# *Vinyl Polymerization. XLVIII.* Polymerization of Methylstyrenes and the Effect of Dimethylaniline on their Polymerization*

By Minoru IMOTO, Kiichi TAKEMOTO and Yuichi IIKUBO

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Previously we have carried out polymerization of styrene and *p*-methylstyrene initiated by the azobisisobutyronitrile (ABIN)-dimethylaniline (DMA) system. Consequently a peculiar effect was observed in the polymerization of *p*-methylstyrene(1). In this paper, the polymerization of *p*-methylstyrene with the ABIN-DMA system was studied repeatedly, and some different conclusions were obtained. The value of $k_1$ in this system was also measured by the ferric chloride method of Bamford et al.(2)

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* XLVII of this series: M. Imoto and I. Soematsu, in contribution.

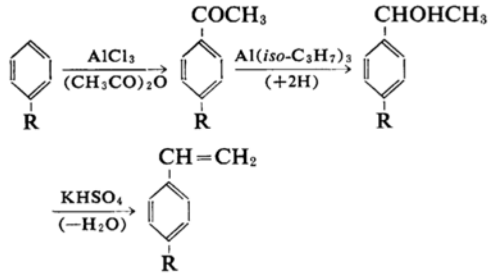
1) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **19**, 205 (1956).

2) J. C. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc.*, **A241**, 364 (1957).

As the polymerization of other monomethyl- and dimethylstyrenes has been little investigated, it was interesting to carry out the polymerization of these monomers. The polymerization with ABIN was studied in benzene, and rates of polymerization and intrinsic viscosities were determined.

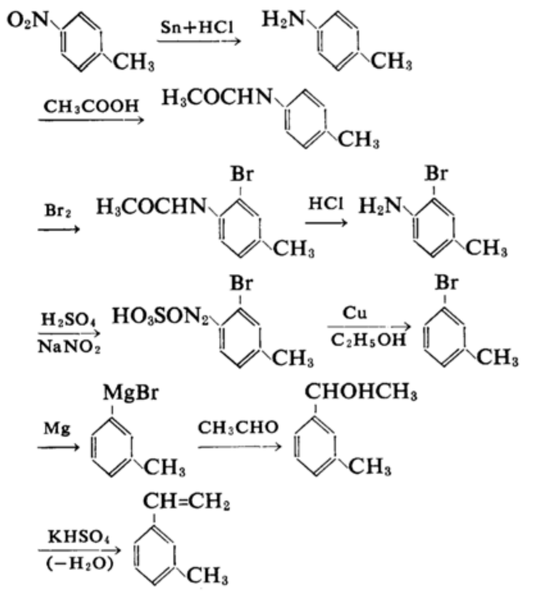
## Experimental

**Syntheses of Monomers.**—*Syntheses of p-Alkylstyrenes.*—*p*-Methyl-, *p*-ethyl- and *p-tert*-butylstyrene were synthesized from corresponding alkylbenzenes, according to the following sequence of reactions⁽³⁾:



(R : $CH_3$, $C_2H_5$, *tert*-$C_4H_9$)

*Synthesis of m-Methylstyrene.*—*m*-Methylstyrene was synthesized from *p*-nitrotoluene as follows⁽⁴⁾:



*Syntheses of Dimethylstyrenes.*—2, 4-Dimethyl-, 2, 5-dimethyl- and 3, 4-dimethylstyrene were synthesized from corresponding xylenes in a manner similar to that used in the case of *p*-alkylstyrenes⁽⁵⁾.

The Meerwein-Ponndorf reduction of the substituted acetophenones was found to be unsuccessful in the case of 3, 4-dimethyl derivative. By the direct hydrogenation in autoclave, using copper-chromium oxide or Raney nickel as catalyst, 3, 4-dimethylphenylcarbinol was obtained with yield of 90%.

*Purification of Monomers.*—All monomers were purified by distillation in vacuo under flushing of nitrogen after drying over calcium chloride. Before use, they were distilled again through a 40 cm. Stedman column. Reflux ratios were 10 : 1∼6 : 1. Physical constants of the monomers were shown in Table I. Infrared spectroscopic analyses were also made for all the monomers to ascertain their structures.

Styrene was purified by distillation in the same manner as the substituted styrenes (b. p. 145°C/760 mmHg).

**Purification of Reagents.**—2, 2′-Azobisisobutyronitrile (ABIN) was purified by recrystallization from methanol and dried in vacuo (m. p. 103°C). Dimethylaniline (DMA) was distilled in a nitrogen atmosphere and stored. Before use, it was again distilled under reduced pressure through a Vigreux column (b. p. 68°C/10 mmHg). Benzene was distilled, after thiophene was removed, dried over calcium chloride and again distilled over metallic sodium (b. p. 80°C). Ferric chloride ($FeCl_3 \cdot 6H_2O$), commercial pure grade, was used after crushing. Benzoquinone was synthesized from hydroquinone by oxidation with sodium dichromate and purified by sublimation under reduced pressure twice before use (m. p. 113∼114°C). Nitrogen was purified by washing through alkaline pyrogallol solution and concentrated sulfuric acid and by passing over reduced copper at 550°C.

