The Effect of Conversion on the Mechanism of Vinyl Polymerization. I. Styrene

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Introduction

Although the detailed mechanism of the initial stage of vinyl polymerization has been studied by many workers with various methods, little has been published which clarifies the effect of conversion on the chain mechanism of polymerization. As already reported, the polymerizations of several vinyl monomers in the liquid phase are strongly accelerated after certain conversions[1),2),3)], and this rate of acceleration has been attributed by Trommsdorff[4)] to a decrease in the termination rate constant of polymer radicals with the increasing viscosity of the system. His suggestion has recently been confirmed by Matheson and his coworkers[5)] with the measurement of the lifetime of kinetic chains, but the further investigations at high conversions may yet be necessary to make clear the chain mechanism in the later stage of polymerization.

In an attempt to obtain further information on this point the present author has studied photochemically the polymerizations of several vinyl monomers in the range 0 to about 70% conversion. This paper reports the work on styrene.

Theoretical

The following facts are implicitly assumed in this work (1) The radical polymerization consists of four kinds of elementary reactions; thermal or light initiation, propagation, transfer with monomer and termination. (2) These elementary rate constants are independent of the length[6)] or valence character (mono- or di-radical) of the polymer radicals, and further the rate constants of propagation and transfer are assumed to be approximately independent of conversion[7)]. (3) The irradiated light is absorbed uniformly in the reaction cell and causes no decomposition of the monomer or of the polymer. (4) The rate of light initiation is proportional to the absorbed light intensity, this intensity being proportional to that of illumination. (5) The light absorption by the polymer is negligible compared to that by the monomer. (6) An instantaneous steady state is reached in the light initiation. (7) The rate of thermal initiation is unaffected by light. (8) The assumptions in the sector experiment are almost the same as those described in Matheson's papers[5)]; precautions to insure the correctness of the assumptions (3) to (8) except (6) were made in the present experiment.

On the basis of the absorption spectra of styrene and its polymer[8)], the assumptions (4) and (5) may be adequate and the absorbed light intensity, $\boldsymbol{I}_{\mathrm{abs}}$, will be represented by

$$\boldsymbol{I}_{\mathrm{abs}} = \varepsilon\, l[M]\, \boldsymbol{I}_0 \,, \qquad (1)$$

where $\boldsymbol{I}_0$ is the intensity of illumination, $[M]$ the monomer concentration, l the depth of the reaction cell and ε the mean molecular extinction coefficient of the monomer in the neighborhood of 3660 Å. In the present work, the production and disappearance of kinetic chains are mainly discussed, but neither the question whether the active polymer is monoradical or biradical or whether the termination is a recombination or a disproportionation are considered. From this stand-point by the concentration of kinetic chains, $[R]$, will be given by

$$\frac{d[R]}{dt} = q\boldsymbol{I}_{\mathrm{abs}} + k_{\mathrm{i}}[M]^2 - k_{\mathrm{t}}[R]^n \qquad (2)$$

and also the rate of monomer consumption at any stage by

$$-\frac{d[M]}{dt} = V_{\mathrm{p}} = k_{\mathrm{p}}[R][M] \qquad (3)$$

Here q is the quantum efficiency of production of kinetic chains, and k_{t}, k_{p} and k_{i} are the rate constants of termination, propagation and thermal initiation respectively.

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

2) G. M. Burnett and H. W. Melville, *Nature*, **155**, 661 (1945); *Proc. Roy. Soc. London*, **A189**, 456 (1947).

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

4) Trommsdorff, "*Colloquium on High Polymers*" Freiburg, 1944.

5) (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).

6) F. R. Mayo, *J. Am. Chom. Soc.*, **70**, 3689 (1948); R. A. Cregg and F. R. Mayo, ibid., **70**, 2373 (1948).

7) M. F. Vaughan, *Trans. Faraday Soc.*, **48**, 576 (1952).

8) (a) T. G. Majury and H. W. Melville, *Proc. Roy. Soc. London*, **A205**, 496 (1951); (b) J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. trav. Chim.*, **52**, 709 (1933).

