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Technical Report No. 5

Model Filled Polymers. V. Synthesis of Crosslinked
Monodisperse Polymethacrylate Beads

by

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Prepared for Publication

in

Journal of Polymer Science: Polymer Chemistry

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September 25, 1990

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 5			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Southern California		6b. OFFICE SYMBOL (If applicable) MC 1211		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) University of Southern California Department of Chemical Engineering Los Angeles, California 90089-1211		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217-5000			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR/DARPA		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER ONR N00014-88-K-0302	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 22217-5000		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO. WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Model Filled Polymers. V. Synthesis of Crosslinked Monodisperse Polymethacrylate Beads					
12. PERSONAL AUTHOR(S) D. Zou, S. Ma, R. Guan, M. Park, L. Sun, J. J. Aklonis, and R. Salovey					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 9/1/89 TO 9/1/90		14. DATE OF REPORT (Year, Month, Day) September 25, 1990	
15. PAGE COUNT 21					
16. SUPPLEMENTARY NOTATION Submitted to <u>Journal of Polymer Science: Polymer Chemistry</u>					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Polymer Beads; Crosslinked Monodisperse Beads; Polymethacrylates; Filled Polymers		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Monodisperse polymethacrylate beads of varied size and crosslink density are prepared by emulsion copolymerization of methacrylate and divinyl monomers in the absence of emulsifiers. The sizes of polybutyl and polyethyl methacrylate beads decreased with increasing polymerization temperature, while polymethyl methacrylate beads were largely unchanged in size. The molar mass of polymer in polymethyl methacrylate beads markedly exceeded that in polystyrene beads. The rate of polymerization increased, and bead size decreased, with increasing initiator concentration or decreasing monomer concentration. The polymethacrylate beads are used as filler particles in polymer composites.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Milliken			22b. TELEPHONE (Include Area Code) (703) 696-4409		22c. OFFICE SYMBOL ONR

Model Filled Polymers. V. Synthesis of Crosslinked Monodisperse Polymethacrylate Beads

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Introduction

Recently, we reported on the synthesis of crosslinked monodisperse polystyrene beads [1] and the preparation of model filled polymers by the inclusion of beads in a polystyrene matrix [2]. In order to ensure that the beads were uncontaminated by surfactant, we conducted synthesis by emulsion polymerization in the absence of emulsifier [3]. For persulfate initiated polymerization, resultant latex particles are stabilized by sulfate groups from the initiator, bound to the surface [4]. Several mechanisms have been proposed for bead nucleation and growth during polymerization without emulsifiers [5, 6]. The actual process may depend on the solubility of the monomer in water.

Since styrene monomer is very slightly soluble in water [7, 8], it has been suggested that oligomeric polystyrene-free radicals, with sulfate end groups, are surface active and form micelles in an emulsion polymerization [5]. Subsequent polymerization would occur with styrene monomer contained in the micelles and continue in styrene swollen polystyrene particles. However, in the absence of emulsifier, particle sizes are increased and each bead contains simultaneously growing chains [9]. As a result, molecular weight distributions are broader than in conventional emulsion polymerization and depend on conversion [9].

For more water soluble monomers, such as methacrylates, it has been proposed [10, 11], that the initial growing particles in the polymerization of beads are formed by the

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precipitation of oligomeric free radicals from the aqueous medium, upon achievement of a critical chain length. Subsequent polymerization occurs in monomer swollen polymer particles.

The homologous series of methyl, ethyl and n-butyl methacrylate, includes monomers of decreasing aqueous solubility, which may enable us to conduct emulsifier-free emulsion polymerizations differing in mechanism. In this paper, we examine the synthesis of crosslinked monodisperse polymethacrylate beads and compare the kinetics and mechanism of polymerization with those of polystyrene beads.

EXPERIMENTAL DETAILS

Materials

Methyl methacrylate monomer with assay 98% inhibited with 25 ± 5 ppm hydroquinone (HQ) is a product of Fisher Scientific Co. Ethyl methacrylate and n-butyl methacrylate monomers both 99% purity are inhibited with 15 ppm and 10 ppm hydroquinone monomethyl ether (MEHQ), respectively, and are produced by Aldrich Chemical Co. Crosslinking agents, allyl methacrylate and ethylene glycol dimethacrylate, both 98% purity, are inhibited with 50-185 ppm hydroquinone and 100 ppm hydroquinone monomethyl ether, respectively, and are purchased from Aldrich Chemical Co.

The initiator, potassium persulfate, is a certified Fisher Scientific product; the water used for polymerization is deionized water from Sparkletts; methanol is analytical reagent grade purchased from Mallinckrodt Co. and nitrogen is obtained from MG Industries Gas Products.

Polymerization

Prior to polymerization, phenolic inhibitors added to the methacrylate monomers, are removed by washing with aqueous sodium hydroxide and water [1] or are deactivated by bubbling nitrogen [12, 13]. Since we have observed that washing the inhibitor out often leads to coagulation during polymerization, we prefer to treat the inhibitor with nitrogen for at least 15 minutes before polymerization.

Polymerizations are carried out in a 1 liter resin reaction flask with internal stirring. The flask is immersed in a thermostated water bath to maintain constant temperature. A water-cooled condenser which is connected to the atmosphere via a wash-bottle containing water, to prevent back-diffusion of oxygen into the reaction system, is fixed to the reactor. Nitrogen is bubbled through a thin teflon tube into the reactor.

