JOURNAL OF POLYMER SCIENCE VOL. XI, NO. 5, PAGES 455-470

Kinetics of Chlorotrifluoroethylene Polymerization*

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INTRODUCTION

While the polymerization of fluorinated monomers has been investigated extensively from the viewpoint of obtaining and characterizing polymeric products, and products so obtained have shown outstanding physical properties, there have been few data reported from kinetic measurements on such polymerizations. This paper presents a survey of the kinetics of the polymerization of chlorotrifluoroethylene in bulk and in solution, and of its copolymerization with several monomers.

Two experimental problems were encountered at the start. First, the polymer is insoluble in the monomer and in all other solvents at the polymerization temperatures, so that it was impossible to carry out the polymerization in a homogeneous system. Anomalies in the kinetic results may be related to precipitation of polymer molecules in process of growth. Second, the monomer is gaseous at ordinary temperatures, so that the sealed tube technique rather than the more sensitive dilatometric technique was used to follow the reaction.

In preliminary experiments it was found that acetyl peroxide is a more effective initiator for this monomer than is either benzoyl peroxide or azobisisobutyronitrile. Since acetyl peroxide decomposition had received little kinetic study but could be expected to be complex in view of recent results for benzoyl peroxide, we made a number of kinetic experiments with a view to characterizing this decomposition sufficiently for our main purpose.

EXPERIMENTAL

Materials

Chlorotrifluoroethylene. Freon 113 (Kinetic Chemicals, Inc.), CF_2Cl-CCl_2F, was dechlorinated with zinc in ethanol,[1] passed over P_2O_5, and distilled through a Stedman column (b.p. −27°C.). It was stored in a steel

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* Presented at the Chicago Meeting, American Chemical Society, September, 1950. Taken from a dissertation submitted by W. M. Thomas to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in June, 1950, in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

cylinder without inhibitor. No bands attributable to ethanol were detected by infrared,[2] and a colorimetric chromic acid method[3] indicated less than 0.02% ethanol. The liquid density was determined in the range −41 to +13°C. by the sink-float method and is given by:

$$d = 1.38 - 0.0029t$$

where d is the density in g./cc. and t is the centigrade temperature.

The unusually favorable increase in density from monomer to polymer (1.3 to 2.1) prompted rate study trials with a dilatometer encased in a steel pressure chamber having heavy glass windows. It was found that precipitation of polymer in the capillary necessitated the use of an auxiliary liquid. None was found which was immiscible with $CF_2{=}CFCl$ and inert toward both monomer and peroxide catalysts.

Acrylonitrile. The American Cyanamid Co. product was washed with 10% H_3PO_4, steam-distilled, dried, and redistilled.

Styrene. Dow Chemical Co. monomer was washed with dilute NaOH, steam-distilled, dried, and redistilled.

Other Monomers. Commercial products were freshly distilled.

Solvents. The best commercial grades were further purified by standard methods.[4]

Catalyst. Porofor N (Naugatuck Chemical Co., azobisisobutyronitrile), benzoyl peroxide (Peters Chemical Co.), and 30% acetyl peroxide in dimethyl phthalate (Buffalo Electro-Chemical Co.) were used as received. The iodide-thiosulfate titration method of Nozaki[5] gave 99.0 ± 0.2% peroxide for the benzoyl peroxide and approximately 32% peroxide (depending on age) for the acetyl peroxide. In titrating acetyl peroxide it was important to use sodium iodide rather than potassium iodide.

Procedure

Polymerization studies were carried out in sealed 18 × 150 mm. Pyrex combustion tubes protected by screens or by vented brass pipes. Tubes were evacuated; the presence of air made results erratic. Tenperature control was afforded by ice water or by a water or glycol bath controlled to ±0.1°C.

