

## Copolymerization of Styrene and *p*-Divinylbenzene. Initial Rates and Gel Points

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### Synopsis

Initial rates of polymerization were measured at 70.0 and 89.7°C. for styrene, *p*-divinylbenzene, and mixtures of the two monomers initiated with 1% benzoyl peroxide. The rates relative to styrene increased linearly with mole fraction of *p*-divinylbenzene; the latter monomer polymerized faster than styrene by a factor of 2.50 at 70.0°C. and 3.54 at 89.7°C. Times to gelation were also measured for those samples containing *p*-divinylbenzene, and from these times the corresponding fractional conversion at the gel point was calculated. The conversion at the gel point passed through a minimum with increasing content of *p*-divinylbenzene. The gelation behavior is explained by concurrent interchain crosslinking to give a network and intrachain crosslinking to give microgels which accumulate to give macrogel, the latter process being dominant at all but low concentrations of *p*-divinylbenzene. The higher the content of crosslinker, the less swollen the microgels, and the greater the conversion required to give gelation by this process. The linear increase in rate with increasing *p*-divinylbenzene content was also explained by intrachain crosslinking: growing polymer radicals which undergo this process have a reduced rate of termination. The factor by which the termination rate constant is reduced with increasing divinylbenzene content is the same factor as that by which the conversion required to give gelation by accumulation of microgels is increased.

### INTRODUCTION

The copolymerization of divinylbenzene with styrene was first carried out by Staudinger<sup>1</sup> in order to demonstrate that crosslinking caused by the divinyl monomer would make the polystyrene insoluble in all solvents. In recent years, the insoluble gels obtained from copolymerization of these two monomers have become important as backbones for synthetic ion exchange resins. The properties of the finished copolymers have been studied,<sup>2</sup> but the copolymerization process itself has been virtually ignored. There is a practical reason for this: commercial divinylbenzene is a complex mixture containing both *meta* and *para* isomers of divinylbenzene as well as other related hydrocarbons, and its composition is not a variable easily controlled in polymerization studies. This work was undertaken to remedy the lack of information on the rates and gel points of polymerizing styrene-divinylbenzene mixtures. The problems associated with commercial divinylbenzene were avoided by using pure *p*-divinylbenzene, which can be separated from the commercial mixture by a bromination-debromination sequence.

### The Problem of Gelation

When a monovinyl monomer is copolymerized with a divinyl monomer, the reaction mass will usually gel at a conversion characteristic of the monomers and the reaction conditions. The transition from fluid to gel is that point at which a gas bubble or glass ball moving gently through the polymerizing mixture suddenly becomes immobilized. In other words, it is that point at which the mixture appears to develop a very small but finite yield stress. The actual measurement made is that of time to gelation; coupled with the known rate of polymerization, the fraction of monomer converted to polymer at the gel point can be calculated.

Gelation is taken to mean the formation of a three-dimensional polymer network in the polymerizing mixture, the implication being that such a network is required for the development of the observed yield stress. The usual method of observing the gel point—subjecting the reaction mass to low shear stress by a slowly moving probe—will show a gel point not only with a three-dimensional network but also with a polymer of high enough molecular weight to immobilize the probe by high viscosity alone. The latter “gel point” can be easily avoided by running the polymerization so as to give short chain lengths; the transition to gel also becomes much sharper under these conditions. (For these reasons, a relatively high initiator concentration of 1 wt.-% was used in this study.) There is a third method by which gelation may occur: the accumulation of microgels. This form of gelation was elegantly demonstrated by Shashoua and Beaman,<sup>3</sup> who prepared special microgels by emulsion polymerization and with them gelled a swelling solvent for the polymers at a definite volume fraction of microgel.

Flory's equation<sup>4</sup> relating the gel point to the amount of crosslinker and chain length of the uncrosslinked polymer states that:

$$\alpha_g = (\bar{Y}_w X_D)^{-1} \quad (1)$$

where  $\alpha_g$  is fractional conversion at the gel point,  $X_D$  is the fraction of double bonds belonging to the divinyl monomer in the mixture, and  $\bar{Y}_w$  is the weight-average degree of polymerization of the “backbone chain.” In practice,  $\bar{Y}_w$  is taken to be the weight-average degree of polymerization of the homopolymer from the monovinyl monomer polymerized under the same conditions. Equation (1) presupposes that the following conditions are met: first, the vinyl groups in the system are of equal reactivity; second, the pendent vinyl group of a singly reacted divinyl monomer is consumed only in interchain polymerization. Walling<sup>5</sup> showed that eq. (1) held for vinyl acetate–divinyl adipate and methyl methacrylate–ethylene dimethacrylate, i.e., systems with vinyl groups of equal reactivity, at low crosslinker levels. At higher crosslinker levels, eq. (1) predicts the gel point at conversions that are much too low. The most reasonable explanation for the deviation is that crosslinks are wasted by intrachain polymerization.<sup>4,6</sup> Considerable evidence for this wastage has been put forward by Loshaek and Fox<sup>7</sup> and Hwa and Fox<sup>8</sup> in the methacrylate–dimethacrylate system.

### Reactivity Ratios for Styrene and *p*-Divinylbenzene

The styrene-*p*-divinylbenzene system appeared to be a good candidate to study the effect of intrachain polymerization on gelation. The position of the two vinyl groups of the crosslinker *para* to each other prevents the formation of small rings by cyclopolymerization; intrachain polymerization should occur by a true "back-biting" reaction to give large, strain-free rings. If back-biting is prevalent in this system, it should be prevalent in most vinyl-divinyl systems. The extent of intrachain reaction can be inferred by comparing the observed gel-point with that predicted by the Flory equation. For the comparison to be valid, the relative reactivities of the vinyl groups of the styrene and *p*-divinylbenzene must be essentially equal to one. The reactivity ratios of styrene and the isomeric divinylbenzenes were determined by Wiley, who used styrene labeled with C<sup>14</sup> to get the composition of the copolymer formed. He obtained  $r_1 = 0.92$ ,  $r_2 = 1.00$  for styrene ( $M_1$ )-*o*-divinylbenzene ( $M_2$ ) mixtures,<sup>9</sup> which give soluble polymer by cyclopolymerization, and  $r_1 = 0.65$ ,  $r_2 = 0.60$  with *m*-divinylbenzene<sup>10</sup> as  $M_2$ , the  $r_2$  values referring to one of the double bonds of the divinylbenzene. A set of values for  $r_1$  and  $r_2$  which were constant with changing monomer composition were not obtained with *p*-divinylbenzene; the variability was attributed to concurrent polymerization of pendent vinyl groups, which would be equivalent to a three-component system.<sup>10</sup> An estimate made from runs of lower divinylbenzene content gave the improbable values of  $r_1 = 0.14$  and  $r_2 = 0.5$ .<sup>9</sup> There is no apparent reason why a vinyl group *para* to the reacting vinyl group should have such a profound influence on the latter's reactivity, while the same group *ortho* to the reacting group shows none.

