A Thermistor Method for the Determination of Velocity Coefficients of Vinyl Polymerization. IV

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Introduction

In the Previous paper[1] the variation of the ratio of velocity constants of propagation and termination, k_p/k_t, was studied with use of a thermistor method against the conversion in vinyl acetate polymerization. In that study, however, each value of k_p and k_t could not be obtained. The author wishes to report, in this paper, the determination of the values of k_p and k_t through the study of the decomposition velocity of the sensitizer 1, 1'-azo-biscyclohexanecarbonitrile, under the same conditions.

Theoretical

Polymerization velocity $-\mathrm{d}M/\mathrm{d}t$ of vinyl acetate, as is well known, can be given as follows[2], provided that the concentration of activated molecule is constant and that the chain is long enough for the initiation velocity against the propagation to be ignored.

$$-\mathrm{d}M/\mathrm{d}t=k_p(V_{init.}/k_t)^{1/2}M \qquad (1)$$

where $V_{init.}$ represents the velocity of initiation and M the concentration of the monomer. Therefore, fractional velocity V can be given by

$$V=-(1/M)\mathrm{d}M/\mathrm{d}t=k_p(V_{init.}/k_t)^{1/2} \qquad (2)$$

V and k_p/k_t are known, as reported in the previous paper, hence k_p can be calculated by the following equation when $V_{init.}$ is determined.

$$k_p=V^2\times(k_t/k_p)\times(1/V_{init.}) \qquad (3)$$

As to the mechanism of photosensitized polymerization by 1, 1'-azo-biscyclohexanecarbonitrile, it is considered probable that sensitizer S is decomposed by photon $h\nu$ and two activated products or radicals R^* are formed from a molecule of the sensitizer,

$$S+h\nu\rightarrow 2R^* \qquad (4)$$

and this radical further activates the monomer M

$$R^*+M\rightarrow R+M^* \qquad (5)$$

If the following equation is taken in this mechanism, as Matheson et al.[3] assumed in the styrene polymerization with use of 2, 2'-azo-bisisobutyronitrile,

$$V_{init.}=2V_s \qquad (6)$$

then equation (3) can be written as follows

$$k_p=V^2\times[2(k_p/k_t)V_s]^{-1} \qquad (7)$$

When V and k_p/k_t values obtained in the previous paper and V_s which can be measured, are applied to the above equation (7), k_p and k_t values can be obtained.

Results

Experimental apparatus and purification of samples were the same as described before[1] and the measurement was carried out at 20°C. As mentioned in the previous paper, 1, 1'-azo-biscyclohexanecarbonitrile shows a big absorption band at ca. 3500 Å. Beer's law could be applied for the optical density at certain wave lengths and concentrations of the sensitizer and this relation at 3660 Å is shown in Fig. 1. D was

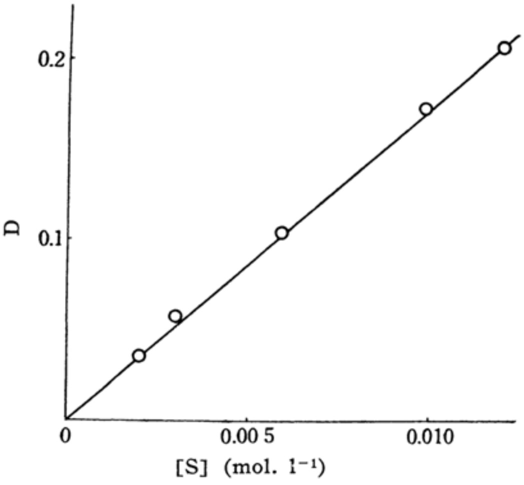

Fig. 1. Variation of the optical density with concentration of 1, 1'-azo-biscyclohexanecarbonitrile.

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[1] H. Miyama, This Bulletin, **29**, 711, 715, 720 (1956).

[2] C. E. H. Bawn, "Chemistry of High Polymers," London (1948), p. 68.

[3] M. S. Matheson, E. E. Auer, E. B. Bevilacquer and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).

measured by use of Hitachi Spectrophotometer EPB-U in vinyl acetate and the thickness of the cell was 1 cm. Thus the decomposition velocity of the sensitizer could be determined from the optical density which, in turn, showed the concentration during the polymerization. A relation between decomposition velocity of sensitizer in vinyl acetate and initial concentration when intensity of illumination is constant, is shown in Fig. 2 and that between intensity of light and decomposition velocity when concentration of sensitizer is constant (0.012 mol./l.), in Fig. 3. In Figs. 2 and 3, decomposition velocity $-\Delta D/\Delta t$ is a decrease of the optical density of sensitizer after one hour irradiation.