Tubes were weighed to 0.01 g. dry and after successive addition of catalyst, solvent (when used), comonomer (when used), and finally after introduction of an estimated quantity of $CF_2{=}CFCl$ and sealing. After the designated reaction period, bulk polymerization tubes were either simply weighed after being vented to remove residual monomer or else opened and the contents extracted with acetone or methanol. Solution polymers were worked up by extraction of solvent and residual monomer from the solid polymer. The polymer was insoluble in the monomer and in all common solvents and precipitated as formed.* Copolymers were usually

* Lack of suitable solvents has impeded the study of molecular weights. Following the observation of Padbury[6] that chlorinated benzotrifluoride dissolves the polymer at temperatures above about 110°C., some viscosity measurements were made in that solvent at 130°C. Specific viscosities at 10 g. per liter were in the range 0.1 to 1.7. See also Kaufman and Muthana[7a] and Hall.[7b]

precipitated in methanol, dissolved in benzene and reprecipitated; vinyl acetate copolymers were precipitated from methyl ethyl ketone with petroleum ether.[8] All polymers and copolymers were dried in a vacuum oven at 70°C.

The composition of copolymers was calculated from the chlorine content (Parr bomb) or from Kjeldahl nitrogen determinations.

In catalyst decomposition studies, 5 ml. of the dilute solutions was pipetted into 18 × 150 mm. tubes, which were then sealed under vacuum. After heating for the appropriate reaction time, the tubes were cooled and opened, and the contents analyzed by the method of Nozaki.

Results

Bulk Polymerization. Preliminary experiments of 42.2 hours' duration at 60°C., with 0.5% initiator, showed: for acetyl peroxide (associated with dimethyl phthalate as a 32% solution and used without separation), 87% yield of white polymer; benzoyl peroxide, 14% of brownish, spotted

TABLE I

BULK POLYMERIZATION OF CHLOROTRIFLUOROETHYLENE WITH APPROXIMATELY 0.55% ACETYL PEROXIDE

Temp. (°C.)	Reaction time (hours)	% conversion to polymer
0.0	70.0	0.9
	217.0	2.8
	457.5	5.0[a]
	1233.0	17.2
25.0	19.2	4.1
	43.8	9.6
	65.2	16.6
	113.8	24.1
	162.5	38.9
	239.6	56.6
	353.0	81.4
	696.2	97.3
40.0	17.5	13.4
	41.5	30.9
	65.2	52.1
	96.0	80.3
	164.5	97.3
60.0	1.8	6.6
	3.2	10.4
	7.8	28.6
	9.8	31.0
	13.2	40.6
	13.2	42.5
	21.0	63.3
	30.8	86.1
	54.5	97.6

[a] Small loss in handling.

polymer; azobisisobutyronitrile, 29% of white polymer. Azobisisobutyronitrile was of very limited solubility in the monomer. Accordingly, acetyl peroxide, in the form of its 32% solution in dimethyl phthalate, was chosen as initiator for most of the kinetic studies.

Experiments in which the extent of polymerization of solutions of 0.55% (0.060 mole/liter at 25°C.) of acetyl peroxide (plus 1.18% or 0.078 mole per liter at 25°C. of dimethyl phthalate) in pure monomer was determined after various periods of time, at the temperatures 0, 25, 40, and 60°C., yielded the results summarized in Table I and Figure 1. The polymerization is zero order to over 80% conversion, at least at the higher temperatures. There is no indication of any induction period. The over-all activation energy which best fits the zero order constants is 17 kcal./mole.

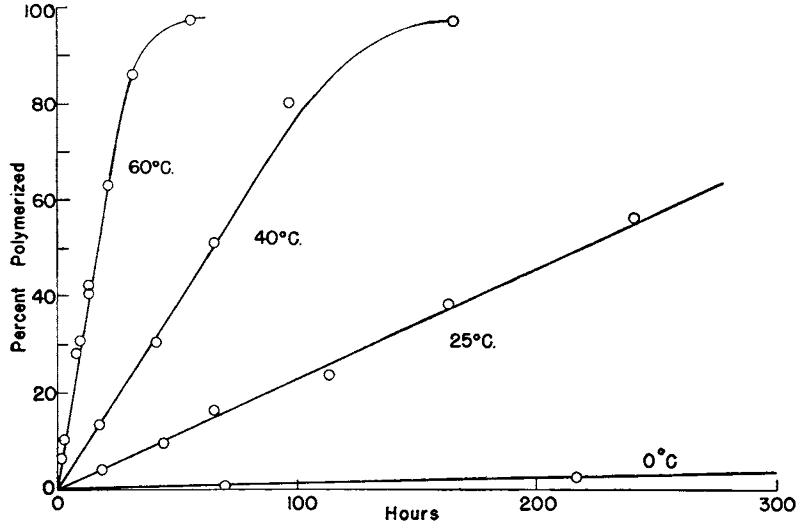

Fig. 1. Bulk polymerization with 0.55% acetyl peroxide.