The relative reactivity of one vinyl group of *p*-divinylbenzene may be estimated by making use of Walling's observation that the reactivities of substituted styryl radicals towards styrene and of styryl radicals towards substituted styrenes follow the Hammett  $\sigma$ - $\rho$  relation.<sup>11</sup> The  $\sigma$  value for the *p*-vinyl group was found in these laboratories to be  $-0.05$  by comparison of the  $pK_a$  of *p*-vinylbenzoic acid in 50% ethanol, which is 5.80,<sup>12</sup> with that of benzoic acid in the same solvent, which is 5.73.<sup>13</sup> Walling found  $\rho$  for these radical reactions to be only 0.5;<sup>11</sup> therefore the relative reactivities of the vinyl groups of styrene and *p*-divinylbenzene can be taken as equal to one within experimental error. This result is in accord with the values of  $r_1$  and  $r_2$  obtained for *o*-divinylbenzene, as expected. In view of this accord and of the large uncertainty in the values determined directly, the  $r_1$  and  $r_2$  values for the styrene-*p*-divinylbenzene system are taken as equal to one in this paper.

The correct equation defining instantaneous copolymer composition for the vinyl-divinyl case was shown by Wiley<sup>10</sup> to be:

$$m_2/m_1 = 2M_2(2r_2M_2 + M_1)/M_1(r_1M_1 + 2M_2) \quad (2)$$

where  $m_2$  and  $m_1$  refer to divinyl and monovinyl units in the polymer and

$M_2$  and  $M_1$  are the molar concentrations of divinyl and monovinyl monomer, respectively. For  $r_1 = r_2 = 1$ , the equation simplifies to

$$m_2/m_1 = 2M_2/M_1 \quad (3)$$

and the mole fraction of divinyl units in the polymer is just equal to the fraction of vinyl groups belonging to the divinyl monomer, or  $X_D$ .

$$m_2/(m_1 + m_2) = 2M_2/(M_1 + 2M_2) = X_D \quad (4)$$

The fraction  $X_D$  can also be expressed in terms of mole fraction of divinyl monomer,  $n$ :

$$X_D = 2n/(n + 1) \quad (5)$$

## EXPERIMENTAL

### Materials

Styrene was either Koppers Company or Dow material. It was distilled prior to use in a series of runs and stored under prepurified nitrogen in the refrigerator. In a few cases, the monomer was redistilled on a spinning band column just before use in a kinetic run; no difference in rate of polymerization was observed. Analysis of the distilled and redistilled samples showed that 0.3% ethylbenzene was present and no other impurities.

*p*-Divinylbenzene was isolated from Koppers divinylbenzene concentrate, which contained 55–60% divinylbenzene with a ratio of *meta* to *para* isomer of about 2.5, by bromination to the crystalline tetrabromide.<sup>14</sup> A 170-g. portion of concentrate was combined with 500 ml. of carbon tetrachloride, to which was added 320 g. (110 ml.) of bromine over the course of 1 hr., with stirring and cooling to keep the temperature at 20–25°C. The bromine color was discharged immediately at first, then more slowly, until the color persisted for about 15 min. Then 10-ml. portions of concentrate were added at 15 min. intervals until the bromine color disappeared; two portions usually sufficed. Crystals began to form during the late stages of bromine addition. The mixture was cooled to 0°C. and stirred for 1 hr.; the mass of crystals which had formed was filtered with suction and sucked as dry as possible. The yield of crude tetrabromide was 90–125 g. After four recrystallizations from benzene, 50–70 g. of product melting at 163°C. was obtained; further recrystallization did not raise the melting point. *p*-Divinylbenzene tetrabromide [*p*-bis(1,2-dibromoethyl)benzene] with a melting point of 163°C. was needed to get *p*-divinylbenzene of the desired purity. The debromination was carried out by dissolving 58.2 g. (0.129 mole) of tetrabromide and 0.5 g. of *p*-methoxyphenol in 300 ml. of dioxane and 26 ml. of water, heating to 85°C., and then adding 18.9 g. (0.29 mole) of zinc dust during 15 min. at such a rate as to keep the reaction temperature at 95°C. The reaction mixture was held at 95°C. for an additional 5 min., cooled with an ice bath to 20°C., and then filtered to remove excess zinc. A 500-ml. portion of ethylene dichloride was added to the filtrate which was then washed with five 250-ml. portions of water to remove zinc bromide and dioxane. The organic layer was dried with anhydrous sodium

sulfate and the bulk of the ethylene dichloride removed under reduced pressure with a water pump. Distillation of the residue under vacuum through a spinning band column yielded a product with boiling point 40–43°C./0.7 mm., melting point 25–26°C. Analysis by vapor-phase chromatography showed only 0.2–0.5% *p*-ethylvinylbenzene, and no other impurities. Yields were about 60% of theory. The capillary boiling tube must be open to the air during the vacuum distillation to allow trace amounts of oxygen to enter; otherwise the monomer polymerizes in the still pot.

Benzyl peroxide was recrystallized from chloroform by precipitation with methanol.

### Density Determinations

The densities of the monomer mixtures were measured in 5 ml. pycnometers; results are shown in Table I. A trace of *tert*-butylcatechol was added to inhibit polymerization.