Further if the condition, $q\boldsymbol{I}_{\mathrm{abs}} \gg k_i[M]^2$, is held in the stationary state of this chain reaction, the following two equations are easily derived from eqns. (1), (2) and (3).

$$\ln V_{\mathrm{pL}} = \ln\left\{(q\varepsilon l)^{1/n}\frac{k_{\mathrm{p}}}{k_{\mathrm{t}}^{1/n}}[M]^{1+\frac{1}{n}}\right\} + \frac{1}{n}\ln \boldsymbol{I}_0 \qquad (4)$$

and

$$E_{\mathrm{a}} = -R\frac{\partial(\ln V_{\mathrm{pL}})}{\partial(1/T)} = E_{\mathrm{p}} - \frac{1}{n}\left\{E_{\mathrm{t}} + R\frac{\partial(\ln q)}{\partial(1/T)}\right\} \qquad (5)$$

where V_{pL} is the stationary rate of photo-polymerization, E_{a} the over-all activation energy of photo-polymerization, T the absolute temperature, and E_{p} and E_{t} are the activation energies of propagation and termination respectively. These eqns. (4) and (5) will be used in the discussion of the experimental results.

Next, if the chain termination is of the second order ($n=2$), the average life-time of kinetic chains, τ_{s}, in the stationary state of polymerization may be defined by

$$\tau_{\mathrm{s}} = \frac{1}{k_{\mathrm{t}}[R]_{\mathrm{s}}} \qquad (6)$$

and then

$$\frac{\tau_{\mathrm{s}} V_{\mathrm{pL}}}{[M]} = k_{\mathrm{p}}/k_{\mathrm{t}} \qquad (7)$$

is obtained from eqn. (3). Thus, by measuring τ_{s} the value of $k_{\mathrm{p}}/k_{\mathrm{t}}$ can be estimated.

Under the present experimental conditions the value of τ_{s} at low conversion (0∼1%) was of the order of second and could be measured with rotating sector technique, but the one at high conversions became so long (over 10^{3} seconds) that the photochemical after-effect could easily be observed dilatometrically. For the after-effect the equation governing $[R]$ after the interruption of illumination will be

$$-\frac{d[R]}{dt} = k_{\mathrm{t}}[R]^n - k_{\mathrm{i}}[M]^2 \qquad (8)$$

This equation can be integrated in the case of $n=2$ under the conditions ($[R]=[R]_{\mathrm{s}}$ at $t=0$, $[R]=(k_{\mathrm{i}}/k_{\mathrm{t}})^{1/2}[M]=[R]_{\mathrm{d}}$ at $t=\infty$) and combined with eqns. (3) and (6) to give

$$\ln\left(\frac{V_{\mathrm{p}}+V_{\mathrm{d}}}{V_{\mathrm{p}}-V_{\mathrm{d}}}\right) = \ln\left(\frac{V_{\mathrm{pL}}+V_{\mathrm{d}}}{V_{\mathrm{pL}}-V_{\mathrm{d}}}\right) + 2\frac{V_{\mathrm{d}}}{V_{\mathrm{pL}}}\frac{t}{\tau_{\mathrm{s}}} \qquad (9)$$

where V_{d} is the steady rate of thermal polymerization (dark rate) V_{p} the rate of polymerization at the time, t, after the interruption of illumination. Hence if

$$\left[\frac{V_{\mathrm{pL}}}{2V_{\mathrm{d}}}\ln\left(\frac{V_{\mathrm{p}}+V_{\mathrm{d}}}{V_{\mathrm{p}}-V_{\mathrm{d}}}\right)\right]$$

is plotted as a function of t, a straight line will be obtained with a slope of $1/\tau_{\mathrm{s}}$, that is, τ_{s} can be estimated.

The theory and experimental method of the rotating sector are fully presented in Matheson's papers⁵⁾. In the present experiment the ratio of the dark period to the light period was 3 and the thermal initiation during light periods was negligible compared to the light initiation. Therefore the theoretical ratio of the intermittent light rate to the steady light rate as a function of flash time and dark rate is the same as the one calculated by Matheson and his co-workers.⁵ᵃ⁾

Experimental

Styrene was prepared by the dehydration of pure β-phenyl-ethyl alcohol with solid potassium hydroxide over 240°C. and purified by successive washing with dilute sulphuric acid, dilute sodium hydroxide and distilled water. After drying with calcium chloride it was distilled twice through a fractionating column of 1 meter long at 15 mm. pressure, and the fraction boiling at 40.0°C. was collected and stored in an evacuated flask in the dark. Immediately before use this monomer was allowed to polymerize to about 5% thermally and with the illumination of ultra-violet light longer than 3300 Å, and then it was redistilled with dry ice into the reaction cell. These procedures were carried out in a glass system evacuated to 10^{-3}mm. pressure.

