The Effect of Conversion on the Mechanism of Vinyl Polymerization. II. Methyl Methacrylate

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In the first paper of this series[1] the author described the application of the photochemical method to the study of vinyl polymerization at various conversions and reported the results on styrene not containing any initiator or chain-transfer substance at room temperatures. It was noted there that the course of polymerization was accompanied by the strong rate acceleration, an extreme increase in kinetic chain lifetime and considerable decrease in apparent activation energy and in the reaction order of chain termination. Those kinds of kinetic behaviour could be explained by the supposition that, with increasing conversion of the system, the mutual termination of polystyrene radicals becomes diffusion-controlled or prevented by the shielding effect of the polymer network.

The author has now applied the same method to methyl methacrylate in an attempt to compare it with the above results on styrene[1]

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[1] S. Fujii, This Bulletin **27**, 216 (1954).

and with those found by several authors[2,3,4,5,6a] for the polymerization of methyl methacrylate in the later stages. This paper reports and discusses the results obtained under the analogous conditions as described in the first paper.[1]

Experimental

Commercial methyl methacrylate was purified by successive washing with dilute sulphuric acid, dilute sodium hydroxide and distilled water, and was dried with calcium chloride over a day. Then it was distilled three times through a fractionating column of 1 meter long at 105 mm. pressure, and the fraction boiling at 45.1°C. was collected and stored in an evacuated flask in the dark. This product was allowed to polymerize to about 10% at 100°C. under the irradiation of ultra-violet light longer than 3300 Å., and then the residual monomer was redistilled with dry ice into a dilatometer used for rate measurements. This operation was carried out in an all glass system evacuated to 10^{-3} mm. pressure. All of the above treatments were necessary to obtain the pure monomer completely free from impurity which may sensitize or retard the polymerization. Unless otherwise noticed, neither photosensitizer nor thermal initiator was added to the reaction system.

The experimental apparatus and procedure were essentially those described in the first paper.[1] The filteration of light from the mercury lamp and the maximum intensity of 3660 Å. light at the front of the reaction cell (4×10^{-8} Einsteins/sec.) were the same as those in the previous experiment.[1] The photo-polymerization was mainly caused by the light of 3660Å., at which wave-length the absorption by the monomer is very little (the molecular extinction coefficient is of the order of 10^{-3})[7] so that the concentration of the radicals within the cell must be uniform. The free radical initiation by the light-excited polymer must be negligible, for the polymer shows no absorption band in the neighborhood of 3660 Å.[8] The rates of photo-and thermal-polymerizations were followed dilatometrically and computed by the use of Matheson's data[6a] on the densities of the monomer and the polymer in monomer. In the same manner as described in ref. (1), all the rate measurements were corrected for the thermal reaction taking place in the unilluminated appendages to the cell. The kinetic chain lifetimes at low conversions (of the order of seconds) were measured with a rotating sector, while those at high conversions were estimated from the photochemical after-effects, which were easily observed dilatometrically. After the experiments at low conversions, the reaction system was polymerized to a desirable conversion under the intense irradiation of 3660 Å. light, left alone at room temperature over half a day, and then the experiments at high conversions were carried out.

The main different feature from styrene was the fact that the polymerization of methyl methacrylate by the same light intensity is much faster (about seven times) than that of styrene in spite of the smaller extinction coefficient. To avoid the undesirable temperature elevation and change of conversion in the reaction system, therefore, the rates of photo-polymerization at high conversions were reduced with calibrated screens. The stationary light rates at high conversions were measured after the long period of preliminary illumination.

Results

The polymerization rates and the reaction order of chain termination—The stationary rates of photo-polymerization at three different temperatures were measured at low conversions under the full intensity (4×10^{-8} Einsteins/sec.) of light from the lamp and at high conversions under the intensities reduced with calibrated screens. Table I shows the data obtained on light rate V_{pL}, thermal rate V_d, and the apparent activation energy, E_{app}, of polymerization.

