total solution, treated with activated charcoal. A similar Raman sample for the anion, $B_{12}D_{12}^{=}$, in D_2O solution was prepared by successive exchange with D_2O. Since the exchange was at least 90% complete, the concentration distribution of $B_{12}D_nH_{12-n}^{=}$ anion species is in accord with the binomial expansion, *e.g.*, ~30% $B_{12}D_{12}^{=}$. While this incomplete deuteration is not ideal, it does not appear to introduce serious complications in interpretation, perhaps because of the relative insensitivity of the boron cage vibrations to the degenerate deuterium substitution. Raman samples for the other anions listed were limited to about 4 grams of salt in 10 ml. of total solution.

The Raman spectra were taken using blue line excitation (4358 Å.) using an instrument designed by Rank and similar to that described by Rank and Wiegand.[11] The instrument is equipped with a helical Toronto mercury arc source and a straight mercury arc source for depolarization measurements, both with water-cooled electrodes. The Raman frequencies presented here are from direct electron multiplier photocell recordings and are accurate to an estimated ±3 cm.$^{-1}$. Qualitative features of the Raman spectra were checked by photography. The infrared measurements of the F_{1u} species were on water or deuterium oxide solutions, using a Perkin–Elmer model 21 infrared spectrometer and NaCl prism, except for 596 cm.$^{-1}$, which was taken using a KBr wafer on a Perkin–Elmer "Infracord"® with KBr prism. KBr wafers were found to cause infrared band shifts and splittings when compared to data on "Nujol"® mulls or water solutions.

Acknowledgments are due to Mrs. J. D. Carberry, Miss N. E. Schlichter and Messrs. W. H. Aughey and J. Q. Townley for valuable technical assistance in determining the spectra.

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[11] E. H. Rank and R. V. Wiegand, *J. Opt. Soc. Am.*, **36**, 325 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Kinetics of Anionic Polymerization of Styrene in Tetrahydrofuran

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A flow technique suitable for studying the kinetics of fast polymerizations is described. The time of polymerization may be as short as 0.08 sec. The anionic polymerization of styrene in THF was investigated and was shown to be first order with respect to the monomer concentration, but the apparent first order rate constant seems to increase with decreasing concentration of "living" ends. No satisfactory explanation was found for this phenomenon. The activation energy of the polymerization was found to be 1.0 kcal./mole, and the entropy of activation was by ~14 e.u. more negative than the respective $\Delta S^{\ddagger}$ of propagation in a radical polymerization. This decrease in $\Delta S^{\ddagger}$ is attributed to the immobilization of the counter-ion in the transition state. In this respect the reaction resembles the anionic polymerization of α-methyl styrene in THF which proceeds with even a lower entropy of activation. On the other hand, the anionic polymerization of styrene in dioxane seems to require a much higher activation energy and its entropy of activation seems to be "normal."

Anionic polymerization may be carried out under conditions preventing the occurrence of any termination, and the polymer produced in this manner is referred to as a "living" polymer.[1] Addition of monomer to a "living" polymer is kinetically a pseudo-unimolecular reaction since the process involves the propagation step only, and the concentration of "living" ends remains constant during the whole course of the reaction. Hence

$$-d[M]/dt = k_p \cdot [\text{"living" ends}] \cdot [M]$$

where [M] denotes the monomer concentration and k_p is the rate constant of the propagation step. The plot of $\ln[M_0]/[M]$ as a function of time should therefore result in a straight line passing through the origin, its slope giving $k_p \cdot$["living" ends]. Since the concentration of the "living" ends may be determined by a direct titration or by a photometric technique—the method gives the absolute value of k_p.

The growth of "living" polymers is often very rapid. This is not surprising since the concentration of the growing species in this polymerization is about 10^{-2}–10^{-3} *M*, whereas in a conventional radical polymerization the stationary concentration of growing radicals is 10^{-7}–10^{-8} *M*. Thus, the anionic polymerization of styrene in tetrahydrofuran solution is virtually completed in a second or two. Studies of such fast reactions require therefore special techniques, and in this investigation the capillary flow method[2] was adopted for this purpose.

Experimental

Although the capillary flow technique is well known, its application to the investigation of anionic polymerization poses a few problems. A description of details of our apparatus and its operation are therefore desirable.

The apparatus used in this study is shown in Fig. 1. Two cylindrical reservoirs contained the solution of the "living" polymer and of the monomer respectively. Each reservoir was calibrated and the level of the liquid could be measured with a cathetometer to 0.1 mm. accuracy. A narrow tube linked the bottom of each reservoir to 1 mm. wide capillaries forming arms of a T-shaped, three-way stopcock. The third vertical arm of the stopcock was immersed in a beaker containing wet tetrahydrofuran or methyl iodide dissolved in dry tetrahydrofuran. The stopcock contained a Teflon barrel with specially drilled 1 mm. holes which served as a mixing chamber. No greasing of the stopcock was required.

The liquid from each reservoir was pressed into the stopcock by dry and rigorously purified nitrogen introduced through special tubes which reached almost to the bottom of each vessel. This device ensured a constant rate of flow of each liquid, in spite of the fact that their levels, *i.e.* the hydrostatic pressures, varied in the course of the experiment. Of course, the pressure of nitrogen had to be kept constant during each experiment, and its possible fluctuations were minimized by inserting in the nitrogen line a 3 l. flask which acted as a barostat.

