Radiation-induced Polymerization of α-Methylstyrene[*]

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It has been considered till recently that α-methylstyrene (αMS) is not easily polymerizable, i. e. it can not be polymerized by radical initiators, but can be polymerized by cationic[1] or anionic initiators[2] at low temperatures. Therefore, it will be interesting to study the effect of ionizing radiation on αMS, i. e. to investigate the possibility of radiation-induced polymerization*, and to make clear the kind of mechanism, if it can be polymerized. After the research was advanced to some extent[3], it was found, however, that the first problem was answered affirmatively, and also that the polymerization seemed to proceed by a radical mechanism[3b]. Therefore, a new problem was encountered. This was why αMS did not polymerize by use of such a radical initiator as benzoyl peroxide. It is the object of the present paper to investigate the three problems mentioned above.

Experimental

Materials. — α-Methylstyrene of guaranteed grade of Tokyo Kasei Kogyo K. K. was used. It was treated with aqueous solutions of 20% NaOH and of 20% $NaHSO_3$ successively. Then, it was dried with dehydrated calcium chloride and also with potassium hydroxide freshly fused, and vacuum-distilled under nitrogen atmosphere. The sample thus purified was stored in a closed vessel. According to gas chromatographic analysis, the water content in it was negligible ($<0.002\%$). Naphthalene of chemical pure grade was used after repeated recrystallization. Other reagents (carbon tetrachloride, benzoquinone, cyclohexane and nitrobenzene) were of guaranteed grade and were used without further purification.

Procedure of Irradiation.—Two γ-ray irradiation sources of Co-60 were used; one was 350 curie source, while the other 1000 curie source**. Samples will therefore be classified in series B or J, according as the irradiation was carried out at the former or at the latter. In order to avoid direct contact with air and water, αMS was always vacuum-distilled (10^{-4} mmHg) into irradiation tubes. However, as it is known that the presence of oxygen and water brings about an undesirable effect on polymerization, one of the samples (J 9) was distilled over an evaporated film of sodium in advance of irradiation for the sake of comparison. The irradiation tube was made of hard glass and could contain 5~16 g. of αMS. Being required by the discussion on the mechanism of polymerization, ultraviolet irradiation was also attempted by utilizing the sunlight in summer, enclosing the sample in a quartz ampoule.

Treatment of the Irradiated Samples. — The irradiated sample was taken out by opening the tube and was poured into methanol, which was five times as much as the sample in volume. White polymers thus precipitated were filtered, washed with methanol, and dried in vacuo at room temperature until the weight became constant. The molecular weight of the polymer was determined with the osmotic pressure method or the viscosity method. In the latter method,

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[*] When the authors' preliminary research was announced at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958, they could not find any research of this kind in literature.

[1] D. J. Worsfold and S. Bywater, *J. Am. Chem. Soc.*, **79**, 4917 (1957); S. Okamura et al., Presented at the 7th Annual Meeting of the Society of Highpolymer Science of Japan, Tokyo, May, 1958.

[2] G. C. Jones et al., *Ind. Eng. Chem.*, **48**, 2123 (1956).

[3] (a) K. Hirota, K. Kuwata and K. Makino, *Isotopes and Radiation* (*Tokyo*), **1**, 104 (1959). (b) Presented at the Symposium of Radiation Chemistry, Tokyo, Nov., 1958.

** The 350 curie source is installed at Institute for Microbial Diseases of Osaka Univ., and the 1000 curie source at Osaka Laboratory of Japanese Association for Radiation Research on Polymers. The authors express sincere thanks to Drs. T. Noguchi, H. Hayashi and M. Hatada for the help in irradiation procedure.

TABLE I. CO-GAMMA IRRADIATION. TOTAL DOSE: 6×10^6 r

	Additives		Conversion %	$\overline{M}_n$	m. p. of polymers °C
	Compounds	Mole fraction %			
B-1	None	—	4.4	3.8×10^4	220
B-2	Carbon tetrachloride	18.1	8.2	1.4×10^4	185
B-3	Naphthalene	7.9	0.27	6.0×10^4	195
B-4	Oxygen	air-saturated	0[a]	—	—
B-5	*p*-Benzoquinone[b]	0.41	0	—	—

a) However, when the irradiated sample was poured into methanol, a turbid solution was obtained.

b) Total dose of 7.3×10^6 r; dose rate of 5.3×10^4 r/hr.

the following viscosity formula was used[4].

$$[\eta]=3.50\times10^{-5}(\overline{M}_n) \qquad (1)$$

$\overline{M}_n$: average molecular weight

As the molecular weight of the polymer was low in case of photopolymerization, the cryoscopic method was adopted.

