, phenylethyl acrylate,

TABLE 1. Conversion to Polymer on Irradiation of Monomers in Vacuo

Monomer	Conversion (%) with various irradiation times													
	3 sec	4 sec	5 sec	6 sec	7 sec	8 sec	9 sec	10 sec	15 sec	20 sec	30 sec	40 sec	45 sec	50 sec
Bromoethyl acrylate		0.1	0.65	0.8	0.4	4.4	6.0	14.1						
			0.60											
Phenylethyl acrylate			0.7	0.64	3.9	24.9	22.0							
Phenoxyethyl acrylate			0.2	0.35				0.78	3.8	7.3				
Methoxyethyl acrylate	0.2	2.4	2.9	3.3	3.8			5.3		9.3	12.6			
			2.2					6.1						
Ethyl acrylate								0.6		0.2	2.8	6.7	6.4	10.1
											4.7			
											6.2			

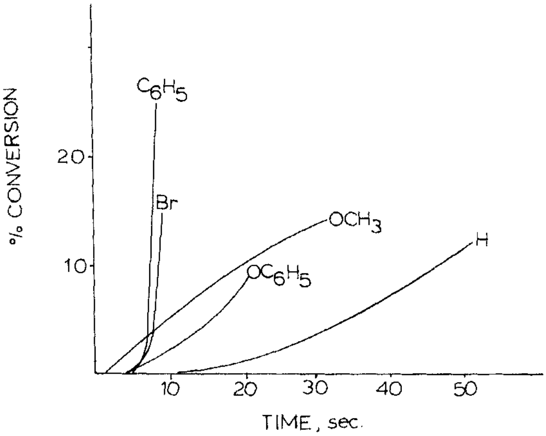
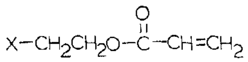


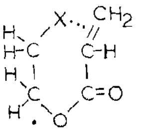
FIG. 1. Results from irradiation in vacuum.

methoxyethyl acrylate, phenoxyethyl acrylate, and unsubstituted ethyl acrylate under a vacuum. Each point on the curves represents conversion obtained from each individual run. As can be seen, the rates of conversion varied with each monomer. These variations in rate can hardly be attributed to any electronic effects of the substituent X on the double bond since it is too far removed from that portion of the molecule:



$$X{-}CH_2CH_2O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2$$

Nor does it appear likely that the double bond reactivity from the β-substituent is affected by a quasi six-membered ring formation and the substituent interacting with the π electron cloud:



However, steric factors could conceivably play some role, and in fact, Burnett et al. [1, 2] attributed the differences in rates of polymerizations of butyl and methyl acrylates to steric effects.

TABLE 2. Conversion to Polymer on Irradiation of Monomers in Vacuo in the Presence of an Inhibitor

	Conversion (%) at various irradiation times								
Monomer	4 sec	5 sec	10 sec	12 sec	20 sec	30 sec	40 sec	45 sec	60 sec
2-Methoxyethyl acrylate	0.5	2.2	6.1						
Ethyl acrylate						2.5	5.6	6.4	19.1
							6.2		
2-Bromoethyl acrylate	0.6	2.8	10.4	14.3					

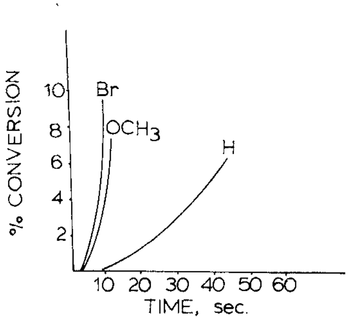


FIG. 2. Irradiated in vacuum, with inhibitor.

Wunderlich [7] felt that the reasons that radical polymerizations of butyl acrylate deviate from the ideal kinetic model could possibly be due to primary radical termination and chain transfer. The same conditions may apply here with each substituent affecting the process of chain transferring differently or in some cases not at all. In addition, one might also consider the possibility of different amounts of solvation of the growing macroradicals by corresponding monomers and, perhaps, also formation of electron donor-acceptor complexes between macroradicals and monomers, as described by Henrici-Olivé and Olivé [8-10]. Other factors which could contribute to variations in rates are: diffusion control of termination through viscosity build-up and through-cage effects. Our data do not permit conclusions about the mechanism involved.