The reservoirs were immersed in larger vessels through which water, maintained at constant temperature by a

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[1] M. Szwarc, *Nature*, **178**, 5557 (1956); *Makromolek. Chem.*, **53**, 132 (1960).

[2] H. Hartridge and F. J. W. Roughton, *Proc. Roy. Soc.* (London), **B104**, 376 (1923); see also for a review, F. J. W. Roughton in "Techniques of Organic Chemistry," Vol. VIII, Interscience Publishing Co., New York, N. Y., 1953, p. 674.

thermostat, was flowing. In this way the temperature of both solutions was kept constant to within $^1/_2$°. The polymerization is exothermic, but though it proceeded under essentially adiabatic conditions, the heat capacity of the reagents was such that the temperature at the end of the capillary did not rise by more than $^1/_2$°. Hence, the temperature remained constant within less than 1° during the whole course of polymerization.

The solution of "living" polystyrene was prepared by a slow addition of styrene solution to a solution of di-anions of α-methyl styrene "tetramer,"[3] the amount of added styrene being such that a polymer of $\overline{\text{DP}}$ of about 20 was formed. The preparation was carried out on a high vacuum line, breakseals being used instead of stopcocks, and all the reagents were rigorously purified and dried. An aliquot of such a solution was titrated and the bulk of it sealed in the container which was eventually attached to the appropriate reservoir. If the experiment had to be delayed, the prepared solution was stored in a deep freeze. However, we made an effort to use it not later than a day or two after its preparation. The solution of styrene in tetrahydrofuran was also prepared on a high vacuum line. The solvent was dried with sodium-potassium alloy, a trace of anthracene or benzophenone being used as an indicator, and then it was distilled into the container. Styrene was purified in the conventional way, then digested for a day or two with calcium hydride and finally distilled on a high vacuum line into a measuring cylinder and thereafter into the container. The latter was then sealed to the respective reservoir, and the initial concentration of styrene was determined spectrophotometrically.

After having both containers attached to the respective reservoirs, the apparatus was evacuated and kept for a few hours under high vacuum to remove traces of moisture. Thereafter the breakseals on the containers were crushed and the reagents admitted to the respective reservoirs. An aliquot of "living" polystyrene solution was removed through the vertical capillary into a solution of methyl iodide in tetrahydrofuran. Titration of the sodium iodide, which remained after evaporating the solvent and excess methyl iodide, determined the concentration of "living" ends in the reservoir. A second aliquot of a mixture of the "living" polymer solution and of the monomer solution was then withdrawn and titrated. Actually, such aliquots were removed at the beginning and at the end of each series of experiments and the average value of the respective titrations was used in the calculation. In a reliable series of experiments the results of all these titrations did not differ by more than 5%. The concentration of "living" ends in each individual experiment was calculated as $V_1C_1/(V_1 + V_2)$, where V_1 and V_2 are the volumes of "living" polymer solution and styrene solution which passed through the capillary and C_1 is the concentration of "living" ends in the "living" polymer reservoir.

A series of experiments was performed with each set of reagents. In each series the time of polymerization was varied by changing the nitrogen pressure in the reservoirs. This introduced a small change in the composition of the reacting mixture since the flow of each reagent is affected to a slightly different degree by the pressure. The change in the composition was taken into account in the calculation.

For each experiment the time of polymerization was calculated as the ratio of the capillary volume to the sum of the rates of flow of both solutions. The latter were calculated by determining with a cathetometer the initial and final positions of the respective menisca in a timed run. During the flow the polymer was gradually deposited on the walls of the capillary thus changing its volume. To avoid any errors arising from this cause, the capillary was thoroughly cleaned with a pipe cleaner after each run. The initial rates of flow of the liquids, during a short period after opening the stopcock, must differ from that established in the stationary flow. It seems, however, that the stationary flow was established in less than a second, and since each run lasted for at least 1 minute this disturbance was of no significance in our work. Consequently, no attempt was made to correct for this phenomenon or to eliminate it by changing the experimental set-up.

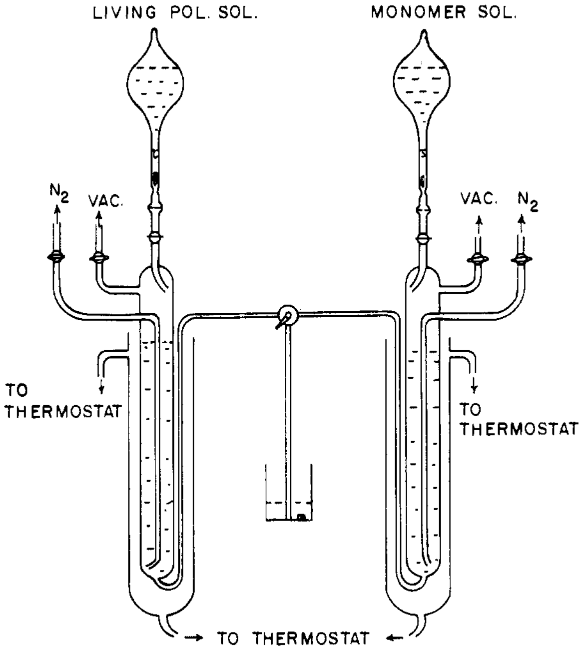

Fig. 1.—Flow apparatus for measuring rates of fast polymerizations.