Usually, the ratio of monomer to water medium is 1/10 by weight, and the initiator concentration is 0.5×10^{-3} mol/l. Typically, 650 ml of water and 70 g monomer are placed into the reactor and nitrogen is bubbled through to deactivate the inhibitors by excluding oxygen from the reacting system [12, 13]. The stirring speed is adjusted to 350 RPM with a digital controller. The system is allowed to sit for at least 15 minutes to deactivate the inhibitor, attain temperature equilibrium and saturate the aqueous phase with monomer. Then, a specified amount of initiator dissolved in 30 ml water is added and washed in with 20 ml water. The reaction is sustained for several hours, depending on temperature, initiator and monomer concentrations and the amount of crosslinking agent. At selected intervals, aliquots are removed from the reactor in order to determine conversion and bead size. Usually, when foam forms on the surface of the emulsion in the reactor, the conversion exceeds 90%. Solid beads are separated from the latex by freezing [1] and washed with water and methanol repeatedly to remove unreacted initiator and monomer. Subsequently, beads are dried in a vacuum oven at 50° C.

Characterization

Bead size and distribution are examined in a scanning electron microscope (SEM), Cambridge Stereoscan, Model 360. The molecular weight of uncrosslinked polystyrene and polymethyl methacrylate beads are determined by gel permeation chromatography (Perkin-Elmer, liquid chromatograph, with a series 10 pump and LC-75 spectrophotometric detector or a Waters, Model M-6000A), using a mixed bed polystyrene gel column and calibrations determined with PS or PMMA standards, as appropriate.

RESULTS

The monodispersity in size of beads from typical polymethacrylate polymerization is illustrated in Figure 1, for polyethyl methacrylate beads, crosslinked with 1 weight % ethylene glycol dimethacrylate.

The effect of polymerization temperature on uncrosslinked bead size is illustrated in Figure 2 for the synthesis of uncrosslinked polymeric beads. The sizes of uncrosslinked polystyrene (PS) beads synthesized in a tumbling reactor [1] are included for comparison. Bead sizes were ordinarily measured at maximum conversion, which approximated 100%. For polymethyl methacrylate (PMMA), however, conversions were not complete, although, unreacted monomer was not observed, because some monomer was lost by evaporation. For PMMA, observed bead sizes were corrected to 100% conversion. For example, for PMMA beads prepared at 60 to 80° C, conversions were about 75%, while for 90° C synthesis, the conversion was about 40%. All data shown for PMMA, were averages of repeated runs. For corresponding crosslinked systems, bead sizes were very close to those shown in Figure 2. Crosslinking of methacrylate systems was effected by the inclusion of ethylene glycol dimethacrylate (EGDMA) or allyl methacrylate (AMA). In all these cases, the dry polymer bead sizes are largely independent of the degree of crosslinking, or the nature of the crosslinking agent.

The copolymerization of ethyl methacrylate (EMA), with up to 20 weight percent AMA, was examined at 70° C and at a constant initiator (potassium persulfate) concentration of 5×10^{-4} mol/l. In all cases, conversions were virtually complete. The content of AMA crosslinker, has only slight effect, <5%, on bead size. Indeed, for AMA concentrations between 1 and 10%, the bead size equaled 378 nm. However, the rate of polymerization increased uniformly with the addition of up to 10% AMA. For methacrylates initiated by potassium persulfate, the rate of polymerization increases with temperature. Typical results are plotted in Figure 3 for EMA.

The homopolymerization of EMA to form a linear polymer, without crosslinker, at

various initiator concentrations, is illustrated in Figure 4. Corresponding final bead sizes are also indicated and decrease with increasing initiator concentration. The apparent rate of reaction, or change in fractional conversion, also increases with decreasing monomer concentration. Results are illustrated for EMA at 70° C in Figure 5. Corresponding bead sizes are indicated and increase with increasing monomer concentration.

Under the same reaction conditions, the rates of reaction and bead sizes are illustrated in Figure 6 for methyl methacrylate (MMA), EMA and butyl methacrylate (BMA). A comparison of AMA and EGDMA crosslinking, by copolymerization with these three monomers, indicates that the rates of copolymerization are slightly faster for reaction with EGDMA than with AMA. However, the sizes of polymeric beads were unaffected by the nature of the crosslinking comonomer.

The molecular weights of PS and PMMA were measured by GPC at various reaction times during the polymerization of the respective monomers at 60 °C. Data are tabulated for PS and PMMA in Table I.

DISCUSSION

Among the monomers examined, the monomer of lowest aqueous solubility, styrene, exhibits the most sensitive dependence of bead size on polymerization temperature (Figure 2). The solubility of styrene (S) in water is 0.0026 mol/l at 25° C and increases with temperature to 0.0037 at 50° C [7, 8]. The solubility of BMA monomer in water is 0.0042 mol/l [5]. Although, the solubility of BMA monomer in water is close to that of S, BMA shows a reduced temperature dependence of bead size. Perhaps, the presence of polar methacrylate groups affects bead nucleation. Also, EMA, with a markedly increased aqueous solubility of 0.045 mol/l [5], shows a similar behavior to BMA. The corresponding curves in Figure 2 are almost parallel. However, polymeric bead sizes are about 100 nm lower for EMA than for BMA. For PMMA, with an aqueous solubility of 0.15 mol/l [5, 8], bead sizes approximated 300 nm, almost independent of polymerization temperature. In surfactant free polymerization, PMMA bead sizes have been reported to be smaller than PS

