Abnormal Acceleration of the Rate of Bulk Polymerization of Styrene[*]

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It is well known that an acceleration in rate can be observed during polymerization reactions. In the early stage of this investigation, Trommsdorff et al.[1] ascribed this phenomenon to the increase in viscosity of the reaction system. It is now currently accepted that the increase in both rate and degree of polymerization is brought about by a decrease in termination constant due to the gel effect (or Trommsdorff effect). In a viscous solution, the termination constant is affected first. Propagation and transfer reactions involving small monomer and catalyst molecules are less affected by viscosity.

There have been some investigations on the effect of viscosity on the reaction rate and the individual rate constants[1-4].

Recently, Tobolsky et al.[5] have shown that the limiting fractional conversion at infinite time of a radical initiated vinyl polymerization could be predicted from a knowledge of the kinetic rate constants under certain conditions where the gel effect does not invalidate the theory.

Experimental

Reagents. — Commercial 2,2′-azobisisobutyronitrile was recrystallized twice from ether solution m. p. 103~103.5°C. Styrene monomer was washed with 10% sodium hydroxide and then with water. After drying over calcium chloride, the monomer was distilled and stored in the dark. Just before use, it was fractionated at 25 mmHg and the middle fraction was used. Benzene was washed in turn with concentrated sulfuric acid, dilute sodium hydroxide and water. Then it was dried over calcium chloride, then over metallic sodium wire and distilled. *n*-Butanol of reagent grade was used after distillation.

Procedure.—All polymerizations were carried out in glass dilatometers, the type of which was similar to that used before[6]. After being filled with the requisite amounts of catalyst and monomer, the tubes were connected to a vacuum line and sealed off. The tubes were then held in a thermostat at 60°C.

The volume contraction of the solution was

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[1] E. Trommsdorff, H. Köhle and P. Lagally, *Makromol. Chem.*, **1**, 169 (1948).

[2] S. W. Benson and A. M. North, *J. Am. Chem. Soc.*, **81**, 1339 (1959).

[3] H. Miyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 714 (1957).

[4] M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).

[5] G. V. Tobolsky, C. E. Rogers and R. D. Brickman, *J. Am. Chem. Soc.*, **82**, 1277 (1960).

[6] S. Hasegawa, N. Hirai, N. Nishimura and T. Kawano, This Bulletin, **31**, 696 (1958).

followed with a travelling microscope. At high conversion where dilatometric technique could not be applied because of high viscosity, the gravimetric method was used. In order to calculate the degree of conversion from the contraction of the solution, the densities of polystyrene in the monomer (solution polymer density) and styrene monomer at 60°C were taken as 1.0563 and 0.869(7), respectively. Hence, for bulk polymerization of styrene, 100% conversion corresponds to a 17.7% contraction in volume of the original monomer.

The induction period could not be observed in every experiment. At specified times, the contents of the tubes were properly dissolved in benzene and then poured dropwise into a much greater quantity of ice-methanol. The precipitate was filtered off and dried in vacuo.

The intrinsic viscosities of the benzene solutions of polystyrene were determined at 30±0.01°C using an Ostwald viscometer. The number average degree of polymerization was estimated from the following equation(8)

$$\bar{P}_{\mathrm{n}}=1770[\eta]^{1.40}$$

In order to obtain the distribution of the degrees of polymerization at high conversion, *n*-butanol was slowly added to the benzene solution of the polymer (about 1.5%). The addition of the *n*-butanol was stopped before precipitation of the polymer appeared. By slow evaporation of the relatively volatile benzene, the solution becomes richer in less volatile *n*-butanol, and the precipitation of polystyrene results. After temperature equilibrium was attained in a thermost at 30°C, the precipitate in a gel state was separated by decantation from the solution and the same procedure was repeated. The precipitate was then dissolved again in benzene and poured into ice-methanol followed by drying in vacuo. This method is almost the same as that adopted by Chitani et al.(9)

Theoretical

Notation

M—Number of moles of monomer,
P—Number of moles of polymer,
I—Number of moles of catalyst,
f—Catalyst efficiency,
k_{p}—Rate constant for propagation,
k_{t}—Rate constant for termination,
k_{d}—Rate constant for the first order decomposition of catalyst,
α—Total volume shrinkage for the complete conversion of monomer to polymer,
$\bar{P}_{\mathrm{n}}$—Cumulative value for number average degree of polymerization,
$\bar{\bar{P}}_{\mathrm{n}}$—Instantaneous value for number average degree of polymerization.