The rate of monomer consumption was measured with a dilatometer shown in Fig. 1, and a reading-microscope was used to read the mercury level in the capillary C to 0.01 mm. This dilatometer was immersed in a thermostat, which was regulated to ±0.001°C. In the experiments at high conversions the reaction cell A in Fig. 1. was heated in a small electric furnace at 130±5°C. for desirable duration⁹⁾, left alone at room

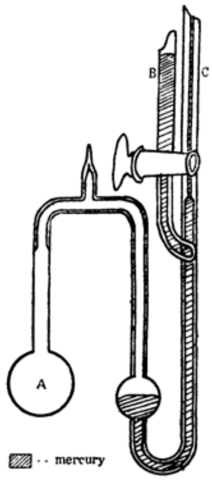

Fig. 1. Dilatometer

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9) The number average degree of polymerization for the polymer formed by this procedure may be estimated as about 1700 (R. A. Gregg and F. R. Mayo, *Discussions of the Faraday Soc.*, No. 2 (1947). *The Labile Molecule.* p. 328.)

temperature over half a day, and then the experiments were carried out, where the polymer concentration in A was estimated from the lowering of the mercury level in B. Matheson's data[5b)] about the densities of the monomer and of the polymer in monomer were used to estimate the rate of polymerization and the polymer concentration in the cell.

The source of light was a 200 watt ultra high pressure mercury lamp fed from a constant voltage transformer. The light was passed through a 5 % aqueous solution of copper sulphate and through two lenses made of soda glass. Considering the intensity distribution of absorbed light the photo-polymerization may be mainly caused by the light of 3660 Å.[10)] During an experiment the constancy of light was checked by a vacuum photocell with a Mazda UVD$_1$ filter (for 3660 Å). Also, using the above optical filter, the light intensity at the front of the reaction cell was measured with an uranyl-oxalate actinometer and its full intensity was 4×10^{-8} Einsteins per second.

The sector was made of a 46 cm. diameter aluminum disk and one-fourth part of it was cut off to a radical depth of 7 cm. The disk speed could be varied in steps from 1/20 to 150 r. p. m. The set of sector apparatus and the method of sector experiment were almost the same as the ones reported by Matheson and his co-workers.[5a)]

Unless otherwise noticed, the reaction system did not contain any photo-sensitizer or thermal catalyser. The rate of photo-polymerization under the present experimental conditions did not exceed over 10^{-4} mol./l./sec., so that the apparent change of monomer concentration may be negligible during illumination. When the lifetime of kinetic chains was very long, a long period of preliminary illumination was necessary to the determination of the stationary rate of photo-polymerization.

Results

The stationary rates of photo-polymerization under a constant light intensity (4×10^{-8} Einsteins/sec.) and of thermal polymerization were measured at three different temperatures between 0 to 60 % conversion, and these were found to be strongly accelerated with increasing conversion (Table I). Plotting log (relative rate) against the reciprocal of the absolute temperature gives an overall activation energy at each conversion and the result is indicated in the last column of Table I.

TABLE I

RATES* OF PHOTO- AND THERMAL-POLYMERIZATIONS AND OVER-ALL ACTIVATION ENERGIES FOR STYRENE

Conversion %	25°C.	30°C.	40°C.	E$_{act.}$ (k cal./mol.)
(a) Light rate (unit; 10^{-6}mol./l./sec.)				
0~1	1.15	1.52	2.65	10.4
38±1	6.25	7.91	12.0	8.1
60±2	21.3	25.8	37.2	6.9
(b) Thermal rate (unit; 10^{-6}mol./l./sec.)				
0~1	0.097	0.170	0.417	18.1
38±1	0.396	0.630	1.40	15.7
60±2	0.645	1.01	2.17	14.5

* All the rate measurements were corrected for the thermal reaction taking place in the unilluminated appendages to the reaction cell, by subtracting the proper fraction of thermal rate from the apparently observed rates. The polymer concentration in the unilluminated appendages to the cell did not exceed a few per-cent even after the experiments at high conversions, so that the magnitude of the thermal rate in that part, which was necessary to the above correction, was considered to hold the initial value in a complete run.