beads [14]. However, in the range of temperatures from 50 to 70° C, both monomers showed small decreases in bead size with increasing temperature [14]. For these emulsion polymerizations in aqueous media, without added emulsifier, alternative particle nucleation mechanisms had been proposed [5]. The specific mechanism applicable depends on the solubility of the monomer in water. Monomers such as S, which are poorly soluble in water, polymerize via bead nucleation in micelles formed by the alignment of surface active oligomers produced during the initial stages of polymerization. Relatively water soluble monomers, such as MMA, undergo homogeneous nucleation of primary particles by the precipitation of growing polymer chains from solution, upon the attainment of a critical chain length. It has been suggested [14], that, with increasing monomer solubility in water, the number of growing particles, early in the polymerization, must be increased, leading to smaller particle size. This would, certainly, be true for PS polymerization in micelles, where the concentration of surface active oligomers determines the number of micelles formed. These quantities, in turn, depend on the concentration of S monomer in the aqueous phase, which increases with temperature [7, 8]. Computer simulation [5] indicates that the number of growing particles increases with increasing solubility of the monomer in water. Moreover, we would anticipate that the molecular weight of the polymer would depend on particle size. Assuming chain termination by radical entry into growing particles, the smaller the particles, the longer the lifetime of growing chains, resulting in higher molecular weights. A comparison of the molecular weights of PS and PMMA in Table 1, at low conversion, shows that the molar mass of PMMA considerably exceeds that of PS. The increase in molar mass with conversion, while the beads grow in size [1], is consistent with a reduced efficiency of termination [1].

For more water soluble monomers, such as the methacrylates, and, especially, PMMA, the number of growing particles, and the bead size, depend both on the solubility of monomer in water *and* on the critical chain length for the precipitation of growing polymer chains from solution. These are opposing effects for the determination of primary particle

size. With increasing monomer solubility, the critical chain length for polymer precipitation would also be increased. In the presence of an adequate concentration of water soluble initiator, the former leads to increased chain nucleation, while the latter leads to reduced chain precipitation. As a result, although the monomer solubility varies widely among the methacrylates, the observed bead sizes are rather close. Similarly, the dependence of bead size on polymerization temperature is reduced for BMA and EMA and is almost non-existent for MMA.

Evidence of a markedly different mechanism for S and MMA polymerization is shown by molecular weight and molecular weight distribution measurements (Table 1). The ratio $\overline{M}_w/\overline{M}_n$ is determined by the mechanism of termination. For PS, this ratio "approximates," but always exceeds two. For a most probable distribution, with termination by combination, as ordinarily shown by styrene, the predicted ratio is 1.5 [15, 16]. However, for polymerization in emulsion, termination may not occur by the reactions of *polymeric* free radicals. Moreover, a change in the efficiency of termination with conversion and with molecular weight may account for the deviation, which increases with conversion [1]. For PMMA, this ratio approaches 1.5 with increasing conversion.

We can speculate on the relationship of bead size and molecular weight. For polymerization at 60° C, the bead sizes are 800 nm for PS and 300 nm for PMMA. However, the molecular weight of PMMA is about seven times the molecular weight of PS under comparable conditions. Thus, the molecular weight is approximately inverse to the square of the bead size. It should be noted that, in these emulsion polymerizations, resultant bead sizes are enlarged in the absence of external emulsifier, in order to enhance bead stability, and there are many simultaneously growing chains [9]. Since the end of a polymer chain is surface active, we had suggested that polymerization occurs on the surface of a growing bead, rather than uniformly throughout the bead. Thus, the number of beads would be inverse to the cube of bead diameter, but termination, which may occur on, or near, the surface, is inverse to the surface area, or the square of the bead diameter. Suggestions of an

emulsion polymerization on the bead surface have been proposed for these systems [17].

The efficiency of crosslinking PS by the copolymerization of S with divinylbenzene (DVB) or polymethylmethacrylates by copolymerization with divinyl monomers, EGDMA or AMA, has been examined by swelling measurements [18]. For DVB and EGDMA, the mole % of crosslinked units approximated, but always exceeded, the mole percent of divinyl monomer in copolymerization. However, EGDMA was a more efficient crosslinking monomer than AMA, which had produced only about 60% crosslinking. We also observed, after crosslinking PEMA with AMA, that the bead size was not affected by crosslink density, consistent with reports on PS crosslinked with DVB [1]. However, the rate of polymerization of EMA increased with AMA content. Since, in these cases, conversions approximated 100%, the polymerization is able to tolerate a wide range of rate, without coagulation and resultant bead loss. However, for copolymerization with 20% AMA, the rate of reaction decreased from 10% AMA and approximated the rate curve for 5% AMA. We infer the occurrence of cyclization and a reduced rate of reaction at 20% AMA content.

The effect of initiator concentration and polymerization temperature on the rate of polymerization and bead size is illustrated for EMA in Figures 2-4. As expected, with increasing temperature, the rate of polymerization increases at constant initial initiator concentration. The decomposition of the water soluble initiator, potassium persulfate, increases with temperature, and, so, the concentration of initiated chains increases with temperature. Therefore, PEMA bead sizes are reduced on raising the temperature. Although, as we have discussed, the reduction is compensated by the increased solubility of growing oligomers.