The effect of varying the acetyl peroxide concentration was investigated in other sets of experiments at 25°C. and at 60°C. The plots of percent polymerization *vs.* time were again zero order, with no induction period. The dependence of the zero order over-all rate constants upon acetyl peroxide concentration is illustrated in Figure 2, which indicates that the rate of bulk polymerization varies with the 0.7 power of the acetyl peroxide concentration at 25°C. and with the 0.8 power at 60°C. These data clearly depart from the normal half-order dependence of polymerization rate upon initiator.

Solution Polymerization. Preliminary experiments indicated that chlorotrifluoroethylene polymerizes when dissolved in a variety of solvents, with acetyl peroxide added, but that the rate of polymerization varies from solvent to solvent. Table II reports the initial and final molarity of monomer in solution polymerization experiments in several solvents and at several temperatures. From these results one may generalize roughly

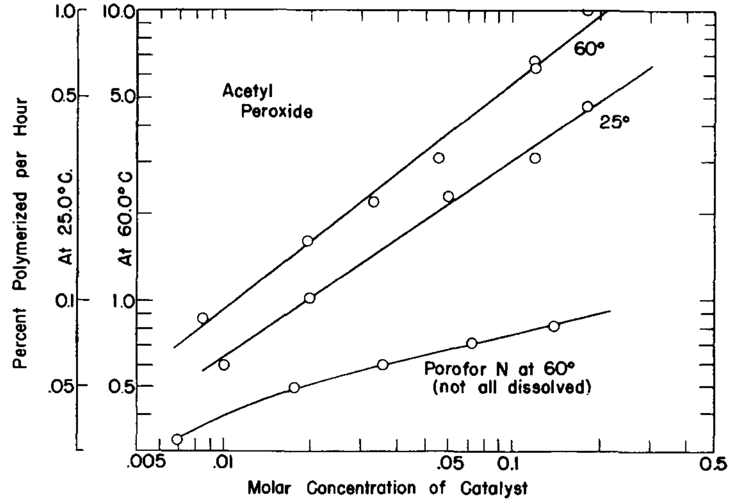

Fig. 2. Effect of catalyst concentration on bulk polymerization.

that the rate is smallest in hexane and cyclohexane, considerably greater in benzene, and still greater in chlorobenzene, *o*-dichlorobenzene, perfluorodimethylcyclohexane, *tert*-butyl alcohol and chloroform. Other results pointed to strong inhibition of the polymerization by ethyl alcohol and even by residual traces of primary and secondary alcohols in a solvent sample which was ostensibly *tert*-amyl alcohol. The rates of the acetyl peroxide initiated polymerization of chlorotrifluoroethylene appear to bear an inverse relationship to the rates of decomposition of acetyl peroxide in these solvents, as will be seen below.

TABLE II

Solution Polymerization of $CF_2{=}CFCl$ at 60.0°C. with Acetyl Peroxide

Solvent	Initiator concn. at start (molar)	Monomer concn.		Time (hours)	k (× 10^6) (sec.$^{-1}$)
		Initial	Final		
Hexane	0.052	4.15	4.09	6.33	0.6
	0.052	4.07	3.80	14.0	1.4
Cyclohexane[a]	0.049	4.44	4.17	13.2	1.3
	0.055	4.29	4.01	12.25	1.5
Benzene	0.055	3.95	3.65	3.00	7.2
	0.052	4.19	3.53	6.13	7.8
	0.055	4.08	2.98	12.25	7.1
	0.055	4.12	2.43	23.68	6.2
	0.055	4.07	1.61	47.00	5.5
Perfluorodimethylcyclohexane	0.053	4.11	3.29	6.33	9.7
	0.057	4.10	2.25	15.4	10.8
tert-Butyl alcohol	0.057	4.15	3.03	6.33	13.6
	0.056	4.17	1.62	15.4	17.0
Chloroform	0.053	2.16	0.54	13.2	29.1
	0.052	4.25	1.58	13.2	20.7

[a] Cyclohexane with 0.034 *M* Porofor N gave a value of $k = 0.1 \times 10^{-6}$.

