*Steady-state Studies by the ESR Method of the Photopolymerization of Vinyl Acetate and Methyl Methacrylate**

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(Received March 20, 1963)

In the free radical-initiated photopolymerization of vinyl monomers, free radical intermediates paly an important role as chain initiators or chain carriers or both. In the kinetic studies[1] it has already been shown that both the rate and the degree of polymerization are closely related to steady-state concentration of the radical intermediates. It becomes important, therefore, not only to identify the free radical intermediates, but also to determine their concentration in the course of the reaction.

The use of the ESR method in identifying such radical intermediates in nonsteady-state photopolymerization has given us very useful knowledge about the initiating step[1-4], the propagating step[2-4] and the terminating step[3]. The structures of the decomposition products of initiators and those of both initiating and propagating free radicals formed by the reaction of the primary radical fragment of the initiator with monomers have been investigated.

It has now become possible to determine by the ESR method the rates of initiation, propagation, and termination steps on some plausible assumptions and also to determine the steady-state concentration of the radical chain carriers. Therefore, the steady-state study by the ESR method, as abopted by Piette et al.[5] in the photo-dissociation of some alkyl hydroperoxides, should be very effective in a detailed investigation of the kinetic process of the present photopolymerization.

By a comparison of the steady-state concentration determined experimentally with the one derived by a simple steady-state treatment of the polymerization, it will be possible to

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* A preliminary report was presented to the 1st Meeting of ESR (Japan), October, 1962, Osaka.

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[1] Cf. C. H. Bamford et al., "The Kinetics of Vinyl Polymerization by Radical Mechanisms", Butterworths Scientific Publications, London (1958).

[2] D. J. E. Ingram, M. C. R. Symons and M. G. Townsend, *Trans. Faraday Soc.*, **54**, 409 (1958).

[3] K. Hotta and R. S. Anderson, The 4th International Symposium on Free Radical Stabilization, Washington, D. C., 1959.

[4] K. Kuwata and K. Hirota, The 10th Annual Meeting of the Association of Polymer Science of Japan, Tokyo, May, 1961.

[5] L. H. Piette and W. C. Landgraf, *J. Chem. Phys.*, **32**, 1107 (1960).

analyze the kinetic data of polymerization. It is particularly important to reconsider the use of an average rate constant for various polymeric chain carriers of different molecular weights. Therefore, we attempted in the present investigation to apply such a steady-state method to the photopolymerization of vinyl acetate and methyl methacrylate, using hydrogen peroxide as the initiator; a reasonable accordance was found to exist between experiment and theory.

Experimental

Materials.—Commercial vinyl acetate and methyl methacrylate were repeatedly distilled and used. Commercial hydrogen peroxide (ca. 30%) was concentrated by vacuum-distillation up to ca. 90%.

Apparatus and Procedure. — To each monomer was added a small amount of enriched hydrogen peroxide so that the latter concentration became ca. 1 mol.%. The sample thus prepared was poured into a quartz tube in which a capillary tube, charged with diphenyl picryl hydrazil (DPPH) or ultramarine of a known spin concentration so as to serve as an analytical internal standard, has been set coaxially. The sample tube thus set up was repeatedly degassed in vacuo and was then sealed off.

Ultraviolet light from a high pressure mercury lamp (1 kW) was focussed with a quartz lens onto the sample tube, which had been inserted into a resonant cavity of a spectrometer. The spectrometer was a high frequency field modulation type, operated at 455 kc. The resonant cavity was a rectangular H_{102} one of the Ingram type and was dipped in a low temperature bath charged with liquid nitrogen as a coolant. The temperature in the cavity was measured with a thermocouple of copper versus constantan, its accuracy being ± 1°K. The temperature in the cavity was adjusted by controlling the level-height of the coolant. The design of this part of the cavity has already been published[6].

The Determination of Rate and Rate Constant. —Before the polymerization reached a steady state, the growth rate of the initiating radical* was measured at such a low temperature (ca. 100°K) that the recombination could be assumed completely quenched. Then, warming the sample up to the temperature where the radical concentration remained constant, i. e., when the steady-state polymerization was realized, the steady-state concentration of the radical was measured, and the rate of decay was determined at the same temperature by cutting off the irradiation source. The temperatures when the steady-state concentration was attained were 115°K for vinyl acetate and 180°K for methyl methacrylate.