The mixing of reagents appeared to be satisfactory if the rate of flow was not too low. Any faulty mixing could be recognized visually by the appearance of streaks in the capillary, and these were easily perceptible since one of the solutions was colored, whereas the other was colorless. In a few runs "living" polymer solution was mixed with a solution of THF containing an equivalent amount of water. "Killing" of "living" ends was completed in the barrel of the stopcock, proving that the mixing was adequate. Since the time of residence of the liquid in the barrel was about 0.003 sec. in those experiments, the time of mixing had to be less than this value. The ultimate "killing" of the polymer solution extruded into the beaker was also extremely fast and its speed depended upon the rate of dispersion of the reagents in the wet tetrahydrofuran. The progress of the "killing" reaction could be followed visually by observing the length of the colored "tail" of the liquid extruded from the capillary. This provided an approximate estimate of the time of "killing" which seemed to shorten as the flow rate increased. Apparently, the negative pressure resulting from the suction-action of the extruded liquid speeded up the mixing of the reagents with the surrounding solution. Further reduction in the "killing" time was achieved by placing the bottom of the beaker against the outlet of the capillary. In such a set up the "killing" time was estimated to be less than 0.005 sec.

Three techniques have been used to determine the monomer's conversion. In an earlier series of experiments the solution obtained at the end of each run was acidified with a drop of hydrochloric acid, and then the solvent was evaporated. The remaining solid polymer was freed from residual monomer by dissolving it in benzene and then by freeze-drying in high vacuum. The drying was continued until the weight of the residue remained constant. The same procedure was applied to samples of the starting polymer solution, and thus the difference in weights of the polymers obtained in an experiment and in the "blank" gave the weight of the polymerized monomer. To ascertain that no polymer was present in the monomer solution, we always determined its content by evaporating to dryness an aliquot of the monomer solution and weighing the residue. If polymer was found, the appropriate correction was introduced in calculations. Usually the amount of polymer in the monomer solution was not greater than 1% of the monomer.

In most of the experiments a spectrophotometric technique was used to determine the concentration of the

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(3) A solution of di-anions of α-methyl styrene "tetramer" is prepared by keeping a 0.5 M solution of α-methyl styrene in tetrahydrofuran in contract with a sodium mirror overnight. The solution is then transferred through a sintered glass filter to the reaction vessel. Numerous titrations demonstrated that the ratio Na : α-methyl styrene in such a preparation is 1 : 2.

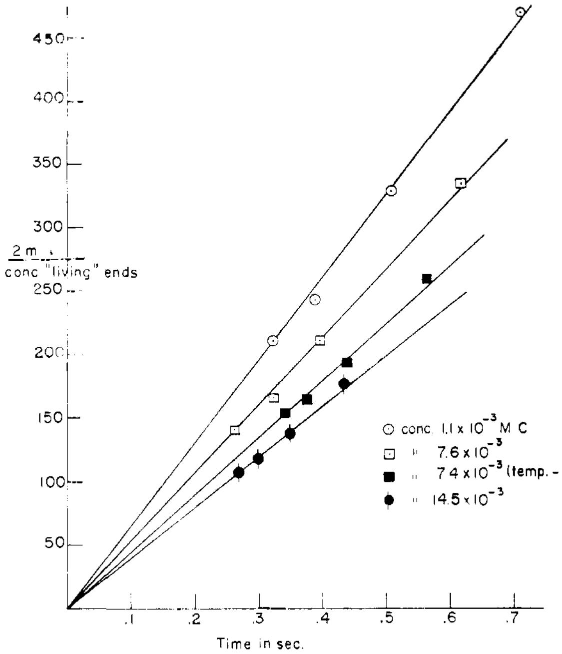

Fig. 2.—Rate of polymerization of living polystyrene at 25° and at varying concentrations (calculated by method I).

residual monomer in the final solution obtained at the end of each run. In determining the styrene concentration the optical density was measured at 291 mμ, by placing the investigated solution in one beam of the spectrophotometer and simultaneously placing in the second beam a solution of polymer, having the same concentration of polystyrene as that of the investigated sample. This arrangement eliminated any errors due to the polymer absorption.

In the last series of experiments the concentration of the residual monomer was determined by vapor phase chromatography, using ethyl benzene as an internal standard. This seems to be the most convenient technique, and the results are not affected by the presence of polymer. The reproducibility of all these methods was good and the results obtained by different techniques agreed closely.