The solution polymerization was studied most intensively in benzene. Figure 3 is a first-order plot of the concentration of monomer, initially approximately 4 molar, *vs.* time in benzene at 60 °C. with 0.05 *M* acetyl peroxide. It will be observed that the first three points fall quite close to a straight line, the slope of which may be taken as a first-order rate constant for the disappearance of monomer under these conditions. The points at 24 and 48 hours lie well above this line. At least part of their deviation is attributable to initiator depletion.

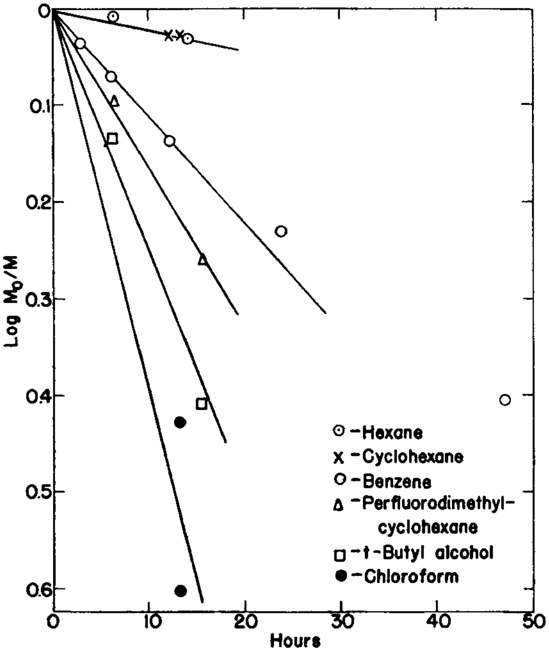

Fig. 3. Solution polymerization at 60 °C.
Initial monomer, 4 *M*. Initial acetyl peroxide, 0.05 *M*.

If we anticipate later discussion and estimate* k_1 for the disappearance of acetyl peroxide in benzene plus monomer at 60 °C. as 1×10^{-5} sec.$^{-1}$, we obtain 19.2 hours as the half life of the peroxide; the initiator concentrations at the 24 and 48 hour points would be 42% and 18% of the initial initiator concentration and $d \log M/dt$ at these times should be considerably smaller than at the start, as observed.

A quantitative estimate of the change in $d \log M/dt$ from this source requires more certain knowledge than we possess of the order of the polymerization with respect to initiator and particularly of the rate of initiator decomposition in benzene plus varying concentrations of monomer at 60 °C.

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* In toluene at 80 °C., 4.0 moles per liter of monomer raises k_1 from 7.4×10^{-5} sec.$^{-1}$ to 15×10^{-5} sec.$^{-1}$. At 60 °C., k_1 in benzene and in toluene is 5×10^{-6}. Extrapolating the effect of monomer from benzene to toluene and from 80° to 60° we obtain a 50% acceleration to $k_1 = 1.0 \times 10^{-5}$.

The data for the other solvents are too sketchy to admit of quantitative interpretation. For purpose of rough comparison of rates, a number of single polymerization experiments were carried out using 4.0 molar solutions of the monomer in several solvents, at several temperatures, with either acetyl peroxide or Porofor N used as initiator. In two series at 60°C. the initiator concentration was varied. From the extents of polymerization observed at the scheduled conclusions of these single experiments apparent first-order rate constants were calculated. These "constants" assume that the solution polymerizations in question were first-order in monomer throughout and that initiator depletion was inappreciable; it is clear that they are not more than rough measures of relative rate under the various conditions. The results of these experiments are summarized in Table III, which compares solvents, temperatures (via calculated activation energies) and acetyl peroxide and Porofor N as initiators; and Figure 4, which represents the dependence of rates on initiator concentration.

TABLE III

APPARENT FIRST-ORDER CONSTANTS[a]

Solvent	Initiator	$k \times 10^6$ at 60°C.	Over-all activation energy (kcal./mole)
Benzene	Acetyl peroxide	7.2	24.8
tert-Butyl alcohol	Acetyl peroxide	16.1	18.3
Chloroform	Acetyl peroxide	19.5	19.6
Benzene	Porofor N	1.1	18.5
tert-Butyl alcohol	Porofor N	1.4	17.4
Acetonitrile	Porofor N	*ca.* 2	—

[a] Initiator, 0.05 *M*. Monomer, 4 *M*.