It is well known that the rate of radical polymerization initiated by a catalyst is expressed as

$$-\frac{\mathrm{d}[M]}{\mathrm{d}t}=K[I]^{1/2}[M] \tag{1}$$

where

$$K\equiv\frac{k_{\mathrm{p}}}{k_{\mathrm{t}}^{1/2}}k_{\mathrm{d}}^{1/2}f^{1/2} \tag{2}$$

If the decomposition rate of the catalyst is of the first order with respect to its concentration, then the conversion x at time t may be expressed by

$$x=1-\exp\{A(e^{-(1/2)k_{\mathrm{d}}t}-1)\} \tag{3}$$

where

$$A\equiv\frac{2K}{k_{\mathrm{d}}}[I]_0^{1/2} \tag{4}$$

The value of K can easily be obtained from the slope of the initial rate of polymerization against the square root of the catalyst concentration. From Eq. 3 it may be seen that the fractional conversion x reaches a limiting value x_∞ when $t\to\infty$.

$$x_\infty=1-\exp(-A) \tag{5}$$

Tobolsky(10) showed this relationship and compared it with experimental results. In the previous paper(6), which describes the polymerization of vinyl acetate in the benzoyl peroxide-iron(II)-benzoin redox system, the same concept of the limiting conversion was proposed by us. Later Tobolsky et al.(5) proposed a modified form of the kinetic expressions. The equations derived above have not been corrected for a net volume shrinkage of the system. If the volume shrinkage is taken into account, then the effective monomer and catalyst concentrations are

$$[M]=\frac{[M]_0}{(1-\alpha x)}(1-x) \tag{6}$$

$$[I]=\frac{[I]_0}{(1-\alpha x)}e^{-k_{\mathrm{d}}t} \tag{7}$$

respectively. From Eqs. 1, 6 and 7, one obtains

$$\frac{(1-\alpha x)^{3/2}}{(1-x)}\mathrm{d}x=K[I]_0^{1/2}e^{-(1/2)k_{\mathrm{d}}t}\cdot\mathrm{d}t \tag{8}$$

Integration of Eq. 8 leads to

$$\frac{2}{3}y^3+2a^2y+a^3\ln\frac{(y-a)}{(y+a)}=Ae^{-(1/2)k_{\mathrm{d}}t}+C \tag{9}$$

where

$$\left.\begin{aligned}&C\equiv\frac{2}{3}+2a^2+a^3\ln\frac{(1-a)}{(1+a)}-A\\&y\equiv(1-\alpha x)^{1/2};\quad a\equiv(1-\alpha)^{1/2}\end{aligned}\right\} \tag{10}$$

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7) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. T. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

8) D. H. Johnson and A. V. Tobolsky, ibid., **74**, 938 (1952).

9) T. Chitani, G. Meshitsuka and Y. Matsui, *High Polym. Chem. (Kobunshi Kagaku)*, **10**, 175 (1953).

10) A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 5927 (1958).

Eqs. 8 and 9 are somewhat different from the similar expressions derived by Tobolsky et al.[5]

It is rather complex to calculate the limiting conversion x_∞ from Eq. 9. But if the corresponding value of y is expressed by y_∞, then from Eq. 9,

$$Z\equiv\frac{2}{3}(y^3-y_\infty^3)+2a^2(y-y_\infty)+a^3\ln\frac{(y-a)(y_\infty+a)}{(y+a)(y_\infty-a)}=Ae^{-(1/2)k_{\mathrm{d}}t} \tag{11}$$

or taking the logarithm,

$$\ln Z=\ln A-\frac{1}{2}k_{\mathrm{d}}t \tag{12}$$

Therefore, if the values of K and k_{d} are accurately known, it is possible to draw an $x\sim t$ curve over the whole course of polymerization and compare it with the experimental curve. And if a deviation between them is seen, it might be explained as indicative of a change in circumstance such as gel formation. In a case where no such deviation occurs, one can obtain K and k_{d} directly by applying Eq. 12. In Eq. 12, if $\ln Z$ is plotted against time t, a straight line should be obtained and the slope and the intercept will give $(1/2)k_{\mathrm{d}}$ and $\ln A$, respectively.