Method of Calculation.—Every determination of the rate constant of propagation, k_p, resulted from a series of experiments performed with a particular solution of "living" polystyrene and a particular solution of the monomer. In each series of experiments the pressure of nitrogen, and hence the time of polymerization, was the only variable, and the results gave the concentration of the monomer M as a function of time. It has been explained in the preceding section that the time of polymerization was calculated as the *average* time of flow, *i.e.*

$$\bar{t} = (\text{capillary volume})/(\Sigma \text{ rates of flow})$$

If we assume that the reacting liquid flows as a solid block then the dependence of M on $\bar{t}$ is given by the usual unimolecular expression $M = M_0 \exp\,(-k_p\cdot[\text{"living" ends}]\cdot\bar{t})$. Hence, k_p["living" ends] is given by the slope of the straight line obtained by plotting $\ln(M_0/M)$ *versus* time. We shall refer to this method of calculation as Method I.

On the other hand, if the flow of the liquid is laminary in character, then the various concentric ring-layers flow with a different velocity. Let us denote by r the distance from the center of the capillary of a ring-layer of thickness dr, and by R the radius of the capillary. At distance r the gradient of the velocity of the liquid

$$-\mathrm{d}u/\mathrm{d}r = pr/2\eta$$

where p is the pressure gradient and η the viscosity of the liquid. The volume of the liquid flowing through the capillary in one second is therefore

$$q = \int_0^R 2\pi r\cdot u\,\mathrm{d}r = \pi R^4 p/8\eta,$$

and the "average" time of residence is

$$\bar{t} = 8V\eta/\pi R^4 p = 8L\eta/R^2 p$$

where V denotes the volume of the capillary and L its length.

If we neglect the diffusion of the reagents (radial or axial) the concentration M_r of the monomer at the end of the capillary and at a distance r from its center is given by the equation

$$M_r = M_0 \exp(-k_p C_{LE} L/u) = M_0 \exp(-\alpha/u)$$

where C_{LE} is the concentration of "living" ends. Hence, the average concentration of the monomer at the end of the capillary is

$$M = (1/q)\cdot M_0 \int_0^R 2\pi\, r\mathrm{d}r\cdot u \exp(-\alpha/u)$$

Integration gives

$$\bar{M}/M_0 = e^{-m}\,[1 - m + F(m)]$$

where $m = 4\alpha\eta/pR^2 = {}^1/_2\, k_p C_{LE}\,\bar{t}$ and

$$F(m) = m^2 e^{-m} \int_m^\infty e^{-x}\,\mathrm{d}x/x$$

Numerical values of $\bar{M}/M_0$ as a function of m are given in Table I, and these data permit to draw a plot of $\bar{M}/M_0$ *versus* m, from which m may be read if $\bar{M}/M_0$ is determined experimentally. Plotting $2m$["living" ends]$^{-1}$ *versus* $\bar{t}$ should give a straight line through the origin with a slope k_p. This method of calculating k_p is referred to as Method II.

Consideration of both kinetic treatments show that for $\bar{M}/M_0$ approaching unity the results are independent of the method of calculation. This means that for a very low % of conversion, *i.e.* for a short time of polymerization and/or for a low concentration of living ends, the calculated k_p's are reliable whatever method is used for their derivation. On the whole, Method II gives higher results than Method I, the deviation increases with increasing $\bar{M}/M_0$.

The two methods of calculation give the extreme values for k_p; the true value is undoubtedly an intermediate one. We feel, however, that Method I is probably more reliable. The actual flow is somewhat turbulent, since the mixing introduces an initial turbulence. The Reynolds number calculated for a typical experiment is ~3000. A laminary flow requires Reynolds numbers smaller than 2100, while a turbulent flow develops for those greater than 3000. In a turbulent flow the kinetics of the reaction resemble that expected in a block flow rather than that in a laminary flow. Moreover, radial diffusion of the monomer, which is unavoidable, also makes Method II less reliable. However, it is gratifying to find that the maximum uncertainty in k_p, arising from the choice of the method of calculation, is not more than about 25% (see Table V).

Results

The results obtained for anionic homo-polymerization of styrene in tetrahydrofuran at 25° are given in Table II, and, for some typical experiments, the calculations of k_p's are illustrated by Fig. 2 (Method I) and 3 (Method II). Table III gives some k_p values calculated from the experimental data by the least square method. The values on the left are derived from the slope of the "best" straight line passing through the experimental

TABLE I

VALUES OF THE AUXILIARY VARIABLE *m* NEEDED FOR THE CALCULATION OF THE RATE CONSTANT IN A FLOW TECHNIQUE BY METHOD II

$$C/C_0 = e^{-m}\left[1 - m + m^2e^{m}\cdot\int_{m}^{\infty}\frac{\mathrm{d}x}{x}\,e^{-x}\right]$$

m	0.000	0.005	0.010	0.020	0.030	0.040	0.050	0.075	0.100	0.150
C/C_0	1.000	.990	.981	.961	.943	.925	.908	.868	.832	.765
m	0.200	.250	.300	.350	.400	.450	.500	.550	.650	.750
C/C_0	.704	.652	.600	.555	.515	.477	.443	.412	.357	.310
m	.850	1.000	1.150	1.350	1.50	1.75	2.00	2.25	2.50	3.00
C/C_0	.274	0.219	0.179	0.138	0.113	0.082	0.060	0.044	0.028	0.018

points, while those on the right are based on the "best" straight line passing through the origin. The agreement between these two sets of data shows that the times of mixing and killing were much shorter than the time of polymerization. Table IV gives results obtained at various temperatures and, in some cases, in the presence of salts.