In this experiment the rate acceleration was found to be accompanied with the photochemical inital- and after-effects (Fig. 2) and also with by a decrease in the reaction order of chain termination (Table II). Here Fig. 2 was obtained in the direct observation of the volume change with time of the reaction system after the interruption of light, where these results had been confirmed to be mainly caused by the chemical after-effect but not by the temperature depression of the system. In the low rate of polymerization used in these experiments (of the order of 10^{-5} mol./l./sec.) the temperature within the reaction cell exceeded that of the thermostat

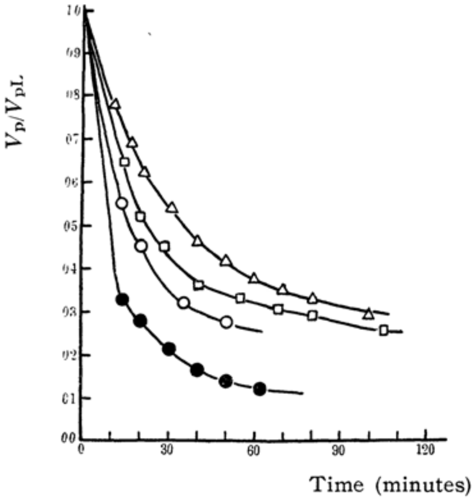

Fig. 2. Photochemical after-effects at 30°C.

	Conversion %	V_{pL} mol./l./sec.	V_d/V_{pL}
●	38	7.91×10^{-6}	0.081
○	38	3.58×10^{-6}	0.180
□	43	9.32×10^{-6}	0.054
△	60	25.8×10^{-6}	0.038

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10) G. M. Burnett, *Trans. Faraday Soc.*, **46**, 772 (1950).

bath only by the order of 0.01°C. under the stationary conditions, and the volume change due to the disappearance of this temperature difference might be negligible, at high conversions, compared to the total change caused by the after-effect. The data in Table II were obtained, with the use of eqn. (4), from the measurement of V_{pL} in one run in the same reaction cell, (i) under the full intensity from the lamp and (ii) with the intensity reduced by covering the window with calibrated screens.

TABLE II
REACTION ORDER OF CHAIN TERMINATION AT 25°C.

(a) An example at 68 % conversion

Transmission of screen, S	V_{pL} (10^{-5} mol./l./sec.)	log S	log (Relative rate	n
1.00	2.25	0.00	0.00	
0.41	1.24	−0.38	−0.25	1.5
0.19	0.79	−0.73	−0.45	1.6

(b) Summarized result

conversion, %	n
0	1.9∼2.1
38±1	1.9∼2.1
60±2	1.7∼1.8
68±2	1.4∼1.6

Also the lifetime of kinetic chains was measured or estimated at several conversions in order to obtain the relationship between the above results and the relative change of k_t with increasing conversion. Since the overall rate of photo-polymerization in the initial stage was proportional to the square-root of the absorbed light intensity ($n=2$, as shown in Table II) and was constant during a considerable period of illumination, τ_s at extremely low conversions could be measured with rotating sector. A typical run in the sector experiments is indicated in Fig. 3.

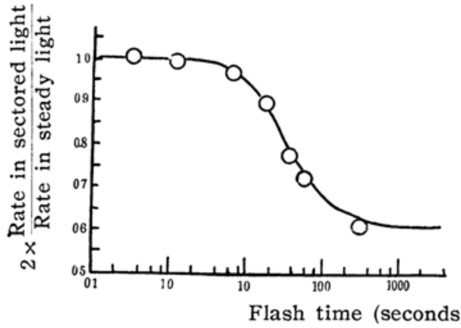

Fig. 3. Rates of polymerization in intermittent light for different times of flash: Curve, theory for dark rate 7 % of steady light rate; ○, experimental point under the conditions (temp. 30°C., coversion 0 % and steady light rate $=2.27\times10^{-6}$ mol./l./sec.)

