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Model Filled Polymers IX. Synthesis of Uniformly Crosslinked Polystyrene Microbeads

by

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ABSTRACT

Monodisperse sized crosslinked polystyrene (PS) beads prepared by reaction of styrene (S) and divinylbenzene (DVB), in batch emulsion copolymerization in the absence of emulsifiers, are *not* uniformly crosslinked, because DVB is more reactive than S. For copolymerization of 1 to 10 mole % DVB and S, within each crosslinked PS microbead, the crosslink density varies by a factor exceeding two and decreases with increased conversion. A semicontinuous copolymerization, involving incremental additions of DVB, produces uniformly crosslinked PS beads. For both copolymerization techniques, T_g correlates well with crosslink density and PS beads are spherical and monodisperse in size.

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INTRODUCTION

Crosslinked polystyrene (PS) is often prepared by the copolymerization of styrene (S) monomer with small amounts of divinylbenzene (DVB). In general, the composition of a copolymer from binary copolymerization depends on the composition and relative reactivity of the monomers [1-3]. As a result, the (instantaneous) composition of a copolymer is, usually, different from the composition of the monomer feed mixture, as one of the monomers may be consumed more rapidly than the other. Ordinarily, the composition of the monomer mixture, varies, as the reaction proceeds, while the composition of the resulting copolymer, also, changes with conversion. Only when the reactivity ratios in copolymerization are both unity, or, for an azeotropic composition of monomers, will the copolymer and monomer compositions be identical.

In order to characterize the crosslinked structure of copolymers of S and DVB, Wiley *et al.* measured the reactivity ratios of S and DVB in binary copolymerization, under various conditions [4-10], and studied properties of the copolymer [11-16]. Although, reported values of the reactivity ratios were not completely consistent, results indicated that DVB is more reactive than S. This will result in depletion of DVB in the monomer mixture during copolymerization,

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before the S is consumed, and a drift in copolymer composition with conversion. As a result, it is possible that crosslinked PS beads, prepared by batch emulsion copolymerization, may have tightly crosslinked cores, to which more lightly crosslinked or uncrosslinked PS chains are attached [4, 9]. Indeed, it has been suggested that emulsion polymerization occurs on the surfaces of growing particles [17] leading to inhomogeneous polymerization, especially for large particle sizes [18]. Small angle neutron scattering analyses of PS latex particles indicate that the particles have a core-shell structure, with the locus of polymerization at the particle surface [19-21].

Using a recently reported technique of swelling crosslinked polymeric beads on an ultrafiltration membrane [22], we directly examined the relationship between crosslink density and reaction time, or conversion, in the synthesis of crosslinked PS beads. In addition, we measured the glass transition temperatures (T_g) of the beads by differential scanning calorimetry (DSC). We also proceeded to add DVB incrementally, during copolymerization, in order to synthesize uniformly crosslinked PS beads.

EXPERIMENTAL DETAILS

A. SYNTHESIS

1. Batch Copolymerization

Crosslinked PS microbeads were prepared by emulsion copolymerization in the absence of emulsifier [23]. Commercial DVB obtained from Aldrich Chemical Company, was used as crosslinker and consists of 55% DVB isomers, 42% ethylvinylbenzene and 3% diethylbenzene. In calculating the composition of the monomer mixture, the ethylvinylbenzene was included with S. Polymerization was carried out in a 2 l reactor immersed in a thermostat bath at 80 ± 1°C. The concentration of the initiator, potassium persulfate, was 0.0014 mole/l in water. Every hour from the onset of the reaction, 10 ml aliquots of reaction mixture were removed during continuous agitation, each placed in a 50 ml beaker, covered with aluminum foil, weighed, opened and dried in an oven at 70-80°C for more than 15 hours. Partially dried samples were dried in a vacuum oven at 70°C and less than 1500 Pa pressure for 4 hours (to constant weight). Dried samples are weighed and conversions calculated. Dried samples were used to measure crosslink density and T_g.

2. Copolymerization with Successive Addition of DVB

Using a synthesis method otherwise the same as that for batch reaction, further DVB was repeatedly added to the reactor. The initial concentration of DVB for a desired crosslink density was selected by trial. Following the conversion curve previously determined for batch copolymerization, DVB would be added for every 10% of comonomer consumed in polymerization. The concentration of DVB in the monomer mixture was continually calculated and readjusted to its initial concentration by incremental addition of DVB. For experimental convenience, a mixture of DVB and S was actually added.