The density measurements on the monomers were reproducible to  $\pm 0.0003$  g./cm.<sup>3</sup> The densities of the polymers were also taken in pycnometers, using inhibited styrene or xylene as solvent or swelling liquid. The polymers were cured for 16 hr. at 125°C.; samples cured under vacuum had the same density as those cured in air. The densities were not reproducible with all samples; however, the values were independent of divinylbenzene content and all clustered about the value of polystyrene swollen in monomer at the same temperature. At 70.1°C., the value was 1.051 g./cm.<sup>3</sup> in agreement with Matheson's result;<sup>15</sup> at 89.7°C., it was 1.041 g./cm.<sup>3</sup>. These density values for polymer and monomer were used to compute the volume shrinkage in passing from monomer to polymer for the different mixtures. The insensitivity of polymer density to divinylbenzene content implies that the volume shrinkages resulting from the polymerization of divinylbenzene and of styrene are about the same, which is reasonable because the volume change results from the collapse of separate monomer molecules into a polymer chain. The volume shrinkage contributed by a pendent vinyl group on the chain should be negligible.

TABLE I  
Densities of Mixtures of Styrene and *p*-Divinylbenzene

DVB, %	Density, g./cm. <sup>3</sup>	
	70.1°C.	89.7°C.
0	0.8624	0.8455
4	0.8626	0.8456
10	0.8631	0.8471
20	0.8650	0.8493
35	0.8729	0.8560
50	0.8820	0.8606
65	0.8837	0.8656
75	0.8878	0.8695
100	0.8957	0.8763

### Polymerization Rates

Initial rates of polymerization for the styrene-divinylbenzene mixtures were determined by measuring the volume shrinkage of the reacting mixture as a function of time by means of a recording dilatometer developed in these laboratories. A diagram of the dilatometer in the upright position is shown in Figure 1. The device works as follows: as the monomer, which is trapped in the reaction bulb by the mercury, shrinks in volume during polymerization, the level of the mercury column in the precision bore tubing drops in direct proportion. A metal probe follows the mercury level by means of a special motor which drives the probe into the mercury, thereby closing the circuit through the platinum wire shown in the figure. Closing the circuit causes the motor to reverse, which removes the probe from the mercury, thereby opening the circuit. The latter action starts the probe anew towards the mercury. This on-off drive keeps the probe just at the surface of the mercury. The probe is connected to a linear potentiometer, which is in turn connected to a recorder. The recorder trace gives the lin-

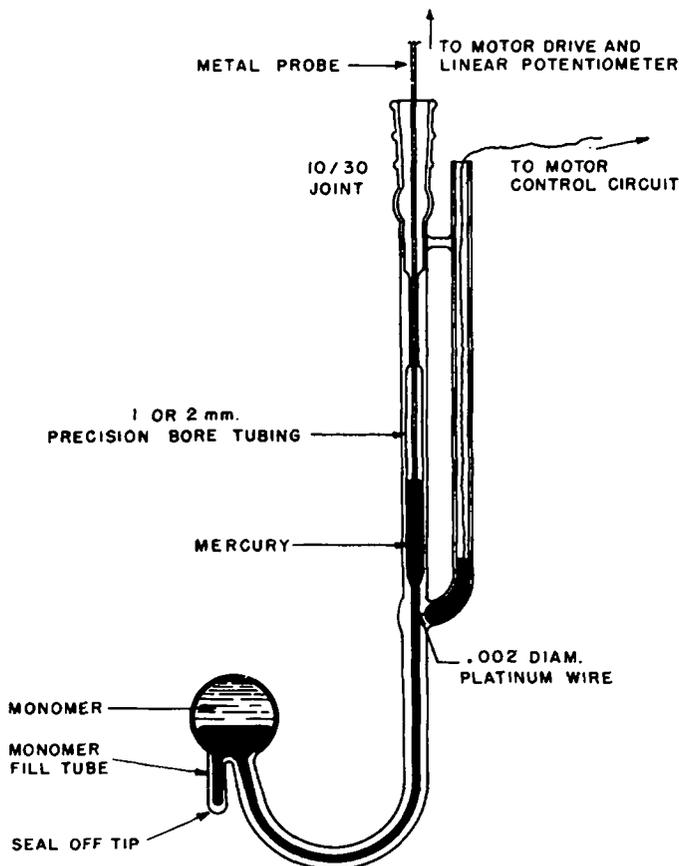


Fig. 1. Recording dilatometer for determining rates of polymerization.

ear travel of the probe as a function of time; since the cross section of the precision bore tube is known and constant, the volume shrinkage as a function of time is easily calculated. The volume shrinkage is assumed to be linear in conversion, and the rate of conversion can be calculated directly. In practice, the polymerization is taken to low enough conversion—6% or less—that the recorder trace is a straight line whose slope can be measured accurately. In one set of runs, the potentiometer was changed to let the trace follow the runs to high conversion.

The dilatometer assembly shown in Figure 1 was prepared as follows. The empty dilatometer tube was hung on a balance so that the monomer bulb and precision bore section hung downward. The monomer mixture was weighted into the bulb through the monomer fill tube whose tip was then sealed off. The dilatometer tube, still upside down to keep the monomer in the bulb, was attached to a vacuum line by means of the standard taper joint. The monomer was alternately frozen and thawed three times under vacuum to remove dissolved gases; helium was admitted after each thaw to sweep out the released gases. The monomer was frozen for the final time, the dilatometer tube put under full vacuum, and mercury allowed to flow into the evacuated tube to confine the monomer. The tube was then put in the upright position and removed from the vacuum line. Excess mercury was removed from the tube with a syringe and a small amount placed in the side arm to provide contact between the platinum wire embedded in the tube and the wire leading to the drive motor.

The kinetic run was started by immersing the dilatometer tube in a constant temperature bath held at  $\pm 0.02^\circ\text{C}$ . so that the mercury surface was well below the bath surface. The mercury rose in the dilatometer barrel until thermal equilibrium had been achieved; the time to equilibrium was usually less than 1 min. The probe was set at the mercury surface and the run allowed to proceed to the desired conversion.

The use of narrow-bore dilatometer tubes, small dilatometer bulbs, and monomer samples about 100 mg. in size ensured that thermal equilibrium was reached rapidly and that the heat of polymerization did not change the sample temperature. The latter point was checked in some runs by changing the sample size by a factor of two with no effect on the rate.