TABLE I

RATES OF PHOTO- AND THERMAL-POLYMERIZATIONS AND OVER-ALL ACTIVATION ENERGIES FOR METHYL METHACRYLATE

Transmission of screen, %	Conversion %	30°C.	40°C.	50°C.	E_{app} kcal./mol.
	(a) Light rate (unit; 10^{-6} mol./l./sec.)				
100	0~1	7.94	11.0	14.1	5.6
27.4	27±1	32.9	41.9	53.4	4.7
12.0	52±2	43.1	54.6	65.8	4.1
	(b) Thermal rate (unit; 10^{-6} mol./l./sec.)				
	0~1	0.29	0.48	0.81	10.1
	27±1	1.58	2.57	3.94	8.9
	52±2	3.49	5.63	8.32	8.5

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[2] G. V. Schulz and F. Blaschke, *Z. physik. Chemie*, **B50**, 305 (1941).

[3] Trommsdorff, "Coloquium on High Polymers," Freiburg, 1944.

[4] G. V. Schulz and G. Harborth, *Die Makromolekulare Chemie*, **1**, 106 (1947).

[5] M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.*, **45**, 323 (1949).

[6] (a) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); (b) ibid., **73**, 1700 (1951); (c) ibid., **73**, 5395 (1951).

[7] T. G. Majury and H. W. Melville, *Proc. Roy. Soc. London*, **A205**, 496 (1951).

[8] The absorption band of the system shifts to the shorter wave length in the disappearance of vinyl double bond.

This table as a whole shows that the indicated values were reproducible within the error of 10% or less. Also a measurement of light rate in a complete run to 60% conversion was carried out in the same reaction cell at 30°C. under the constant intensity of illumination and the result is shown diagrammatically in Fig. 1. At the same time the reaction order of chain termination, *n*, i. e., the reciprocal of the intensity exponent of the stationary light rate, was determined in one run in the same reaction cell at several conversions and the results are given in Table II.

TABLE II

THE REACTION ORDER OF CHAIN TERMINATION, *n*

Conversion %	*n*
0∼1	1.9∼2.1
45±2	1.8∼1.9
60±2	1.6,∼1.8

It is concluded from the above tables and figure that the strong rate acceleration after about 10% conversion is accompanied with some decreases in E_{app} ane *n*. This kinetic behavior is analogous to that of styrene.[1]

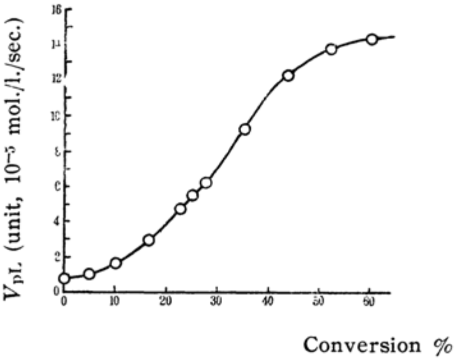

Fig. 1. The rate of photo-polymerization at 30°C. as a function of conversion.

Photochemical after-effect and kinetic chain lifetime—In the measurement of light rates, the reaction showed no detectable induction period in the initial stages, while the prolonged initial- and after-effects were clearly observed in the later stages. Since the rates were followed with a dilatometer, the temperature change of the system in the beginning of illumination and after the interruption of light caused some volume change on the system and more or less disturbed the detection of pure chemical initial- and after-effects. However the ratio of the volume change caused by this undesirable temperature change to the total one by the after-effect became very small at high conversions, so that the allowance for this temperature change was neglected, as the first approximation, in the present discussion of these effects. In a similar manner described in the previous paper,[1] it was confirmed that these effects resulted from an extreme increase in kinetic chain lifetime but not from the decomposition of any unstable substance produced during the previous illumination. A few examples of the observed after-effects are illustrated in Fig. 2, where the relative rate after the interruption of illumination is represented as a function of time.

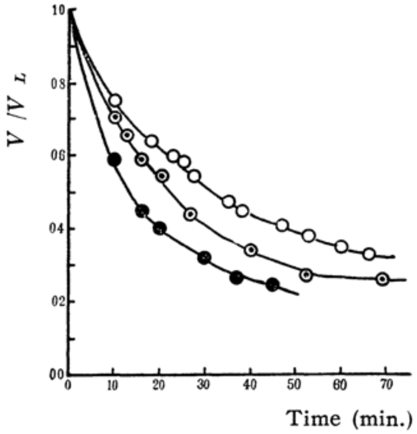

Fig. 2. Photochemical after-effects.