The radical concentration was evaluated by comparing the intensity of the absorption of the radical with that of DPPH in the case of vinyl acetate. However, due to the closeness of g-factors between DPPH and the radicals, the two absorption spectra overlapped each other, thus lowering the accuracy of the concentration determination. In the case of methyl methacrylate, therefore, ultramarine ($g=2.030$) was used instead of DPPH.

Results and Discussion

It is shown by Fig. 1 that the initiating radical increases linearly with time in the case of vinyl acetate, though it is not clear if an induction period exists. Similarly, a linear relation was obtained also in the case of methyl methacrylate, as Fig. 2 shows. Assuming the initiation step of the photopolymerization to be of the zeroth order reaction*, the rate of radical growth can be determined from the slope of the curve in Figs. 1 and 2. Stricktly speaking, the radical concentrations

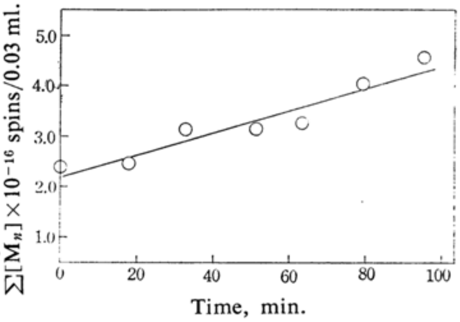

Fig. 1. Radical growth of vinyl acetate against irradiation time at 100°K.

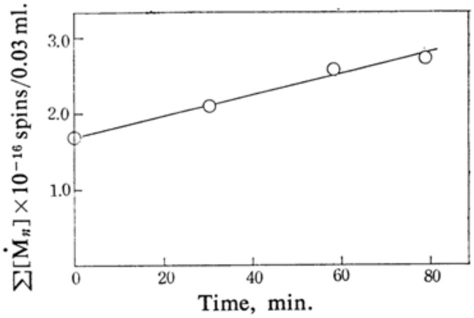

Fig. 2. Radical growth of methyl methacrylate against irradiation at 100°K.

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[6] K. Kuwata and K. Hirota, This Bulletin, **34**, 458 (1961).

* It has been confirmed[4,7] that by irradiating such a system, occluding H_2O_2 at 77°K, an asymmetric signal appears which can be ascribed to the OH or O_2H radical, but if it is kept at 90～100°K, another signal increases its intensity and replaces the first one finally. The initiating radical in the present paper corresponds to the second signal.

[7] K. Kuwata, T. Ichikawa and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 652 (1962).

* This is due to the fact that the production of $\dot{M}$ is very fast compared with that of $\dot{X}$ in Eq. 1.

TABLE I. RATE CONSTANTS AND STEADY-STATE RADICAL CONCENTRATIONS

		Vinyl acetate	Methyl methacrylate
Rate of radical growth, v_i		$1.2_2\times10^{-5}$ molec./l./min.	$8.3_1\times10^{-6}$ molec./l./min.
Rate constant of radical decay, k_t		$2.7_1\times10$ l./molec./min.	$1.8_1\times10$ l./molec./min.
Steady-state radical concn. $\sum_n[\dot{M}_n]$	Obs.	$1.1_1\times10^{-3}$ molec./l.	$7.2_2\times10^{-4}$ molec./l.
	Calcd.	$6.7_1\times10^{-4}$ molec./l.	$6.7_8\times10^{-4}$ molec./l.
	% dev.	−40%	−8%

thus determined include that of the propagating radicals, but since their amount equals that of the initiating radical which disappeared, the above procedure to determine the rate of radical growth may be said to be justified. The procedure was applied to both monomers, and the rates of radical growth, v_i, obtained are described in Table I.

Next, the rate of the termination step was that determined in a similar manner by assuming the radical concentration decays only by way of the termination reaction of the second order. The rate constants of radical decay, k_t, thus obtained are shown in Table I. The decay rate is shown for vinyl acetate by Figs. 3 and 4, where the open circles denote the experimental values, while the curve is the calculated value. These rate constants correspond to the ones defined by the following reaction scheme:

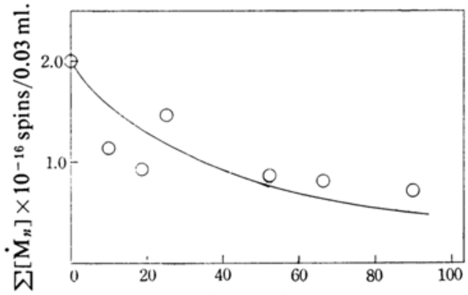

Fig. 3. Radical decay of vinyl acetate at 115°K.