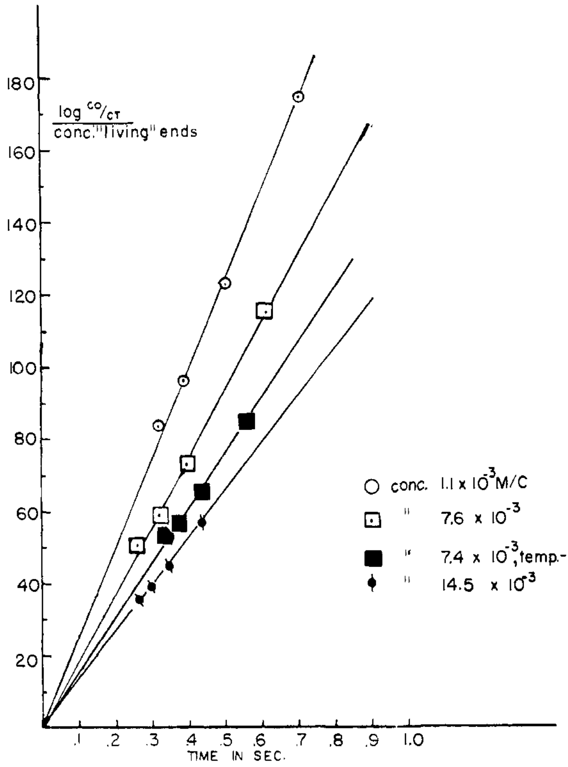

Fig. 3.—Rate of polymerization of "living" polystyrene at 25° and at varying concentrations as calculated by method II.

Table V gives the propagation rate constants calculated by Method I (k_p) and by Method II (k_p'). Inspection of these data shows that k_p (or k_p') is independent of the monomer concentration, *e.g.* in series 24d, 21b, 21c and 28a for which the [LE] was approximately constant ($1.14 - 1.7 \times 10^{-3}$), k_p was found to be constant, namely 570 ± 15, although $[M]_0$ varied from 1.97×10^{-2} to 9×10^{-2}. On the other hand, k_p seemed to decrease with increasing concentration of the living ends. This is shown clearly in Fig. 4, where k_p (or k_p') is plotted as a function of [living ends]. In three experiments a THF solution of perchlorate (sodium and lithium perchlorate are easily soluble in THF) was added to the polymerized solution of living polystyrene. The results show that the presence of this salt did not affect the rate of polymerization (see Fig. 4).

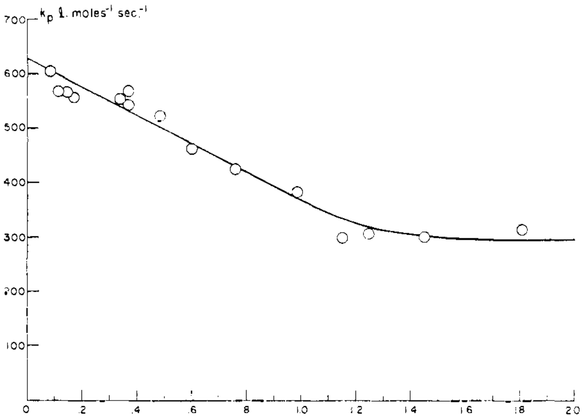

Fig. 4.—Dependence of k_p in the anionic polymerization of styrene on the concentration of the living ends.

One series of experiments was carried out at −7° and only a small change was observed in the rate constant of propagation. Comparing this result (27c) with that obtained in series 24b (the same [LE]), one calculates the activation energy of propagation to be ~1.0 kcal./mole.

Discussion

The results show that the anionic polymerization of styrene in THF is a pseudo-unimolecular chain reaction which does not involve a termination step, thus confirming the concept of "living" polymers.[1] Similar kinetic results were obtained by Worsfold and Bywater[4] for the anionic polymerization of α-methyl styrene in THF, by Dainton, Wiles and Wright[5] for the polymerization of styrene initiated

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(4) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **36**, 1141 (1958).

(5) F. S. Dainton, D. M. Wiles and A. N. Wright, *J. Polymer Sci.*, **45**, 111 (1960).