In order to ascertain the effects of initiator concentration, without changes in monomer or oligomer solubility, we directly vary the initiator concentration at constant temperature (Figure 4). Here, the polymerization rate increases with the initiator concentration. As expected, bead sizes decrease with increasing initiator concentration as more growing particles are formed. However, the decrease in size is much less pronounced than an inverse

cube root dependence on initiator concentration, implying that the number of growing particles may not be simply inverse to the volume of growing beads. It has been proposed [17, 19] that, following primary nucleation by the precipitation of growing chains, agglomeration and particle coalescence occur and fix the number of beads nucleated.

In the preparation of PS beads, it has been shown [1] that a simple way to limit bead size is to reduce the concentration of monomer, so that the growing bead runs out of monomer. Similarly, for PEMA, bead size and reaction rate are sensitive to EMA concentration (Figure 5). Again, since we plot fractional conversion versus time, the rate of reaction appears to increase as we reduce monomer concentration. However, the actual rate of bead growth is constant, in terms of moles polymerized per unit time. Here, bead diameter is less variable than the cube root of monomer concentration. This may reflect bead formation by the agglomeration of primary particles [17, 19-21].

If we compare rates of polymerization and bead sizes among the various methacrylate monomers (Figure 6), we observe that the slower the rate of fractional conversion, the larger the bead size, showing that fewer particles grow. However, PEMA and PMMA rates and bead sizes are extremely close. As we have suggested, simultaneous variations in monomer and oligomer solubility in water may have reduced differences. Further studies, in our laboratories, have shown that crosslinking the methacrylate monomers, with either 5% AMA or 5% EGDMA, leads to the same bead size. However, PBMA beads were very close in size to PEMA beads, but slightly larger than PMMA beads.

CONCLUSIONS

Monodisperse polymethacrylate beads have been prepared by emulsion polymerization of methacrylate monomers in an aqueous medium in the absence of surfactant. Sizes of uncrosslinked beads were less sensitive to polymerization temperature than polystyrene and varied with the nature of the monomer. The sizes of polybutyl methacrylate and polyethyl methacrylate beads decreased with increasing polymerization temperature, while polymethyl methacrylate beads remained fairly constant in size. The

molecular weights at several conversions of the polymer in polymethyl methacrylate beads were almost an order of magnitude larger than those in polystyrene beads. It is clear that these monomers exhibit diverse particle nucleation mechanisms. It is suggested that the effect of polymerization temperature on polymethacrylate bead size is suppressed, to an extent depending on the monomer, by a balance between monomer solubility and the critical chain length for the precipitation of growing polymer chains from solution. In addition, emulsion polymerization on the bead surface is proposed.

Monodisperse crosslinked polymethacrylate beads have been prepared by copolymerizing methacrylate monomers with ethylene glycol dimethacrylate or allyl methacrylate. The rate of polymerization of methacrylate monomers increases with increasing polymerization temperature and with initiator concentration. Bead sizes decreased with increasing initiator concentration as more growing beads are produced. For polymethacrylates, bead sizes decrease and fractional conversions increase by reducing the concentration of monomer. The slower the rate of fractional conversion, the larger the bead size, as fewer particles must grow. In general, among the polymethacrylates studied, reaction rates and bead sizes are close, under similar experimental conditions.

ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research and by DARPA.

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**Table 1. Molecular Weights during
Polymerization of Beads***

Reaction Time	Polystyrene		Polymethyl methacrylate	
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$
15 minutes	67,700	30,800		
45 minutes	74,700	32,900	538,000	274,000
1 hour 30 minutes	86,600	37,400	865,000	656,000
4 hours	105,000	44,100	855,000	674,000
6 hours	116,000	47,400	928,000	628,000
8 hours	142,000	57,400	1,000,000	714,000

* polymerization at 60°C.

LIST OF FIGURES

1. Monodisperse crosslinked polymethyl methacrylate beads, prepared by copolymerization of ethyl methacrylate and 1% ethylene glycol dimethacrylate. Bead diameter 345 nm. Scanning electron micrograph, magnification 10,000 $\times$.
2. Effect of polymerization temperature on the size of uncrosslinked beads:
 - (A) polystyrene (PS);
 - (B) polybutyl methacrylate (PBMA);
 - (C) polyethyl methacrylate (PEMA);
 - (D) polymethyl methacrylate (PMMA).
3. Conversion of uncrosslinked polyethyl methacrylate beads at various polymerization temperatures.
4. Conversion of uncrosslinked polyethyl methacrylate beads at various initiator concentrations; 70° C; 10% ethyl methacrylate:
 - (A) 2.0×10^{-3} mol/dm³, final bead size 282 nm;
 - (B) 1.0×10^{-3} mol/dm³, final bead size 314 nm;
 - (C) 0.5×10^{-3} mol/dm³, final bead size 347 nm;
 - (D) 0.25×10^{-3} mol/dm³, final bead size 378 nm.
5. Conversion of uncrosslinked polyethyl methacrylate beads at various monomer concentrations prepared at 70° C; initiator concentration = 0.50×10^{-3} mol/dm³:
 - (A) 2.5% monomer by weight, final bead size 252 nm;
 - (B) 5.0% monomer by weight, final bead size 275 nm;
 - (C) 10% monomer by weight, final bead size 347 nm;
 - (D) 20% monomer by weight, final bead size 455 nm.
6. Conversion of uncrosslinked polymethacrylate beads prepared with 10% monomer by weight at 70° C; initiator concentration 1.0×10^{-3} mol/dm³:
 - (A) polymethyl methacrylate, final bead size 313 nm;
 - (B) polyethyl methacrylate, final bead size 314 nm;
 - (C) polybutyl methacrylate, final bead size 378 nm.