The number average degrees of polymerization of a polymer instantaneously formed and cumulatively formed are related to each other by Eq. 13.

$$\bar{\bar{P}}_{\mathrm{n}}=\frac{\bar{P}_{\mathrm{n}}}{1-\dfrac{x}{\bar{P}_{\mathrm{n}}}\cdot\dfrac{\mathrm{d}\bar{P}_{\mathrm{n}}}{\mathrm{d}x}} \tag{13}$$

Applying Eq. 13, one can calculate $\bar{\bar{P}}_{\mathrm{n}}$ from the $\bar{P}_{\mathrm{n}}\sim x$ curve which can be obtained experimentally. Eq. 13 was derived by Schulz et al.[11] and Wall et al.[12], independently.

It is of great interest to note that according to Eq. 13, the value of the instantaneous degree of polymerization will become infinitely large when the value of $(x/\bar{P}_{\mathrm{n}})\cdot(\mathrm{d}\bar{P}_{\mathrm{n}}/\mathrm{d}x)$ approaches unity. So, one can tentatively refer $\bar{\bar{P}}_{\mathrm{n}}\rightarrow\infty$ as a measure of gel formation.

In a bulk polymerization of vinyl monomer, if chain transfers to monomer and initiator are both neglected, $\bar{P}_{\mathrm{n}}$ may be expressed as

$$\bar{P}_{\mathrm{n}}=\frac{[M]_0-[M]}{f\{[I]_0-[I]\}} \tag{14}$$

for combination termination.

In a case where volume shrinkage can be neglected,

$$\bar{P}_{\mathrm{n}}=\frac{[M]_0}{f[I]_0}\cdot\frac{x}{1-\exp(-k_{\mathrm{d}}t)} \tag{15}$$

Taking the volume shrinkage into account, it follows that

$$\bar{P}_{\mathrm{n}}=\frac{[M]_0}{f[I]_0}\cdot\frac{x}{1-\alpha x-\exp(-k_{\mathrm{d}}t)} \tag{16}$$

It was pointed out by Robertson[13] that the catalyst efficiency f started to decrease rapidly as bulk polymerization proceeded in the case of styrene and methyl methacrylate. In this case, remembering that $\bar{P}_{\mathrm{n}}$ is a cumulative value for the number average degree of polymerization, the catalyst efficiency f in Eq. 14 must also be a cumulative one. Then, rearranging Eq. 14 and inserting $\bar{f}$ instead of f,

$$\bar{f}=\frac{[M]_0-[M]}{\bar{P}_{\mathrm{n}}([I]_0-[I])} \tag{17}$$

The true value of f at conversion x may be expressed by

$$f=\bar{f}+x\frac{\mathrm{d}\bar{f}}{\mathrm{d}x} \tag{18}$$

It is well known that an abnormal explosive reaction is followed by an increase in the degree of polymerization. Hence, the comparison of the experimental molecular weight distribution with the theoretical one will offer interesting information.

According to rigorous kinetics, the molecular distribution for combination termination is given by[14]

$$\begin{aligned}r[M_{\mathrm{r}}]=\frac{1}{2}R_{\mathrm{i}}\delta^2\Bigg[&\left(\frac{r}{[M]_0}+\frac{1}{R_{\mathrm{i}}{}^{1/2}\delta}\right)\\&\exp\left\{-\frac{R_{\mathrm{i}}{}^{1/2}\delta}{[M]_0}(r-1)\right\}\\&-\left(\frac{r}{[M]}+\frac{1}{R_{\mathrm{i}}{}^{1/2}\delta}\right)\\&\exp\left\{-\frac{R_{\mathrm{i}}{}^{1/2}\delta}{[M]}(r-1)\right\}\Bigg]\end{aligned} \tag{19}$$

where M_{r} is the number of moles of a polymer having r monomer nuits, δ a quantity approximated to $k_{\mathrm{t}}{}^{1/2}/k_{\mathrm{p}}$ and R_{i} the rate of initiation.

Results and Discussion

The bulk polymerizations of styrene catalyzed by 2, 2′-azobisisobutyronitrile were carried out at 60°C, and the fractional conversion x was

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[11] G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

[12] F. T. Wall and L. F. Beste, *J. Am. Chem., Soc.*, 69, 1761 (1947).

[13] E. R. Robertson, *Tsans. Faraday Soc.*, **52**, 426 (1956).

[14] E. F. Herrington and A. Robertson, ibid., **40**, 236 (1944); G. M. Burnett, "Mechanism of Polymer Reactions", Interscience Publishers, New York (1954), p. 106.