TABLE II

ANIONIC POLYMERIZATION OF STYRENE IN THF AT 25°; Na^+-COUNTERION

Series	[Living ends] $M \times 10^3$	$[M]_0$, mole/l.	t, sec.	% conversion
18	4.86	0.223	0.792	87.3
	4.86	.222	.455	65.8
	4.85	.224	.305	53.9
19	3.40	.097	.743	78.4
	3.37	.098	.574	69.4
	3.39	.097	.447	56.9
	3.37	.098	.331	45.9
20	3.74	.131	.750	78.2
	3.70	.128	.551	67.6
	3.70	.127	.414	53.5
	3.67	.128	.310	45.2
20a	3.79	.130	.706	81.7
	3.73	.132	.561	69.0
	3.71	.133	.400	57.9
	3.68	.134	.297	47.4
21c	1.49	.0882	.798	50.0
	1.48	.0893	.605	41.5
	1.41	.0901	.373	26.2
	1.39	.0901	.279	19.1
21b	1.72	.0668	.821	55.7
	1.70	.0660	.551	40.1
	1.67	.0674	.408	29.8
	1.66	.0676	.285	23.1
22c	9.89	.0778	.500	89.3
	9.89	.0778	.382	76.0
	9.89	.0776	.296	60.6
	9.85	.0778	.260	64.3
23a	12.41	.0603	.442	81.5
	12.42	.0600	.366	75.4
	12.40	.0602	.301	69.0
	12.40	.0603	.264	65.5
23b	18.1	.073	.393	89.9
	18.2	.073	.334	86.4
	18.1	.073	.285	81.8
	18.1	.073	.262	80.4
24a	14.5	.0568	.432	84.8
	14.5	.0567	.348	77.7
	14.5	.0569	.298	73.0
	14.5	.0568	.267	70.3
24b	5.95	.0468	.608	78.8
	5.9	.0468	.422	68.0
	5.9	.0468	.315	56.3
	5.9	.0468	.278	52.2
24g	7.75	.0118	.616	85.4
	7.75	.0118	.395	71.6
	7.60	.0120	.261	58.0
	7.60	.0120	.324	62.9
	7.60	.0120	.978	91.4
24c	0.835	.0194	.740	32.6
	.834	.0198	.456	20.5
	.830	.0198	.376	17.1
	.820	.0200	.320	15.0
24d	1.14	.0195	.711	36.9
	1.15	.0197	.506	27.9
	1.14	.0198	.388	22.2
	1.14	.0200	.321	19.8

TABLE III

CALCULATION OF k_p (METHOD I), USING THE LEAST SQUARE METHOD FOR THE EXPERIMENTAL POINTS AND THE LEAST SQUARE METHOD FOR A STRAIGHT LINE PASSING THROUGH THE ORIGIN

Run	k_p (least square) l. mole^{-1} sec.$^{-1}$	k_p (least square through origin) l. mole^{-1} sec.$^{-1}$
18	552	523
19	572	554
20	554	545
20a	521	570
21c	595	570

TABLE IV

ANIONIC POLYMERIZATION OF STYRENE IN THF

Series	Temp., °C.	[Living ends] $M \times 10^3$	$[M]_0$, mole/l.	t, sec.	% conversion
27	−7	7.43	0.0514	0.561	76.8
	−7	7.46	.0521	.437	67.6
	−7	7.44	.0521	.375	62.2
	−7	7.42	.0524	.340	59.9
21	0	1.01	.0102	.414	25.2
28[a]	25	4.10	.0739	.580	74.4
	25	4.18	.0708	.416	61.4
	25	4.23	.0698	.326	52.2
	25	4.24	.0695	.255	46.2
28[b]	25	1.55	.0700	.536	38.6
	25	1.53	.0703	.399	29.0
	25	1.55	.0696	.315	25.2
	25	1.55	.0700	.262	18.8
32a	25	2.92	.0544	.574	62.1
	25	2.86	.0553	.364	45.0
	25	2.82	.0556	.255	37.4
	25	2.86	.0553	.209	34.1

[a] 10 times excess of $NaClO_4$ added. [b] 20 times excess of $NaClO_4$ added.

by the blue solution of potassium in THF or dimethoxyethane, and by Allen, Gee and Stretch[6] for the anionic polymerization of styrene in dioxane.

The studies of Worsfold and Bywater,[4] like our own, show that the first order character of the polymerization is obeyed even for 90% conversion. However, in contradistinction with our findings, the pseudo-unimolecular rate constant for α-methyl styrene polymerization, *i.e.* k_p[LE], remains linear with the concentration of living ends in the range [LE] = $\sim 10^{-4} M$ up to $3 \times 10^{-3} M$, although the straight line drawn through the experimental points (at −40°) shows a small intercept. The authors remarked that this intercept may be an artifact, arising from the destruction of a small fraction of catalyst, but they emphasized also that the observed effect may be real. Their data obtained at −77° seem to indicate again a decrease of k_p with increasing concentration of the catalyst, whereas for those results which were obtained at −10°, the experimental scatter is too

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(6) G. Allen, G. Gee and C. Stretch, *J. Polymer Sci.*, **48**, 189 (1960); see also C. Stretch and G. Allen, *Polymer*, **2**, 151 (1961).

TABLE V

CALCULATION OF k_p (METHOD I) AND k_p' (METHOD II) FOR ANIONIC POLYMERIZATION OF STYRENE IN THF AT 25°

Series	[Living ends] $M \times 10^3$	$[M]_0$, mole/l. $\times 10^2$	k_p, l./mole sec.	k_p', l./mole sec.
24c	0.830	1.97	609	638
24d	1.145	1.97	565	640
21c	1.45	9.0	570-595	650
21b	1.70	6.7	556	625
19	3.40	9.8	554–572	663
20	3.70	13.0	545–554	650
20a	3.75	13.2	510–570	675
18	4.85	22.3	523–552	620
24b	5.90	4.7	458	560
24g	7.70	1.2	426	539
22c	9.89	7.8	385	520
22b	11.4	10.5	300	390–465
23a	12.4	6.0	309	405
24a	14.5	5.7	300	402
23b	18.1	7.3	315	444
28[a]	4.2	7.0	535	..
28[b]	1.55	7.0	580	..
32[b]	2.9	5.5	574	..
27[c]	7.45	5.2	352	..