A typical preparation of 5 mol% crosslinked PS beads was carried out as follows: 1450 ml deionized water was added to a 2 l reactor. The reactor was immersed in a thermostat bath at 80 ± 1°C. Nitrogen was bubbled through the water in the reactor while stirring at 400 rpm for 30 min, to remove oxygen from the system. Then, 113.27 g S and 6.73 g DVB, which had been washed with a 10% aqueous sodium hydroxide solution and, then, deionized water for four times, respectively, were added to the reactor. Here, the initial concentration of DVB in the monomer mixture is 2.5 mol%. The reactor was left for 20 minutes to attain thermal equilibrium. Then, 571 mg initiator, potassium persulfate, dissolved in 30 ml deionized water, was added and washed into the reactor with another 20 ml deionized water, and the polymerization began. The initial concentration of initiator was 0.0014 mol/l water. Nitrogen flow was continued throughout the reaction, at a low flow rate to minimize evaporation. A mixture of DVB and S, in a weight ratio of 3:7, was added to the reacting system according to Table I.

The reaction was carried out for a total of 300 min. Before each addition of DVB, 10 ml aliquots were removed from the reactor. Polymer samples were isolated and analyzed, as previously described.

B. CROSSLINK DENSITY

The crosslink density of all samples was determined by swelling on an ultrafiltration membrane, as recently reported [22].

C. GLASS TRANSITION TEMPERATURE (T_g)

T_g was determined by calorimetry using a Differential Scanning Calorimeter (Perkin-Elmer DSC-4). The midpoint of the endothermic shift, characteristic of the transition, was selected as T_g.

RESULTS

In the preparation of 1-10 mole% crosslinked PS microbeads by batch copolymerization of S and DVB, the crosslink density and T_g of samples, corresponding to different conversions, were determined. Figure 1 illustrates the variation of conversion, crosslink density and T_g with reaction time for 5 mole% crosslinked PS beads. By adding DVB incrementally during copolymerization, we synthesized 1, 2, 5 and 10 mole% "uniformly"crosslinked PS microbeads. By analogy to the preparation of 5 mole% crosslinked PS beads, described in the Experimental Details and in Table I, incremental additions of DVB (in S) were added in order to readjust the calculated concentration of DVB to its initial value. Exact additions are summarized in Tables 2-4. Figures 2-5 indicate the relationship between crosslink density and reaction time for 1, 2, 5 and 10 mole% crosslinked PS microbeads, respectively, for both batch copolymerization of S and DVB and for "semicontinuous" processes involving incremental monomer addition. Figures 6 and 7 are SEM photomicrographs of 2 and 5 mole% crosslinked PS microbeads, respectively, resulting from semicontinuous copolymerization.

DISCUSSION

Reactivity ratios of S and DVB, determined under various conditions, indicate that DVB is a more reactive monomer than S [4-10], so that the mole fraction of DVB in the feed decreases with copolymerization. This is directly reflected in variations in crosslink density. In Figure 8, we plot crosslink density versus conversion for 5 mole% DVB in PS beads from batch copolymerization. The crosslink density of the copolymer formed at low conversion is much higher than the initial concentration of DVB in the monomer feed. As the conversion increases, the crosslink density of the copolymer rapidly decreases. In this case, the integral crosslink density approaches 5 mole% at high conversion.

As a result of crosslinking, polymer chains are immobilized and T_g increases [24-27]. As shown in Figure 1 for batch copolymerization, T_g correlates well with crosslink density, as a function of conversion, although, there was some variability in T_g at high conversion. Perhaps this results from traces of monomer trapped in largely polymeric beads.

It has been reported [23, 28-33] that the emulsion polymerization of S in the absence of emulsifier can yield monodisperse sized microbeads. Apparently, the number of growing particles in the reaction mixture remains constant with increasing conversion, with growth proceeding in the absence of new particle nucleation [28, 29, 31]. In the course of polymerization, polymer particles increase monotonically in size [23]. In this work, we demonstrate that the crosslink density decreases with increasing conversion. If we assume that newly formed copolymer adds to the surfaces of growing beads [17, 18], the crosslink density of a PS bead decreases from center to surface, and copolymer at the particle surface may be uncrosslinked or lightly crosslinked. Therefore, the PS bead from batch copolymerization is heterogeneously crosslinked, with a crosslink density gradient through the bead.

For batch copolymerizations of S containing 1, 2, 5 or 10 mole% of DVB, we observe that the crosslink density of resultant PS beads decreases markedly with reaction time (Figures 2-5).

We anticipate that crosslink density curves should level off at initial concentrations of DVB, as the cumulative mole fraction of DVB in the copolymer polymerized to high conversion should approach the mole fraction of DVB in the feed. This is approximately true at 2 and 5 mole% DVB, but is about 20% lower at 1 and 10 mole% DVB (Figure 5). Moreover, if we plot crosslink density versus conversion for 5 mole% DVB, the curve does not appear to level off at high conversion (Figure 8). We suggest that, in a heterogeneously crosslinked system, the crosslink density determined by swelling may not correspond exactly to the mole fraction of crosslinker in the copolymer. This is intrinsic to the swelling calculation [2] and is increasingly true at higher crosslink densities. Moreover, in batch copolymerization, final conversions attained 70-80%.