### Gel Point Determinations

The gel point tube is shown in Figure 2. The monomer chamber was filled about three-quarters full with monomer. The monomer mixture was degassed by three freeze-thaw cycles under vacuum, after which the tube was filled with helium. A melting point capillary tube containing iso-octane colored red was inserted quickly into the tube, as shown, and the tube was tightly stoppered. Upon immersion of the gel point tube in the constant temperature bath, the red iso-octane rose in its capillary until thermal equilibrium had been reached, which usually took less than 1 min. The rate measurements had shown that, with the degassed, uninhibited monomer mixtures used here, induction periods were negligible; zero time was there-

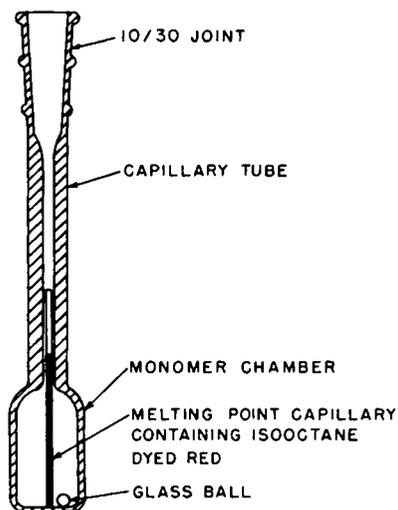


Fig. 2. Gel point tube for determining time to gelation.

fore taken at thermal equilibrium. The vibration of the motor stirring the constant temperature bath caused the little glass ball to spin in the bottom of the gel point tube. The point at which the ball stopped spinning was taken as the gel point; the endpoint was usually sharp, except at very low levels of divinylbenzene. The determination of zero time was more difficult and one of the main sources of error; the end of the thermal expansion of the isooctane was a little hard to judge, and there always remained the possibility of a significant induction period caused by an unknown impurity. The gel points were calculated from the gel times and initial rates; first-order disappearance of monomers was assumed for this region of conversion.

#### Calculation of Weight-Average Degree of Polymerization, $\bar{Y}_w$

The value of  $\bar{Y}_w$  for uncrosslinked polystyrene in this system was calculated from the number-average degree of polymerization, which in turn was calculated from eq. (16):<sup>4b</sup>

$$(\bar{Y}_n)^{-1} = C_M + \{(k_t/k_p^2)R_p/[M]^2\} + (C_I[I]/[M]) \quad (6)$$

In this equation,  $C_M$  is the chain transfer constant for monomer,  $R_p$  is the overall rate of polymerization,  $[M]$  is the monomer concentration,  $C_I$  is the chain transfer constant for the initiator, and  $[I]$  is the initiator concentration. At 60°C.,  $C_M = 0.60 \times 10^{-4}$  and  $C_I = 0.055$ .<sup>16</sup> The temperature dependence of these constants is not known; it was estimated as follows: The value of  $C_M$  for styrene is nearly equal to that for ethylbenzene;<sup>4c</sup> the two molecules have structures similar enough that one can reasonably assume that their chain transfer constants will have the same temperature dependence. This assumption gives the estimated values of  $C_M$ :  $0.75 \times 10^{-4}$  at 70.0°C. and  $1.16 \times 10^{-4}$  at 89.7°C. Benzoyl peroxide, the initiator, has a transfer constant only six times that of  $\text{CCl}_4$  in the

styrene system.<sup>4c</sup> For lack of a better estimate,  $C_1$  is assumed to have the same temperature dependence in the styrene system as does  $\text{CCl}_4$ . This assumption yields the estimated values of  $C_1$ : 0.069 at 70.0°C. and 0.096 at 89.7°C. Using the values for the rate of polymerization of styrene with 1% benzoyl peroxide determined in this study and the estimated values listed above, one obtains  $\bar{Y}_n = 400$  at 70.0°C. and  $\bar{Y}_n = 229$  at 89.7°C. Polystyrene radicals combine when they react,<sup>17</sup> in which case  $\bar{Y}_w = 1.5 \bar{Y}_n$ . Hence at 70.0°C.,  $\bar{Y}_w = 600$  and at 89.7°C.,  $\bar{Y}_w = 344$ . These values correspond to molecular weights of 62,400 at 70.0°C. and 35,800 at 89.7°C. The viscosity-average molecular of two polystyrene samples polymerized with 1% benzoyl peroxide at the two temperatures, and isolated by methanol precipitation at 16% conversion, was 70,000 at 70.0°C. and 34,600 at 89.7°C. The agreement is satisfactory, considering the approximations made in the calculation and the inevitable loss of low molecular weight polymer in the isolation step. The calculated values of  $\bar{Y}_w$  are used in this paper in calculations with the Flory gel point equation.

## RESULTS

### Rates of Polymerization

The overall first-order rate constants for polymerization with 1% benzoyl peroxide of styrene-*p*-divinylbenzene mixtures ranging in composition from straight styrene to straight divinylbenzene are reported in Table II. These values obtain from the start of polymerization to the gel point and, at low crosslinker levels to a little beyond the gel point. The initial rate constants relative to that for styrene at the same temperature increase linearly with mole fraction of divinylbenzene, as shown in Figure 3. The increase for *p*-divinylbenzene over styrene at both temperatures studied is

TABLE II  
Overall First-Order Rate Constants  $K$  for the Polymerization  
of Styrene-*p*-Divinylbenzene Mixtures Initiated with 1% Benzoyl Peroxide<sup>a</sup>

<i>p</i> -DVB		$K, \text{min.}^{-1} \times 10^3$	
Wt.-%	Mole fraction	Temp. = 70.1°C., [Bz <sub>2</sub> O <sub>2</sub> ] = 0.0356 <i>M</i>	Temp. = 89.7°C., [Bz <sub>2</sub> O <sub>2</sub> ] = 0.0349 <i>M</i>
0	0	1.34 ± 0.00	6.9 ± 0.3
4	0.032	1.42 ± 0.04	7.8 ● 0.0
10	0.082	1.48 ± 0.02	8.9 ● 0.2
20	0.167	1.62 ± 0.02	9.5 ± 0.4
35	0.301	1.90 ± 0.01	12.5 ± 0.1
50	0.445	2.33 ± 0.04	14.9 ± 0.2
65	0.598	2.69 ± 0.03	16.7 ± 0.3
75	0.706	2.85 ± 0.01	18.7 ± 0.5
900	1.00	3.25 ± 0.07	25.0 ± 0.5

<sup>a</sup>  $K$  defined by the equation:  $-d[M]/dt = K[M]$ , where  $[M]$  is the concentration of monomer. Values of  $K$  are averages from two or three runs; precision limits are standard deviations.