Results

Preliminary Experiments. — As shown in Table I, it has been found that αMS polymerizes with total dose of 6×10^6 r, dose rate being 1.2×10^5 r/hr. The polymer obtained is of fairly high molecular weight. Its melting point is also high if compared with the polymer obtained by photo-polymerization[5]. Moreover, it has been found that polymerization was sensitized by the addition of carbon tetrachloride, but was retarded by the presence of naphthalene and perfectly inhibited by oxygen and benzophenone. Such effects of additives seem to suggest that the polymerization proceeds by the radical initiation of γ-rays.

Effect of Total Dose. — In Table II, the effect of total dose on conversion and intrinsic viscosity is shown by keeping the dose rate constant. Conversion of polymerization increases linearly with the total dose after an induction period (ca. 5 hr.). On the other hand, judging from the relation between the intrinsic viscosity and total dose, the molecular weight of the polymer seems to be constant.

TABLE II. EFFECTS OF TOTAL DOSE ON CONVERSION AND INTRINSIC VISCOSITY

Run	Dose rate r/hr.	Dose r	Conversion, %	[η]
J 6-1	1.56×10^5	5.8×10^6	28.2	0.110
J 6-2	1.56×10^5	4.34×10^6	21.4	0.116
J 6-3	1.56×10^5	1.74×10^6	4.4	0.113

Effect of Dose Rate. — In Table III, the effect of dose rate on conversion is shown. In order to investigate the effect of dose rate on velocity of polymerization in detail, the conversion rate V_p is plotted against dose rate I in Fig. 1. It is clear that the velocity of polymerization of αMS is first order of I on the assumption that it is proportional to the rate of conversion. For the sake of comparison, the result of

TABLE III. EFFECT OF DOSE RATE ON CONVERSION

Run	Dose rate r/hr.	Dose r	Conversion, %	[η]
J 1-2	2.6×10^4	3.5×10^6	8.6	0.105
J 1-3	1.4×10^4	1.8×10^6	4.6	0.106
J 1-4	8.8×10^3	1.2×10^6	7.5	0.115
J 7-3	1.6×10^5	3.3×10^6	20.5	0.118
J 7-4	1.6×10^5	7.6×10^6	19.1	0.116

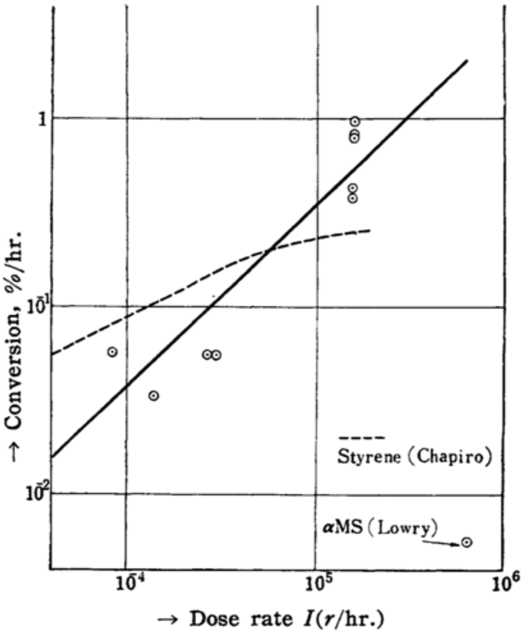

Fig. 1. Conversion per hour vs. dose rate.

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[4] C. P. Brown and A. R. Mathieson, *J. Chem. Soc.*, 1958, 3445.

[5] C. E. Schildknecht, *Ind. Eng. Chem.*, **50**, 107 (1958).

