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

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Introduction

In the 1st paper⁽¹⁾ of this series the author described a thermistor method for the measurement of the rate of vinyl polymerization and good results were obtained compared with the thermocouple method. According to this measurement, the k_p/k_t value of styrene at 30°C, when 2, 2′-azobispropare used as photosensitizer, was 2.02×10^{-6}. However, this sensitizer was not very effective and the rate of polymerization was very slow especially when irradiation was weak. Thus the analysis of the curve of oscillograph was very difficult.

In this paper, α-azobisisobutyronitrile which is a very effective photosensitizer for vinyl polymerization is used. The measurement was fulfilled on styrene, vinyl acetate and methyl methacrylate at 30°C, 35°C and 40°C. And, from the value of k_p/k_t at various temperatures, the activation energy difference E_p-E_t of these monomers was obtained, where E_p was the activation energy of propagation process and E_t was the activation energy of termination process.

Experimental

The experimental apparatus and procedure are the same as those described in the previous paper.

The monomers were prepaped according to Fujii's meteod⁽²⁾ as described in the first paper.

α-Azobisisobutyronitrile was a commercial product (Kanto Chemical Co. Inc.) and used after three recrystallizations from carbon tetrachloride.

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1) H. Miyama, This Bulletin, **29**, 711 (1956).

2) S. Fujii, This Bulletin, **27**, 216 (1954); **27**, 238 (1954).

In Fig. 1, its ultraviolet absorption spectrum is shown.

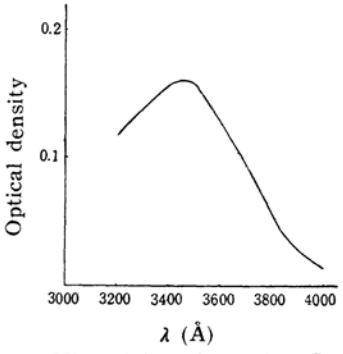

Fig. 1. Ultraviolet absorption Spectrum of α-azo-bisisobutyronitrile α-azolisiso-butyronctrile at the concentration of 0.0122 mol./l. in CCl_4.

Results

Styrene.—As shown in Fig. 6 of the first paper, the amplitude of oscillograph corresponding to the temperature difference of 0.001°C is not the same at different temperatures. These values at 30°C, 35°C and 40°C obtained from that figure are as follows.

$$\begin{aligned} 1\ \text{mm.} &= 3.00\times10^{-4}\,^{\circ}\text{C at } 30^{\circ}\text{C} \\ 1\ \text{mm.} &= 2.94\times10^{-4}\,^{\circ}\text{C at } 35^{\circ}\text{C} \\ 1\ \text{mm.} &= 2.88\times10^{-4}\,^{\circ}\text{C at } 40^{\circ}\text{C} \end{aligned} \tag{1}$$

Although heat capacity and heat of polymerization of styrene depend on the temperature, the values at 30°C are used, since the error caused by these values is small compared with the experimental error[3]. From the relation (1) and constants of styrene at 30°C, the following relations between amplitude-change per second and fractional rate of polymerization can be obtained.

$$\begin{aligned} 1\ \text{mm./sec.} &= 0.785\times10^{-6}/\text{sec. at } 30^{\circ}\text{C} \\ 1\ \text{mm./sec.} &= 0.770\times10^{-6}/\text{sec. at } 35^{\circ}\text{C} \\ 1\ \text{mm./sec.} &= 0.755\times10^{-6}/\text{sec. at } 40^{\circ}\text{C} \end{aligned} \tag{2}$$

In Fig. 2 a recorder trace of a typical experiment is shown, in which A and B are respectively the marks of lighting on and lighting off. This measurement was carried out at 30°C by using 0.0122 mol./l. of α-azoisobutyronitrile as a photosensitizer and other conditions were the same as those described for Fig. 5 of the first paper. From Fig. 5 of the first paper and Fig. 2 it can be shown that the rate of polymerization photosensitized by 0.0122 mol./l. of α-azoisobutyronitrile is sixfold larger than the rate of polymerization photosensitized by 0.0202 mol./l. of 2, 2′-azobispropane and thus the analysis of the curve can be more correctly preformed.