On the other hand the values of τ_s at high conversions were too great to be measured by with the usual sector techniqe and so these were estimated by the use of eqn. (9) from the observed after-effect. The allowance for the deviation of n from 2 was not considered in this estimation. Therefore both the τ_s values estimated on the basis of the eqn. (9) and the corresponding k_p/k_t values on the eqn. (7) may have a considerable error at the conversions over about 60 %, since n becomes less than 2 at those high conversions. Few examples of the analytical representation for the after-effect observed are illustrated in Fig. 4 and the results of all lifetime runs are summerized in Table III.

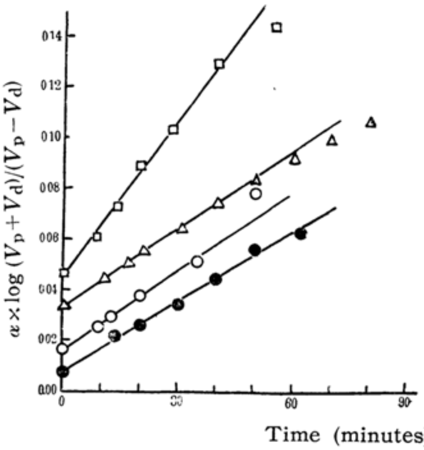

Fig. 4. Analytical representations for the observed after effects; the kinds of experimental points are the same as the ones shown in Fig. 2.

●, ○ ………… $\alpha=0.1$
□, △ ………… $\alpha=1.0$

Discussions

Rate acceleration Trommsdorff[4] examined several vinyl monomers and found that the rates of polymerization were accelerated after certain conversions, styrene alone showing no such acceleration under his experimental conditions. Also it has been well known after Schulz's work[11] that the rates of thermal polymerization of styrene at comparatively high temperatures are apparently proportional to the monomer concentration in the range up to about 90 % conversion. Therefore, compared with these previous results, the abnormal rate acceleration observed in this work seems to throw the possibility (a) on the production of an unstable substance which may induce the rate acceleration and the after-effect or (b)

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[11] G. V. Schulz, *Ergeb. d. exakt. naturwis.*, **17**, 364 (1938).

TABLE III KINETIC CHAIN LIFETIMES AND RATE CONSTANT RATIO IN RTYRENE

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_{to} [(b)]
0	20	2.18×10^{-5} 1.12×10^{-5}	0.26 0.35	0.48	0.55×10^{-6} [(a)]	
	30	2.27×10^{-6} 1.52×10^{-6}	9.8 12.	2.0	2.36×10^{-6}	1
38 ± 1	30	7.91×10^{-6} 3.58×10^{-6}	453. 1000.	358.	6.36×10^{-4}	3.75×10^{-3}
43 ± 2	30	9.32×10^{-6}	1356.	1261.	2.56×10^{-3}	9.22×10^{-4}
60 ± 2	30	2.58×10^{-5}	1932.	4980.	1.30×10^{-2}	1.81×10^{-4}
70 ± 2	30	1.76×10^{-5}	2274.	4002.	1.37×10^{-2}	1.71×10^{-4}

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

(b) The ratio of k_{tx} at x % conversion to k_{t0} at nearly 0 %; the assumption (2) was used in this estimation.

on the abnormal increase of q. However the theoretical examination for the case (a) will give a constant τ_s value, which is independent of V_{pL} and conversion, in contradiction to the present result, and also the simple calculation for the case (b) will lead to the unreal conclusion that the few hundred-fold increase of q must be necessary to explain the observed rate acceleration. On the other hand, if the rate acceleration is attributed to a decrease in k_t as suggested by Tromsdorff in the other vinyl polymerizations, the expected ratios of V_{pL} at 38 % and 60 % conversions to the initial value may eb estimated as about 7.9 and 18.8 respectively at 30°C. by the use of eqn. (4) with the data in the last column of Table III, while the corresponding experimental ratios are about 5.2 and 16.9 respectively. The difference between the above two values at each conversion is accepted to be within an experimental error under the present conditions. Thus the allowance for the above discussions will lead to the conclusion that the rate acceleration is due to an extreme decrease in k_t as the system becomes more viscous.