Experimental point	⊙	●	○
Conversion	47 %	52 %	72 %
Temperature	30°C.	50°C.	30°C.
V_{pL}(10^{-5}mol./l./sec.)	4.03	6.58	5.17
V_d/V_{pL}	0.08	0.13	0.18

With several assumptions previously justified[1] and under the case of $n=2$, the mathematical analysis of the photochemical after-effect results in the equation,

$$log\left(\frac{V_p+V_d}{V_p-V_d}\right)=log\left(\frac{V_{pL}+V_d}{V_{pL}-V_d}\right)+\frac{2\,V_d}{2.303\,V_{pL}}\times\frac{t}{\tau_s}\,, \quad (1)$$

and slso the accepted polymerization mechanism leads to the equation,

$$\frac{{}_sV_{pL}}{[M]}=k_p/k_t\,. \quad \cdots\cdots\cdots\cdots\cdots (2)$$

Here V_p is the rate at the time, *t*, after the interruption of illumination, k_p and k_t the propagation and termination rate constants of growing radicals respectively $[M]$ the monomer concentration and τ_s the average lifetime of kinetic chains at the light rate of V_{pL}, but not the one of each growing radical. Plotting the value of the left hand side of Eq. (1) against the time will lead to a straight line and then the τ_s value can be estimated from the slope of this line. The k_p/k_t value can be estimated from Eq. (2).

Although the deviation of n from 2 was observed at high conversions as shown in Table II, it may be admitted in the present qualitative discussion that the τ_s and k_p/k_t values at high conversions are estimated, as the first approximation was, by the use of these equations. On the basis of the above, the analytical representations of the observed after-effects are illustrated in Fig. 3, and the τ_s and k_p/k_t values obtained are summarized in Table III.

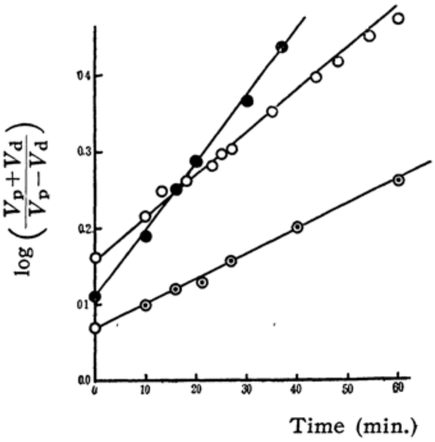

Fig. 3. Analytical representations for the observed after-effects; the experimental conditions for the indicated points are the same as those in Fig. 2.

On the other hand the kinetic chain lifetimes at low conversions were of the order of 10 seconds at the V_{pL} values indicated in Table I, and consequently these were measured with a rotating sector. A typical run in the sector experiments is indicated in Fig. 4, and the initial values of τ_s and k_p/k_t are also summarized in Table III.

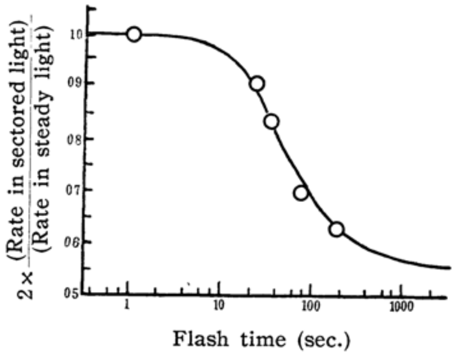

Fig. 4. Rates of polymerization of methyl methacrylate in intermittent light for different times of flash: curve, theory for dark rate 3% of steady light rate; ○, experimental point at 40°C. and steady light rate $=1.06\times10^{-5}$ mol./l./sec.

As noted previously[1,6a)] the propagation step in free radical polymerizations has been admitted to be only slightly dependent upon conversion as compared with the termination step, so that the relative decrease in k_t with increasing conversion may be estimated from the k_p/k_t values shown in Table III under the assumption of constant k_p. The evaluated result is indicated in the last column of Table III, and such decrease in k_t is analogous to that previously reported on styrene.