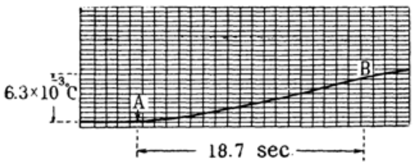

Fig. 2. A reconder trace of a typical experiment for the polymerization of styrene sensitized by α-azobisisobutyronitrile at 30°C.

By varying the intensity of light, the relation between log *I* and log *V* at 30°C, 35°C and 40°C were obtained as shown in Fig. 3. From this

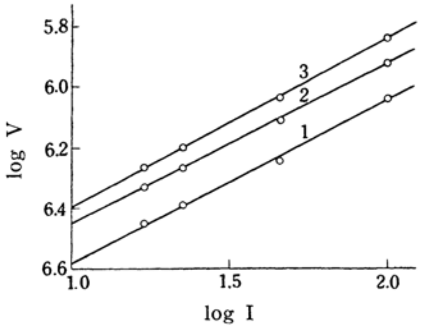

Fig. 3. Variation of the rate with the light intensity for styrene; Curve 1, at 30°C: Curve 2, at 35°C; Curve 3, af 40°C.

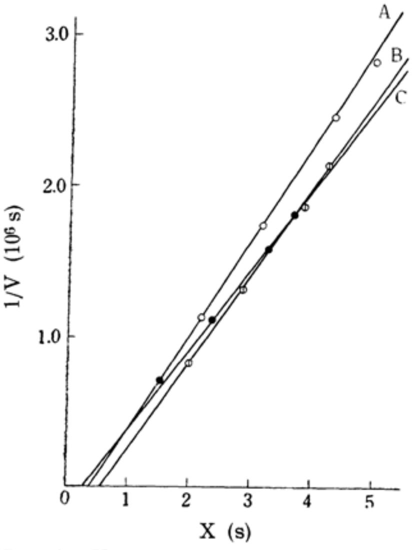

Fig. 4. Variation of the rate with the measured intercept for the polymerization of styrene.

○ Curve A, at 30°C; ◑ Curve B, at 35°C; ● Curve C, at 40°C.

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[3] Heat capacities and heat of polymerization of styrene at different temperatures are as follows[4].

	Heat Capacity	Heat of Polymerization
30°C	43.9 cal./mol.	16.76 kcal./mol.
35°C	44.3 cal./mol.	16.84 kcal./mol.
40°C	44.6 cal./mol.	16.90 kcal./mol.

From these values and (1), the relations between the amplitude-change per second and the fractional rate can be obtained.

$$\begin{aligned} 1\ \text{mm./sec.} &= 0.785\times10^{-6}/\text{sec. at } 30^{\circ}\text{C} \\ 1\ \text{mm./sec.} &= 0.775\times10^{-6}/\text{sec. at } 35^{\circ}\text{C} \\ 1\ \text{mm./sec.} &= 0.760\times10^{-6}/\text{sec. at } 40^{\circ}\text{C} \end{aligned}$$

These Values coincide with (2) within the error of ca. ±0.3%, which is small compared with the usual experimental error.

[4] Ray H. Boundy and Raymond F. Boyer; "Styrene", Reinhold, New York (1952), pp. 67, 68.

straight-line's slope, it can be shown that the exponent is 0.53 at 30°C, 0.53 at 35°C and 0.54 at 40°C. Therefore the theory described in the first paper is applicable.

The relation between $1/V$ and X is shown in Fig. 4 and from this straight-line's intercept the instrument's lag in response is 0.25–0.5 sec. This value coincides approximately with 0.6 sec. obtained in the first paper. From the slope of this line, the values k_p/k_t of styrene are 2.28×10^{-6} at 30°C, 2.50×10^{-6} at 35°C and 2.77×10^{-6} at 40°C.