Decreases in the overall activation energy and n It is an expected result in this work that an extreme decrease in k_t is accompanied with a considerable decrease in the over-all activation energy, and this kinetic behaviour has also been found by the present author in the thermal- and photo-polymerizations of methyl methacrylate near room temperatures[12] and by Cowley & Melville[13] in the photo-degradation (by 2537 Å line) of polymethyl methacrylate over 130°C. This result can be explained by the fact that E_t in eqn. (5) increases steadily as the mutual termination of polymer radicals become diffusion-controlled with the increasing viscosity of the system. Using the following equation, which has been suggested by Spencer and Williams[14],

$$\eta=3.63\times10^{-10}\,exp\{0.0572\sqrt{M}+\sqrt{w_2}(22.54-0.045\sqrt{M}+5000/T)\},$$

where η = bulk viscosity of the styrene-polystrene system in centipoises, M = Staudinger molecular weight and w_2 = weight fraction of polymer, it may be estimated that the activation energies of diffusion of polymer radicals at 38 % and 60 % conversions are about 6.1 and 7.7 kcal./mole respectively. If 2.4 kcal./mole is used as an apparent E_t value in the initial stage[5b)], the estimated increase in E_t will cause it to decrease E_a (in eqn. (5)) by about 1.8 kcal./mole at 38 % and by about 3.0 kcal./mole at 60 %, while Table I shows the decreases in the over-all activation energies as 2.3∼2.4 kcal./mole at 38 % and as 3.5∼3.6 kcal./mole at 60 %. The difference between the above estimated and experimental decreases in E_a may be within an experimental error.

The value (1.9∼2.1) of n, the reaction order of chain termination, measured in the range 0 to nearly 40 % conversion shows that mutual termination only takes place. However its decrease over about 60 % conversion suggests strongly that self-termination occurs considerably in the highly viscous medium. It is not difficult to visualize a mechanism by which polymer radicals become apparently terminated without mutual collision. There will be a finite probability that the active end of a growing radical will become shielded by the coiling of the molecule. The fine net of polymer chains at high conversion would be expected greatly to enhance the

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[12] Unpublished work from this Laboratory.

[13] P. R. E. J. Cowley and H. W. Melville, *Proc. Roy. Soc. London*, **A211**, 320 (1952).

[14] Spencer and Williams, *J. Colloid Sci.*, **2**, 117 (1947).

degree of shielding. Thus a considerable portion of radicals become unable to react freely with monomer for steric reasons and appear to be deactivated by itself alone. In this sense the extreme decrease in k_t is an inevitable result and also the rate constants of propagation and transfer may be more or less reduced at very high conversions. On the other hand such a shielding effect may be expected to be diminished by the following factors; (i) thermal disturbance, (ii) a decrease in the molecular weight of polymer present and (iii) the addition of a chain transfer substance which is able to pass freely through the polymer network. The factor (iii) has been confirmed experimentally by the addition of a small amount of carbon tetrachloride as a chain transfer substance in the photo-polymerization of styrene[15]. Also it is expected from the factor (i) that neither the extreme decrease in k_t nor the change of $\dot{n}$ are observed at comparatively high temperatures. The discrepancy between the present experimental results and those of the previous authors may perhaps be due to a great difference in the degree of this shielding effect, though it can not be explained precisely at present.

Summary

The polymerization of pure styrene has been studied photochemically near room temperatures and in the range 0 to about 70 % conversion, and the following results have been obtained.

With increasing conversion; (1) both the direct photo-polymerization and the thermal polymerization are accelerated strongly, (2) the over-all activation energies in both polymerizations decreases, (3) the lifetime of kinetic chains increased steadily and the photochemical initial and after effects are easily observed dilatometrically over 30 % conversion. Also (4) the reaction order of chain termination is 2 in the range 0 to about 40 % conversion, but it becomes less than 2 at the conversions over 60 %.

Thus these results have been discussed on several assumptions and it has been concluded that they are attributed to a considerable change in the mechanism of radical termination with increasing conversion of the reaction system, i. e., the change from an activation-controlled termination to a diffusion-controlled one.

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[15] Unpublished work by the present author.