**Procedures.**—*Measurement of Rate of Polymerization.*—In order to determine the initial rate of polymerization, the dilatometric and usual sealed tube methods were adopted. In some experiments, the dilatometer reported earlier⁽⁶⁾ was used. In another case, a dilatometer in a different form was used, the total capacity being about 4.5∼5.5 ml. and the diameter of the capillary tube about 0.3∼0.5 mm.

Polymerization was carried out as described in the previous paper. The polymerization temperature was regulated within ±0.02°C in the case of dilatometry, and ±0.05°C in the case of the sealed tube method.

*Measurement of Intrinsic Viscosity.* — Intrinsic viscosities $[\eta]$ of polymers were measured in benzene solution at 30±0.1°C, using Ostwald's viscometer. Assuming that the following equation given by Tobolsky et al.⁽⁷⁾ for polystyrene can also be available for substituted polystyrenes, the number-average polymerization degree $\bar{P}_n$ of all polymers was computed.

$$\bar{P}_n = 1770[\eta]^{1.40}$$

*Measurement of Rate of Decomposition of ABIN.*—The rate of decomposition of ABIN was measured, with the volume of nitrogen evolved⁽⁸⁾.

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3) C. G. Overberger, C. Frazier, J. Mandelman and H. G. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1951).

4) C. S. Marvel, C. G. Overberger, R. E. Allen and J. H. Saunders, ibid., **68**, 736 (1946).

5) C. S. Marvel, J. H. Saunders and C. G. Overberger, ibid., **68**, 1085 (1946).

6) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **18**, 377 (1955).

7) D. H. Johnson and A. V. Tobolsky, *J. Am. Chem. Soc.*, **74**, 938 (1952).

8) M. Imoto, T. Otsu, T. Ota, H. Takatsugi and M. Matsuda, *J. Polymer Sci.*, **22**, 137 (1956).

TABLE I. PHYSICAL PROPERTIES OF SUBSTITUTED STYRENES

| Styrene | B. p., °C | (mmHg) | S. g. | Refractive index |
|---|---|---|---|---|
| *p*-Methylstyrene | 58 | ( 7) | $d_4^{25}=0.890$ | $n^{25}=1.5393$ |
| *p*-Ethylstyrene | 68 | (10) | $d_4^{20}=0.9070$ | $n^{25}=1.5349$ |
| *p-tert*-Butylstyrene | 90～92 | (10) | $d_4^{23}=0.8739$ | $n^{20}=1.5212$ |
| *m*-Methylstyrene | 90～91 | (30) | $d_{25}^{25}=0.9032$ | $n^{24.5}=1.5392$ |
| 2, 4-Dimethylstyrene | 90 | (25) | $d_{25}^{25}=0.9048$ | $n^{20.5}=1.5425$ |
| 2, 5-Dimethylstyrene | 81～83 | (23) | $d_{25}^{25}=0.9050$ | $n^{20}=1.5389$ |
| 3, 4-Dimethylstyrene | 86～88 | (20) | $d_{25}^{25}=0.9200$ | $n^{20}=1.5420$ |

TABLE II. RATES OF POLYMERIZATION AND DEGREES OF POLYMERIZATION FOR SUBSTITUTED STYRENES

| Monomer | Rate of polymerization |  | Degree of polymerization $\bar{P}_n$ |
|---|---|---|---|
|  | Sealed tube method, 50°C (mol./l. sec.) | Dilatometry, 70°C (mol./l. sec.) |  |
| Styrene | $11.13\times10^{-6}$ | $5.10\times10^{-6}$ | 700 |
| *p*-Methylstyrene | 14.30 | 5.32 | 190 |
| *p*-Ethylstyrene | — | 2.13 | — |
| *p-tert*-Butylstyrene | — | 1.73 | — |
| *m*-Methylstyrene | 4.20 | — | 280 |
| 2, 4-Dimethylstyrene | 6.52 | — | 150 |
| 2, 5-Dimethylstyrene | 6.86 | — | 300 |
| 3, 4-Dimethylstyrene | 10.96 | — | 490 |

* Monomer concentration = 3.43 mol./l., ABIN concentration = $1.097\times10^{-2}$ mol./l.