While the nature of these experiments and these constants discourages quantitative interpretation, they show clearly that the rates with acetyl peroxide as initiator are greater by an order of magnitude and more dependent on the identity of the solvent than the rates with Porofor N. This is particularly noteworthy in view of the first-order rate constants for the decomposition of these initiators. Porofor N is generally assumed to decompose by a first-order mechanism with rate essentially independent of solvent identity; at 60°C., k_1 is approximately 1×10^{-5} sec.$^{-1}$.[9] Results below (Table IV) show that the decomposition of acetyl peroxide in the solvents of Table III is first-order or nearly so and that k_1 is 3 to 5×10^{-6} sec.$^{-1}$ and may be raised to *ca.* 1×10^{-5} sec.$^{-1}$ by acceleration by monomer. Figure 4 shows that the polymerization is 0.7 order in acetyl peroxide (as in bulk) but 0.5 order in Porofor N (if two unexplained low rates at very low Porofor N concentration are neglected). The temperature dependence of the rate of these solution polymerizations is well represented by $E_a = 18 \pm 2$ kcal./mole except for acetyl peroxide initiation in benzene solution; there it is *ca.* 25 kcal./mole.

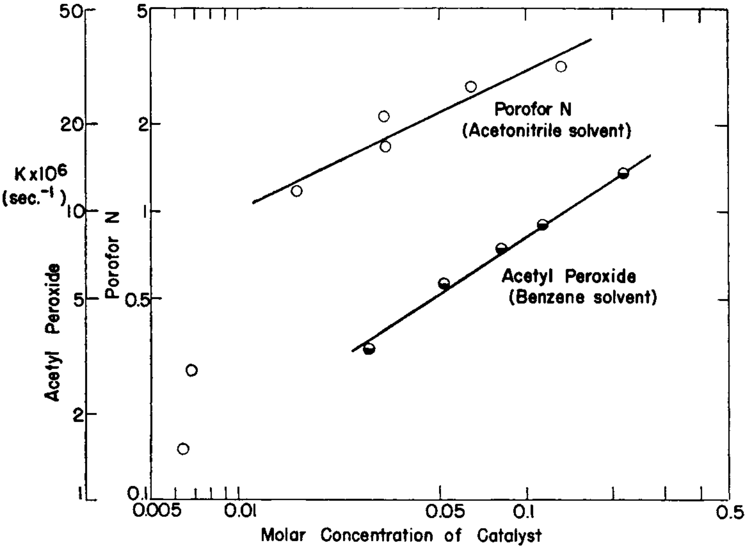


Fig. 4. Effect of catalyst concentration in solution polymerization at 60°C.

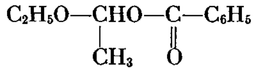
Decomposition of Acetyl Peroxide. The rate of the decomposition of benzoyl peroxide in solution has been found to vary widely with solvent, increasing from chlorinated solvents through aromatics, saturated aliphatics, alcohols, and ethers, and amines, in that order.[11] With the exception of the very fast reaction in amines, the variation in rate and the complex kinetics observed have been explained on the assumption that a secondary radical induced decomposition of chain character accompanies the spontaneous unimolecular decomposition into radicals, with the rate of the radical induced process (and the length of the chain) strongly dependent upon the identity of the radicals formed from the solvent. Schematically, reactions are postulated of the types:

$$P \longrightarrow 2R\cdot (R{=}C_6H_5COO\cdot \text{ or } C_6H_5\cdot + CO_2) \quad (1)$$

$$R\cdot + SH \longrightarrow RH + S\cdot \quad (2)$$

$$S\cdot + P \longrightarrow \text{product} + R\cdot \quad (3)$$

plus termination steps. In support of this postulate we may note, among other evidence: (*1*) that in the rapid decomposition in diethyl ether Cass[12] has identified the product:



$$C_2H_5O{-}\underset{\displaystyle CH_3}{CHO}{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}C_6H_5$$

(1-ethoxyethyl benzoate) resulting from reaction (3), and (*2*) that O'-Shaughnessy and Epstein have found a quantum yield of ~300, at 30°C., for the photochemically induced decomposition in ethanol, also a "fast" solvent. The decomposition of acetyl peroxide has received much less investigation[13-15] but there is no *a priori* reason for ruling out a similar complex mechanism in this case.