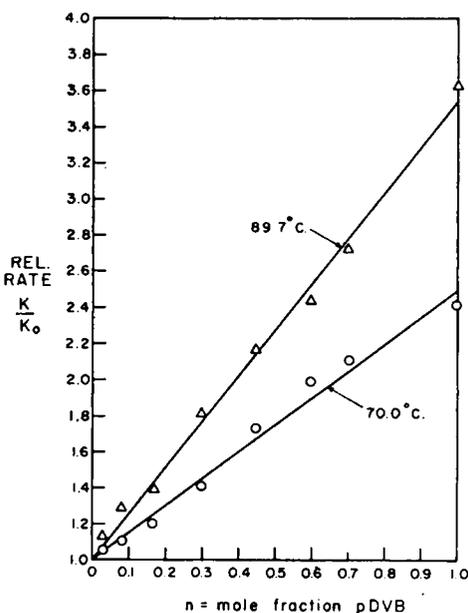


Fig. 3. Rate relative to styrene of the polymerization of styrene-*p*-divinylbenzene mixtures.

greater than the factor of two expected on a statistical basis for the divinyl over the monovinyl monomer; at 70.0°C. the factor is 2.50, at 89.7°C. it is 3.54.

The overall constant  $K$  is a composite; in terms of more familiar constants,

$$K = (\bar{k}_d[I])^{1/2}k_t^{-1/2}k_p \quad (7)$$

where  $[I]$  is the initiator concentration,  $k_d$  is the rate constant for decomposition of initiator to free radicals,  $k_p$  is the rate constant for polymer radical propagation, and  $k_t$  is the rate constant for polymer radical termination. The value of  $k_d$  for benzoyl peroxide in toluene solution was measured at different temperatures by Bawn and Mellish<sup>17</sup> using diphenyl picryl hydrazyl to trap the radicals generated; the value of  $k_p/k_t^{1/2}$  was obtained at different temperatures by Matheson.<sup>16</sup> From their results, the value of  $K$  for styrene is calculated to be  $1.35 \times 10^{-3} \text{ min.}^{-1}$  at 70°C. and  $6.6 \times 10^{-3} \text{ min.}^{-1}$  at 90°C., in good agreement with the results of this work. The calculation assumes that the efficiency of initiation is unity, which was found to be the case at 60°C.<sup>16</sup>

After the gel point, the polymerization rates increase, the increase being greater at the higher divinylbenzene content. The shape of the conversion curves obtained from the dilatometric measurement is shown in Figure 4 for 4, 10, and 20% divinylbenzene at 70.0°C.; a similar set of curves is obtained at 89.7°C. The reproducibility of the polymerization curves after the gel point was fairly satisfactory up to 20% divinylbenzene; at higher

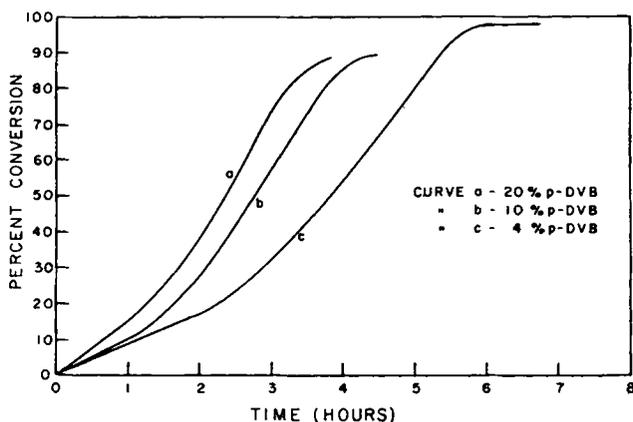


Fig. 4. Per cent conversion as a function of time for mixtures of styrene and (a) 20% *p*-DVB, (b) 10% *p*-DVB, and (c) 4% *p*-DVB; 70.0°C.

crosslinker contents only the initial rates were reproducible. The shape of the curves is that to be expected for systems which, as polymerization proceeds show progressively reduced termination rates due to reduced rate of polymer radical diffusion.<sup>18</sup> Gelled systems of this type would be just the ones expected to slow down radical termination by trapping polymer radicals in the gel.

TABLE III  
Conversions at the Gel Point for Polymerizing Mixtures of Styrene-*p*-Divinylbenzene Initiated with 1% Benzoyl Peroxide

<i>p</i> -DVB		Temp. = 70.1°C., [Bz <sub>2</sub> O <sub>2</sub> ] = 0.0356 <i>M</i>		Temp. = 89.7°C., [Bz <sub>2</sub> O <sub>2</sub> ] = 0.0349 <i>M</i>	
Wt.-%	Mole fraction	Gel time, min. <sup>a</sup>	Conversion at gel point, %	Gel time, min. <sup>a</sup>	Conversion at gel point, %
0.5 <sup>b</sup>	0.004	131 ± 2	16.1	73 ± 3	39.5
1.0 <sup>b</sup>	0.008	112 ± 4	14.1	40.5 ± 0.9	24.5
2.5 <sup>b</sup>	0.020	57.4 ± 2.0	7.6	17.1 ± 0.4	11.3
4	0.032	54.5 ± 0.4	7.4	12.45 ± 0.01	9.2
10	0.082	36.4 ± 0.5	5.2	7.65 ± 0.06	6.5
20	0.167	28.3 ± 0.1	4.5	5.80 ± 0.22	5.4
35	0.301	24.0 ± 0.3	4.5	4.83 ± 0.03	5.8
50	0.445	19.8 ± 0.6	4.5	4.23 ± 0.01	6.1
65	0.598	19.4 ± 0.5	5.1	3.84 ± 0.04	6.2
75	0.706	18.1 ± 0.4	5.0	3.49 ± 0.06	6.3
100	1.00	15.4 ± 0.6	4.9	2.62 ± 0.16	6.3

<sup>a</sup> Gel times are averages from two or three runs. Precision limits are standard deviations.

