steps in the reaction sequence were acid-catalyzed. The support for the ester hypothesis could be found in the similarity between tungsten and chromium: the facility with which chromic acid esterifies alcohols is well known.[33] The ester hypothesis could perhaps explain why tungstic acid appears to catalyze the opening of the oxirane ring more efficiently during the course of epoxidation of allyl alcohol than in the absence of the latter. Were the path of eq. 35 the correct one, then a "cage effect" might be invoked.

Acknowledgments.—The author wishes to express his appreciation to Prof. P. D. Bartlett of Harvard University and Drs. P. L. Dietz and H. C. Stevens of this Laboratory for stimulating discussions. Thanks are also due to Mr. E. M. Pflueger who performed part of the experimental work.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dead-end Radical Polymerization. II

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RECEIVED AUGUST 13, 1959

In the absence of retardation of the termination reaction, the radical initiated polymerization of vinyl monomers ceases short of complete conversion, a phenomenon that has been termed dead-end radical polymerization. The modified kinetic expression describing the polymerization may be used with experimentally determined conversion–time data to calculate simultaneously the specific rate of initiator decomposition k_d and the kinetic constant $f^{1/2}k_p/k_t^{1/2}$. If the quantity $k_p/k_t^{1/2}$ is known for the monomer, the initiator efficiency f may be found. If k_d and $f^{1/2}k_p/k_t^{1/2}$ for the system are known, the course of conversion with time may be accurately predicted. When the theoretical value for the dead-end conversion is fairly high, acceleration of polymerization to nearly complete conversion may occur due to the retardation of the termination step; in such cases, the dead-end theory is inapplicable. Data for the bulk polymerization of styrene at several temperatures with 2,2′-azobisisobutyronitrile as initiator illustrate the application of the dead-end theory for kinetic measurements and also the limitations imposed by the "gel" effect.

Introduction

In the previous article,[1] it was shown that the limiting fractional conversion at infinite time of a radical initiated vinyl polymerization is less than unity (neglecting thermal polymerization) and can be predicted if the kinetic constants describing the system are known accurately. Under certain conditions of temperature and initiator concentration the limiting conversion may in fact be very low. This situation applies only in the absence of such complicating features at high conversion as the retardation of the termination step, the so-called Tromsdorff–Norrish[2,3] "gel" effect.

This present work shows experimental conditions where the dead-end theory appears to apply exactly and other conditions where the "gel" effect invalidates the theory. Where the theory is valid, it has been used to obtain values for the specific rate constant of initiator decomposition and for the initiator efficiency.

Theoretical

The rate of radical initiated vinyl polymerization, assuming a steady-state radical concentration, is

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} k_d^{1/2} f^{1/2} [\text{Cat}]^{1/2}[M] \qquad (1)$$

This disregards the polymer produced by purely thermal polymerization concurrent with the catalyzed polymerization. In this equation, $[M]$ represents the concentration of unreacted monomer, $[\text{Cat}]$ the concentration of unreacted catalyst and f the catalyst efficiency, that is, the fraction of radicals produced by the primary cleavage of catalyst that actually start polymer chains. The quantity k_d is the specific rate constant for the first-order primary cleavage of catalyst, k_p is the specific rate of propagation, $k_t = k_{tc} + k_{td}$ is the sum of the specific rates of combination and disproportionation, respectively.

If the catalyst is such as 2,2′-azobisisobutyronitrile, the rate of disappearance of catalyst is

$$\frac{-d[\text{Cat}]}{dt} = k_d[\text{Cat}] \qquad (2)$$

If the initial catalyst concentration is $[\text{Cat}]_0$ and if the catalyst is all added at the beginning of the polymerization, one obtains

$$[\text{Cat}] = [\text{Cat}]_0 e^{-k_d t} \qquad (3)$$

As the polymerization proceeds, there is a net volume shrinkage of the system as monomer is converted into polymer of lesser specific volume. This results in an effective increase of the initial catalyst and monomer concentrations so that at a fractional conversion x

$$x = ([M]_0 - [M])/[M]_0 \qquad (4)$$

the effective unreacted catalyst and monomer concentrations are

$$[\text{Cat}] = \frac{[\text{Cat}]_0}{(1 - \alpha x)} e^{-k_d t} \qquad (5)$$

$$[M] = \frac{[M]_0}{(1 - \alpha x)} (1 - x) \qquad (6)$$

where $[M]_0$ is the initial monomer concentration and α is the total volume shrinkage for the complete conversion of monomer to polymer.