Vinyl Acetate.—The rate of polymerization of vinyl acetate was ca. ninefold larger than that of styrene under the same conditions. Hence the sensitivity of the amplifier was lowered as follows.

$$\begin{aligned}1\text{ mm.}&=1.20\times10^{-3}{}^\circ\text{C at }30^\circ\text{C}\\1\text{ mm.}&=1.18\times10^{-3}{}^\circ\text{C at }35^\circ\text{C}\\1\text{ mm.}&=1.15\times10^{-3}{}^\circ\text{C at }40^\circ\text{C}\end{aligned}\qquad(4)$$

The necessary constants of vinyl acetate are as follows[5].

Heat capacity 40.5 cal./mol.
Heat of polymerization 21.3 kcal./mol.

From these values the relation between the conversion and the temperature-rise can be obtained.

$$1\%=5.28^\circ\text{C} \qquad (4)$$

From (3) and (4) the following relations were obtained.

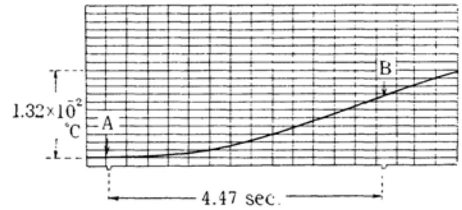

Fig. 5. A recorder trace of a typical experiment for the polymerization of vinyl acetate sensitized by α-azobisisbutyronitrile at 30°C.

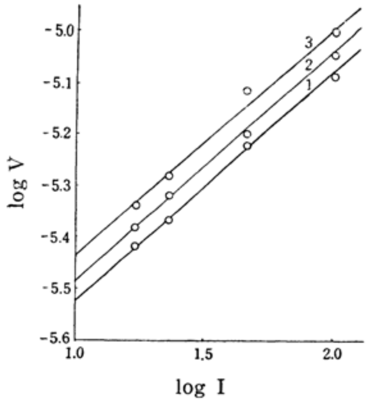

Fig. 6. Variation of the rate with the light intensity for the polymerization of vinyl acetate. Curve 1, at 30°C; Curve 2, at 35°C; Curve 3, at 40°C.

$$\begin{aligned}1\text{ mm./sec.}&=0.228\times10^{-5}/\text{sec. at }30^\circ\text{C}\\1\text{ mm./sec.}&=0.223\times10^{-5}/\text{sec. at }35^\circ\text{C}\\1\text{ mm./sec.}&=0.218\times10^{-5}/\text{sec. at }40^\circ\text{C}\end{aligned}\qquad(5)$$

In Figs. 5, 6 and 7, the exprimental results obtained under the same conditions as in styrene are shown. From Fig. 7 the instrument's lag in respones is 0.5–0.9 sec. and the k_o/k_t values of vinyl acetate are 1.21×10^{-5} at 30°C, 1.34×10^{-5} at 35°C and 1.44×10^{-5} at 40°C.

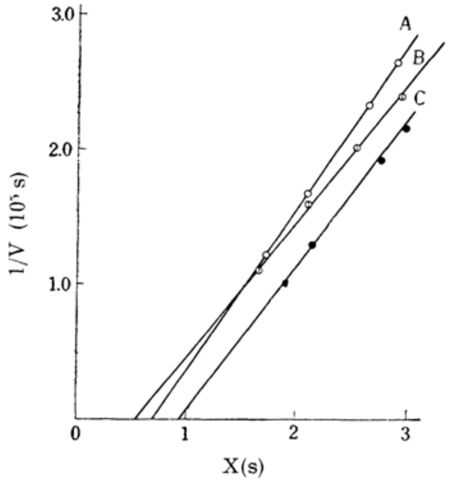

Fig. 7. Variation of the rate with the measused intercept for the polymerization of vinyl acetate.
○ Curve A, at 30°C; ⦶ Curve B, at 35°C; ● Curve C, at 40°C.

Methyl Methacrylate.—The rate of polymerization of methyl methacrylate was ca. threefold larger than styrene under the same conditions. As the sensitivity of amplifier, (1) was used. The constants of methyl methacrylate used were as follows[5].

Heat capacity	49.0 cal./mol.
Heat of polymerization	13.0 kcal./mol.