<sup>b</sup> Initial rates for these *p*-DVB concentrations calculated from straight lines in Figure 3.

### Gel Points

Times to gelation and conversions at the gel point are presented in Table III for the various styrene-divinylbenzene mixtures. The gel points show a minimum around 20% divinylbenzene and actually increase with increasing crosslinker content beyond this point. This system, therefore, is also one which shows marked deviation from the Flory equation. The hypothesis that this deviation is probably due to intrachain crosslinking to form microgels is supported by the increasing sharpness of the gel point with increasing crosslinker. At high divinylbenzene contents, the mixture remains very fluid right up to gelation, at which point it sets up very suddenly. The same sort of sudden transition to macrogel was observed by Shashoua and Beaman<sup>3</sup> in their microgel experiments. At lower divinylbenzene contents, the mixture becomes quite viscous, and the transition to gel is less sudden. This was particularly true of the runs made with 0.5, 1.0, and 2.5% divinylbenzene, and the gel points determined at these levels are less reliable than those obtained at 4% divinylbenzene and higher.

### DISCUSSION

The results of the gel point determination on polymerizing mixtures of styrene and *p*-divinylbenzene imply that intrachain crosslinking to produce microgels is an important reaction even at low crosslinker levels and is the dominant reaction at moderate to high levels. It seems a reasonable hypothesis that the increase in initial polymerization rate with increasing divinylbenzene content is also a consequence of this same reaction. A reaction scheme is proposed below which relates both the gel point and the polymerization rate to the same intrachain crosslinking reaction.

#### Dependence of the Gel Point on *p*-Divinylbenzene Content

Two mechanisms appear to be operating in this system to produce gelation. One is the conventional buildup of a three-dimensional network by interchain crosslinking. The other is accumulation of sufficient intramolecularly crosslinked microgels to cause macrogelation. A simple gel point equation expressing this idea can be written for vinyl-divinyl monomer polymerizations, based on the following postulates. (a) all double bonds in the system are of equal reactivity; (b) gelation occurs by both interchain crosslinking and by accumulation of microgels, the effects being strictly additive; (c) the volume of a microgel decreases as the crosslinker content increases by a factor  $(1 + \epsilon X_D)^{-1}$ , where  $\epsilon$  is a constant.

The first postulate is common to all gel point equations of this type and avoids the mathematical difficulties resulting from the introduction of monomer reactivity ratios. The postulate appears to be valid for the styrene-*p*-divinylbenzene system. The second postulate is made to simplify the mathematics and is admittedly arbitrary. Its physical basis derives from the fact that interchain crosslinking and microgel accumulation should give quite different gel structures which can exist side by side

without interference. The great difference in viscosity and sedimentation behavior in solvents of microgels and linear polymers supports this picture.<sup>3</sup> The third postulate states that the volume of a microgel is inversely proportional to the number of divinylbenzene units incorporated in the basic chain, which in turn is presumed to control the number of intrachain links in each microgel. The greater the number of these links, the more tightly crosslinked is the microgel, and hence the smaller is its swollen volume.

The contribution to gelation from interchain crosslinking is given directly by the Flory equation:

$$\alpha_t = (Y_w X_D)^{-1} \quad (1a)$$

where  $\alpha_t$  is now the fraction of monomer converted to chains with no internal crosslinks at the gel point. If the volume of a microgel containing but one internal crosslink at nearly zero crosslinker concentration is taken as  $V_0$ , then the average volume  $V$  of a microgel with a divinylbenzene content corresponding to  $X_D$  is:

$$V = V_0(1 + \epsilon X_D)^{-1} \quad (8)$$

The contribution to gelation by microgel accumulation,  $\alpha_M$ , is expressed by:

$$\alpha_m = \alpha_{m_0}(1 + \epsilon X_D) \quad (9)$$

where  $\alpha_{m_0}$  is the fractional conversion at the gel point corresponding to  $V_0$  if gelation were solely due to accumulation of swollen microgels with volume  $V_0$ . The sum of  $\alpha_t$  and  $\alpha_m$  then gives the actual gel point for the system:

$$\alpha_g = (\bar{Y}_w X_D)^{-1} + \alpha_{m_0}(1 + \epsilon X_D) \quad (10)$$

Qualitatively, eq. (10) is of the type which should give the observed gel point minimum. A quantitative test of the equation will be deferred until after discussion of the polymerization rate.

### Dependence of Polymerization Rate on Divinylbenzene Content

A relatively simple reaction scheme, applicable at low conversions, may be written which makes provision for intramolecular crosslinking if the postulates made for the gel point equation are assumed to hold and, in addition, if the following postulates are also admitted. (a) The termination rate constant  $k_{t_g}$  for the reaction of two microgel radicals is less than the termination constant  $k_{t_0}$  for two open chain radicals. Further, the rate constant is less because of the smaller effective volume of the two microgel radicals, and the second-order rate constant  $k_{t_g}$  is related to  $k_{t_0}$  by the relation:

$$k_{t_g} = k_{t_0} (1 + \epsilon X_D)^{-2} \quad (11)$$

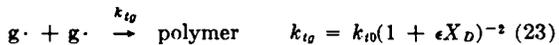
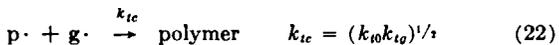
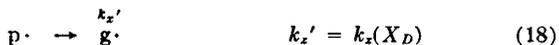
(b) The cross-termination constant  $k_{t_c}$  for the reaction of an open chain radical with a microgel radical is equal to the geometric mean of  $k_{t_0}$  and  $k_{t_g}$ :

$$k_{t_c} = (k_{t_0} k_{t_g})^{1/2} \quad (12)$$

(c) The intrachain reaction is proportional to the mole fraction of divinylbenzene units in the chain, is first-order in open chain radicals, and does not depend on molecular weight if the chain is indeed of polymeric dimensions.