TABLE III

KINETIC CHAIN LIFETIMES AND RATE CONSTANT RATIO IN METHYL METHACRYLATE

Conversion x %	Temp. °C.	V_{pL} mol./l./sec.	τ_s sec.	Av. τ_s at $V_{pL}=10^{-5}$	k_p/k_t	k_{tx}/k_{t0} b)
0∼1	30	3.52×10^{-5}	1.85	a) 7.43		
		6.83×10^{-5}	1.22			
	30	7.95×10^{-6}	21.7	17.9	1.93×10^{-5}	1
		1.08×10^{-5}	17.2			
	40	1.10×10^{-5}	20.3	22.7	2.47×10^{-5}	
		1.60×10^{-5}	14.5			
47±2	30	4.03×10^{-5}	1260	5080	9.20×10^{-3}	2.10×10^{-3}
52±2	30	4.31×10^{-5}	1098	4730	9.33×10^{-3}	2.07×10^{-3}
	40	5.46×10^{-5}	882	4810	9.48×10^{-3}	
	50	6.58×10^{-5}	762	5010	9.86×10^{-3}	
72±3	30	5.17×10^{-5}	1800	9310	2.96×10^{-2}	6.52×10^{-4}

(a) α-Azo-bisisobutyronitrile sensitizer was used in this experiment; no sensitizer in the others.

(b) The ratio of k_t at x % conversion to its initial value was estimated at 30°C.

Discussion

With the several assumptions previously described,1) the accepted mechanism of photopolymerization leads to the equation,

$$V_{\mathrm{pL}} = (q\,\varepsilon\,l\,I_0)^{1/n}\left(k_{\mathrm{p}}/k_{\mathrm{t}}{}^{1/n} \right)[M]^{1+1/n} \qquad (3)$$

and also, if the thermal initiation of kinetic chains is assumed to be proportional to $[M]^{2}$,9) the rate of thermal polymerization may be represented as

$$V_{\mathrm{d}} = k_{\mathrm{p}}\left(\frac{k_{\mathrm{t}}}{k_{\mathrm{i}}} \right)^{1/n}[M]^{1+1/n} \qquad (4)$$

Here q is the quantum efficiency of the production of kinetic chains, ε the molecular extinction coefficient of the monomer, l the depth of the reaction cell, I_0 the intensity of illumination and k_{i} the rate constant of thermal initiation by the monomer. Using these equations and the data in Table III, the rate ratio at 52% conversion to the initial value at 30°C. can be estimated10) as about 11. 8 for V_{pL} and about 8. 7 for V_{d}, while the corresponding experimental ratios are about 17. 3 for V_{pL} from Fig. 1 and about 12. 0 for V_{d} from Table I. If the $k_{\mathrm{tx}}/k_{\mathrm{to}}$ value at 52% conversion is estimated to be half of that indicated in Table III,11) the differences between the above theoretical and experimental ratios in the rate accelerations may be almost eliminated. Therefore it may be concluded that the observed rate accelerations are attributed to the extreme decrease in k_{t}. This conclusion has already been suggested by Trommsdorff4) and several other authors,2,4,5) who found the catalytic- and photo-polymerizations of several vinyl monomers to be strongly accelerated after certain conversions, and has also been confirmed by Matheson and his co-workers6a) with the measurement of kinetic chain lifetimes in the biacetyl photosensitized-polymerization of methyl methacrylate at about 33% conversion. Following the data of the latter authors the value of $k_{\mathrm{tx}}/k_{\mathrm{to}}$ at 33% conversion is in the range $4.6\sim6.6\times10^{-3}$ at 30°C., while the present work shows about 2×10^{-3} in the neighborhood of 50% at the same temperature. Allowing for the different conversions, one may accept the fact that both the results coincide with each other.