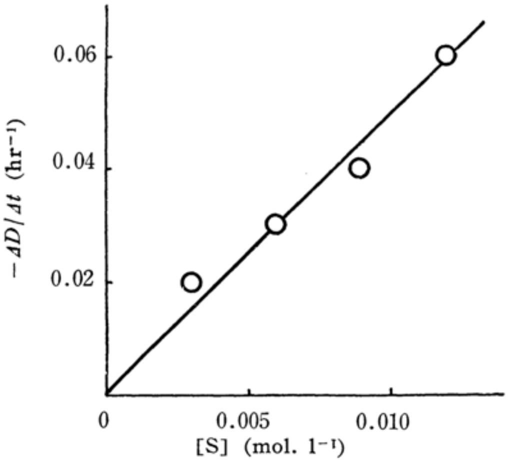

Fig. 2. The relation between decomposition velocity and concentration of 1, 1'-azo-biscyclohexanecarbonitrile.

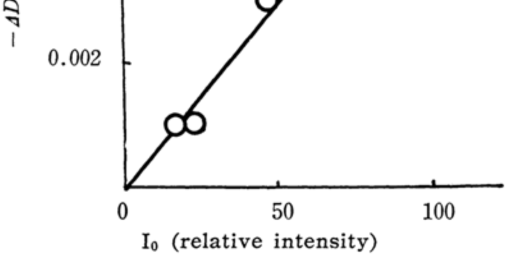

Fig. 3. The relation betweeen decomposition velocity of 1, 1'-azo-biscyclohexanecarbonitrile and intensity of illumination.

The author obtained the results shown in Fig. 4 on determination of variation of the optical density of sensitizer with time when continuous irradiation was applied under the same conditions as described for the vinyl acetate polymerization, which was photosensitized, in the third paper of this series. The initial concentration of the sensitizer was 0.003 mol./l., 0.006 mol./l. or 0.012 mol./l.

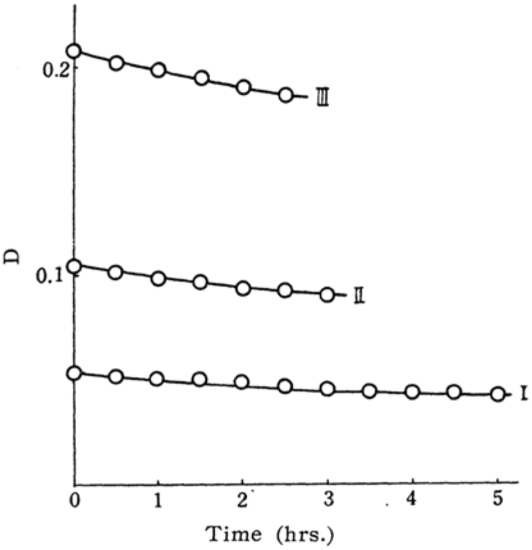

Fig. 4. Variation of the optical density of 1, 1'-azo-biscyclohexanecarbonitrile with time.
I, 0.003 mol. l^{-1}; II, 0.006 mol. l^{-1}; III, 0.012 mol. l^{-1}.

From the results shown in Figs. 2 and 3, it is clear that the decomposition velocity of sensitizer V_s is proportional to the concentration of sensitizer $[S]$ and the intensity of light I_0. Absorbed light $I_{abs.}$ is shown by the next formula

$$I_{abs.}=I_0(1-e^{-\alpha[S]l}) \qquad (8)$$

where α is molar absorption coefficient of sensitizer (40.1) and l is the thickness of the reaction vessel (8 mm.). The value of $\alpha[S]l$ is 0.096 at the concentration of sensitizer 0.003 mol./l., hence the next approximation is materialized within the error

$$I_{abs.}\doteqdot I_0\alpha l[S] \qquad (9)$$

thus V_s is obtainable from the next equation

$$V_s=-\mathrm{d}[S]/\mathrm{d}t=kI_{abs.}=kI_0\alpha l[S] \qquad (10)$$

Since $K=kI_0\alpha l$ can be considered constant during the measurement in Fig. 4, next equation is obtained by integrating equation (10)

$$2.303 \log [S]_0/[S] = Kt \qquad (11)$$

thus there should be a linear relation between $\log [S]_0/[S]$ and time t, where $[S]_0$ is the initial concentration of sensitizer. This relation can be shown in Fig. 5, in which $\log D_0/D$ is used instead of $\log [S]_0/[S]$ the former being obtained from the result of Fig. 4. The equation (11) is apparently materialized. The constant K obtained from the tangent of this line is $4.66\times10^{-2}\text{hr}^{-1}$. The concentration of sensitizer in the case of determining k_p/k_t of vinyl acetate polymerization was 0.003 mol./l. in the third paper of this series and thus V_s at arbitrary time can be calculated by the next equation when the above value of K is used.

$$V_s = K[S]_0 e^{-Kt} \qquad (12)$$

The above equation is obtained by eliminating $[S]$ from equations (10) and (11).