** Monomer concentration = 0.455 mol./l., ABIN concentration = $2.50\times10^{-3}$ mol./l.

## Results

**Polymerization of Substituted Styrenes.**—*Polymerization of p-Alkyl- and Dimethylstyrenes.*—Polymerizations of styrene, *p*-methyl-, *p*-ethyl- and *p-tert*-butylstyrene were carried out dilatometrically in benzene at 70°C. The linear time-conversion relationship was obtained for all runs. Polymerization of *m*-methyl-, 2, 4-dimethyl-, 2, 5-dimethyl and 3, 4-dimethylstyrene were also carried out in benzene at 50°C by the sealed tube method. Time-conversion curves were shown in Fig. 1 (including the curves of styrene and *p*-methylstyrene), where the concentrations of monomer and initiator were kept constant at 3.43, and 1.097 $\times10^{-2}$ mol./l., respectively. The linear time-conversion curves were also obtained. The rate for *p*-methylstyrene was greater than that for styrene. The rates for other monomers were smaller than that for styrene.

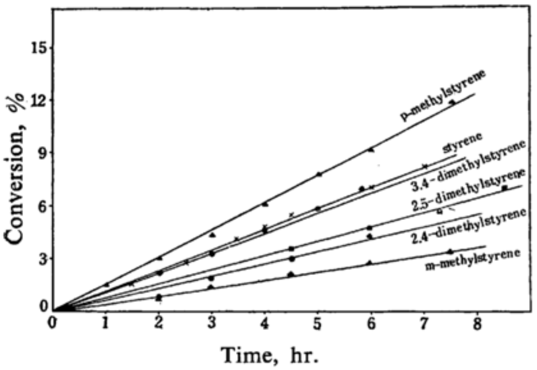

Fig. 1. Time-conversion curves for polymerization of substituted styrenes initiated by ABIN (sealed tube, in benzene, 50°C).
[M] = 3.43 mol./l.
[ABIN] = $1,097\times10^{-2}$ mol./l.
50°C, in benzene

The values of the rate of polymerization obtained were tabulated in Table II. The table includes also the values of degree of polymerization. The polymers used for the determination of [$\eta$] were obtained by 4.5 hr. polymerization.

Comparing the values of $\bar{P}_n$ and $Rp$ of *p*-methylstyrene with these of styrene, it was assumed that *p*-methylstyrene easily underwent chain transfer reaction. This was because in spite of the larger value of $Rp$, the degree of polymerisation was smaller. In order to study the effect of solvents on reaction, polymerization of *p*-methylstyrene was carried out in acetone or dimethylformamide (DMF) in the same manner as in benzene. As shown in Table III, the rates of polymerization in acetone were nearly the same as that in benzene. But the value obtained in DMF was relatively low. Separation of the polymer from benzene or DMF solution was easy, because the polymer separated granulously when the reaction mixture was poured into an excess of methanol.

TABLE III. OVERALL RATES OF POLYMERIZATION OF *p*-METHYLSTYRENE IN SOME SOLVENTS (DILATOMETRY, 60°C)

| Exp. run | Solvent | Rate of polymerization mol./l. sec. |
|---|---|---|
| 1 | Dimethylformamide | $2.13\times10^{-5}$ |
| 2 | 〃 | 2.08 |
| 3 | Benzene | 2.47 |
| 4 | 〃 | 2.46 |
| 5 | 〃 | 2.56 |
| 6 | Acetone | 2.46 |
| 7 | 〃 | 2.47 |

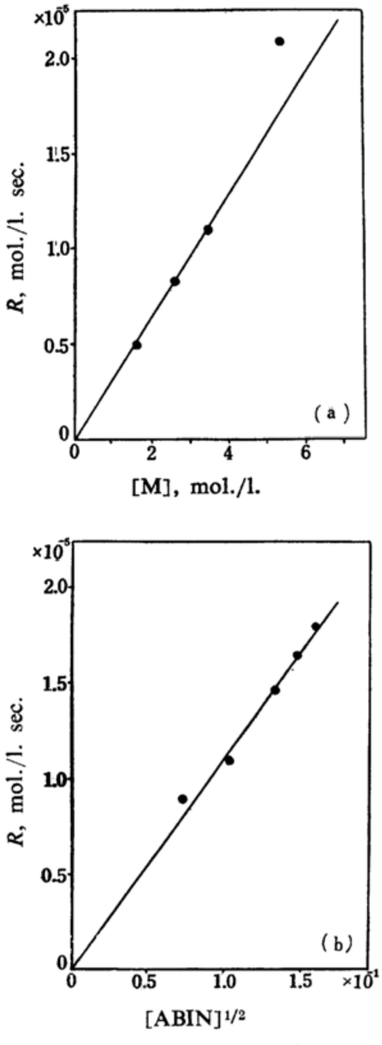

Fig. 2. Polymerization of 3,4-dimethylstyrene initiated by ABIN (sealed tube, in benzene, 50°C).