The variation in polymerization rates with solvent noted above and the 0.8-order dependence of the rates upon acetyl peroxide as initiator pointed to some peculiarity in the initiation step of the polymerization. Accordingly a number of experiments were performed in which the decomposition of acetyl peroxide (always associated with dimethyl phthalate) in several solvents and solvent mixtures was followed by the sealed-ampule technique. In almost every case, the decomposition followed first-order kinetics quite closely in single runs. The observed rate constants, along with approximate half-lives, and activation energies when determined, are listed in Table IV, in which the solvents have been listed in order of increasing rate of peroxide decomposition.

Several important features stand out in Table IV. The first is that the chlorinated solvents chloroform and carbon tetrachloride are the "slowest," along with *tert*-butyl alcohol, followed by benzene and toluene, then *n*-butyl alcohol, and finally *sec*-butyl and ethyl alcohols; the order is substantially the same as with benzoyl peroxide. The comparison among the butyl alcohols fit excellently with the hypothesis[11] that the radical involved in an induced decomposition is formed by removal of an alpha hydrogen from an alcohol. Benzene and dimethyl phthalate retard the decomposition in ethyl alcohol just as aromatic substances have been formed by Cass[12] to retard the benzoyl peroxide decomposition in "fast" solvents, particularly ethers. Finally, however, monomer appears to accelerate the decomposition of the peroxide—to about the same total rate in *tert*-butyl

TABLE IV

DECOMPOSITION OF ACETYL PEROXIDE IN SOLVENTS

Solvents	$k \times 10^5$ sec.$^{-1}$		E_a (kcal./mole)	$t_{1/2}$ (hours at 60°C.)
	60.3°C.	80.3°C.		
Carbon tetrachloride	0.3^a	—	—	60–70
Chloroform	—	~5	—	—
tert-Butyl alcohol	0.31	4.9	32	62
Benzene	0.50	—	—	38
Toluene	0.5	7.4^b	31	38
Toluene plus monomer (4 *M*)	—	15	—	—
tert-Butyl alcohol plus monomer (4 *M*)	—	15	—	—
n-Butyl alcohol	3.4	—	—	—
sec-Butyl alcohol	3	—	—	6
Ethyl alcohol plus 10% dimethyl phthalate	5.2	—	—	—
Ethyl alcohol plus 10 mole % benzene	7.9	—	—	2.5
Ethyl alcohol plus air	8.6	—	—	—
Ethyl alcohol	10.1	140	31	2
Ethyl alcohol plus ethyl acetate	10.1	—	—	—

[a] Reference 14. [b] Reference 13.

alcohol and in toluene. The wide variation in rates and the correspondence with the rates for benzoyl peroxide are strongly indicative of a similarity in mechanism in these two decompositions. The acceleration of decomposition by monomer is contrary, however, to the retardation of benzoyl peroxide decomposition by several monomers. This and the fact that decomposition of acetyl peroxide in solvents is slow at temperatures at which it initiates rapid polymerization of chlorotrifluoroethylene suggest that the initiation step may involve a reaction between peroxide and monomer.

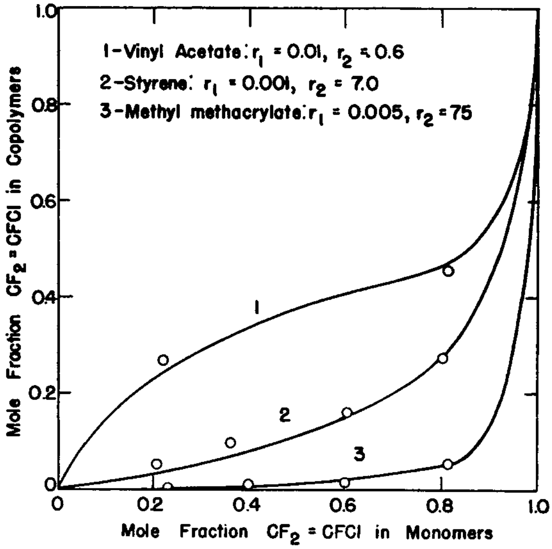


Fig. 5. Copolymerization of chlorotrifluoroethylene.