As noted previously on styrene,1) the observed decreases in k_{t} and E_{app} with increasing conversion can be explained by the fact that the mutual termination of polymer radicals becomes predominantly diffusion-controlled in the later stages. Using Matheson's datum (2. 8 kcal./mole)6a) for the activation energy of chain termination, E_{t}, in the initial stages, the observed decrease in E_{app} (=the increase in $1/2\,E_{\mathrm{t}}$) gives about 5. 8 kcal./mole12) for the E_{t} value at 52% conversion, i. e., the activation energy of the diffusion of polymethyl methacrylate radicals in the reaction system. The E_{t} values of polystyrene radicals at 38 and 60% conversions have been reported by the present author as about 7 and 9 kcal./mole respectively,1) and these values are almost in agreement with those estimated from the viscosity equation of Spencer and Williams.13) Flory14) reported about 8 kcal./mole as the activation energy of the viscosity for several fused polyesters. Cowley and Melville15) studied the photo-degradation of polymethyl methacrylate with the rotating sector technique and reported about 20 kcal./mole as the E_{t} value of the polymer radicals in the fused polymer. Comparing this with the author's data on styrene and Flory's data on polyesters the present value (5. 8 kcal.) may be adequate, while the value (20 kcal.) of Cowley and Melville is beyond the accepted order of magnitude for the self-diffusion of polymer in the fused phase.

Some decrease in n observed over about 50% conversion seems to show that, together with the mutual termination of polymer radicals, the self-termination also takes place at very high conversions. Such self-termination may be supposed to be caused by the strong shielding action of a polymer network on the active ends of growing radicals. This suggested mechanism has been discussed in the first paper of this series1) and supported by Bamford and Jenkins,16) who studied the photopolymerization of acrylonitrile and found

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9) P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).

10) In this calculation $n=1.8$ was used and q assumed to be constant.

11) It can be accepted under the present experimental accuracy to reduce the ratio in kt by a factor of 2.

12) Such increase in Et with increasing conversion is also detected from the temperature dependence of $k\mathrm{p}/kt$. The data of $k\mathrm{p}/kt$ at 52% conversion in Table 3 lead to give about 0.5 kcal./mole as the value of ($E\mathrm{p}$-Et), where $E\mathrm{p}$ is the activation energy of propagation. Using Matheson's datum ($E\mathrm{p}$=6.3 kcal./mole)6a the Et value at 52% conversion is estimated as about 5.8 kcal./mole, the value of which in good agreement with that estimated from the temperature dependence of $V\mathrm{pL}$ or $V\mathrm{d}$ at the same conversion.

13) Spencer and Williams, *J. Colloid Sci.*, **2**, 117 (1947).

14) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

15) P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. London*, **A210**, 461 (1952); ibid., **A211**, 320 (1952); In the latter reference the kt value in the fused polymer at 167°C. was reported as 4×10^{4} l./mol./sec. While Matheson reported 1.22×10^{7} at 30°C. and 1.87×10^{7} at 60°C. as the kt value at low conversion. Using Cowley's value (20 kcal.) of Et in the fused polymer and Matheson's value (2.8 kcal.(of Et in the initial stages, the kt_x/kt_0 value at 100% conversion is estimated as about 1.2×10^{-8} at 167°C. and about 4×10^{-8} at 30°C.

16) C. H. Bamford and A. D. Jenkins, *Proc. Ror. Soc. London*, **A216**, 515 (1953).

that the photo-polymer precipitated near room temperatures occluded the active ends of polymer radicals. Recently the present author has found that the effects of conversion on V_{pL}, V_d, k_t and n are extremely reduced by the addition of chain-transfer substance, such as *n*-butylmercaptan, to the polymerization system.[17] This result seems to throw a powerful datum on the verification of the above mechanism.

Summary

The usual photochemical method and the rotating sector technique have been used to study the effect of conversion on the termination mechanism in the polymerization of methyl methacrylate. The strong rate acceleration, the extreme increase in kinetic chain lifetime and some decreases in the overall activation energy and the reaction order of chain termination have been detected with increasing conversion of the reaction system. These results are in good agreement with those reported on styrene in the first paper of this series and with the available data on this polymerization. These results have been discussed under several assumptions and confirmed to be due to a large change in the termination mechanism, i. e., from the activation-controlled termination of polymer radicals in the initial stages to the predominant diffusion-controlled termination in the later stages.

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[17] Unpublished