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[1] A. V. Tobolsky, THIS JOURNAL, **80**, 5927 (1958).

[2] E. Tromsdorff, H. Kohle and P. Lagolly, *Makromol. Chem.*, **1**, 169 (1948).

[3] R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).

TABLE I[a]

Temp., °C.	60		70		80		90		100		100	
$[\mathrm{Cat}]_0$	0.0216		0.0214		0.0212		0.0210		0.0337		0.0093	
	t	x	t	x	t	x	t	x	t	x	t	x
	0.70	0.093	0.36	0.117	0.18	0.146	0.09	0.172	0.03	0.144	0.03	0.065
	1.4	.190	0.72	.215	.36	.259	.18	.286	.06	.253	.06	.124
	2.9	.332	1.44	.367	.54	.358	.27	.369	.09	.349	.09	.171
	5.8	.642	2.16	.518	.72	.448	.36	.428	.12	.398	.12	.202
	8.6	.87	2.52	.623	.90	.521	.54	.499	.15	.414	.15	.214
	11.5	.955	2.88	.801	1.08	.571	.72	.534	.18	.468	.18	.252
	17.3	.955	3.60	.953	1.26	.629	1.08	.560	.36	.528	.36	.290
	23.1	.956	4.32	.956	1.44	.692	1.44	.579	.72	.507	.72	.320
	46.1	.960	8.64	.965	1.62	.793	1.80	.595	1.44	.558	1.44	.309
					1.71	.847	3.60	.626				
					1.80	.917						
					2.16	.949						
					2.88	.955						
					4.32	.971						

[a] t = time in seconds 10^{-4}; x = fractional conversion corrected for thermal polymerization; $[\mathrm{Cat}]_0$ = initial initiator concentration at $T°$.

TABLE II

				$k_d \times 10^4$, sec.$^{-1}$			f			x_∞	
Temp., °C.	$[\mathrm{Cat}]_0$, mole/l. at $T°$	α	$k_p/k_t^{1/2}$	Eq. 13	Eq. 10	Lit. ref. 7	Eq. 13	Eq. 10	Lit. ref. 4	Predicted by eq. 10	Expt.
60	0.0216	0.163	0.0341	...	(0.12)	0.097	..	(0.71)	0.60	0.94	0.95
70	.0214	.170	.0451	...	(0.45)	0.38	..	(.71)	.60	.85	.95
80	.0212	.179	.0592	...	(1.60)	1.40	..	(.71)	.60	.72	.95
90	.0210	.182	.0739	4.88	5.08	4.80	0.92	.71	.60	.63	.63
100	.0337	.186	.0915	18.4	18.0	16.0	1.04	.76	.60	.54	.56
100	.0093	.186	.0915	18.4	18.0	16.0	1.04	.61	.60	.32	.31

Substituting equations 5 and 6 into equation 1 and integrating in terms of the fractional conversion x, one obtains successively

$$\frac{\mathrm{d}x}{(1-x)(1-\alpha x)^{1/2}} = \frac{k_p f^{1/2} k_d^{1/2}}{k_t^{1/2}(1-\alpha)} [\mathrm{Cat}]_0^{1/2} e^{-k_d t/2}\, \mathrm{d}t \quad (7)$$

$$\ln \frac{y+a}{y-a} = \ln \frac{1+a}{1-a} + \frac{K}{a}\left(1 - e^{-k_d t/2}\right) \quad (8)$$

where

$$y = (1-\alpha x)^{1/2} \qquad K = \frac{2k_p f^{1/2}[\mathrm{Cat}]_0^{1/2}}{k_t^{1/2}\, k_d^{1/2}}$$
$$a = (1-\alpha)^{1/2}$$

In the absence of such complicating phenomena as the Tromsdorff–Norrish effect, as $t \rightarrow \infty$, the conversion reaches a limiting value x_∞, so that

$$\ln \frac{y_\infty + a}{y_\infty - a} = \ln \frac{1+a}{1-a} + \frac{K}{a} \quad (9)$$

Equations 8 and 9 may be combined to give

$$-\ln\left[\ln\left(\frac{y_\infty + a}{y_\infty - a}\right) - \ln\left(\frac{y_i + a}{y_i - a}\right)\right] = -\ln\frac{K}{a} + \frac{k_d}{2}\, t_i \quad (10)$$

where y_i is the value of y at $t = t_i$.