The justification for the first postulate is that microgel radicals have a much reduced effective volume which decreases their rate of reaction with each other. The further assumption that this reduction in volume is proportional to  $(1 + \epsilon X_D)^{-1}$  is the same one made for reduction in microgel volume and is admittedly arbitrary. Since two such radicals must react to give the termination reaction, the rate constant  $k_{t_0}$  should be inversely proportional to  $(1 + \epsilon X_D)^{-2}$ . The second postulate is again arbitrary and is made to simplify the mathematics. It is physically reasonable since the radicals are chemically the same, but differ only in their physical shape. The third postulate rests on the idea that, once a chain has grown to sufficient length, the back-biting reaction depends on the concentration of pendent vinyl groups in the vicinity of the growing chain end rather than on the total number of such groups along the chain.

In the set of reactions, eqs. (13)–(23), written for a fixed divinylbenzene concentration, the symbol  $p\cdot$  is used for an open chain polymer radical and  $g\cdot$  for a microgel radical. The symbols S, D, and I stand for styrene, divinylbenzene, and initiator, respectively. It must be emphasized that these reactions are meant to describe the polymerization process only at low conversion and that the rate expressions derived from them are valid only in this region.



The rate equation for the disappearance of styrene and divinylbenzene based on the reaction scheme is the following:

$$d([S] + [D]) = k_p([S] + 2[D])([p\cdot] + [g\cdot]) \quad (24)$$

If the concentrations of all radicals in the system are assumed as usual to be small and invariant with time, the concentration of polymer radicals is given by the expression:

$$[p\cdot] + [g\cdot] = A(k_d[I]/k_t)^{1/2} \quad (25)$$

where

$$A = \left\{ \frac{k_d^{1/2}[I]^{1/2} + k_x(X_D)/k_{t_0}^{1/2}}{k_d^{1/2}[I]^{1/2} + k_x(X_D)/k_{t_0}^{1/2}} \right\} \quad (26)$$

Substituting eqs. (25) and (26) into eq. (24), one obtains the rate equation:

$$-d([S] + [D])/dt = (k_d[I]/k_t)^{1/2} k_p A ([S] + 2[D]) \quad (27)$$

Equation (16) can be modified slightly to make it correspond to the usual form of the rate equation for polymerization:

$$-d([S] + [D])/dt = k_d[I]/k_t)^{1/2} k_p A (1 + n) ([S] + [D]) \quad (28)$$

where  $n$  is the mole fraction of divinylbenzene in the mixture. The overall first-order rate constant  $K$  is then expressed by:

$$K = (k_d[I]/k_t)^{1/2} k_p A (1 + n) \quad (29)$$

With no divinylbenzene present,  $n = 0$ ,  $X_D = 0$ , and  $A = 1$ , in which case  $K$  is just the overall first-order constant for styrene,  $K_0$ . The overall rate constant at any divinylbenzene content is then

$$K = K_0 A (1 + n) \quad (30)$$

and the product  $A(1 + n)$  equal to  $K/K_0$  must, according to Figure 3, be linear in  $n$  with a slope greater than one.

The quantity  $A$ , defined by equation (26), is a complex ratio which is a function of initiator concentration and of the parameter  $X_D$ . As written, the expression for  $A$  is too complicated to be useful in correlating polymerization rates. However, if intrachain crosslinking dominates in this system to the extent implied by the gel point observations, then the ratios  $k_x(X_D)/k_{t_0}^{1/2}$  and  $k_x(X_D)/k_{t_0}^{1/2}$  should be significantly greater than  $k_d^{1/2}[I]^{1/2}$ , even at low divinylbenzene levels. The expression for  $A$  then simplifies to

$$A \approx k_{t_0}^{1/2}/k_{t_0}^{1/2} = (1 + \epsilon X_D) \quad (31)$$

by combination with eq. (11). The expression for  $K/K_0$  then becomes

$$K/K_0 = A(1 + n) = 1 + (1 + 2\epsilon)n \quad (32)$$

by using the relation between  $X_D$  and the mole fraction  $n$ . This relation fits the requirements of linearity and slope imposed by Figure 3; from the plot, the value of  $\epsilon$  at 70°C. is 0.25 and that at 89.7°C. is 0.77.

### Correlation of Polymerization Rates and Gel Point

The model discussed in the preceding paragraphs for styrene-*p*-divinylbenzene polymerization yields two equations which share the common

parameter  $\epsilon$ . The slope of the lines in Figure 1 allows  $\epsilon$  to be calculated from eq. (32) at the two temperatures studied. The gel point equation eq. (1) contains another quantity  $\alpha_{m_0}$ , whose value is unknown, but which should be independent of divinylbenzene content. With values for  $\epsilon$  available, the value of  $\alpha_{m_0}$  may be calculated from the observed gel points at the different divinylbenzene levels by means of the equation

$$\alpha_{m_0} = [\alpha_g - (\bar{Y}_w X_D)^{-1}] / (1 + \epsilon X_D) \quad (33)$$

which is just eq. (10) suitably rearranged. Values of  $\alpha_{m_0}$  are shown in Table IV; they are independent not only of crosslinker content, but also of polymerization temperature. The average value of  $\alpha_{m_0}$  corresponds to a volume fraction of polymer of about 0.033. According to the original definition of  $\alpha_{m_0}$ , this volume fraction is the minimum required for any assemblage of microgels to cause gelation, since it is the volume fraction occupied by microgels with but one internal crosslink. These hypothetical microgels would have a volume swelling ratio of about 30 from dry polymer to fully swollen state. The gel point equation for bulk polymerization of styrene-*p*-divinylbenzene systems can then be written

$$\alpha_g = (\bar{Y}_w X_D)^{-1} + 0.038 (1 + \epsilon X_D) \quad (34)$$

The equation has the advantage that there is no crosslinking efficiency factor attached to the Flory term, and that it contains only one undefined parameter,  $\epsilon$ , which can be obtained from the rate of polymerization. The fact that the term  $\epsilon$  does tie together the gel point and polymerization rate supports the mechanism of extensive intrachain crosslinking in this system.