(a) Relationship of the initial rate of polymerization with the monomer concentration. ($[ABIN]=1.098\times10^{-2}$ mol./l.)

(b) Relationship of the initial rate of polymerization with the initiator concentration. ($[M]=3.49$ mol./l.)

However, when acetone was used, a turbid emulsion was obtained and the separation by filtration was much more difficult.

**Rate Equation of Polymerization for Substituted Styrene.**—From the results of 3,4-dimethylstyrene as shown in Fig. 2, the following equation was derived. This was identical with that for styrene.

$$R_0=k[M][ABIN]^{1/2}$$

**Determination of Rate Constants for Initiation.**—The rate constants of initiation of the polymerization of styrene and *p*-methylstyrene were determined, according to the $FeCl_3$-method by Bamford et al.[2], using the following equation.

$$\tau=\frac{[FeCl_3\cdot6H_2O]}{2f\cdot k_d[ABIN]}=\frac{[FeCl_3\cdot6H_2O]}{2k_i[ABIN]}$$

where $\tau$ is the induction period (in minutes), $f$ the initiator efficiency, and $k_d$ and $k_i$ the rate constants for decomposition of initiator and for initiation, respectively. The measurement of the value of $\tau$ for *p*-methylstyrene was carried out in DMF at 60°C.

In Fig. 3, examples of the time-conversion curve were illustrated. In Fig. 4, the relationship between the induction period and the amount of ferric chloride was shown. In Fig. 5, the relationship between the concentration of ABIN and the reciprocal of induction period was shown. The rate constants of initiation

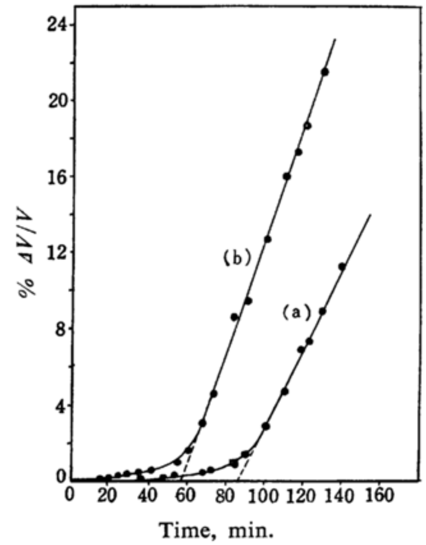

Fig. 3. Time-conversion curve for polymerization of *p*-methylstyrene initiated by ABIN in the presence of ferric chloride (in DMF, 60°C).

$[M]=2.17$ mol./l.

$[FeCl_3\cdot6H_2O]=4.46\times10^{-3}$ mol./l.

(a) $[ABIN]=6.12\times10^{-2}$ mol./l.

(b) $[ABIN]=1.00\times10^{-1}$ mol./l.

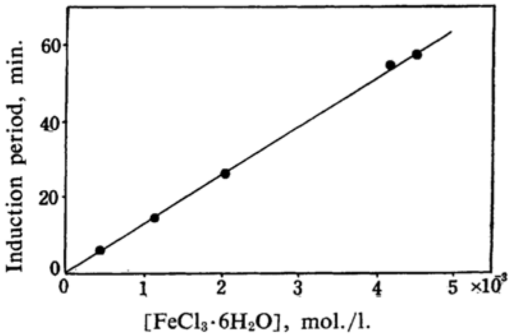

Fig. 4. Relationship between the induction period and the amount of ferric chloride in the polymerization of $p$-methylstyrene (in DMF, 60°C). $[M]=2.17$ mol./l., $[ABIN]=1.00\times10^{-1}$ mol./l.

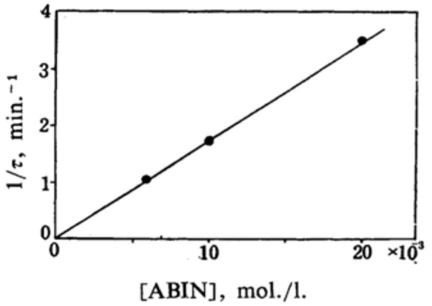

Fig. 5. Relationship between the induction period and the amount of ABIN in the polymerization of $p$-methylstyrene (in DMF, 60°C). $[M]=2.17$ mol./l., $[FeCl_3\cdot6H_2O]=4.46\times10^{-3}$ mol./l.