These expressions represent a small correction to those obtained neglecting volume shrinkage[1]; a quantitative comparison will be given in the subsequent section.

A plot of the left-hand side of equation 10 *versus* t_i will yield a straight line of slope $(k_d/2)$ and of intercept $(-\ln K/a)$. This enables one to obtain simultaneous values of k_d and $f^{1/2}k_p/k_t^{1/2}$; if $k_p/k_t^{1/2}$ is known then the initiator efficiency f can be found.

Experimental

Freshly distilled styrene was polymerized at 60, 70, 80, 90 and 100° for varying lengths of time in evacuated, sealed Pyrex ampoules with and without 2,2′-azobisisobutyronitrile as initiator. All samples were prepared and worked-up in an identical manner[4]; it was found necessary to reprecipitate the glassy high-conversion samples from chloroform in order to free them from residual monomer.

In all cases the amount of thermal polymer was nearly insignificant compared with the total conversion. To account for the small contribution of the purely thermal polymerization, the experimentally determined conversions were corrected by subtracting the measured thermal conversion in a thermal polymerization of the same sample of styrene at the same temperature. At small time values this method is not exact[5] but the amount of thermal polymerization is so small in comparison with the catalyzed polymerization, that this procedure is sufficiently accurate. The procedure is quite valid at the longer times, when the initiator in the catalyzed run has disappeared, except when the fractional conversions approach unity.

The values of α listed in Table II were calculated from the known densities of styrene monomer and polymer at the temperatures used. The values of $k_p/k_t^{1/2}$ in Table II are those given by Offenbach and Tobolsky[6] in terms of the quantity: $A' = (2k_{td} + k_{tc})/k_p^2$; for styrene, $k_{td} = 0$.

Results and Discussion

The theory of dead-end radical polymerization, where applicable, allows the simultaneous determination of the specific rate of initiator decomposition k_d and the initiator efficiency f provided that $k_p/k_t^{1/2}$ is known for the monomer in question. We found conditions under which the dead-end theory does apply and others where it does not apply in the

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[4] J. P. Van Hook and A. V. Tobolsky, *J. Polymer Sci.*, **33**, 429 (1958).

[5] A. V. Tobolsky, *Ann. Rev. Phys. Chem.*, **7**, 167 (1956).

[6] J. Offenbach and A. V. Tobolsky, *J. Polymer Sci.*, **16**, 311 (1955).

bulk polymerization of styrene at various temperatures using 2,2′-azobisisobutyronitrile as initiator.

At 90 and 100°, using the initiator concentrations in Table II, the limiting dead-end conversion is clearly defined and the dead-end theory is quantitatively applicable. Accurate values of k_d and f may be determined by means of the theory.

At lower temperatures, with the initiator concentrations used, acceleration of polymerization due to retardation of the termination step does occur and the dead-end theory is inapplicable. The theoretical dead-end conversions under these conditions are high and the viscosity becomes very great within the time of a few initiator half-lives.

In Table I are listed the corrected fractional conversions with time for the bulk polymerization of styrene at the temperatures and initiator concentrations indicated.

Using points from smoothed curves through the corrected experimental data at 90 and 100°, plots of equation 10 were constructed as in Fig. 1. The values of k_d and f calculated from the slopes and intercepts of these linear plots by equation 10 are listed in Table II. Also in Table II are listed, for comparison, values of k_d and f calculated by the simplified equations describing the radical polymerization but neglecting the effect of the volume shrinkage during polymerization[1]

$$-\ln(1-x) = K(1-e^{-k_d t/2}) \quad (11)$$

so that

$$-\ln(1-x_\infty) + \ln(1-x) = Ke^{-k_d t/2} \quad (12)$$

or

$$-\ln\left[\ln\left(\frac{1-x}{1-x_\infty}\right)\right] = -\ln K + \frac{k_d}{2}t \quad (13)$$

The data in Table II indicate that the determined values of k_d are not sensitive to the correction for volume shrinkage; however, the efficiency f is very significantly affected. The values of f calculated by equation 10, correcting for the effect of volume shrinkage, agree more closely with the values of f determined from initial polymerization rates[4] than do the values of f calculated by equation 13.