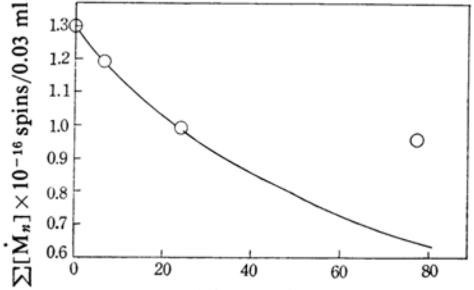

Fig. 4. Radical decay of methyl methacrylate at 180°K.

$$\left.\begin{array}{llll}
\text{Initiator} & \rightsquigarrow & \dot{X} & v_d=\phi I \\
M+\dot{X} & \longrightarrow & \dot{M} & v_i=k_i[M][\dot{X}] \\
\dot{M}_{n-1}+M & \longrightarrow & \dot{M}_n & v_p=k_p[M](\sum[\dot{M}_{n-1}]) \\
\dot{M}_n+\dot{M}_m & \begin{cases}\longrightarrow \\ \longrightarrow\end{cases} & \begin{array}{l} M_{n+m} \\ M_n+M_m \end{array} & \begin{array}{l} v_{tc}=k_{tc}(\sum[\dot{M}_n])^2 \\ v_{td}=k_{td}(\sum[\dot{M}_n])^2 \end{array}
\end{array}\right\} \tag{1}$$

Here, I is the light intensity absorbed by the initiator. k_t is defined by a sum of the rate constant of radical recombination, k_{tc}, and that of the disproportionation, $k_{\ d}$, between two propagating radicals $\dot{M}_n$ and $\dot{M}_m$, as shown by reaction scheme 1, i. e.,

$$k_t = k_{td}+k_{tc} \tag{2}$$

In Table I, the steady-state concentrations of the propagating radicals are compared with those calculated by Eq. 3, which employs a simple kinetic treatment[8]:

$$\sum_n[\dot{M}_n]=(v_i/k_t)^{1/2} \tag{3}$$

which exists among the steady-state concentration, $\sum_n[\dot{M}_n]$, of the propagating radical, the rate of radical growth, v_i, and that of termination, k_t.

Table I tells us that the steady-state radical concentrations calculated by Eq. 3 coincide well with those observed in the cases of both vinyl acetate and methyl methacrylate within a factor of two. This agreement seems to be surprisingly good if one considers that the errors occurred in the determination of the radical concentration and the rate of growth. There remains some doubt about the oversimplifications which were worked out in the simple kinetic treatment. In the calculation, only one decay constant is used as an average value for all the polymer radicals of different molecular weights. However, the observed decay curve corresponds to the one superposed by those of individual polymer radicals of different chain lengths. Therefore, the rate constant of radical decay determined on the assumption of simple second order kinetics

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[8] Cf. Ref. 1, p. 14; J. Laidler, "Chemical Kinetics", McGraw Hill Book Co., Inc., New York (1950), pp. 345—364.

ought not to be used over a wider range of the progress of reaction. Actually, the calculated curve of MMA polymerization (Fig. 4) deviates gradually from the observed values as the polymerization proceeds, i. e., as the chain length of the polymer radical becomes larger. This is probably due to the fact that the reaction rate decreases with the chain length of the polymerizing radicals. A similar tendency seems to occur in the case of VAc as well (Fig. 3), though it cannot be observed so clearly.

There are some modifications of the treatment regarding the direction which will give a more exact feature concerning the radical decay in the case of radical polymerization[9]. However, it can be shown as above that the simple kinetic treatment retains its usefulness in such a limited case of the liquid state photopolymerization at a low temperature as in the present research. One of the reasons why such an accordance was realized seems to be because the error in the determination of the decay rate was canceled out, together with the errors in the determination of the growth rate.

Summary

It has been attempted, by the ESR technique, to study the steady-state photopolymerization of vinyl acetate and methyl methacrylate, using hydrogen peroxide as the initiating substance. The observed steady-state radical concentration has been found to coincide within a factor of two with the calculated value, Eq. 3, derived under the assumption of a simple kinetic treatment. Although, it has been shown that the calculated decay curve deviates from the observed curve in the later period of decay, especially in the case of methyl methacrylate; such a discrepancy seems to be explainable if the reaction rate decreases with the chain length of the polymerizing radicals.

A part of the expense of this research has been defrayed by a special grant given us by the Ministry of Education to which our thanks are due.

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[9] G. Gee and H. W. Melville, *Trans. Faraday Soc.*, **40**, 240 (1944).