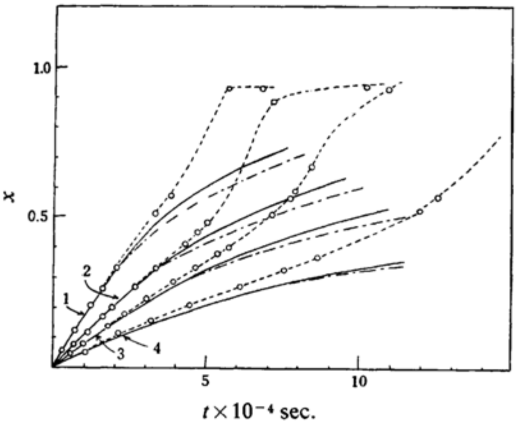

Fig. 1. Fractional conversion x vs. t for the bulk polymerization of styrene at 60°C, using 2, 2′-azobisisobutyronitrile as initiator.

--○-- experimental ——— calcd. by Eq. 9 —·—·— by Eq. 3 $[I]_0 \times 10^2$ mol./l. : 1, 5.00; 2, 2.00; 3, 1.00; 4, 0.36

plotted against time t over the whole course of polymerization as shown in Fig. 1.

The initial rates of the reaction R_0 obtained from the figure were plotted against the square root of the initial concentrations of the catalyst, giving a straight line as expected from Eq. 1. This is shown in Fig. 2. From the slope, the value of K was found to be 0.86×10^{-4} mol$^{-(1/2)}$ l$^{1/2}$ sec^{-1}, which is in good agreement with the value obtained by Tobolsky et al.[8] The spontaneous decomposition of 2, 2′-azobisisobutyronitrile has been widely studied and various values for the rate constant k_d have been reported. Using the ^{14}C labelled initiator, Bevington[15] proposed the value of 1.20×10^{-5} sec^{-1} as the best. Using this value together with the above-mentioned value of K, one can calculate the whole course of the

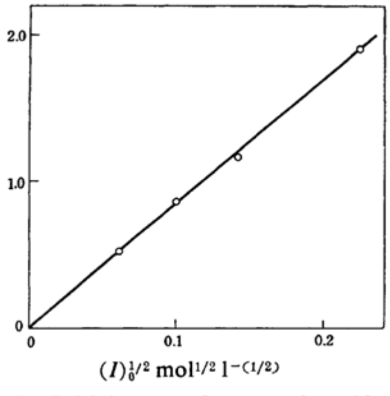

Fig. 2. Initial rate of conversion $(dx/dt)_0$ vs. $[I]_0^{1/2}$.

TABLE I. EXPERIMENTAL VALUES OF x, $\bar{P}_n$ AND $\bar{f}$

$[I]_0$ mol./l.	$t \times 10^{-4}$ sec.	x	$\bar{P}_n$	$\bar{f}$ (Eq. 15)	$\bar{f}$ (Eq. 16)
0.05	0.72	0.130	375	0.70	0.79
	1.80	0.297	353	0.72	0.82
	3.96	0.595	579	0.45	0.52
	5.76	0.937	1920	0.16	0.20
	6.84	0.934	1879	0.15	0.17
0.02	1.26	0.141	608	0.69	0.69
	2.70	0.274	608	0.68	0.68
	4.32	0.420	739	0.59	0.59
	7.20	0.891	2835	0.23	0.26
	10.26	0.941	3123	0.18	0.19
0.01	1.80	0.150	890	0.72	0.69
	3.24	0.249	948	0.68	0.65
	5.76	0.405	1010	0.67	0.65
	8.46	0.674	2023	0.44	0.44
	10.98	0.931	4671	0.23	0.24
0.0036	2.16	0.120	1684	0.72	0.66
	6.12	0.277	1921	0.64	0.58
	8.82	0.380	2246	0.60	0.55
	12.54	0.577	3598	0.48	0.45
	17.28	0.903	6853	0.35	0.35

TABLE II. CALCULATED VALUES OF x AND $\bar{P}_n$ APPLYING EQS. 3 AND 15*

$t \times 10^{-4}$ sec.	$[I]_0$ mol./l.	x	$\bar{P}_n$
0	0.05	0.000	382
1		0.170	359
2		0.304	340
3		0.411	324
4		0.495	310
5		0.564	298
7		0.667	280
10		0.765	261
∞		0.960	229
0	0.02	0.000	605
1		0.111	585
2		0.203	568
3		0.285	562
4		0.351	549
5		0.409	540
7		0.501	525
10		0.600	511
∞		0.869	517
0	0.01	0.000	852
1		0.080	843
2		0.149	833
3		0.210	828
4		0.263	822
5		0.309	816
7		0.388	814
10		0.475	810
∞		0.761	906
0	0.0036	0.000	1423
1		0.049	1435
2		0.093	1445
3		0.132	1447
4		0.167	1451
5		0.200	1468
7		0.255	1486
10		0.321	1520
∞		0.577	1910

* $K = 0.86 \times 10^{-4}$ mol$^{-(1/2)}$ l$^{1/2}$ sec^{-1}, $k_d = 1.20 \times 10^{-5}$ sec^{-1} and $\bar{f} = 0.70$ was used.