Chapiro⁽⁶⁾ on styrene is plotted as a broken line, by which it is shown that the order of polymerization of styrene is one half if the dose rate is small. The same order is often reported in the γ-ray-induced polymerization. Therefore, it may be noteworthy that an exceptional order of reaction has been obtained in the present research. This problem will be taken up again in the part of discussion in relation to the mechanism of polymerization. However, the polymerization velocity seems of the same degree in both monomers, while the recent data of Lowry⁽⁷⁾ on αMS is very small as compared with that of the present research. The intrinsic viscosity [η] is shown to be independent of dose, i. e. 0.110, being similar to that of Lowry. The molecular weight of poly-α-methylstyrene is smaller than that of polystyrene by Chapiro.

Effect of Solvent. — As mentioned in the part of the preliminary experiment, effect of several solvents on the reaction rate was already investigated. However, an additional experiment was carried out in other solvents, in order to make the mechanism of polymerization clearer. To meet this requirement, nitrobenzene and cyclohexane were selected as the solvents to be studied, each dielectric constant being 36 and 1.9, respectively. If the reaction proceeds by an anionic or cationic mechanism, αMS will polymerize very rapidly in a solvent of high dielectric constant⁽⁸⁾ such as nitrobenzene, while if the reaction proceeds by a radical mechanism, the polymerization must be inhibited by the solvent on the contrary. According to the result shown in Table IV, nitrobenzene behaves as an inhibitor, while cyclohexane behaves as a simple diluent. The result, in addition to the preliminary experiments, confirms the conclusion that the reaction proceeds by a radical mechanism.

Effect of Temperatures.—Hitherto, radical polymerization of αMS has been attempted at higher temperatures, but the result was found always negative. Though the data here obtained seem to contradict the above results, the situation may be brought about by the condition that the irradiation was carried out at ordinary temperature. Such being the case, the effect of temperature on radiation-induced polymerization was investigated over the range 9∼72°C, the result being summarized in Table V.

As shown by the value of intrinsic

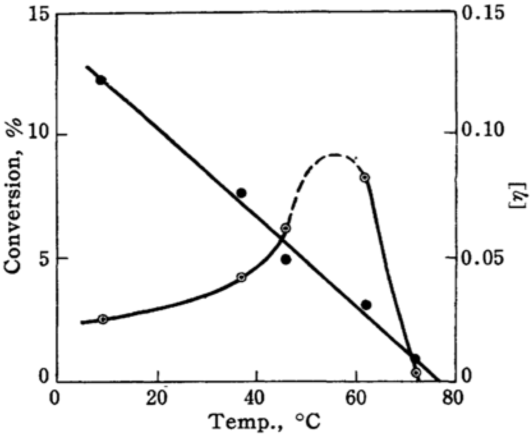

Fig. 2. Conversion and intrinsic viscosity vs. temperature.

⊙: Conversion, %
●: Intrinsic viscosity, [η]

TABLE IV. EFFECT OF SOLVENT ON THE RATE OF POLYMERIZATION

Run	Additive compounds	Mol. %	Dose rate r/hr.	Dose r	Conversion %	[η]
J 7-1	Cyclohexane	29.0	1.6×10^5	3.4×10^6	13.2	0.101
J 7-2	Nitrobenzene	37.3	1.6 〃	3.4 〃	0	—

TABLE V. EFFECT OF TEMPERATURE ON CONVERSION etc.

Run	Temp. °C	Dose rate r/hr.	Dose r	Conversion %	[η]	$\overline{\text{DP}}$
J 9-1	9	3.1×10^4	1.2×10^6	2.5	0.123	29.6
J 9-2	37	〃	〃	4.2	0.076	18.6
J 9-3	46	〃	〃	6.1	0.049	11.9
J 9-4	62	〃	〃	8.2	0.030	7.3
J 9-5	72	〃	〃	0.33	0.009	2.2

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6) A. Chapiro and P. Wahl, *Compt. rend.*, **238**, 1803 (1954).

7) G. G. Lowry, *J. Polymer Sci.*, **31**, 187 (1958).