The values of k_d determined by equation 10 are close to but slightly greater than values found from studies of the decomposition of this same initiator in benzene or toluene solution,[7] as shown in Table II. The "experimental" values of k_d from equation 10 at 60, 70 and 80° were calculated from an Arrhenius plot using our experimental points at 90 and 100° and with an activation energy of 30.8 kcal./mole degree.[5]

Using the values of k_d and f determined by this method, the predicted curves of conversion *versus* reduced time, $t/t_{1/2}$, ($t_{1/2}$ is the half-life of the initiator at the given temperature) are plotted in Fig. 2 as solid lines with the corresponding experimental values plotted as points and dashed lines. From an inspection of Fig. 2 and a comparison of the predicted and experimental values of x_∞ given in Table II, it is obvious that, whereas the polymerization behavior follows the curves predicted by equation 10 at 90 and 100°, at the lower temperatures there are marked deviations.

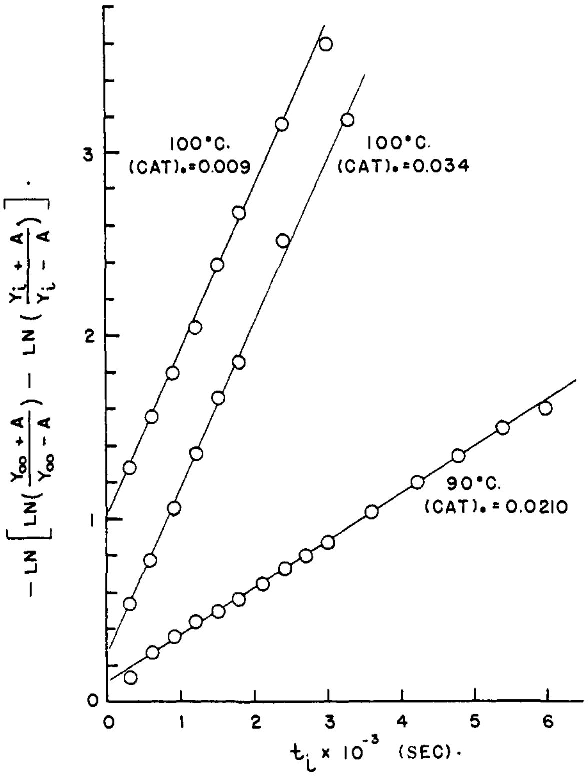

Fig. 1.—Plot for the determination of k_d and f (equation 10). Bulk polymerization of styrene using 2,2′-azobisisobutyronitrile as initiator.

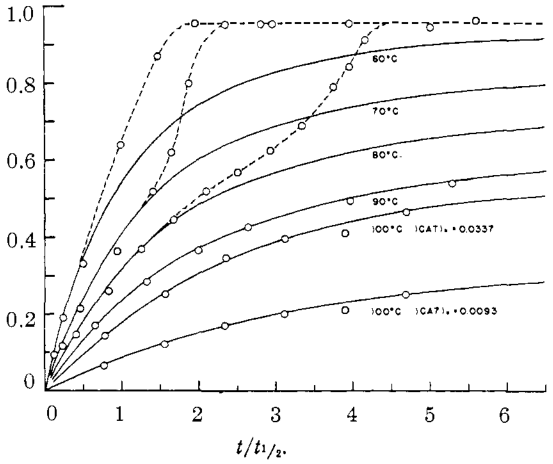

Fig. 2.—Fractional conversion x *versus* reduced time $t/t_{1/2}$ for the bulk polymerization of styrene using 2,2′-azobisisobutyronitrile as initiator. Solid lines predicted by equation 10; dashed lines experimental.