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[15] J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).

polymerization by Eq. 3 or, exactly, by Eq. 9. Some experimental and calculated values of x at various times are listed in Table I and Table II, and predicted $x \sim t$ curves are also shown in Fig. 1, $\alpha=0.177$ being used in Eq. 9.

As seen in the figure, these two calculated curves coincide with each other almost perfectly below 20% conversion, and above it, they separate gradually. At high convertion, the difference becomes fairly appreciable. Such a fact must be taken into account when polymerization, are followed by large valume shrinkage as seen in the bulk polymerization of vinyl acetate. Comparing the predicted and experimental values of x in each catalyst concentration, it seems that, at very low conversion, these values agree fairly well. In the second step, however, there appears a clear deviation between them which seems to appear at lower conversion in lower initial catalyst concentration. The accelerated polymerizations proceed almost linearly with respect to time. Then, there is a third step where the rate of the polymerization becomes explosive, and at the beginning of the step, production of gas bubbles was always seen. It made the dilatometric analysis impossible. Above 90% conversion, the viscous solution changed into hard plastic and the reaction ceased few percent less than perfect conversion. Since this anomalous rate acceleration cannot be considered as associated with change in k_d, it must be owing to change in K. The values of K at any fractional conversions can be calculated by Eq. 8, in which the slope dx/dt at x may be obtained from Fig. 1, the value of k_d being taken again as $1.20\times10^{-5}\,\mathrm{sec}^{-1}$ and as constant at any conversions. It must be noted that in deriving the values of K from Eq. 8, it was tacitly assumed that the steady state for radicals holds even at the explosive step.

Remembering that $K=k_p k_d^{1/2} f^{1/2}/kt^{1/2}$, the values of $f^{1/2}k_p/kt^{1/2}$ were plotted against x as shown in Fig. 3. The form of the curves in the figure is quite similar to one which was reported by other investigators[5,13].

From Fig. 3, it is obvious that the values of $f^{1/2}k_p/k_t^{1\ 2}$ are almost constant up to 20~30% conversion in every initial catalyst concentration. They increase gradually and then rapidly as x increases. It is clear that the increase in $f^{1/2}k_p/k_t^{1/2}$ occurs at lower fractional conversion the lower the initial catalyst concentration is. The reasonable explanation is as follows: As has been pointed out by some investigators, the termination constant k_t including two large growing polymer chains is first diffusion-controlled. The lower the catalyst concentration, the greater becomes the degree of polmerization and hence the viscosity of solution. If k_t is affected first, the increase in viscosity will result in the decrease in k_t.

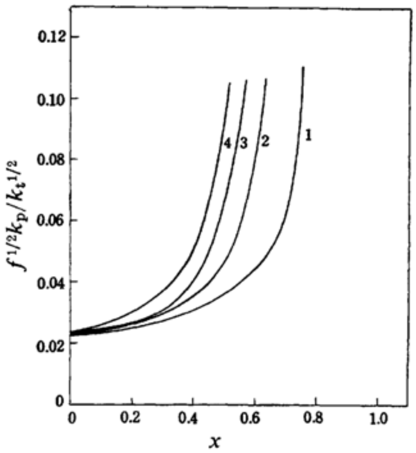

Fig. 3. $f^{1/2}k_p/k_t^{1/2}$ determined from the rate of polymerization data (Eq. 8) vs. x. $[I]_0\times10^2$ mol./l.: 1, 5.00; 2, 2.00; 3, 1.00; 4, 0.36

The increase in $f^{1/2}k_p/k_t^{1/2}$ may also be reflected on the fact that the experimental conversions were higher than the predicted ones in each experiment with one exception. According to Eq. 5, as A and hence $f^{1/2}k_p/k_t^{1/2}$ increase, the value of x approaches unity.