In order to prepare homogeneously crosslinked PS beads from copolymerization of S and DVB, the initial concentration of DVB in the monomer mixture must be reduced and, then, continuously supplemented during copolymerization. Addition of DVB during copolymerization, according to the schemes in Tables 1 to 4, yielded relatively uniformly crosslinked microbeads (Figures 2-5). Moreover, resultant crosslinked PS beads were spherical and monodisperse in size (Figures 6, 7).

The crosslink density of uniformly crosslinked PS beads was particularly sensitive to the initial concentration of DVB in the monomer mixture. For example, if the initial concentration of DVB is increased from 2.5 to 3 mole%, the crosslink density increased from 5 to 7.5 mole%. Similarly, for a change in initial concentration of DVB from 1.2 to 1.5 mole%, the corresponding crosslink density increased from 2 to 3 mole%. We have indicated the initial concentration of DVB for the preparation of uniformly crosslinked PS beads (Tables 2-4). Since published values [4-10] of reactivity ratios for S and DVB were derived from solution or bulk copolymerization, they may not apply to the initial stages of *emulsion* polymerization and, so, cannot be used to directly predict the initial concentration of DVB.

For the synthesis of uniformly crosslinked PS beads, the incremental addition of DVB was determined from the conversion curve for batch copolymerization. Therefore, the stability of operating conditions and the reproducibility of reactions were very important. Small variations in reaction rates lead to marked deviations in crosslink density, as changes in DVB concentration in the monomer mixture were reflected in drifts in crosslink density.

In later stages of emulsion copolymerization, the reaction rate often changes as monomer droplets in emulsion are depleted and the monomer concentration decreases in growing swollen beads. Therefore, the maximum conversion often varied by as much as 5%. However, in "semicontinuous" copolymerization at high conversion, it was occasionally observed that the conversion levelled off prematurely. This would imply that the reaction rate increased at final stages of copolymerization. Perhaps, final increments of DVB and S, which are always enriched in DVB, are not completely incorporated into growing beads. This may produce microbeads surrounded by a hard shell of increased crosslink density. In order to avoid an abrupt increase in crosslink density at the end of copolymerization, it is necessary to terminate incremental additions of DVB and S *before* the rate of copolymerization decreases.

CONCLUSIONS

Monodisperse sized crosslinked PS beads prepared by reaction of S and DVB, in batch emulsion copolymerization in the absence of emulsifier, are *not* uniformly crosslinked. Since DVB is more reactive than S, the mole fraction of DVB in the monomer feed decreases with copolymerization, leading to reductions to T_g and crosslink density with increasing conversion. For copolymerization of S and 1 to 10 mole % DVB, crosslinked PS microbeads, isolated at various stages of conversion, decrease in crosslink density by a factor exceeding two. At final conversions, approximating 75%, the cumulative mole fraction of crosslinks in the copolymer approaches the mole fraction of DVB in the feed for copolymerizations of 2 and 5 mole % DVB, but is about 20% lower at 1 and 10% DVB.

Techniques for semicontinuous copolymerization, involving incremental additions of DVB, were devised to produce uniformly crosslinked PS microbeads. Here, the initial concentration of DVB in the monomer mixture was markedly reduced, for example, to 2.5% to produce 5 mole % crosslinking. By comparison to kinetic curves for corresponding batch copolymerization, subsequent additions of DVB were made at 10% conversion intervals, in order to readjust the calculated concentration of DVB to its initial value.

For both batch and semicontinuous processes, T_g correlates well with crosslink density. Moreover, crosslinked PS beads, from either process, are spherical and monodisperse in size.

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Table I. Addition of DVB Mixtures for 5 mole% DVB-PS Beads (DVB:S = 3:7 by weight)

Reaction Time (min.)	60	96	123	147	165	183	204	231
Amount (g)	2.73	2.51	2.31	2.13	1.97	1.80	1.67	1.55

Table II. Addition of DVB mixtures for 1 mole % DVB-PS Beads (DVB: S = 1:9)

Initial Concentration of DVB in Monomer Mixture: 0.6 mole %

Reaction Time (min.)	51	81	105	123	141	156	168	186	219	260
Amount (g)	2.43	2.23	2.07	1.91	1.77	1.59	1.50	1.37	1.26	1.18

Table III. Addition of DVB mixtures for 2 mole % DVB-PS Beads (DVB: S = 1:9)

Initial Concentration of DVB in Monomer Mixture: 1.2 mole %

Reaction Time (min.)	57	84	108	128	147	165	181	196	218	248
Amount (g)	3.00	2.73	2.55	2.33	2.16	2.02	1.86	1.69	1.58	1.46

Table IV. Addition of DVB mixtures for 10 mole % DVB-PS Beads (DVB: S = 1:1)

Initial Concentration of DVB in Monomer Mixture:3.5 mole %

Reaction Time (min.)	57	94	129	154	175	193	210	225
Amount (g)	4.07	3.77	3.51	3.26	3.04	2.83	2.63	2.46

LIST OF FIGURES

1. Variation of Conversion, Crosslink Density (XLD) and Glass Transition Temperature (T_g) with reaction time for 5 mol% DVB/PS beads from batch copolymerization.

