

An Analytical Method to Determine Time–Conversion Relationship for a Multicomponent Monomer Mixture in a Suspension Polymerization System

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Synopsis

A precise method has been developed for the quantitative measurement of individual monomers during suspension polymerization. Since no simplifications or assumptions are made regarding the components of the polymerization system, this method can be used to study the conversion kinetics of monomers in the actual suspension polymerization reaction.

INTRODUCTION

Suspension polymerization is commonly used to prepare insoluble, crosslinked polymer beads for ultimate use in ion exchange resin synthesis. Because of the heterogeneous character of the system and the crosslinked polymer structure, the evaluation of the course of this polymerization reaction is difficult. The copolymerization of styrene with crosslinker divinyl benzene (DVB) or ethylene glycol dimethacrylate (EGDM) has been studied widely in bulk or solution polymerizations.¹⁻³ Initial reaction rate⁴ and reaction kinetics with small quantities of crosslinker⁵ have also been measured. However, the kinetics of the multicomponent system, styrene, divinyl benzene, and ethylene glycol dimethacrylate have never been explored.

This article describes a simple and precise method which can be used to elucidate the kinetics of any multicomponent suspension polymerization system.

EXPERIMENTAL

Materials

Divinyl Benzene (DVB). A commercial mixture supplied by Dow Chemical Co., contained (by GLC): 57% DVB (the mixture of *m*-, *p*-isomers), 41.7% ethyl vinyl benzene, EVB (the mixture of *m*-, *p*-isomers), and 1.2% saturates primarily diethyl benzene.

Ethylene Glycol Dimethacrylate (EGDM). A commercial grade supplied by The Ware Co.

Styrene. A commercial grade supplied by Gulf Oil Co.

Methanol. Baker analytical grade was dehydrated by standing over molecular sieves (activated Linde 5A from Matheson Coleman and Bell Co.) for at least 24 hr before use.

Suspension Media. Prepared by using commercial grades of precipitated calcium phosphate, sodium chloride, and deionized water having conductivity $<10 \mu\text{mho cm}^{-1}$.

***t*-Butyl Catechol (TBC).** A commercial grade, Dow Chemical Co.

Sampling Procedure

Samples (1–1.5 ml) of the polymerization slurry taken from the reaction vessel at known intervals were immediately added to a solution of ~0.3 g of *t*-butyl catechol, as inhibitor, dissolved in ~16 g of methanol, a monomer extracting agent, in a screw-cap test tube. All the materials in the solution were weighed accurately to ± 0.0001 g and the mixture was weighed again after addition of the sample slurry. The test tube was sealed, tumbled occasionally, and kept in the refrigerator for 24 hr, after which time it was found that all monomers had been extracted. The test tube was then centrifuged to separate insoluble salts and solid polymer from liquid methanol, unreacted monomers and water. The clear supernatant (methanol extract) was saved for GLC analysis, while solid residue was soaked in 3*N* HCl for 48 hr to dissolve all the inorganic precipitates. The residual polymer obtained was washed successively with copious amounts of 3*N* HCl, deionized water, and finally methanol on a filter paper, then aspirated and dried in a vacuum oven at 50°C for 24 hr, and finally weighed to ± 0.0001 g.

Water, DVB, EGDM, EVB, and Styrene Analysis

The analysis for individual unreacted monomers was carried out using a Perkin–Elmer 3920 gas chromatograph equipped with a Hewlett–Packard 33805 integrator and flame ionization detector using a 9-ft 1/8-in. stainless-steel column packed with 5% Sp-1200/1.75% bentone 34 on 100/120 Supelcoport. The temperature program was set from 80–160°C with an 8°C/min rate. The GLC correction factors for each monomer were calculated from standard solutions prepared for the expected range of monomer concentrations. The impurity peaks (less than 0.5% total in the raw materials) were neglected in the material balance, therefore, only the intensities of DVB, EVB, EGDM, and styrene were considered in the residual monomer calculations. After taking correction factors into account, the true percentage of unreacted monomer in the sample was determined.

The methanol phase was analyzed with a Gowmac 550 gas chromatograph equipped with a thermal conductivity detector and a 6-ft 1/8-in. stainless-steel column packed with porapak Q 80/100 mesh at 90°C to determine weight ratio of water and methanol in the test tube. Knowing the weight of methanol, an internal reference, the weight of water in the sample is readily calculated.

Calculation

The weight of unreacted overall monomers in the sample was calculated as follows:

$$A = B - C - D$$

where *A* = total wt of unreacted monomers in the sample; *B* = total wt of sample taken from polymerization slurry; *C* = wt of suspension media taken from polymerization slurry = (wt of water in the sample)/(wt fraction of water in the aqueous phase calcd. from the original formulation); and *D* = wt of polymer formed during the polymerization.