The explosive polymerization is usually followed by an increase in the degree of polymerization. In the polymerization of styrene, the chain transfer to monomer is small and so, its contribution to the degree of polymerization may be neglected if catalyst concentration is properly chosen.

Since chain termination by combination is exclusive in the polymerization of styrene, the cumulative number average degree of polymerization $\bar{P}_n$ may be expressed approximately by Eq. 14. In Figs. 4 and 5, $\bar{P}_n$ is plotted against x.

Applying Eq. 14 ($f=0.7$ was used), the theoretical plots of $\bar{P}_n$ vs. x are expressed by curves I and I′ in each figure, the volume shrinkage being neglected for simplicity. As seen in the figure, the predicted value of $\bar{P}_n$ is not so much affected by the fractional conversion unless the catalyst concentration is extremely small or very large. The experimental plots of $\bar{P}_n$ vs. x which are denoted by curves II and II′, show that the values of $\bar{P}_n$ in each run agree fairly well with the predicted value up to 20~30% conversion. With $[I]_0=0.0036$ mol./l., the deviation is the greatest. However the value of $\bar{P}_n$ increases gradually thereafter, then more rapidly toward the last.

According to Eq. 14, $\bar{P}_n$ is a function of

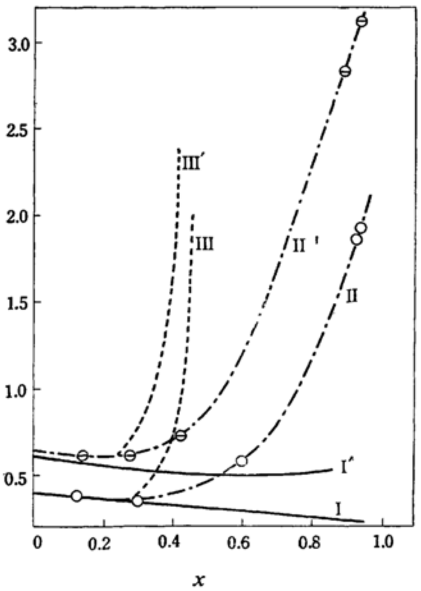

Fig. 4. Cumulative and instantaneous average degree of polymerization $\bar{P}_n$ and $\bar{\bar{P}}_n$ vs. x. —— theoretical (Eq. 15) —·— experimental plots of $\bar{P}_n$; ---- experimental $\bar{\bar{P}}_n$ (Eq. 13) I, II and III for $[I]_0=0.05$, I', II' and III' for $[I]_0=0.02$ mol./l., respectively

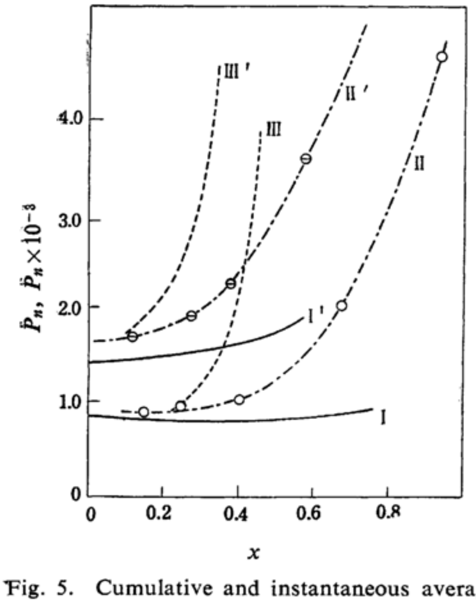

Fig. 5. Cumulative and instantaneous average degree of polymerization $\bar{P}_n$ and $\bar{\bar{P}}_n$ vs. x. —— theoretical (Eq. 15) —·— experimental plots of $\bar{P}_n$; ---- experimental $\bar{\bar{P}}_n$ (Eq. 13) I, II and III for $[I]_0=0.01$, I', II' and III' for $[I]_0=0.0036$ mol./l., respectively

monomer and catalyst concentrations and catalyst efficiency. Accordingly, the (cumulative) catalyst efficiency $\bar{f}$ can be obtained on inserting the experimental values of $\bar{P}_n$, $[M]$ and calculated values of $[I]$ into Eq. 17. In Table I are listed some values of $\bar{f}$ which were calculated by Eqs. 15 and 16, the volume shrinkage being taken into account in the latter equation. As may be seen in Fig. 6, the values of $\bar{f}$ are plotted against x. The average value of $\bar{f}$ at low conversion is about 0.7, which is very close to the value obtained by Tobolsky et al.[5] It is of interest to note that the catalyst efficiency $\bar{f}$ seems to depend only upon conversion and not upon the initial concentration of the catalyst. The instantaneous catalyst efficiency f which was calculated by Eq. 23 may also be seen in Fig. 6.