Copolymerization. Preliminary trials indicated some degree of copolymerization of chlorotrifluoroethylene with vinyl chloride, butadiene, styrene, vinyl acetate, 2-vinylpyridine, and methyl methacrylate, on the basis of qualitative analysis for F or Cl or both by sodium fusion. With vinylidine chloride and acrylonitrile this qualitative test was negative. The copolymerization with vinyl acetate was quite rapid and about 20 experiments were conducted with this comonomer, first in the process of adjusting conditions to secure a yield of the order of 10% or less and next in the process of discovery that the estimation of chlorine by hydrolysis by the method of Bevilaqua[17] gave erratic results with these copolymers. The Parr bomb analysis for chlorine was finally adopted for the copolymerization experiments upon which conclusions were to be based.

These final copolymerization experiments are reported in Table V and Figure 5. The solvents listed therein were added to secure either compatibility of the monomers at the composition indicated or solubility of the copolymer at least to the indicated conversion.

TABLE V

Copolymers of Chlorotrifluoroethylene

Hrs. at 60.3°C.	% conv.	% Cl[a]	Mole fraction $CF_2{=}CFCl$ Monomer[b]	Mole fraction $CF_2{=}CFCl$ Copolymer
		Methyl Methacrylate (M_2)		
2.5	15.6	0.23	0.234	0.0065
3	6.8	0.45	0.400	0.0127
3.5	6.3	0.49	0.602	0.0138
12.5[c]	7.4	1.95	0.817	0.0554
		Styrene (M_2)		
3	9.5	1.94	0.204	0.057
5	10.2	3.29	0.362	0.098
7.25	9.3	5.38	0.603	0.161
16.2[c]	10.1	9.05	0.803	0.274
		Vinyl Acetate (M_2)		
1[d]	11.9	10.11	0.220	0.269
1.3[d]	13.6	16.15	0.815	0.454

[a] Parr bomb method; courtesy Mr. T. Harsell, Stamford Research Laboratories, American Cyanamid Co.
[b] Average of initial and final values.
[c] Polymerized in benzene.
[d] Polymerized in methyl ethyl ketone.

Accepted copolymerization theory states that the mole ratio of comonomers, m_1/m_2, in copolymer formed at a given time is related to the molar concentration, M_1 and M_2, of the comonomers at that time and to the ratios of propagation rate constants, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, by the equation:

$$\frac{m_1}{m_2} \approx \frac{dM_1}{dM_2} = \frac{M_1}{M_2}\frac{r_1M_1 + M_2}{r_2M_2 + M_1}$$

The first approximate equality holds for low conversions such that little relative change of M_1 and M_2 has occurred through the reaction. In this paper the subscript (1) always refers to chlorotrifluoroethylene.

Values of r_1 and r_2 are deducible, with fair accuracy, by fitting copolymerization curves to the points in Figure 5 using r_1 and r_2 as adjustable parameters. Since the mole fraction of chlorotrifluoroethylene in the copolymer in no case exceeded 0.5, the selection of values for r_1 is somewhat arbitrary and subject to large error. The results of the computations from these limited data, together with Q and e values in the scheme of Alfrey and Price, are reported in Table VI.

DISCUSSION

The rationalization of the results presented above in terms of existing theory requires adequate explanations for several apparently anomalous facts:

(*1*) The zero-order kinetics in bulk, persisting to very high conversion.

TABLE VI

MONOMER REACTIVITY RATIOS AND Q–e DATA

	Literature values		Experimental		Calc. for $CF_2{=}CFC$	
Reference monomer (M_2)	Q_2	e_2	r_1	r_2	Q_1	e
Styrene	1.0	−0.8	0.001	7.0	0.025	1.4
Vinyl acetate	0.03	−0.3	0.01	0.6	0.025	2.0
Methyl methacrylate	0.8	+0.4	0.005	75	0.016	1.4

(*2*) The 0.8-order dependence upon initiator concentration, with acetyl peroxide as initiator.

(*3*) The dependence of rate upon solvent identity, in solution, and the inhibition by certain solvents.

These kinetic results should be explicable in terms of standard polymerization rate theory, the chemical nature of this monomer and the fact that it precipitates from solution as formed.