The percentage of a specific monomer conversion at each interval was calculated as follows:

$$E = \left[1 - \frac{A \times F}{(B - C) \times G} \right] \times 100$$

where E = % conversion of each individual monomer; F = wt fraction of individual unreacted monomer at known intervals obtained from GLC analysis; and G = wt fraction of individual monomer in the original monomer mixture obtained from GLC analysis.

A plot of percent individual monomer conversion versus reaction time for a typical suspension polymerization system of the composition 90.8% styrene, 2.98% EVB, 4.34% DVB, and 1.88% EGDM is shown in Figure 1.

DISCUSSION

All calculations in the previously discussed procedure were based on mass balances and the values of each repeated measurement was estimated to be within $\pm 3\%$ of the average value. Since no assumption was made to correct these values and no internal standard was required for this method of analysis for each monomer, the method is applicable for following actual plant-scale polymerizations.

The accuracy of A value defined in the calculation section is subject only to errors in weighing. They can be further verified by using a high-resolution GLC, equipped with a thermal conductivity detector, which is calibrated with standard solutions having compositions over the ranges of interest.

If studies on the reactivity of individual DVB isomers and unreacted double-bond content of DVB and EGDM in the solid polymers of known intervals

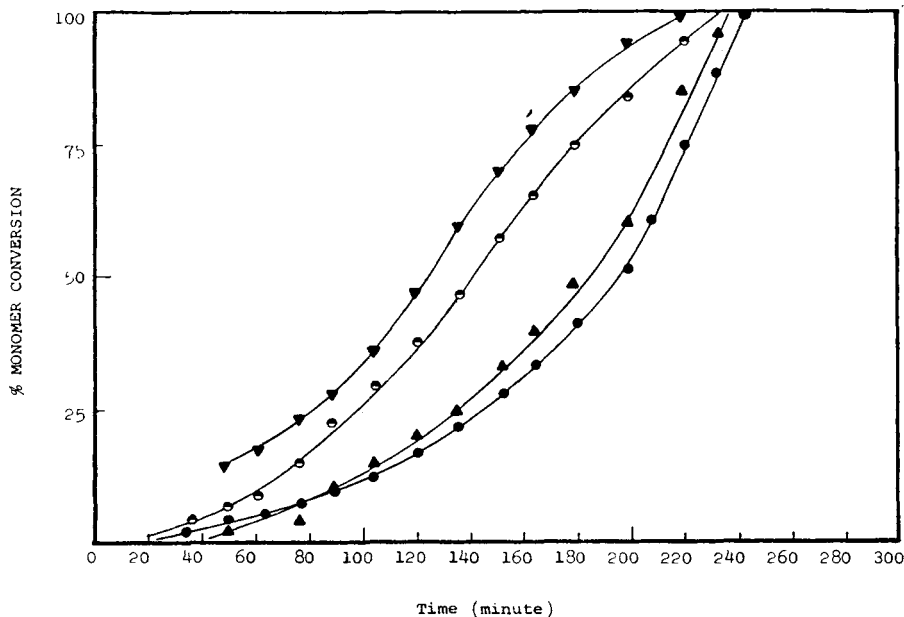


Fig. 1. Percentage of monomer conversion vs. reaction time: (●) styrene; (▲) EVB; (◐) DVB; (▼) EGDM.

are desired, additional steps may be fitted into the procedure. The resolution of the individual DVB isomers may be accomplished by GLC analysis using a 1/8-in. stainless-steel column packed with 5% bentone 34 and 5% di-isodecyl phthalate on chromosorb W/AW 80/100 mesh as indicated by Kwant.⁵

Residual pendant double bonds in the isolated polymer may be determined and differentiated into acrylic and styrenic vinyl groups as follows. The total unreacted pendant double bonds in the solvent-swollen isolated polymer are determined by bromine titration⁶ ($\text{KBr}-\text{KBrO}_3$) in aqueous-glacial acetic acid acidified with sulfuric acid. Loshaek and Fox⁷ reported that an infrared analysis method was used to examine the unreacted EGDM-pendant double bond quantitatively. They used a strong and sharp peak of conjugation of olefin linkage with the ester-carbonyl group [$\text{CH}_2 = \text{C}(\text{CH}_3)\text{C} = \text{O}$] at $6.10 \pm 0.01 \mu$. Once the amount of unreacted EGDM-pendant double bond and the total unreacted double bond are known on each polymer sample at a certain period of polymerization, the amount of unreacted DVB double bond can be determined.

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Received January 28, 1980

Accepted March 13, 1980