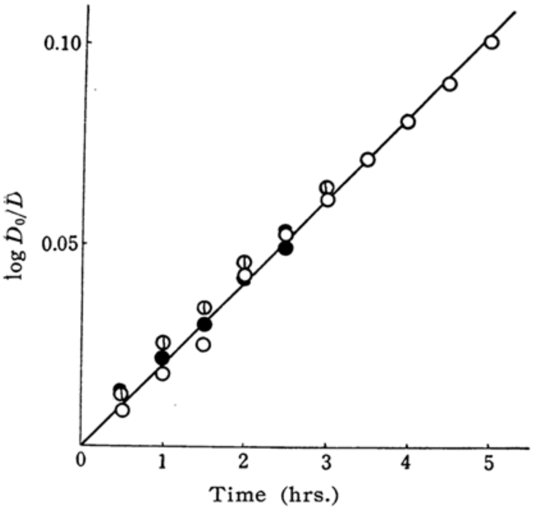

Fig. 5. Variation of $\log D_0/D$ with time. ○, 0.003 mol. 1^{-1}; ⦶, 0.006 mol. 1^{-1}; ●, 0.012 mol. 1^{-1}.

TABLE I
VALUES OF CONVERSION, V_s, V AND k_p/k_t AT VARIOUS IRRADIATION PERIODS

Time (hr.)	Conversion (%)	V_s (mol. 1^{-1}. s^{-1})	V (s^{-1})	k_p/k_t
0	0	3.87×10^{-8}	2.16×10^{-5}	1.08×10^{-5}
3	28.15	3.36×10^{-8}	2.98×10^{-5}	2.82×10^{-5}
4	39	3.21×10^{-8}	3.06×10^{-5}	4.13×10^{-5}
5	49.80	3.06×10^{-8}	2.95×10^{-5}	9.55×10^{-5}
6	59.30	2.92×10^{-8}	2.34×10^{-5}	32.3×10^{-5}
7	66.40	2.79×10^{-8}	1.61×10^{-5}	48.6×10^{-5}
8	71.10	2.66×10^{-8}	1.00×10^{-5}	64.2×10^{-5}

The values of V_s, V and k_p/k_t, the latter two of which were obtained in the previous paper, at various times are shown in Table I. The values of k_p and k_t, which were calculated by using equation (7) and the above values in Table I, were tabulated in Table II.

TABLE II
VALUES OF k_p AND k_t AT VAROUS CONVERSIONS

Conversion (%)	k_p	$k_t\times10^{-5}$
0	559	518
28.15	484	172
39	354	85.8
49.80	149	15.6
59.30	29.0	0.90
66.40	9.52	0.20
71.10	2.93	0.05

Discussion

Since k_p and k_t values at the early stage of polymerization were obtained by many other workers, the results are shown in Table III for comparison.

TABLE III
THE VALUES OF k_p AND k_t OF VINYL ACETATE POLYMERIZATION AT 15°C[4]

Reference	k_p	k_t
This work	505	5.15×10^7
Bengough and Melville (1955)	574	2.4×10^7
Bartlett et al. (1950)	800	5.7×10^7
Dixon-Lewis (1949)	4180	2.2×10^8
Matheson et al. (1949)	630	4.5×10^7
Burnett and Melville (1947)	720	4.5×10^8

The value of k_p obtained by the author is a little lower than the others and the k_t is about the same. The methods of determination and calculation, however, are different, therefore this amount of deviation seems to be reasonable. It is doubtful whether the theory which is used for the explanation of the results at the early stage of polymerization is applicable for the later stage, but, from the results of Table II, it can be qualitatively said that k_p is considered to be constant up to 40% conversion while k_t gradually decreases and thus the polymerization velocity increases up to 40% conversion. As the conversion exceeds 40%, k_p decreases to lower the velocity of polymerization. It is possible to consider that the velocity probably depends on the reactivity of

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[4] The author corrected the values at 15°C assuming that E_p=3.7 kcal./mole and E_t=0. The other values have been summarized in a literature (W. I. Bengough & H. W. Melville, *Proc. Roy. Soc.*, **230**, 429 (1955)) and corrected assuming that E_p=4.2 kcal./mole and E_t=0.

radicals or radical and monomer at the early stage of polymerization and on diffusion at the later stage, because, in the latter, viscosity increases to make diffusion very slow. From Table II, the effect of diffusion first appears in the termination process

$$M_n^* + M_m^* \rightarrow M_{n+m} \qquad (13)$$

On the other hand the propagation process shown by the next formulas is not so greatly affected by viscosity and only in conversion of more than 40% diffusion comes to have some effect on the velocity.

$$\left.\begin{array}{l} M_1^* + M \rightarrow M_2^* \\ M_2^* + M \rightarrow M_3^* \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ M^*_{n-1} + M \rightarrow M_n^* \end{array}\right\} \qquad (14)$$

This difference may be explained by the difference of mobility of monomer M and radical M_n^* in viscous solution.

Summary

Concentration change of sensitizer during vinyl acetate polymerization photosensitized by 1, 1'-azo-biscyclohexanecarbonitrile was measured with use of a spectrophotometer and the initiation velocity of polymerization was determined. Values of k_p and k_t at various degree of conversion were calculated from this value and the results of the previous paper. From this experiment, it was concluded that k_p was nearly constant up to 40% conversion and as the conversion exceeded 40%, it decreased, while k_t gradually decresed with the increase of the conversion.

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