   ● Conversion
   × XLD
   ▲ T_g

2. Variation of XLD with reaction time for 1 mol% DVB/PS beads.

   ···▲·······▲··· batch copolymerization
   —●——●— successively adding DVB

3. Variation of XLD with reaction time for 2 mol% DVB/PS beads.

   ···▲·······▲··· batch copolymerization
   —●——●— successively adding DVB

4. Variation of XLD with reaction time for 5 mol% DVB/PS beads.

   ···▲·······▲··· batch copolymerization
   —●——●— successively adding DVB

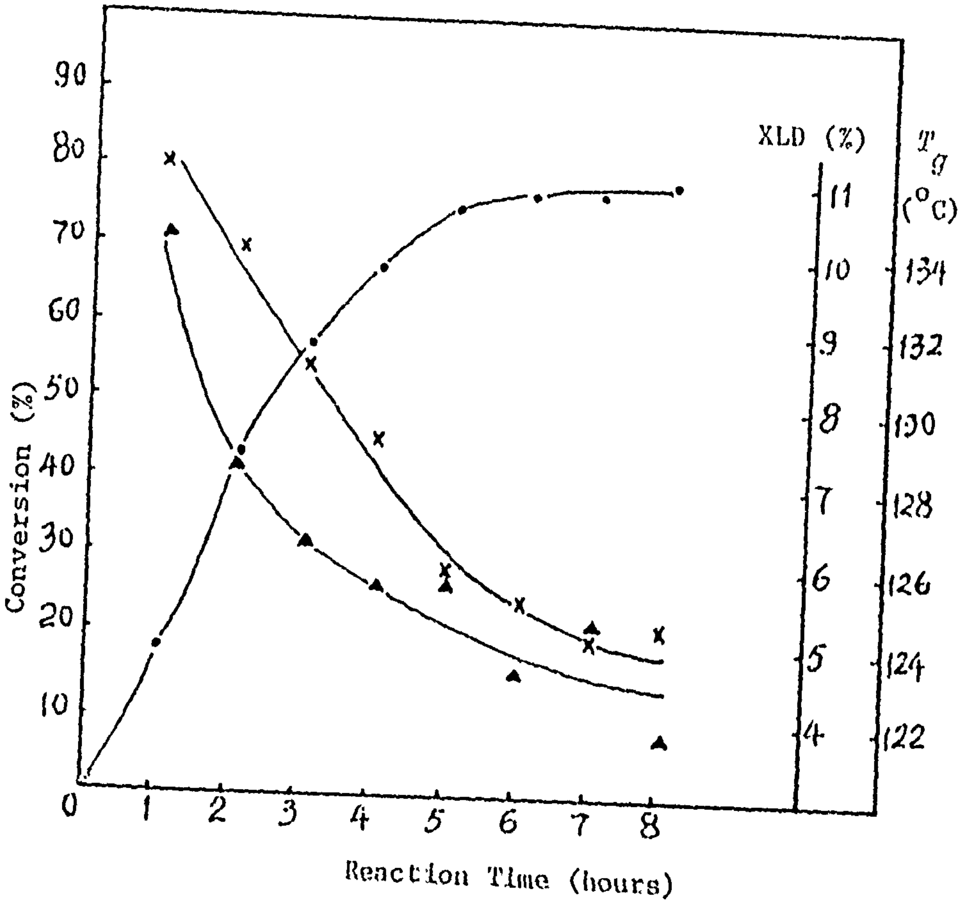
5. Variation of XLD with reaction time for 10 mol% DVB/PS beads.

   ···▲·······▲··· batch copolymerization
   —●——●— successively adding DVB

6. Monodisperse PS beads, crosslinked with 2 mol% DVB, prepared by successively adding DVB, scanning electron micrograph, magnification *10,000* ×, 505 nm.

7. Monodisperse PS beads, crosslinked with 5 mol% DVB prepared by successively adding DVB, scanning electron micrograph, magnification *10,000* ×, 438 nm.