TABLE IV  
Values of  $\alpha_{m_0}$  Calculated from Equation (23)

<i>p</i> -DVB, %	$X_D$	Temp. = 70.0°C., $\bar{Y}_w = 600, \epsilon = 0.25$			Temp. = 89.7°C., $\bar{Y}_w = 344, \epsilon = 0.77$		
		$\alpha_g$	$(\bar{Y}_w X_D)^{-1}$	$\alpha_{m_0}$	$\alpha_g$	$(\bar{Y}_w X_D)^{-1}$	$\alpha_{m_0}$
0.5	0.008	0.162 <sup>a</sup>	0.208	-0.046 <sup>b</sup>	0.395	0.362	0.032
1.0	0.016	0.141	0.104	0.037	0.245 <sup>c</sup>	0.182	0.063 <sup>b</sup>
2.5	0.039	0.076	0.043	0.033	0.113	0.075	0.037
4.0	0.062	0.074	0.027	0.046	0.092	0.047	0.043
10	0.115	0.052	0.011	0.039	0.065	0.019	0.040
20	0.287	0.045	0.006	0.036	0.054	0.010	0.036
35	0.461	0.045	0.004	0.037	0.058	0.006	0.039
50	0.616	0.045	0.003	0.037	0.061	0.005	0.038
65	0.750	0.051	0.002	0.041	0.062	0.004	0.036
75	0.828	0.050	0.002	0.040	0.063	0.004	0.036
100	1.00	0.049	0.002	0.039	0.063	0.003	0.034
			Avg.	0.038		Avg.	0.037

<sup>a</sup> Value apparently too low, probably because of high viscosity prior to actual gel point.

<sup>b</sup> Value not used in computing average.

<sup>c</sup> Value apparently too high, possibly because of impurity causing induction period.

The quantity  $\alpha_{m_0}$  in eq. (10) should increase if a diluent is added to the system, because a greater conversion of monomer to polymer must take place to produce the volume fraction of microgels required for macrogelation. It should, in fact, be possible to select a solvent-monomer system that will not gel, regardless of the crosslinker content of the monomer component. Zimm<sup>19</sup> has demonstrated this by polymerizing a styrene-20% divinylbenzene mixture in carbon tetrachloride to high conversion without gelation. The soluble polymers isolated from that series of experiments behaved like microgels in that they had unusually low viscosity for the molecular weight measured by light scattering. This is further evidence for microgel formation in the styrene-divinylbenzene system.

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### Résumé

Les vitesses initiales de polymérisation du styrène, du *p*-divinylbenzène et du mélange des deux monomères, initiés avec le peroxyde de benzoyle à 1% ont été mesurées à 70°C et à 89,7°C. Les vitesses relatives du styrène augmentent linéairement avec la fraction molaire du *p*-divinylbenzène; ce dernier monomère polymérise plus vite que le styrène et ceci avec un facteur de 2,5 à 70°C et de 3,54 à 89,7°C. Les temps de formation de gels ont été également mesurés pour ces échantillons contenant du *p*-divinylbenzène, et à partir de ces temps on a calculé la conversion partielle correspondante au point de

gélification. La conversion au point de gélification passe par un minimum en augmentant la teneur en *p*-divinylbenzène. Le phénomène de gélification est expliqué par le pontage entre les chaînes polymériques pour donner un réseau et par le pontage dans la chaîne même pour donner des microgels qui s'accumulent pour former un macrogel, ce dernier phénomène étant dominant pour toutes que les faibles concentrations en *p*-divinylbenzène. Au plus il y a d'agent de ramification au moins les microgels sont gonflés, et au plus une plus grande conversion est nécessaire pour former un gel par ce processus. L'augmentation linéaire de la vitesse avec une teneur croissante en *p*-divinylbenzène est également expliquée par pontage dans la chaîne: des radicaux polymériques en croissance, qui subissent ce processus, ont une vitesse de terminaison réduite. Le facteur par lequel la constante de vitesse de terminaison est réduite avec une augmentation de la teneur en divinylbenzène, est identique à celui par lequel la conversion nécessaire pour former un gel par accumulation de microgels est augmentée.

### Zusammenfassung

Die Anfangsgeschwindigkeit der Polymerisation bei 70,0°C und 89,7°C wurde für Styrol, *p*-Divinylbenzol und Mischungen der beiden Monomeren mit Start 1% Benzoylperoxyd gemessen. Bezogen auf Styrol nahm die Geschwindigkeit linear mit dem Molenbruch an *p*-Divinylbenzol zu; letzteres Monomeres polymerisierte bei 70,0°C um einen Faktor 2,50 rascher als Styrol, bei 89,7°C um einen Faktor 3,54. Für die *p*-Divinylbenzol-enthaltenden Proben wurde auch die Gelbildungsdauer gemessen, und aus diesen Zeiten wurde der entsprechende Umsatz beim Gelpunkt berechnet. Der Umsatz beim Gelpunkt ging mit zunehmendem Gehalt an *p*-Divinylbenzol durch ein Minimum. Das Gelbildungsverhalten wird durch gleichzeitige Zwischenkettenvernetzung unter Bildung eines Netzwerkes und Intrakettenvernetzung unter Bildung eines Mikrogels, das sich zu einem Makrogel akkumuliert, erklärt; letzterer Vorgang ist bei allen ausser niedrigen *p*-Divinylbenzolkonzentrationen vorherrschend. Je höher der Gehalt an Vernetzung, umso weniger gequollen sind die Mikrogele und umso grösser ist der für eine Gelbildung durch diesen Vorgang erforderliche Umsatz. Auch die lineare Geschwindigkeitszunahme mit steigendem *p*-Divinylbenzolgehalt wurde durch Intrakettenvernetzung erklärt: Wachsende Polymerradikale, bei denen dieser Vorgang auftritt, besitzen eine herabgesetzte Abbruchgeschwindigkeit. Der Faktor, um welchen die Abbruchgeschwindigkeitskonstante mit wachsendem *p*-Divinylbenzolgehalt herabgesetzt wird, ist der gleiche, um welchen der zur Gelbildung durch Akkumulation von Mikrogele erforderliche Umsatz erhöht wird.

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