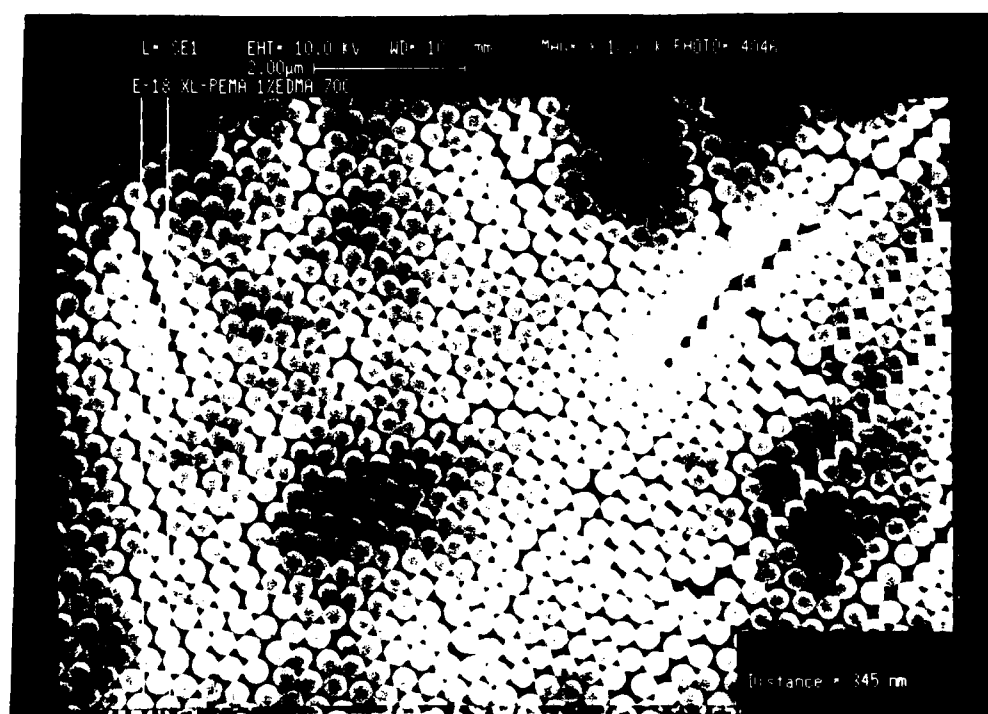


FIGURE 1

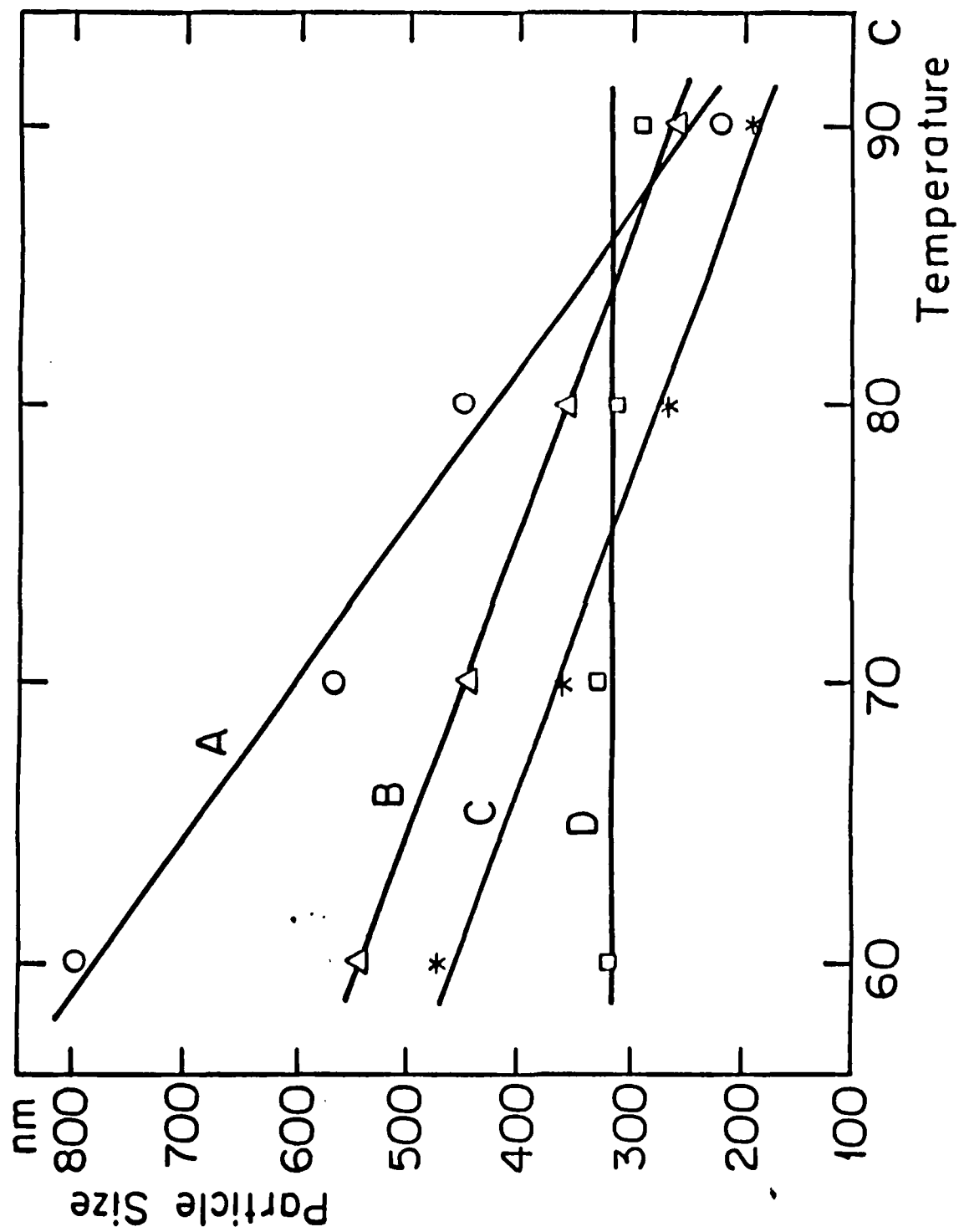