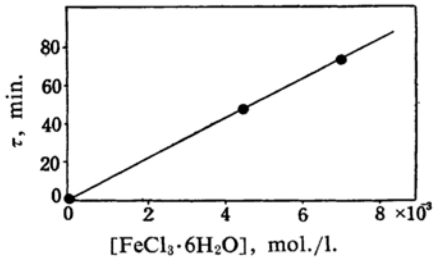

Fig. 6. Relationship between the induction period and the amount of ferric chloride in the polymerization of styrene (in DMF, 60°C). $[M]=2.04$ mol./l., $[ABIN]=1.00\times10^{-1}$ mol./l.

for the polymerization of $p$-methylstyrene were estimated as follows:

$$k_i=0.67\times10^{-5}\ (\text{sec}^{-1})$$

Similar determination was also made for styrene in DMF at 60°C, and the result obtained was shown in Fig. 6. The value of $k_i$ was as follows:

$$k_i=0.76\times10^{-5}\ (\text{sec}^{-1})$$

This value was in good agreement with the value, $k_i=0.70\times10^{-5}$ (sec$^{-1}$), obtained by Bamford et al. From the agreement of our value with that by Bamford et al., the value of $k_i$ for $p$-methylstyrene seemed to be reasonable.

As for $k_i$, the value for $p$-methylstyrene was found to be rather smaller than that for styrene. As shown in the former section of this paper, however, the overall rate of the polymerization of $p$-methylstyrene was greater than that of styrene. These results imply that in the sase of $p$-methylstyrene the rate constant for the propagation would be greater than that for styrene, or, that the rate constant of the termination $k_t$ would be smaller. Further work will be done to clarify this point.

**Polymerization of Substituted Styrene in the Presence of Dimethylaniline.—Polymerization of Styrene and *p*-Methylstyrene.**—*a) Polymerization with $Bz_2O_2$-DMA.*—Polymerization of $p$-methylstyrene was carried out dilatometrically at 70°C, using a system of benzoyl peroxide ($Bz_2O_2$)-dimethylaniline (DMA) as initiator. Time-conversion curves were shown in Fig. 7, where the concentrations of monomer and $Bz_2O_2$ were kept constant at 0.455 and $2.50\times10^{-3}$ mol./l., respectively, and the concentration of DMA was varied from 0 to 0.02 mol./l. Fig. 8 shows the results obtained, where the concentration of monomer and DMA were kept constant at 0.455 and $2.50\times10^{-3}$ mol./l., respectively, and the concentration of $Bz_2O_2$ was varied from 0 to 0.085 mol./l. The initial rates of polymerization were determined by the extrapolation method previously reported⁵⁾.

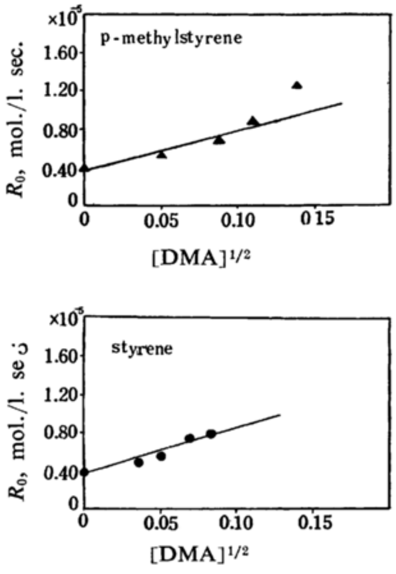

Fig. 7. Polymerization of styrene and $p$-methylstyrene initiated by $Bz_2O_2$ at 70°C (dilatometry).

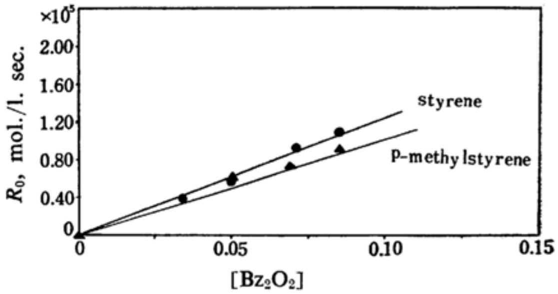

Fig. 8. Polymerization of styrene and *p*-methylstyrene initiated by $Bz_2O_2$ at 70°C (dilatometry).

The polymerization of styrene was carried out in parallel.

It was found that in the polymerization of *p*-methylstyrene, the initial rate of polymerization was also regarded as of 1/2-order with the concentrations of $Bz_2O_2$ and DMA, respectively.

$$R_0 = k' [Bz_2O_2]^{1/2} [DMA]^{1/2}$$

This agrees well with the results reported for the polymerization of several vinyl monomers⁹⁾.

*b) Polymerization with ABIN-DMA.*—Polymerizations of styrene and *p*-methylstyrene were carried out dilatometrically at 70°C by the ABIN-DMA system. Keeping the concentrations of monomer and ABIN constant at 0.455 and $2.50 \times 10^{-3}$ mol./l., respectively, and varying the concentration of DMA from 0 to $2.5 \times 10^{-2}$ mol./l., the initial rates of polymerization were measured.