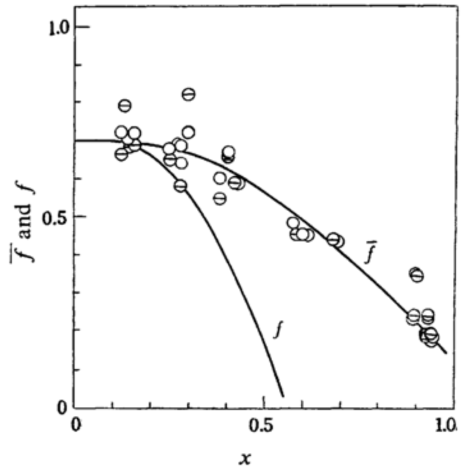

Fig. 6. Apparent dependence of cumulative and instantaneous catalyst efficiency $\bar{f}$ and f upon x.
○ calcd. by Eq. 15; ⊖ calcd. by Eq. 16

The shape of the curves is similar to but somewhat different from that obtained by Robertson[13]. This true value of catalyst efficiciency at any x decreases rapidly with increasing conversion. There is a doubt as to whether or not the catalyst efficiency is much affected by change in environment such as an increase in viscosity. Since the dimensions of the catalyst and the monomer are very small compared with the dimension of the polymer, it is unlikely that those molecules suffer an effect of diffusion in such a low conversion step. Hence it is very doubtful whether the catalyst efficiency is diffusion controlled. In deriving Eq. 16, it was tacitly assumed that the chain transfer to polymer does not take place and hence each polymer produced is a long chain molecule which has two catalyst fragments at its ends. If this is not so and the chain transfer to already dead polymers might occur considerably Eq. 16 would no more be applied. If the chain transfers to polymers occur in such a manner as to cross-link together the polymers previously formed, a rapid increase in the average degree of polymerization will result. The apparent decrease in f might be owing to this fact.

The instantaneous degree of polymerization $\overline{\overline{P}}_n$ at any conversion may be calculated by Eq. 15. In Figs. 4 and 5, $\overline{\overline{P}}_n$ is plotted against x as shown in curves III and III′. As seen in these figures, each value of $\overline{\overline{P}}_n$ increases steeply toward infinity as x increases. Above 40∼50% conversion, the value of $\overline{\overline{P}}_n$ takes a negative value in each experiment.

This interesting phenomenon was first observed by Wall et al.[12] According to them, the formation of cross-linking of polymer molecules not only increases the average molecular weight, but simultaneously, diminishes the number of polymer molecules, thus accounting for the observed results. It is clear from the definition $\overline{\overline{P}}_n=-\mathrm{d}M/\mathrm{d}P$ that $\overline{\overline{P}}_n$ takes a negative sign when $\mathrm{d}P$ is negative.

On account of the fact that any polymers produced by chain reactions must have a certain dispersion of molecular sizes, the study of size distribution in polymers is of great importance in connection with the kinetic mechanisms of polymerizations. Among several experimental techniques for the fractionation of polymers, those based on solubility are most generally used. However, the fractions obtained in any experimental techniques are always heterogeneous with respect to molecular weight and, so far, the problem of the overlapping of the polymer species has never been overcome.

The fractionations of two samples were carried out in order to obtain the distribution of molecular sizes at high conversion, and the results are listed in Table III. As an approximation, the degrees of polymerization in each fraction were calculated from the data of viscosity measurements, using the relation $\overline{P}_n=1770\,[\eta]^{1.40}$ which was applied for the unfractionated polymers.

TABLE III. FRACTIONATION RESULTS OF POLYMERS

Fraction No.	Weight, g.	%	$\overline{DP}$
Unfractionated	6.000		6853
1	1.347	22.7	26980
2	0.575	9.7	11480
3	1.174	19.7	9820
4	0.369	6.2	5681
5	0.745	12.5	4142
6	1.277	21.5	2258
7	0.455	7.7	818
Unfractionated	5.523		3123
1	0.465	8.4	14090
2	0.788	14·3	8048
3	0.392	7.1	4508
4	1.279	23.2	2501
5	1.112	20.1	1183
6	1.140	20.7	652
7	0.344	6.2	242

The integral weight distribution curves were obtained by plotting the weight of each fraction as a function of the degree of polymerization, adding the weight of each fraction to the weight of the preceding fraction. The smooth lines drawn in Fig. 7 are the integral and differential weight distribution curves. The latter lines were obtained by taking the slope of the integral weight distribution curves as a function of the degree of polymerization.