8) D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

viscosity, it seems that the degree of polymerization $\overline{\mathrm{DP}}$ decreases linearly with temperature, and will became practically zero at 77°C. This tendency may be clearly shown by Fig. 2 where conversion and $[\eta]$ are plotted against temperature. It may be estimated that the degree of polymerization at 77°C will be less than five, because telomers of such low polymerization degree are soluble in methanol. On the other hand, the amount of conversion has a maximum and will be zero at 72°C (cf. Fig. 2). The phenomenon here observed must be ascribed to the peculiar property of αMS, and will serve as a key to the mechanism of polymerization***.

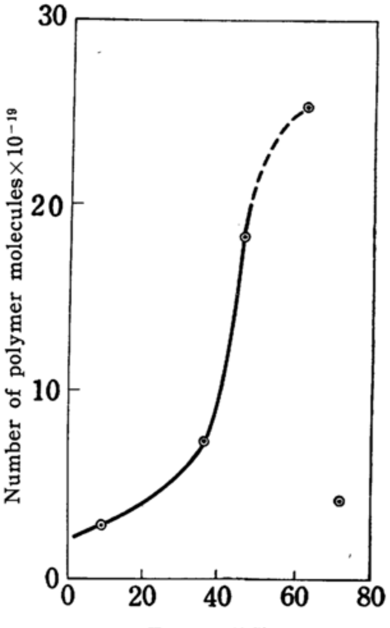

Fig. 3. The effect of temperature on the number of polymer molecules.

Assuming that Eq. 1 can be applied on the poly-αMS, as far as the relative value of average molecular weight is concerned, the number of polymer (n) produced at each temperature was calculated, and it was found that n increases very rapidly if temperature decreases as shown in Fig. 3.

Photopolymerizations. — Recently, it was reported that Schildknecht[5] succeeded to polymerize αMS by irradiating it with ultraviolet light, the detail being not described. Therefore, similar research was carried out by use of the sunlight for the sake of confirmation. Polymers of 0.38 g. in weight could be obtained from the starting material of (αMS 15.7 g. + di-*tert*-BPO 4.0 g.). The molecular weight of the polymers was ca. 640 (cryoscopic method).

Discussion

Mechanism of Polymerization.—Considering the effects of additives and solvents on the yield of polymers, it may be reasonable to conclude that the radiation-induced polymerization of αMS proceeds by a radical mechanism, as already mentioned. Polymerizing power of ultraviolet light also supports the mechanism, though telomers obtained are of low molecular weight. In the course of the present research this conclusion has been justified independently by Lowry[7] who could obtain polymers having the molecular weight of 50000 at 0°C by the redox polymerization method.

Thus, the present research seems merely to have added an example of radiation-induced polymerization, but it may be noteworthy to have found that the polymerization of this monomer has a peculiar dependency upon temperature, especially it will practically stop at higher temperatures than ca. 70°C. Now, it may be clear why the attempts to polymerize αMS did not succeed hitherto. In these attempts the temperatures to supply radical initiators to the sample were too high to obtain polymers. The phenomenon of this kind called "ceiling temperature" was already pointed out experimentally by Snow and Frey[9] in the copolymerization of olefins and sulfur dioxide. Later Dainton and Ivin[10] explained it by assuming the equilibrium

$$\mathrm{M}_j + \mathrm{M} \rightleftarrows \mathrm{M}_{j+1}$$

and derived the existence of a temperature beyond which the reaction chains will fail to grow. Thermodynamically the ceiling temperature T_c may generally be given by

$$T_c = -\Delta H_p / -\Delta S_p = \frac{\Delta H}{\Delta S^\circ + 2.30\,\boldsymbol{R}\log_{10}[\mathrm{M}]} \tag{2}$$

where ΔH_p and ΔS_p denote, respectively, changes of enthalpy and entropy of polymerization, [M] denotes the concentration

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*** Detailed discussion on the relations of conversion and intrinsic viscosity with temperature will be omitted, because it was published already [K. Makino, G. Meshitsuka, K. Kuwata and K. Hirota, *Isotopes and Radiation* (*Tokyo*), **2**, 322 (1959)].

[9] R. P. Snow and F. E. Frey, *Ind. Eng. Chem.*, **30**, 176 (1938); *J. Am. Chem. Soc.*, **65**, 2417 (1943); cf. F. E. Mathews and H. M. Elder, Brit. Pat., 11,635 (1914).