Previously, two of the present authors, M. Imoto and K. Takemoto, published a paper on the polymerization of *p*-methylstyrene by ABIN-DMA¹⁾. There an apparent conclusion was obtained that the initial rate of polymerization increased with the addition of a small quantity of DMA and then decreased with the increasing quantity of DMA, after passing a maximum value (Fig. 9). It had been assumed that this phenomenon was due to the acceleration of the hyperconjugation effect of the *p*-alkyl group by DMA. For four years the study to ascertain this phenomenon was carried out repeatedly. In many cases, it was observed that no such accelerating effect by DMA existed as shown in Fig. 10.

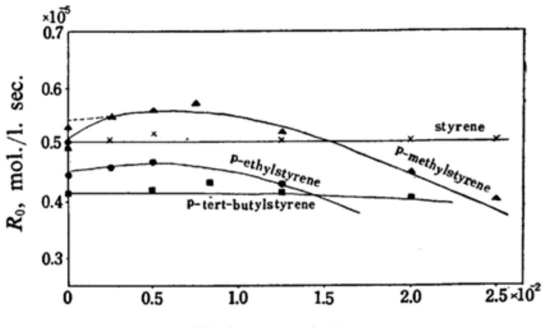

Fig. 9. Polymerization of styrene and *p*-alkylstyrenes initiated by ABIN in the presence of DMF at 70°C.
[M] = 0.455 mol./l.
[ABIN] = $2.50 \times 10^{-3}$ mol./l.

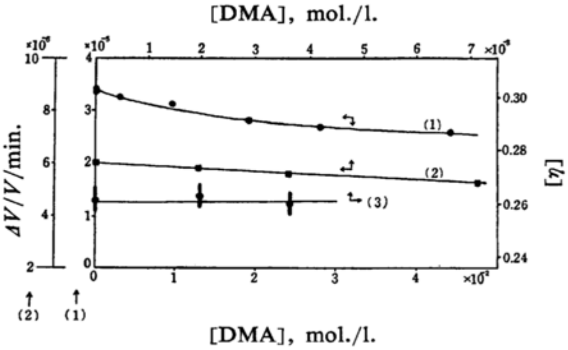

Fig. 10. Relationship of overall rate and intrinsic viscosity with the amount of DMA in the polymerization of *p*-methylstyrene initiated by ABIN at 60°C (in benzene). [M] = 2.17 mol./l., [ABIN], (1) $1.00 \times 10^{-1}$ mol./l., (2), (3) $2.68 \times 10^{-3}$ mol./l.

Granting the dotted line in Fig. 9 to be correct, the former observations coincided with the results obtained in this paper. (As stated above, the rate of polymerization of *p*-methylstyrene was surely greater than that of styrene.) It was now concluded that an accelerating effect by hyperconjugation might be denied, and that the initial rates of polymerization seemed to decrease with DMA as seen from Figs. 9 and 10.

**Polymerization of Dimethylstyrenes and *m*-Methylstyrene.**—We have carried out further

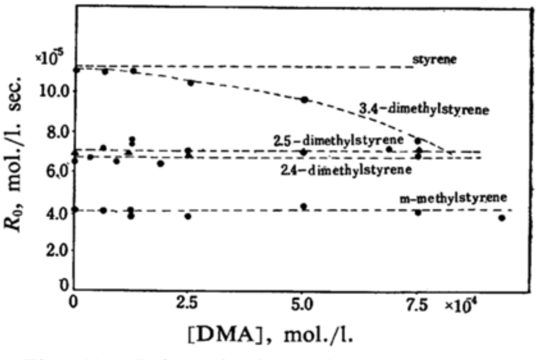

Fig. 11. Polymerization of *m*-methylstyrene and dimethylstyrenes initiated by ABIN in the presence of DMA at 50°C.
[M] = 3.43 mol./l.
[ABIN] = $1.097 \times 10^{-2}$ mol./l.

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9) M. Imoto, T. Otsu and T. Ota, *Makromol. Chem.*, **16**, 10 (1955).

experiments on the polymerization of dimethylstyrenes in order to examine the effect of DMA on the polymerization initiated by ABIN.

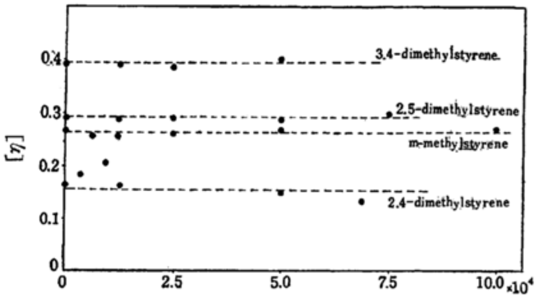
Polymerization was carried out by the sealed tube method at 50°C. The concentrations of the monomer and ABIN were kept constant at 3.43 and $1.097\times10^{-2}$ mol./l. respectively, while the concentration of DMA was varied from 0 to $1.0\times10^{-3}$ mol./l. As shown in Fig. 11, in the case of *m*-methylstyrene no effect of DMA on the initial rate was observed as in the case of styrene, while in the case of 2, 4- and 3, 4-dimethylstyrene a slight decrease with DMA was observed.