8. Variation of XLD with conversion for 5 mol% DVB/PS beads from batch copolymerization.



Conversion (%)
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
Reaction Time (hours)
XLD (%)
11
10
9
8
7
6
5
4
T_g (°C)
134
132
130
128
126
124
122

FIGURE 1

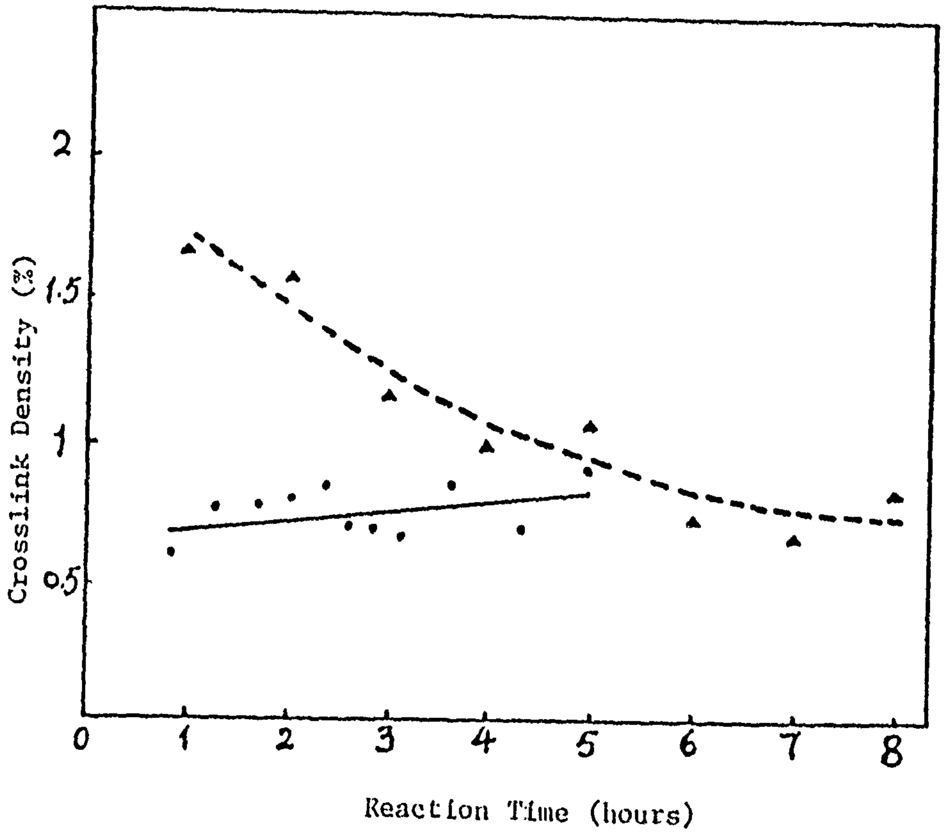


FIGURE 2

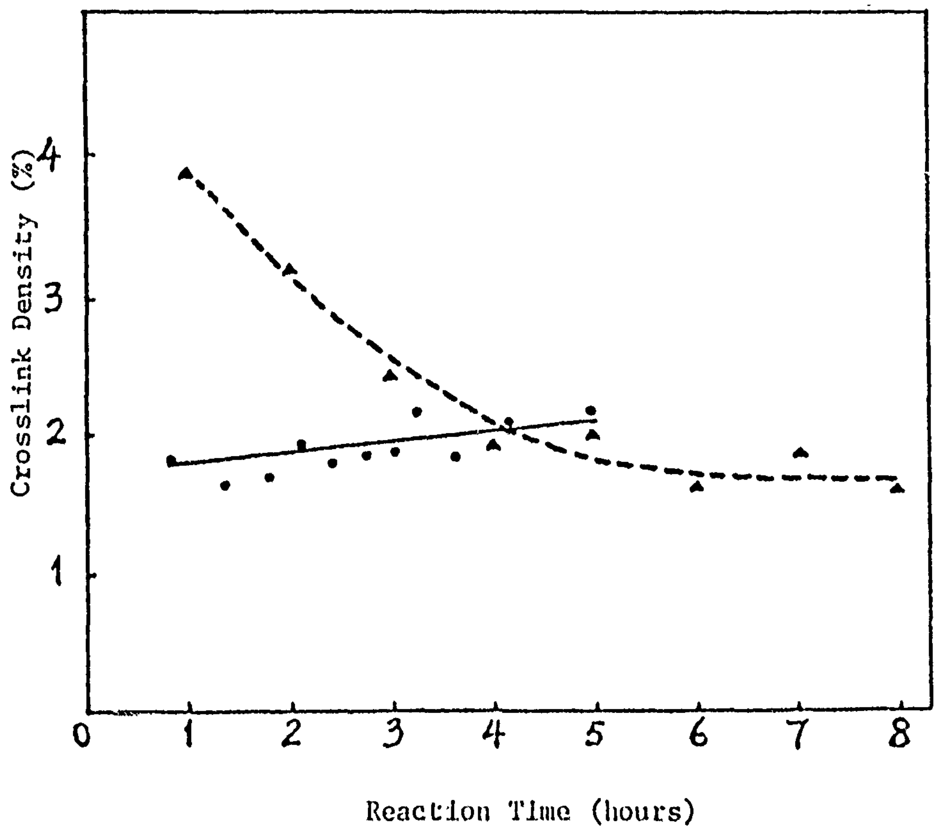


FIGURE 3

Fig. 3

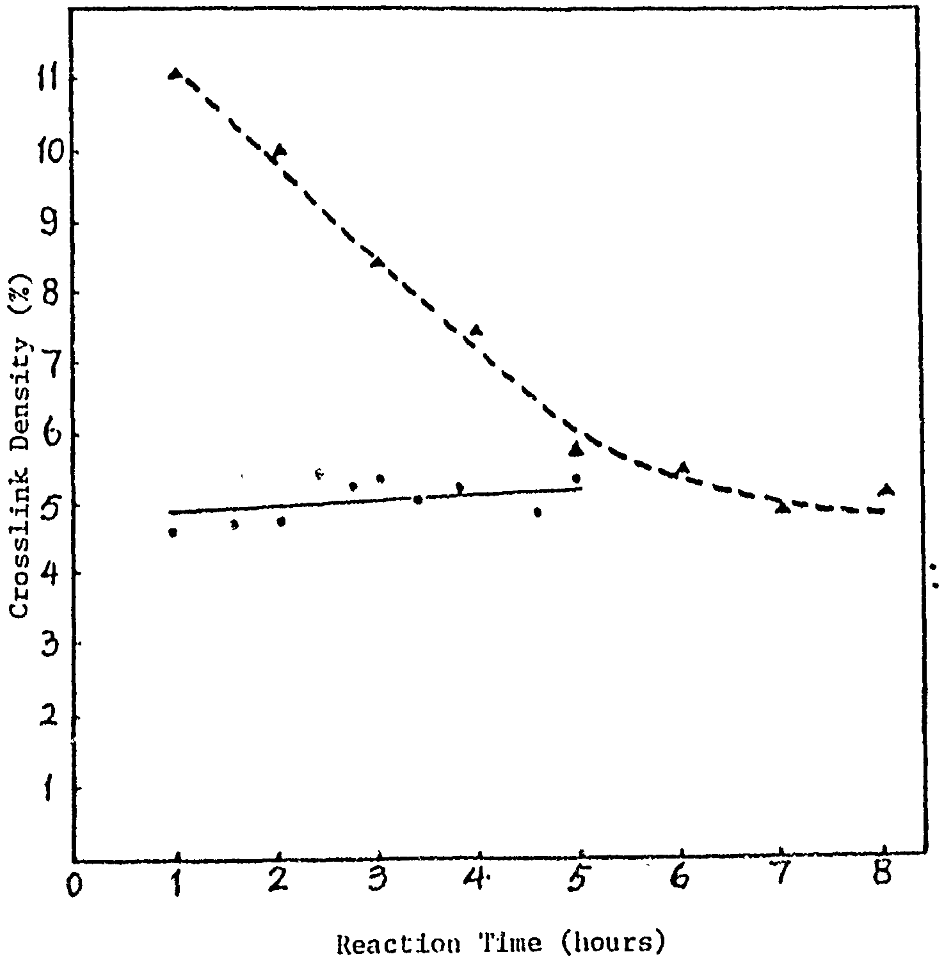

Crosslink Density (%)
11
10
9
8
7
6
5
4
3
2
1
0
1
2
3
4
5
6
7
8
Reaction Time (hours)