We were not able to observe any induction periods in the polymerizations, either for the inhibitor-containing experiments and for the

TABLE 3. Conversion to Polymer on Irradiation of Monomers in the Presence of an Inhibitor under Nitrogen Flush

	Conversion (%) at various irradiation times										
Monomer	5 sec	10 sec	15 sec	20 sec	30 sec	40 sec	50 sec	60 sec	70 sec	80 sec	90 sec
2-Phenylethyl acrylate					1.0	3.0	4.3	11.8			
Ethyl acrylate				0.8		2.7		5.6 5.3			14.4
2-Methoxyethyl acrylate	2.2	6.1	7.7	7.1 10.6		14.0					
2-Bromoethyl acrylate						0.9	2.2	2.9	5.6	11.8	17.3
2-Phenoxyethyl acrylate				0.5	1.0	1.7	4.8	8.9			

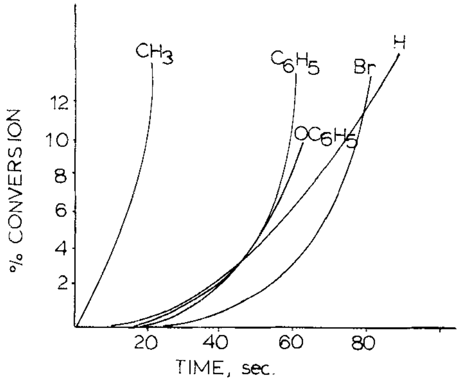


FIG. 3. Irradiated with N_2 purge, with inhibitor.

experiments with pure monomers. This might perhaps be due to the time intervals at which data were gathered. If the induction periods were already finished at the first points obtained then they were already past being measured.

When the above polymerizations were repeated with bromoethyl acrylate, ethyl acrylate, or methoxyethyl acrylate in the presence of 400 ppm hydroquinone monoethyl ether, (Table 2 and Fig. 2), then data were obtained which resemble those obtained with pure, inhibitor-free monomers. However, when nitrogen was merely swept over the surface of these monomers (Table 3 and Fig. 3), then the dissolved oxygen exerted a considerable effect.

EXPERIMENTAL

Purification and Preparation of Monomers

All monomers were washed with sodium hydroxide solution and then vacuum distilled just prior to use. To all these monomers 0.50% of diethoxyacetophenone per mole was added after the distillation.

Irradiation of Monomers

Irradiation was conducted on bulk monomers at 25°C by using approximately 0.1 g of the material which was weighed accurately into Pyrex tubes. A 2.5 cm-long, U-shaped, Hanovia Co., 100 W medium pressure Hg lamp was used for irradiations. The lamp was placed below the tubes at a distance of 23 cm from the bottom of the tubes so that all irradiation occurred through the bottom of the Pyrex glass tube. Upon completion of the irradiation, air was introduced into the tubes and the formed polymer was precipitated with a nonsolvent; the amount of polymer formed was determined gravimetrically as has been done by others [11, 12].

Vacuum Method

The monomer, after being placed into a Pyrex tube, was frozen in a Dry Ice-acetone bath, and then the tube was alternately evacuated to pressures below 0.05 mm Hg and then filled with prepurified, oxygen-free nitrogen. After five purge-evacuation cycles, the tube was sealed under vacuum and the sample was then irradiated.

Nitrogen Flush Method

The sample of monomer was weighed into the centrifuge tube. This was followed by insertion of a glass capillary tube to within 1 cm from monomer. The capillary was suspended from a rubber stopper and held at the mouth of the tube. Nitrogen was blown at the rate of 300 cc/min through the capillary, purging the atmosphere in the tube for 15 sec, after which the sample was irradiated while the flushing continued.

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