FIGURE 2

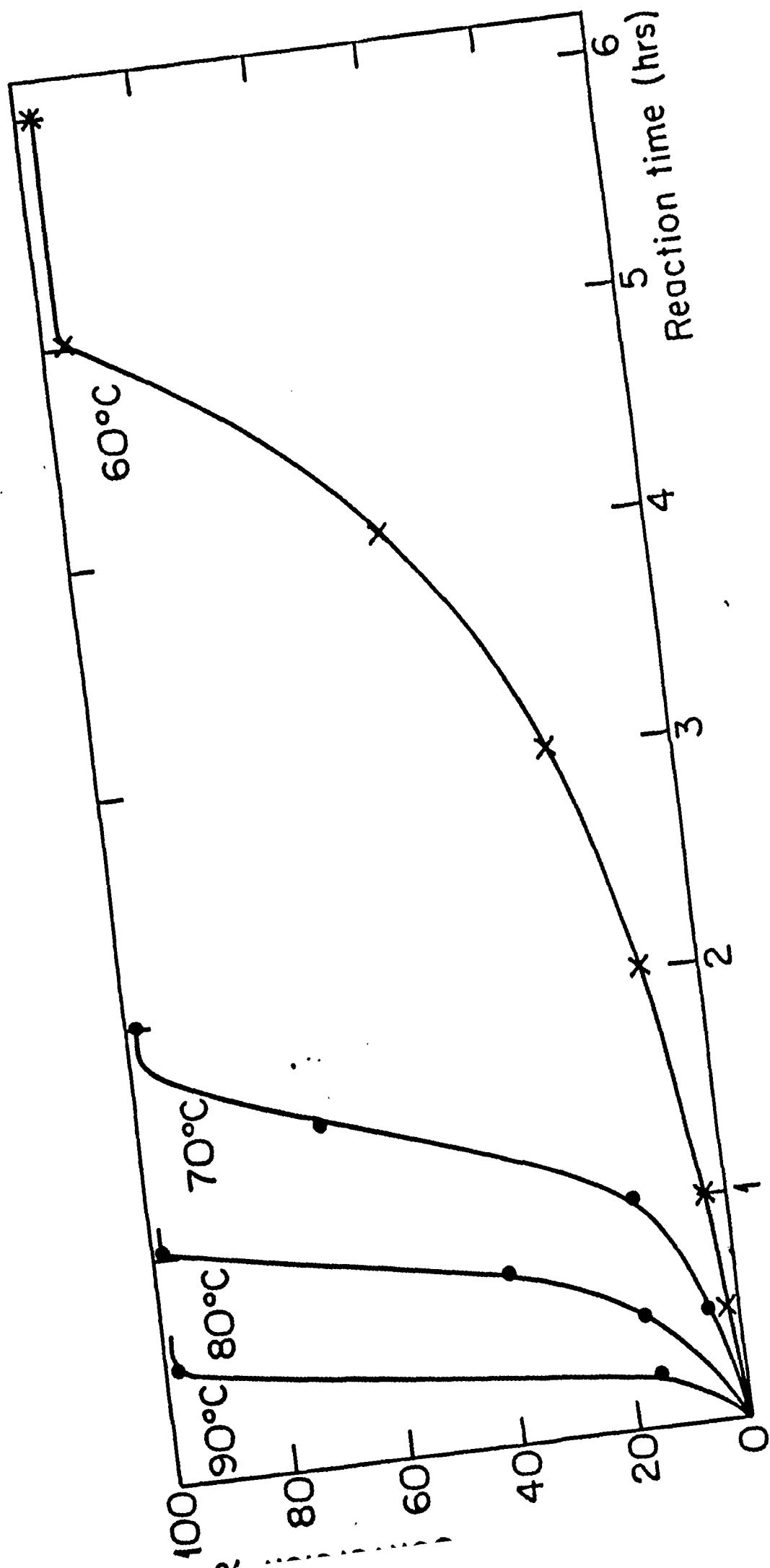


FIGURE 3

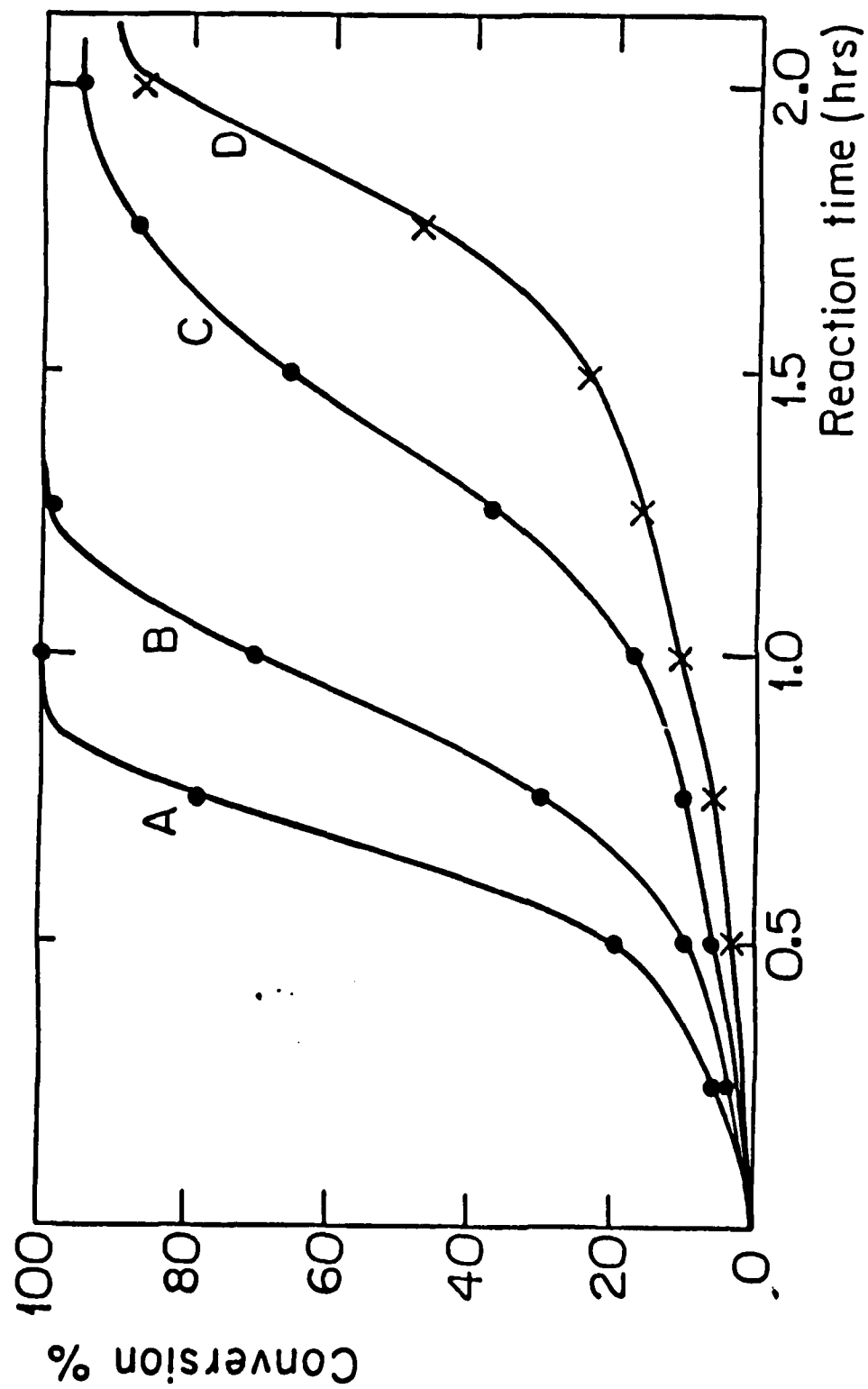