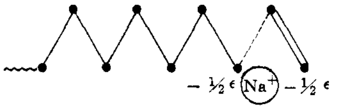
[a] $NaClO_4$ added in 10 fold excess of LE. [b] $NaClO_4$ added in 20 fold excess of LE. [c] Experiment carried out at −7°.

large to permit any reliable conclusion about their concentration dependence.

In our own studies the apparent k_p seems definitely to decrease with increasing concentration of living ends. This decrease might arise from the destruction of some living ends in the capillary since their concentration was always determined at the outlet. However, one expects that the impurities on the capillary wall would be destroyed during the first few seconds of the experiment, and since a constant concentration of living ends was observed at the beginning and at the end of each series, this explanation seems unlikely. Alternatively, the "killing" might be due to some impurities present in the monomer solution. This is also improbable, since the concentration of living ends in the absence and in the presence of monomer solution (corrected for the change in volume) was found to be constant (see Experimental).

The dependence of the apparent k_p on the concentration of living ends is a puzzling phenomenon. Studies of other systems, carried out in this Laboratory (*e.g.* co-polymerization of styrene on the living poly-α-methyl styrene or the anionic homo-polymerization of vinyl pyridine) showed the same concentration dependence of the propagation rate constant. Unfortunately, no satisfactory explanation for this phenomenon may be offered at this time. The suggestion that the isolated ions grow faster than ion-pairs is contradicted by the conductivity studies carried out by Worsfold and Bywater.[7] These workers found that about 1% of ion-pairs dissociates in a 10^{-3} *M* solution of living polystyrene in THF. This would mean that an isolated ion grows about 100 times faster than an ion-pair, and it would require the curve, shown in Fig. 4, to turn sharply up for $C<0.001$. There is no indication of such a behaviour. The alternative suggestion that ion-pairs associate into pairs of ion-pairs is also improbable. Such an association would be manifested by a change in the viscosity of solution on killing living polystyrene. This was not observed, although our polymers possess two living ends per chain. Finally, the addition of a large excess of sodium perchlorate had no effect upon k_p (see Table V) which contradicts such an explanation. It seems, therefore, that more work should be done to clarify this issue.

The low activation energy (1.0 kcal./mole) of the propagation step makes the entropy of activation of the anionic polymerization of styrene substantially more negative than that of the radical polymerization. The available data[8] indicate that the A factor of the propagation step in the radical polymerization of styrene is $\sim 4.5.10^6$ l./mole sec., while the *A* factor for the anionic polymerization in THF (at infinite dilution) is calculated to be $\sim 4 \times 10^3$. Hence, the decrease in the entropy of activation amounts to about 14 e.u. We propose that this decrease should be attributed to the immobilization of the counter-ion (and its solvation shell) in the transition state, as shown below



The large decrease in entropy of activation, characterizing the anionic polymerization of styrene in THF, was also observed by Dainton, *et al.*[5] Their kinetic studies provided only qualitative information; nevertheless, the derived value for k_p is similar to ours, *i.e.* about 1000 l./mole sec. The fact that the reaction proceeded at −78° as well as at 0° was taken as an indication of a low activation energy of the propagation step, and this demands a substantially negative $\Delta S^{\ddagger}$. Dainton, *et al.*, attribute this low value of $\Delta S^{\ddagger}$ to a higher degree of solvation of the transition than the initial state. They assumed that in the transition state the counter-ion is separated from the growing end by a monomer molecule, and this increases the degree of solvation.

A very low A_p is also shown in the anionic polymerization of α-methyl styrene in THF. Actually, from Worsfold and Bywater's data[4] we calculate A_p to be ~ 250 l./mole sec. Unfortunately, no data are available for the absolute value of k_p in the radical polymerization of α-methyl styrene. It is probable that the respective A_p factor may be lower than that observed in the styrene polymerization.

On the other hand, the activation energy of the anionic polymerization of styrene in dioxane seems to be substantially greater,[6] namely 9 ± 3 kcal./mole, and the respective A_p factor appears to be "normal." Undoubtedly, solvents exert a great influence not only upon the rate but also upon the character of ionic polymerization.

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(7) D. J. Worsfold and S. Bywater, *J. Chem. Soc.* (London), p. 5234 (1960).