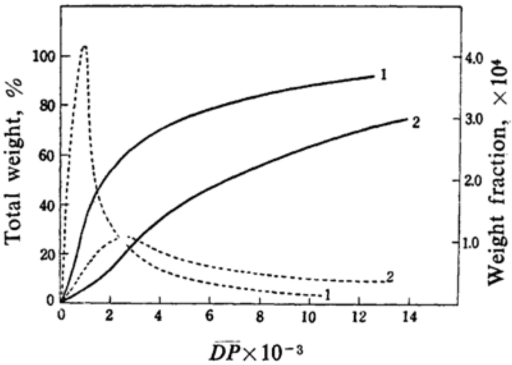

Fig. 7. Molecular weight distribution.

—— integral, ---- differental weight distributions

1 : $[I]_0=0.02$ mol./l., $x=0.941$, $\overline{P}_n=3123$

2 : $[I]_0=0.0036$ mol./l., $x=0.903$, $\overline{P}_n=6853$

It was pointed out by Guzmán[16] that this classical method of approaching the problem about molecular weight distribution is rather imperfect because there is an inevitable source of error such as the overlapping of polymer species. He compared the results obtained by the classical procedure with those obtained statistically, based on the same experimental data, and showed that there was a considerable difference between them. In spite of being more logical and reasonable, the statistical approach involves a great labor of mathematical computation and is not easy to handle.

Instead, the size distribution curves of the polymer at conversion $x=4\%$ were drawn as shown in Fig. 8 in accordance with Eq. 21 which was derived from the kinetic mechanism of the initial polmerization step alone.

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[16] G. M. Guzmán, *J. Polymer Sci.*, **19**, 519 (1956).

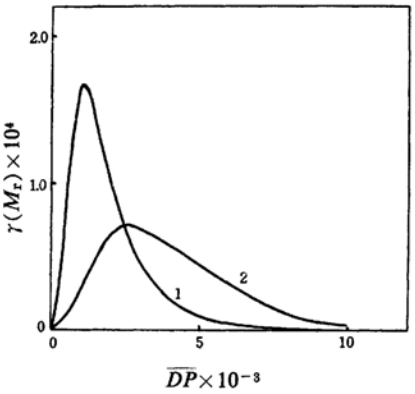

Fig. 8. Theoretical differential weight distributions (Eq. 19) at $x=0.04$.
1: $[I]_0=0.02$; 2: $[I]_0=0.0036$ mol./l.

It is clear from Figs. 7 and 8 that there is a considerable difference between experimental and calculated differential weight distributions. The shape of the corresponding curves up to the maximum weight fraction is very similar. However, beyond this, the experimental curves fall much less rapidly and unsymmetrically than do the calculated ones.

It may reasonably be assumed that the experimental molecular weight distribution consists of two parts, normal and abnormal distributions of molecular species. The part of the normal distribution may correspond to that which can be obtained from the initial stage of polymerization, while the part of the abnormal distribution may arise from the explosive polymerization. The kinetic treatment of such abnormal weight distribution may be complex. Nevertheless, it is of great interest that the result of explosive polymerization is reflected on such weight distribution.

From the study of the molecular weight distribution, it seems that the abnormal increase of the degree of polymerization at high conversion is not owing to the chain transfer to the already dead polymers, but is, probably, owing to the burying of the growing polymer radicals, because the produced polymer at high conversion involves a considerable part of low molecular weight.

Summary

The bulk polymerization of styrene initiated by 2, 2'-azobisisobutyronitrile was carried out up to high conversion at 60°C. The comparison of the experimental conversion~time data with calculated ones showed that there was a considerable deviation between them. The rate of the polymerization became explosively great toward the last.

Assuming the combination termination, the cumulative degree of polymerization was calculated and the values were compared with those obtained experimentally. The deviation at high conversion might be owing to the decrease in the catalyst efficiency as suggested by Robertson. However, the assumption that the polymer molecules have been produced only by combination is very doubtful.

The study of the molecular weight distribution suggested that the abnormal increase in the rate and the degree of polymerization seemed to be owing to the burying of the growing polymer radicals in themselves in the highly viscous solution.

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