FIGURE 4

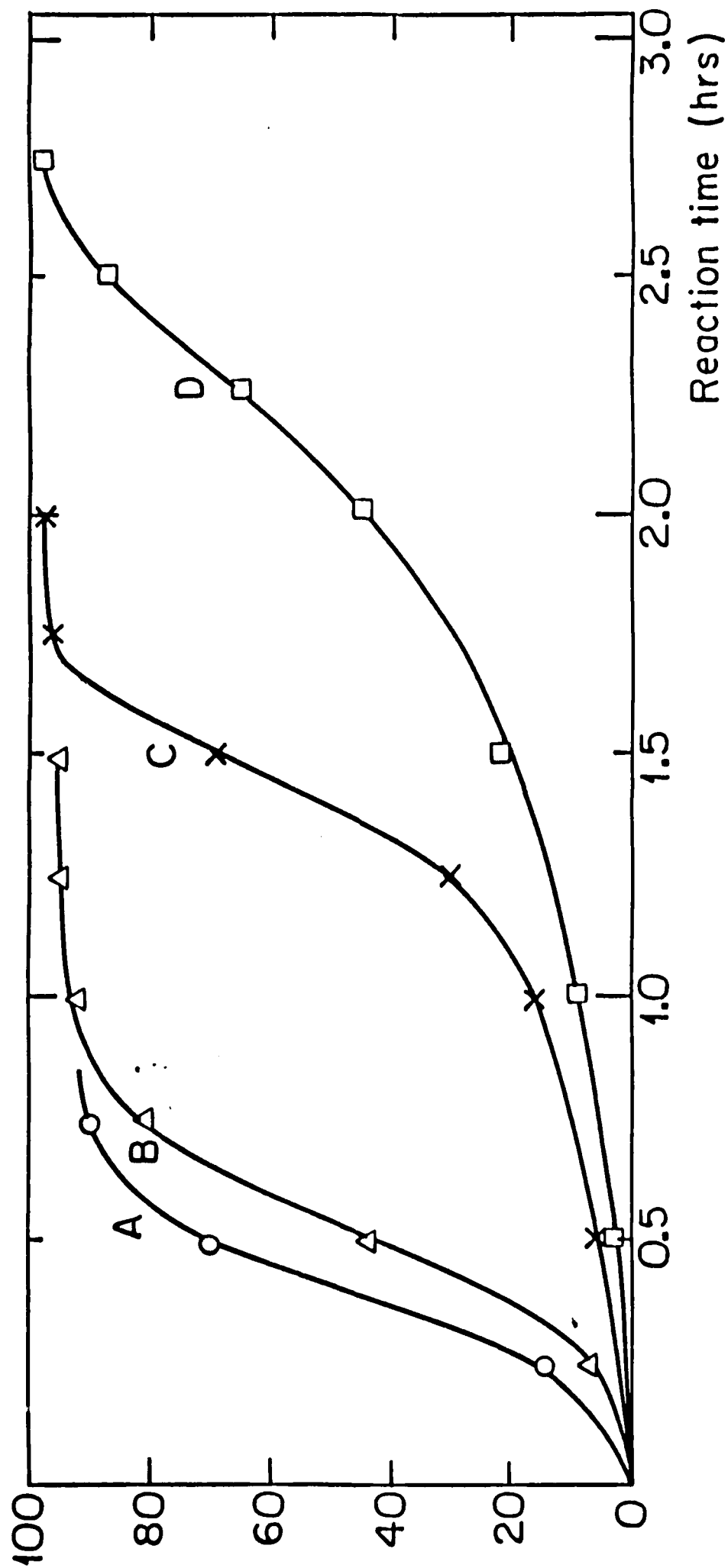


FIGURE 5