(8) C. Walling, in "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

The low activation energy of the investigated propagation of styrene polymerization suggests that the reaction in tetrahydrofuran may involve two steps—a rapid equilibrium

$$S_n{\cdot}S^- + S \rightleftharpoons S_n{\cdot}S^-,S, \ldots, K_{as}$$

in which a complex is formed with the monomer (*e.g.*, a charge transfer complex) followed by an irreversible rearrangement

$$S_n{\cdot}S^-,S \longrightarrow S_{n+1}{\cdot}S^-, \ldots, k_r$$

If $(S_n{\cdot}S^-,S] \ll [S]$, the kinetic result of this scheme would be identical with the conventional bimolecular reaction. However, the over-all activation energy E_p would be $E_p = \Delta H_{as} + E_r$; and since ΔH_{as} is negative, E_p could be very low. Such a scheme may account for the observed dependence of k_p on [LE] if the complex is in equilibrium with its ions, *i.e.*

$$S_n{\cdot}S^-, S, Na^+ \rightleftharpoons S_nS^-,S + Na^+$$

and the rearrangement constant k_r' for $S_n{\cdot}S^-$, S, Na^+ is lower than that for $S_n{\cdot}S^-$, S (k_r''). Since the concentration of $S_n{\cdot}S^-$, S is much lower than that of $S_n{\cdot}S^-$, Na^+, its dissociation into free ions may be considerable. This scheme avoids all the difficulties of the previously considered suggestion, namely, $S_nS^-, Na^+ \rightleftarrows S_nS^- + Na^+$, which made the latter unacceptable, as the explanation of the dependence of k_p on the concentration of living ends.

It is interesting to note that the rate constant of propagation in the anionic polymerization of styrene at 25° is greater only by a factor of 25 or 30 than the k_p of the radical polymerization. Hence, the large increase in the rate of anionic polymerization, when compared to the radical reaction, is due to a higher concentration of growing chains. As was pointed out, the stationary concentration of growing radicals is about 10^{-7}–10^{-8} *M*, while that of the growing anions is 10^{-3}–10^{-2} *M*.

Finally, let us compare the absolute propagation rate constants of styrene and α-methyl styrene polymerizations. The latter is smaller by a factor of 300, while the respective equilibrium constants of propagation differ by a factor of ~10^6. This indicates that the strain caused by the bulky groups present in the α-methyl styrene molecule is much more pronounced in the final state, *i.e.* in the polymer, than in the transition state. This point was clearly recognized by Alfrey.[9]

We wish to acknowledge the financial support of this investigation by the National Science Foundation (Grant No. G14393) and by the Quartermaster Corps (Grant No. DA-19-129-QM-1297).

[9] T. Alfrey in T. Alfrey, J. J. Bohrer and H. Mark, "Co-polymerization," Interscience Publishers, New York, N. Y., 1952; see also T. Alfrey and W. H. Ebelke; *J. Am. Chem. Soc.*, **71**, 3235 (1949).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, CELANESE CHEMICAL COMPANY, A DIVISION OF CELANESE CORPORATION OF AMERICA, CLARKWOOD, TEXAS]

Excited Alkoxy Radicals in the Photolysis of Dialkyl Peroxides[1]

BY G. R. McMILLAN

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The decomposition of alkoxy radicals formed by photolysis (λ 2537 Å.) of diisopropyl, di-*tert*-butyl and isopropyl-*tert*-butyl peroxides is not completely suppressed by nitric oxide. This observation is discussed in terms of excited or "hot" alkoxy radicals formed in the primary process. In the di-*tert*-butyl peroxide–nitric oxide system, the excited radical effect appears to decrease as the peroxide pressure is increased or as propylene is added, suggesting a collisional deactivation process. Such a deactivation is evidence for the participation of excited radicals of finite lifetime, as it weighs against an alternative primary process involving concerted scission of two or three bonds in the peroxide molecule to form products directly. *tert*-Pentoxy radicals are known to decompose by two parallel reactions, a favored path to split off an ethyl radical, and a second path to split off a methyl. *tert*-Pentoxy radicals formed by photodecomposition of ethyl-*tert*-pentyl peroxide with λ 2537 Å. radiation show an increased randomness in the bond scission reaction compared with radicals formed by λ 3130 Å. radiation or by thermal decomposition of the peroxide, a result perhaps to be expected of excited radicals. Indirect evidence points to the absence of an excited radical decomposition of the ethoxy formed by photolysis of ethyl-*tert*-pentyl peroxide.

Introduction

Much of the information about reactions of alkoxy radicals in the vapor phase has been obtained from studies of the photolysis of dialkyl peroxides.[2–6]

It is known that isopropoxy radicals may decompose according to

$$(CH_3)_2CHO \longrightarrow CH_3 + CH_3CHO \qquad (1)$$

but decomposition of the radicals formed by photolysis of diisopropyl peroxide by light of λ 2300–2900 Å. appeared to be complex.[6] In effect, the apparent rate of reaction 1 was expressible not as $k_1[(CH_3)_2CHO]$ but as $K + k_1[(CH_3)_2CHO]$. Furthermore, addition of nitric oxide, a scavenger of known effectiveness for alkoxy radicals, did not eliminate acetaldehyde formation; in fact, the acetaldehyde quantum yield was independent of

[1] Presented in part at the 140th National Meeting of the Society, Chicago, Ill., September, 1961.

[2] L. M. Dorfman and Z. W. Salsburg, *J. Am. Chem. Soc.*, **73**, 255 (1951).

[3] D. H. Volman and W. M. Graven, *ibid.*, **75**, 3111 (1953).

[4] G. R. McMillan and M. H. J. Wijnen, *Can. J. Chem.*, **36**, 1227 (1958).

[5] G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960).

[6] G. R. McMillan, *ibid.*, **83**, 3018 (1961).