This anomalous behavior may be more clearly defined by using equation 7 to calculate the quantity $f^{1/2}k_p/k_t^{1/2}$ with the slope of the time–conversion curve taken as a measure of the rate of polymerization, dx/dt. Plots of $f^{1/2}k_p/k_t^{1/2}$ *versus* conversion, x, at 70, 80 and 90° are shown in Fig. 3. The abrupt increase in $f^{1/2}k_p/k_t^{1/2}$ for the 70 and 80° data at a conversion of about 0.5 to 0.6 is indicative of a reduced chain termination rate

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[7] J. P. Van Hook and A. V. Tobolsky, THIS JOURNAL, **80**, 779 (1958).

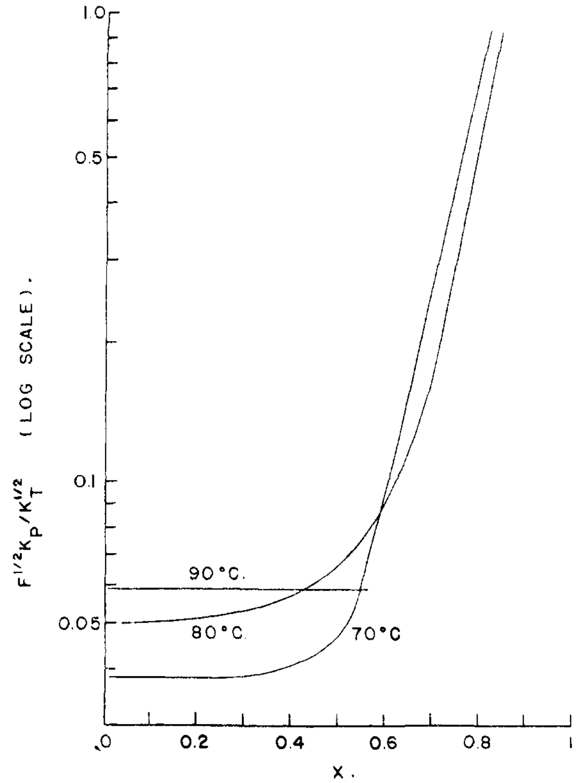

Fig. 3.—$f^{1/2}k_p/k_t^{1/2}$ determined from rate of polymerization data (equation 7) *versus* fractional conversion x for the bulk polymerization of styrene using 2,2′-azobisisobutyronitrile as initiator.

(k_t) probably due to the high viscosity of the monomer–polymer mixtures at these high conversions. The natural mobility of the polymeric radicals is so hindered that the probability is greatly reduced that two radicals will meet and terminate. The propagation reaction, dependent on the diffusion of small monomer molecules, is relatively little affected by changes in the viscosity of the medium.

In such cases, it is not possible to use equation 10 as a means for the simultaneous determination of k_d and f. This limitation may be avoided by using lower initiator concentrations or by conducting the polymerization in some suitable concentration of an appropriate solvent in order to lower the viscosity so that the retardation of termination does not occur.

Conclusion

The theory of dead-end radical polymerization of vinyl monomers is valid when there are no complicating features at high conversion such as the retardation of the termination step. In the absence of anomalous high conversion behavior, the entire course of conversion with time as well as the limiting conversion at infinite time may be predicted from a knowledge of the kinetic constants ($k_p/k_t^{1/2}$), f and k_d.

The dead-end theory is also very useful for kinetic studies. If $k_p/k_t^{1/2}$ is known for a given monomer, then by a determination of the conversion x, as a function of time, including the asymptotic value x_∞, it is possible to determine accurate values for the specific rate of initiator decomposition k_d and for the efficiency f. This method should be especially helpful for investigations of very fast initiators where it is not possible to obtain data easily on the initial rates of polymerization.

Many monomers exist for which $k_p/k_t^{1/2}$ has not been determined. For such monomers, the dead-end theory can be used to obtain the quantities $f^{1/2}k_p/k_t^{1/2}$ and k_d.

If the polymerizing system does tend to show the Tromsdorff–Norrish effect of retarded termination, a very few experiments serve to define the critical conversion range above which the "gel" effect occurs. Provided the quantities $(k_p/k_t^{1/2})f^{1/2}$ and k_d are known for the system, it may be predicted easily whether or not the Tromsdorff effect will occur during a polymerization at a given temperature and initiator concentration by simply calculating the theoretical conversion at infinite time. When this limiting conversion is significantly greater than the critical conversion range, then acceleration of polymerization due to the gel-effect probably will occur sometime during the course of the reaction.

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