**Measurement of Intrinsic Viscosity.**—Intrinsic viscosities of the polymers obtained were measured in benzene at 30°C. Figs. 10 and 12 gave the plots of the intrinsic viscosities to the amounts of DMA added in the polymerization. From the results, it was concluded that no effect of DMA on the intrinsic viscosity was present.

**Rate of Decomposition of ABIN in the Presence of DMA and Monomer.**—The rate of decomposition of ABIN was measured at 50°C in benzene in the presence of monomer and DMA, using the apparatus described in the experimental part. The concentration of ABIN was kept constant at $9.84\times10^{-2}$ mol./l.

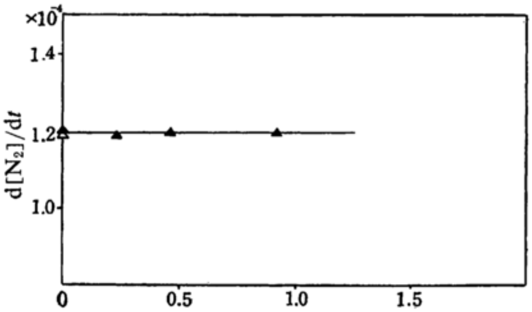
It was established that the rate of decomposition of ABIN was independent of the concentrations of styrene and DMA as shown in Fig. 13.

**Relationship between DMA and Induction Period.**—(*a*) *In DMF, with Ferric Chloride.*—We have already shown that an induction period was observed in the polymerization of styrene or *p*-methylstyrene in the presence of ferric chloride. We have studied further the effect of DMA on the induction period for the polymerization of *p*-methylstyrene initiated by ABIN in DMF, where the concentrations of ABIN and ferric chloride were kept constant at $1.00\times10^{-1}$ and $3.5\times10^{-3}$ mol./l. respectively, and the concentration of DMA was varied from 0 to 2.4 mol./l. As can be seen from Fig. 14 and Table IV, it was found that no effect of DMA on the induction period was observed.



[DMA], mol./l.

Fig. 12. Intrinsic viscosity for the substituted styrene polymers (30°C, in benzene).



[DMA], mol./l.

Fig. 13. Decomposition rate of ABIN in the presence of monomer and DMA at 50°C (in benzene).

$[M]=0.253$ mol./l.

$[ABIN]=9.84\times10^{-2}$ mol./l.

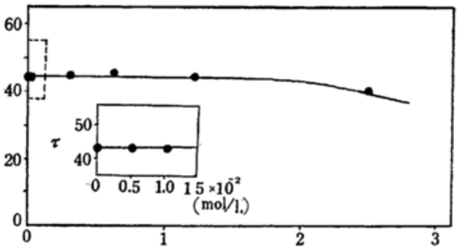
△ In the absence of monomer

▲ In the presence of monomer

TABLE IV. RELATIONSHIP BETWEEN INDUCTION PERIOD AND THE AMOUNT OF DMA AT 60°C (IN DMF)

$[ABIN]=1.00\times10^{-1}$ mol./l., $[M]=2.17$ mol./l., $[FeCl_3\cdot6H_2O]=3.5\times10^{-3}$ mol./l.

| Amount of DMA mol./l. | Induction period min. |
|---|---|
| $5\times10^{-3}$ | 43.0 |
| $1\times10^{-2}$ | 43.0 |
| $3\times10^{-1}$ | 44.0 |
| $6\times10^{-1}$ | 44.5 |
| 1.2 | 43.5 |
| 2.4 | 39.0 |
| 0 | 43.0 |



[DMA], mol./l.

Fig. 14. Relationship between induction period and the amount of DMA in the polymerization of *p*-methylstyrene at 60°C (in DMF). $[M]=2.17$ mol./l., $[ABIN]=1.00\times10^{-1}$ mol./l., $[FeCl_3\cdot6H_2O]=3.5\times10^{-3}$ mol./l.