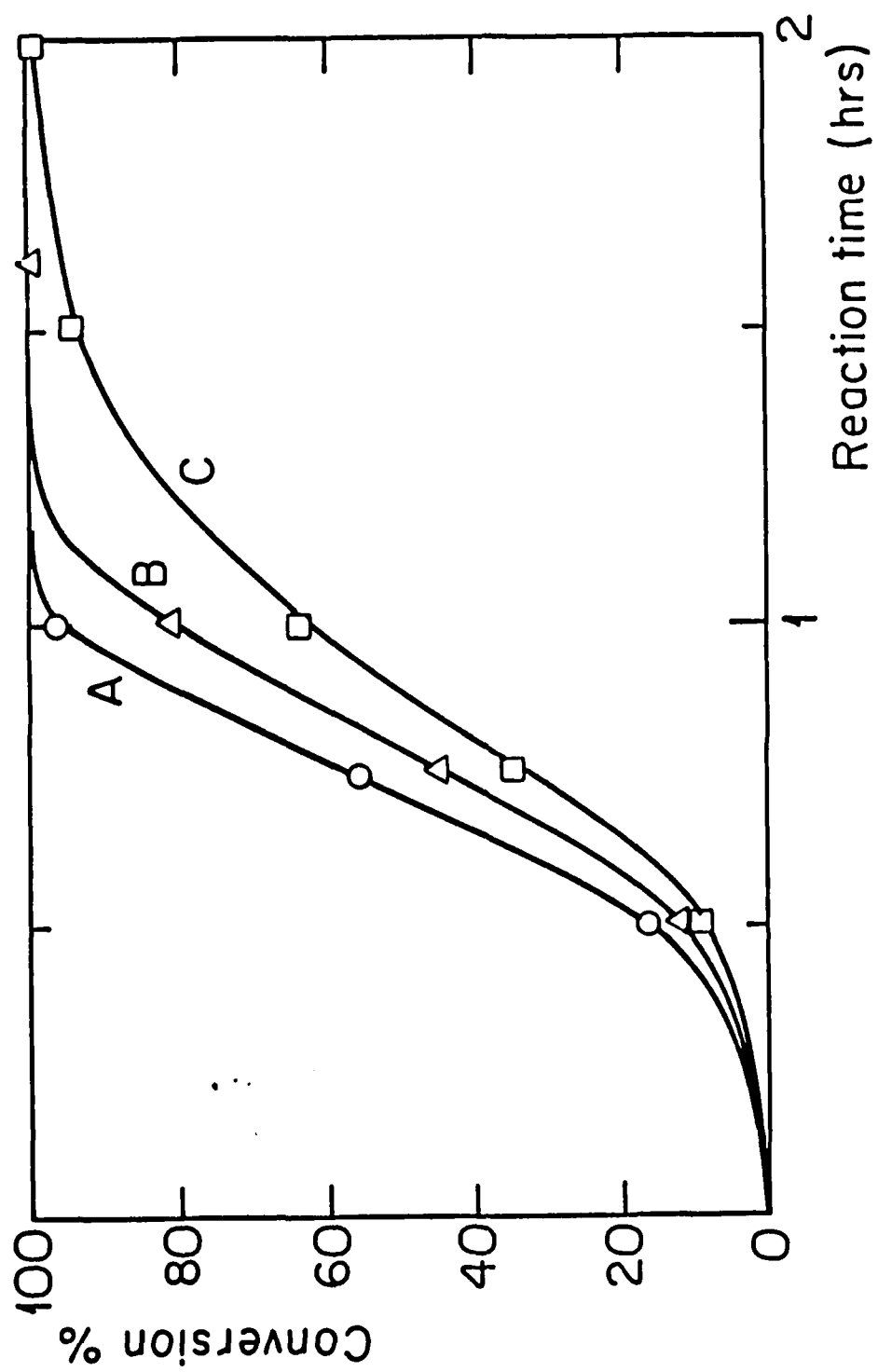


FIGURE 6

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