From these values the relation between the conversion and the temperature-rise is

$$1\%=2.65^\circ\text{C} \qquad (6)$$

From (1) and (6), the following relations were obtained.

$$\begin{aligned}1\text{ mm./sec.}&=1.132\times10^{-6}/\text{sec. at }30^\circ\text{C}\\1\text{ mm./sec.}&=1.110\times10^{-6}/\text{sec. at }35^\circ\text{C}\\1\text{ mm./sec.}&=1.078\times10^{-6}/\text{sec. at }40^\circ\text{C}\end{aligned}\qquad(7)$$

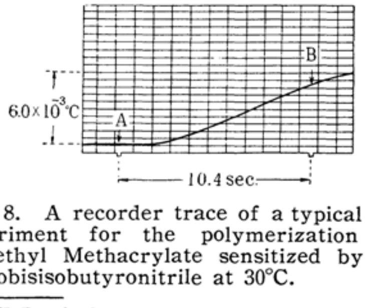

Fig. 8. A recorder trace of a typical experiment for the polymerization of Methyl Methacrylate sensitized by α-azobisisobutyronitrile at 30°C.

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[5] W.I. Bengough and H.W. Melville, *Proc. Roy. Soc.*, **A225**, 330 (1954).

[6] C.H. Bamford and Dewer, *Proc. Roy. Soc. London*, **A 192**, 309 (1948).

In Figs. 8, 9 and 10, the experimental results are shown and the experimental condition is the same as in styrene and vinyl acetate. From Fig. 10 the instruments's lag is 0.5–0.6 sec. and k_p/k_t values of methyl methacrylate are 7.41×10^{-6} at 30°C, 8.08×10^{-6} at 35°C and 8.92×10^{-6} at 40°C.

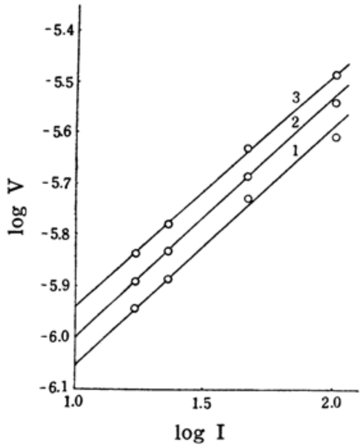

Fig. 9. Variation of the rate with the light intensity for the polymerization of methyl methacrylate. Curve 1, at 30°C; Curve 2, at 35°C; Curve 3, at 40°C.

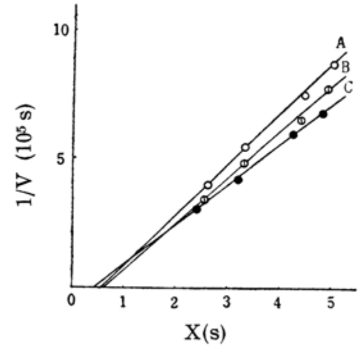

Fig. 10. Variation of the rate with the measured intercept for the polymerization of methyl methacrylate.
○ Curve A, at 30°C; ⦶ Curve B, at 35°C; ● Curve C, at 40°C.

Discussion

From the k_p/k_t value at various temperatures, the difference between the activation energies E_p and E_t, where E_p and E_t are respectively the activation energy of propagation and termination processes, can be calculated. Thus the values of E_p-E_t are 3.71 kcal./mol., 3.25 kcal./mol. and 3.54 kcal./. mol. for styrene, vinyl acetate and methyl methacrylate respectively. Using these values and k_p/k_t values at values temperatures, the following equations can be obtained.

$k_p/k_t=1.09\times10^{-3}\times e^{-3710/RT}$ for styrene
$k_p/k_t=2.72\times10^{-3}\times e^{-3250/RT}$ for vinyl acetate
$k_p/k_t=2.66\times10^{-3}\times e^{-3540/RT}$ for methyl methacrylate (8)

These equations obtained by other workers are as follows.

$k_p/k_t=3.33\times10^{-3}\times e^{-3700/RT}$ for styrene[6)]
$k_p/k_t=5.34\times10^{-3}\times e^{-2080/RT}$ for vinyl acetat[7)]
$k_p/k_t=3.78\times10^{-3}\times e^{-3470/RT}$ for methyl methacrylate[8)]

Using equations (8), the k_p/k_t values at 15°C can be obtained and they are compared with other worker's values in Table I, Table II and Table III.