(*b*) *In Benzene, with p-Benzoquinone.*—It could not be completely denied, that DMF reacted with a free radical. Therefore, it was considered that DMF was not the most suitable solvent. Thus, in the following runs, benzene was chosen as solvent. However, ferric chloride did not dissolve in benzene. We have studied finally the polymerization of *p*-methylstyrene in the presence of *p*-benzoquinone and DMA in benzene and studied the effect of DMA on the induction period, on the rate of polymerization after induction period and on the intrinsic viscosity of polymers. As can be seen from Fig. 15 and Table V, the induction period was decreased with the amount of DMA, which was somewhat different from the result obtained when the ferric chloride-DMA system was used. The rate of polymerization after the induction period had a tendency to increase, while the intrinsic viscosities decreased with DMA.

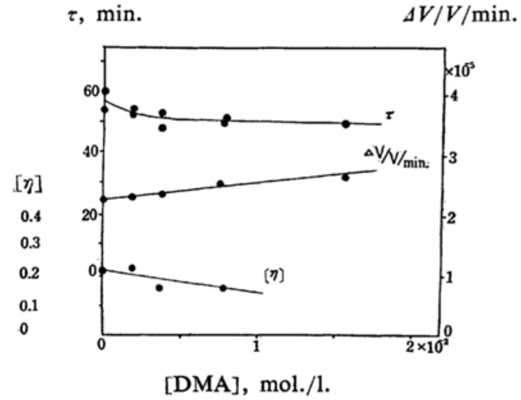


Fig. 15. Relationship of the amount of DMA with induction period, with over-all rate after induction period, and with intrinsic viscosity in the polymerization of *p*-methylstyrene at 60°C (in benzene). $[M]=2.17$ mol./l., $[ABIN]=7.05\times10^{-2}$mol./l., [*p*-Benzoquinone] $=1.06\times10^{-3}$ mol./l.

TABLE V. INDUCTION PERIOD, AND OVER-ALL POLYMERIZATION RATE AFTER INDUCTION PERIOD IN THE POLYMERIZATION OF *p*-METHYLSTYRENE IN THE PRESENCE OF DMA AT 60°C (IN BENZENE)

| DMA mol./l. | Induction period min. | Volume conversion $\Delta V/V$/min. | Rate$\times10^5$ mol./l./sec. |
|---|---|---|---|
| 0 | 56.0 | — | — |
| $2\times10^{-3}$ | 54.0 | — | — |
| $4\times10^{-3}$ | 49.0 | — | — |
| $8\times10^{-3}$ | 52.0 | — | — |
| 0 | 60.5 | 2.24 | 1.69 |
| $1.8\times10^{-3}$ | 53.5 | 2.27 | 1.71 |
| $3.8\times10^{-3}$ | 54.0 | 2.27 | 1.71 |
| $7.8\times10^{-3}$ | 51.5 | 2.43 | 1.82 |
| $15.6\times10^{-3}$ | 49.5 | 2.60 | 1.95 |

Determination of the individual rate constants in the polymerization of *p*-methylstyrene is in progress using the sector method. The results will be reported in near future.

## Summary

1. Solution polymerizations of styrene, *p*-methyl-, *p*-ethyl-, *p*-*tert*-butyl-, *m*-methyl-, 2, 4-dimethyl-, 2, 5-dimethyl- and 3, 4-dimethylstyrene were carried out at 50 and 70°C by ABIN in benzene, and the rates of polymerization and [η]'s of the polymers were determined. For 3, 4-dimethylstyrene, the same equation as for styrene was obtained:

$$R_0=k\,[M]\,[ABIN]^{1/2}$$

2. Rate constants of initiation of the polymerizations of styrene and *p*-methylstyrene were determined, according to the $FeCl_3$-method as follows:

$$k_1=0.67\times10^{-5}\ (\mathrm{sec}^{-1})\quad (\text{for } p\text{-methylstyrene})$$

$$k_1=0.76\times10^{-5}\ (\mathrm{sec}^{-1})\quad (\text{for styrene})$$

3. Polymerizations of styrene and *p*-methylstyrene were carried out at 70°C by the $Bz_2O_2$-DMA system, and the same equation as styrene was derived for *p*-methylstyrene as follows:

$$R_0=k'\,[Bz_2O_2]^{1/2}\{DMA\}^{1/2}$$

4. Polymerizations of styrene, *p*-methyl-, and dimethylstyrenes were carried out at 50 and 70°C by ABIN-DMA system, and the results for the rate of polymerization and the value of [η] were discussed. A correction was made for the results previously obtained.

5. The effect of DMA on the induction period for the polymerization of *p*-methylstyrene was studied at 60°C. In the case of polymerization with $FeCl_3$ in DMF, no effect of DMA on the induction period was observed, while in the case of that with *p*-benzoquinone in benzene, the induction period was decreased with the amount of DMA.

*Faculty of Engineering*
*Osaka City University*
*Kita-ku, Osaka*
*(M. I. & K. T.)*

*Onoda Cement Co. Ltd.*
*Onoda Factory*
*Onoda-shi, Yamaguchi-ken*
*(Y. I.)*