[10] F. S. Dainton and K. Ivin, *Nature*, **162**, 705 (1948).

of monomer, and S° denotes the quantity referred to monomer in a standard state of pure liquid. Recently McCormic[11] determined T_c of αMS to be 61°C from the polymerization in tetrahydrofuran solution by use of a sodium naphthalene complex as initiator. Though the temperature is slightly lower than that of the present research, the discrepancy can be explained by Eq. 2, if it is considered that the degree of polymerization of the present sample is lower than that of McCormic (cf. the formula[12] giving the relation between $\varDelta H_p$ and average molecular weight $\overline{M}_n$: $-\varDelta H_p = 8.424 + 2194/\overline{M}_n$). It is rather interesting that T_c of such a low temperature is obtained in both experiments, notwithstanding the fact that the active species are different in the course of polymerization. Now, a problem remains why T_c of poly-α-methylstyrene is much lower than that of polystyrene. It may be ascribed to the small values of $-\varDelta H_p$ for this monomer as compared with other monomers: e. g. αMS 9.0, styrene 16.0 and ethylene 22, respectively in kcal./mol. per monomer, in spite of the order of magnitude of its $\varDelta S_p$ comparable to the other monomers[13].

Kinetic Formula of Polymerization. — From the above discussion, it seems to be without ambiguity that radiation-induced polymerization of αMS proceeds by a radical mechanism, but an important experimental result still remains to be unexplained. In the pioneer work of Chapiro[6] on the gamma-ray-induced polymerization of styrene and other monomers, he found that velocity V_p of the polymerization can be expressed by the formula

$$V_p \propto I^{1/2} \qquad (3)$$

where I is the dose rate. The formula is generally accepted to be applicable to all the radiation-induced polymerization. Nevertheless, in the present research as shown in Fig. 1, the velocity derived from the conversion (%) is not proportional to $I^{1/2}$ but rather to I. The above result, though it seems to be exceptional, can be understood by the mechanism in which a degradative chain transfer proceeds more frequently than the chain termination between radicals. Therefore, each step of the elementary processes of the present reaction will be summarized as follows:

Initiation: $\mathrm{M} \xrightarrow{\phi I} \mathrm{R}\cdot$

$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k'_i} \mathrm{M}^*$

Propagation: $\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_p} \mathrm{M}^*_{j+1}$

Depropagation: $\mathrm{M}^*_{j+1} \xrightarrow{k_d} \mathrm{M}^*_j + \mathrm{M}$

Chain transfer to monomer:

$\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_{tr}} \mathrm{M}_j + \mathrm{M}^*$

Degradative chain transfer:

$\mathrm{M}^*_j + \mathrm{M} \xrightarrow{k_t} \mathrm{M}_j + \mathrm{M}$

where M^*_j denotes active polymers of j subunits and ϕ radicals produced per unit I in unit volume of monomers. Applying the steady state treatment to the mechanism mentioned above, the kinetic formula may be derived easily:

$$V_p = (\phi I / k_t)(k_p[\mathrm{M}] - k_d)$$

i. e. V_p is proportional to I.

Summary

It has been shown that (a) α-methylstyrene polymerizes at room temperatures by gamma-ray irradiation; that (b) the reaction proceeds by a radical mechanism, considering from the effect of solvents, additives and ultraviolet light; that (c) ceiling temperature for this monomer is exceptionally low (ca. 70°C) among vinyl monomers, so that it is hard to obtain high polymers by the usual method; that (d) the experimental fact that the velocity of polymerization is proportional to dose rate and not to square root of dose rate can be explained by the assumption that degradative chain transfer occurs more frequently than the termination between active polymers.

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[11] H. W. McCormick, *J. Polymer Sci.*, **25**, 488 (1957).

[12] D. E. Roberts and R. S. Jessup, *J. Res. Natl. Bur. Standards*, **38**, 627 (1947).

[13] C. Walling, "Free Radicals in Solutions", John Wiley & Sons, Inc., New York (1957), p. 213; F. S. Dainton and K. J. Ivin, *Quart. Revs.*, **12**, 61 (1958).