FIGURE 4

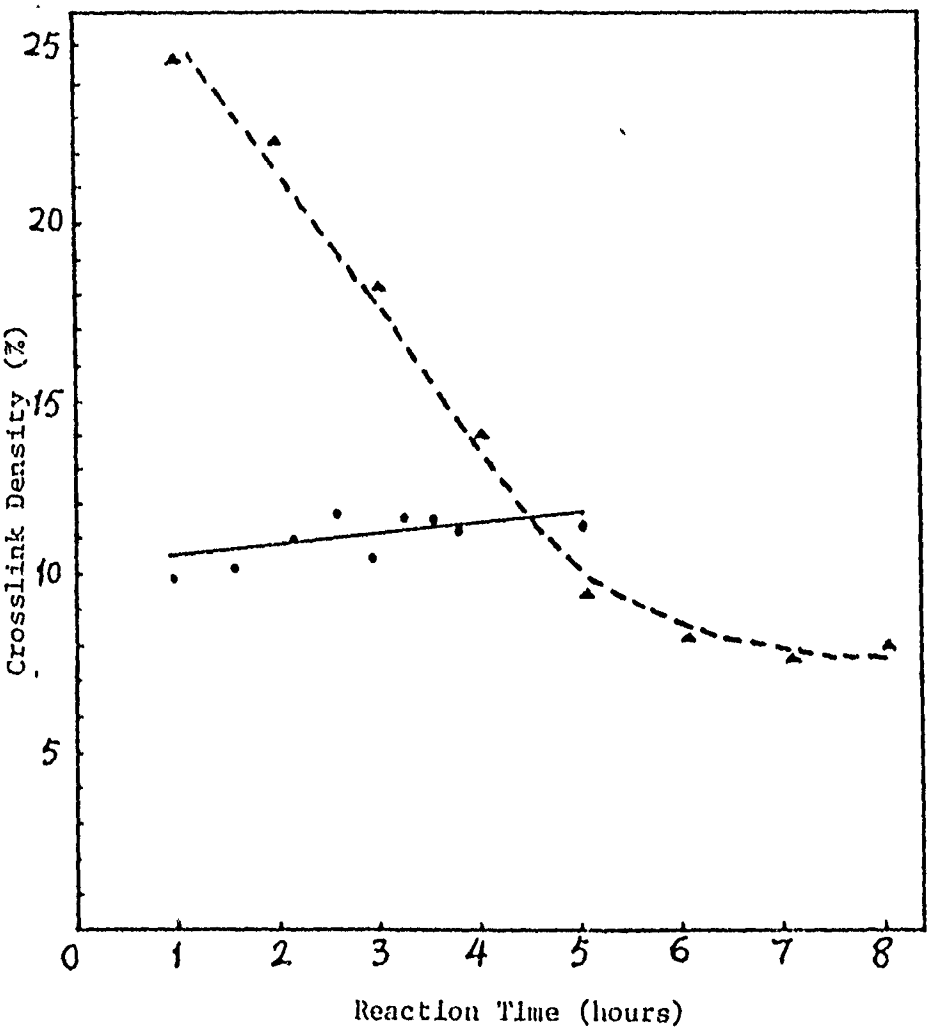


FIGURE 5

Fig. 5

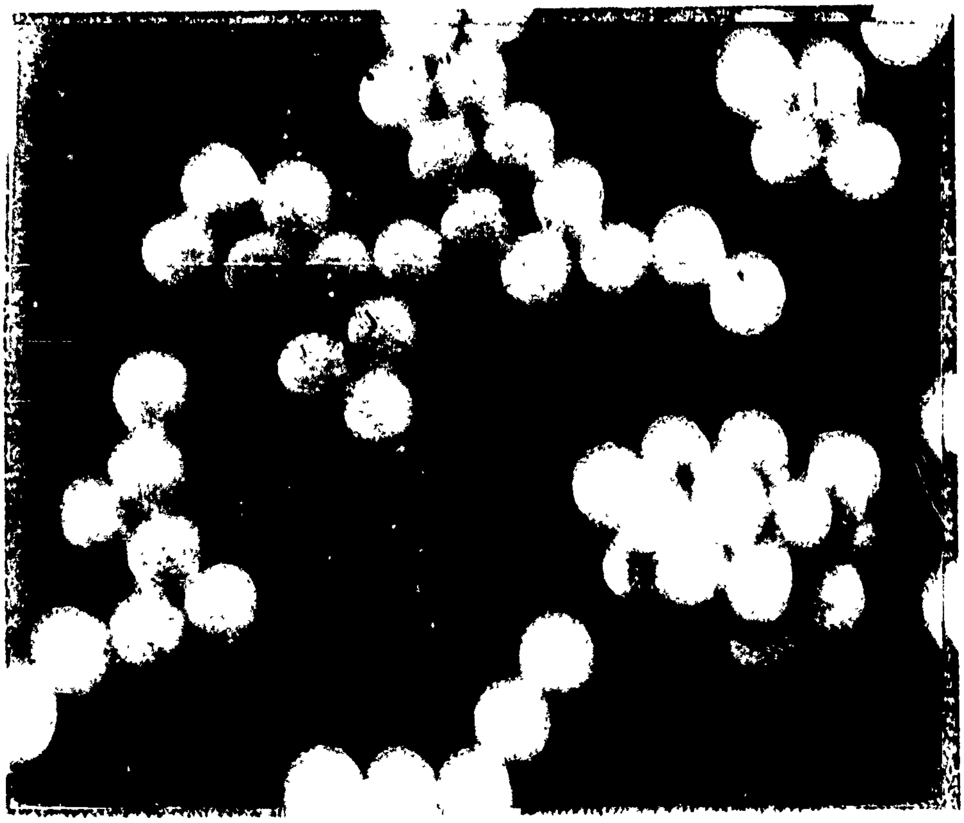


FIGURE 6

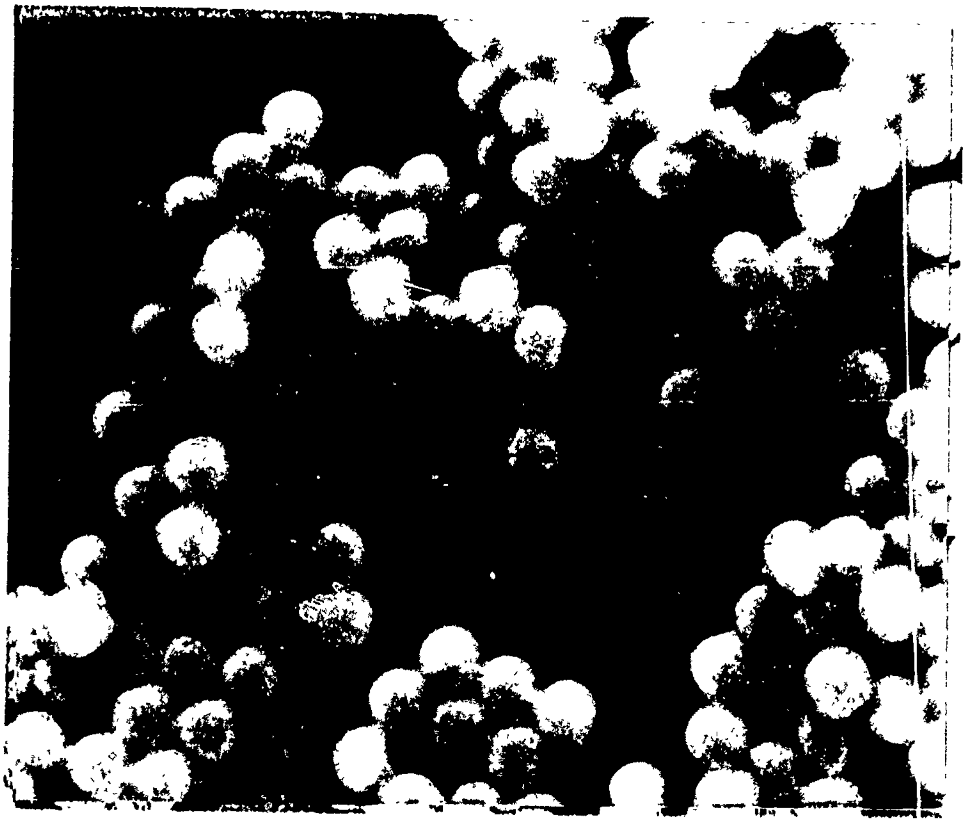
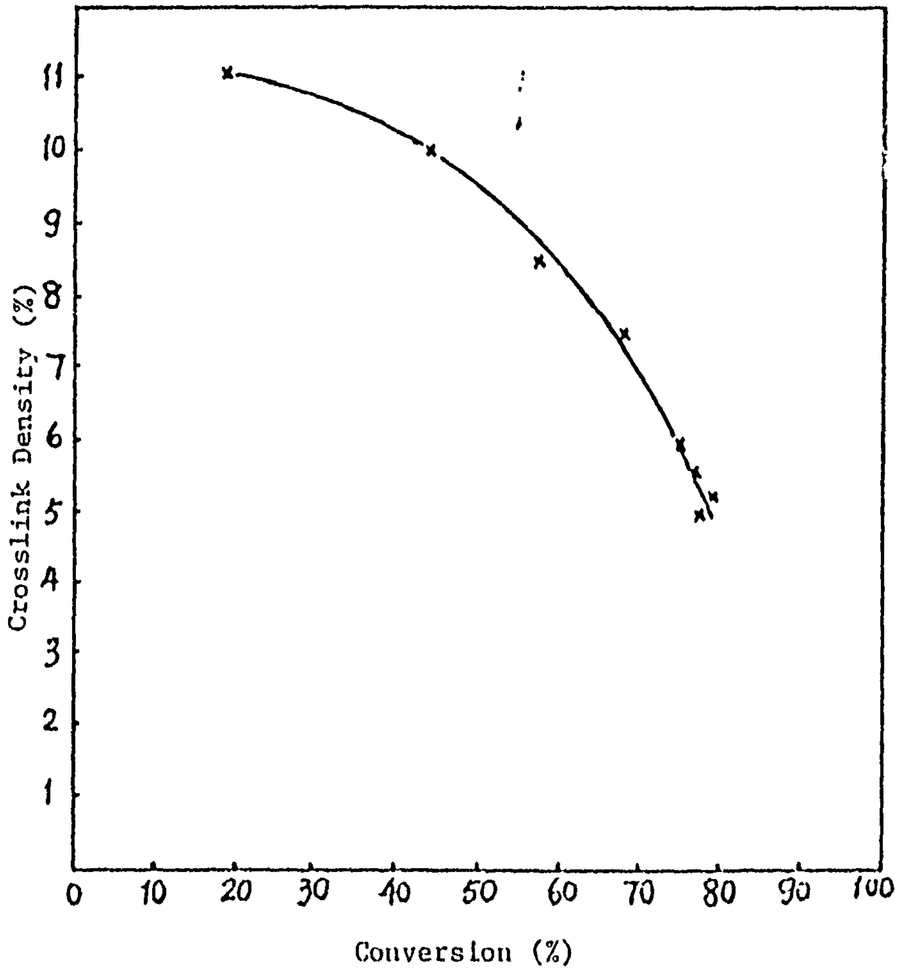


FIGURE 7



Crosslink Density (%)
11
10
9
8
7
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
90
100
Conversion (%)

FIGURE 8

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