Since the above results were, as described in the previous paper, obtained from measurements after the reaction system attained the stationary state and was then irradiated, the reaction in the dark is supposed to be canceled out. However heat-decomposition of α-azobisisobutyronitrile at higher temperature is considerable and accelerates the polymerization in the dark, hence the effect of

TABLE I

THE k_p/k_t VALUE OF STYRENE AT 15°C

Method	Sensitizer	$k_p/k_t\times10^6$	Ref.
Thermistor	Azobisisobutyronitrile	1.3	This work
Interferometer	Benzoyl Peroxide	2.0[9)]	Grassie & Melville (1951)
Sector	Benzoyl Perxide	3.6[9)]	Valentine & Melville (1950)
Sector	Azopropane	0.65[9)]	Matheson (1950)
Dilatometer	None	5.26[9)]	Burnett (1950)
Dielectric Constant	Azobisisobutyronitrile	0.68[9)]	Majury & Melville (1951)
Viscosity	None	5.3[9)]	Bamford & Dewer (1948)

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7) M.S. Matheson, E.E. Auer, E.B. Bevilacpuer and E.T. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949).

8) ibid., 71. 497 (1949).

9) N.G. Grassie and Melville, *Proc. Roy. Soc. London*, **A 207**, 285 (1951).
These values are summarized in this paper and corrected to 15°C assuming an activation energy of 4 kcal./mol. for the k_p/k_t term.

10) These values are summarized in ref. 5) and corrected to 15°C assuming an activation energy of 4.1 kcal./mol. for the k_p/k_t term.

11) These values are summarized in ref. 5) and corrected to 15°C assuming an activation energy of 3.7 kcal./mol. for the k_p/k_t term.

TABLE II

THE k_p/k_t VALUE OF VINYL ACETATE AT 15°C

Method	Sensitizer	$k_p/k_t\times10^5$	Ref.
Thermistor	Azobisisobutyronitrle	0.92	This work
Thermocouple	Azobiscyclohexanecarbonitrile	2.5[10]	Bengough & Melville (1954)
Refractometric	Azobisisobutyronitrile	2.0[10]	Grassi & Melville (1951)
Dielectric Constant	Azobisisobutyronitrile	0.35[10]	Majury & Melville (1951)
Sector	None	0.11[10]	Burnett & Melville (1947)
Sector	None	1.1[10]	Bartlett & Melville (1946)
Sector	Azobisisobutyronitrile	1.1[10]	Matheson, Bevilacqua, Auer, & Hart (1949)
Viscosity	None	1.9[10]	Dixon-Lewis (1949)
Dilatometer	Azobiscyclohexanecarbonitrile	2.4[10]	Bengough (unpublished)
Sector	None	1.4[10]	Bartlett, Broadbent & Kwart (1950)

TABLE III

THE k_p/k_t VALUE OF METHYL METHACRYLATE AT 15°C

Method	Sensitizer	$k_p/k_t\times10^6$	Ref.
Thermistor	Azobisisobutyronitrile	5.4	This work
Thermocouple	Azobiscyclohexanecarbonitrile	9.8[11]	Bengough Melville (1954)
Interferometer	None	6.1[11]	Grassie & Melville (1951)
Sector	None	3.8[11]	Mackay & Melville (1949)
Sector	Benzoine	8.9[11]	Chinmayanandam & Melville (1954)
Viscosity	None	20[11]	Bamford & Dewer (1948)
Sector	Bnnzoyl Peroxide	7.9[11]	Melville & Valentine (1950)

reaction in the dark must be taken in consideration. It is desirable, therefore, to use a photosensitizer which does not accelerate the reaction in the dark but the one in the light only.

Summary

The k_p/k_t value of styrene, vinyl acetate and methyl methacrylate was obtained by using thermistor method reported in the first paper of this series. Moreover from the k_p/k_t values at various temperatures, the activation energy difference between propagation and termination processes was calculated. They were 3.71, 3.25 and 3.54 kcal./mol. for styrene, vinyl acetate and methyl methacrylate respectively. The characteristics of this apparatus were almost the same as described in the first paper, although various monomers were used.

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