The zero-order kinetics of the bulk polymerization appears to be too reproducible, under varied conditions of temperature and of initiator concentration, to be the result of chance balancing of tendencies to slow and to accelerate the reaction. Yet it is not what the usual theory would predict, for a system in which precipitation of polymer as formed leads to progressive decrease in liquid volume as the reaction proceeds, with the monomer molarity remaining substantially constant at its initial value. For the usual polymerization scheme:

$$\begin{array}{lr} \mathrm{I} \longrightarrow 2\mathrm{R}\cdot & k_1 \\ \mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}\cdot & k_2 \\ \mathrm{R}\cdot + \mathrm{R}\cdot \longrightarrow \text{polymer} & k_3 \end{array}$$

with all steps taking place in the liquid phase, the kinetic analysis under conditions of substantially constant monomer concentration in a shrinking liquid volume ($V = n_M V_M$) gives for the total rate of polymerization in moles of monomer polymerized per second:

$$R_p = -\frac{dn_M}{dt}, = k_2' n_R, = k_2' V C_R$$

where n_R is the total number of moles of active radicals present in the liquid volume V at any time. From the steady state assumption for the radical concentration at any instant, we have:

$$\frac{dC_R}{dt} = 0, \quad = k_1 C_I - k_3 C_R^2$$

$$C_R = \left(\frac{k_1}{k_3} C_I\right)^{1/2}$$

$$n_R = VC_R, = V\left(\frac{k_1}{k_3}\frac{n_I}{V}\right)^{1/2}, \quad = \left(V\frac{k_1}{k_3} n_I\right)^{1/2}$$

and, since $V = n_M V_M$ (where V_M is the molar volume of monomer):

$$n_R = \left(\frac{k_1}{k_3} V_M n_M \, n_I\right)^{1/2}$$

and:

$$R_p = k_2' \left(\frac{k_1}{k_3} V_M n_M n_I\right)^{1/2}$$

or:

$$R_p = k(n_M n_I)^{1/2}$$

Thus, even in the most favorable case of inappreciable depletion of the initiator through the reaction, the rate should decrease as the square root of the amount of monomer remaining. The rate at 50% conversion should be less than the initial rate by the factor 0.707, whereas experimentally only one run shows indication of any decrease of rate in the first 50% of reaction.

The observed zero order in monomer, along with first-order dependence of rate on initiator, can be derived for the present case as consequences of the following assumptions: (*1*) initiation second-order in acetyl peroxide; (*2*) propagation as usual; (*3*) termination, as usual, second-order in active radicals, with the implication that termination precedes precipitation of polymer molecules. Alternatively, the same orders follow from: (*1*) first-order initiation; (*2*) propagation as usual; and (*3*) first-order termination, which could perhaps be attributed to effective cessation of chain growth upon precipitation of active chains.

We consider the assumption of second-order initiation highly questionable. It is an *ad hoc* hypothesis which is at variance with our data for peroxide disappearance in solution and with most commonly held ideas of peroxide behavior, and is, furthermore, not related to the obvious peculiarities of our system. The assumptions based on first-order termination appear satisfactory at first sight and it may be that they are essentially true. We encounter difficulty, however, as soon as we try to explain the first-order termination in concrete terms. Degradative chain transfer is a possible explanation but again it is an *ad hoc* hypothesis, unrelated to the heterogeneity of the reaction system. Termination by precipitation of growing chains would be expected to increase in rate with the accumulation of solid polymer in the reaction mixture, and is subject to the further objection that it leaves unspecified the actual radical termination process.

Two facts which are probably important in this connection are the normal 0.5 order dependence of polymerization rate upon initiator when Porofor N was used as initiator in solution polymerizations, and the acceleration of the decomposition of acetyl peroxide in toluene and in *tert*-butyl alcohol by the addition of 4 moles per liter of monomer (Table IV). The first of these implies kinetically normal bimolecular termination of radicals, at least in the solution polymerization in which it was observed. The second may simply be the result of induced peroxide decomposition by attack of polymer radicals upon peroxide. Alternatively, it may be evidence that in addition to initiation by radicals from spontaneously dissociated peroxide there is reaction between monomer and peroxide molecules resulting in initiation. If such a reaction occurs and doubles or triples the rate of initiator decomposition in solution it should be even more important in pure monomer. If it were second-order in initiator it would, in combination with normal initiation, lead to an over-all order of initiation between 0.5 and 1.0, and go far toward explaining the zero over-all order of polymerization. The greater effectiveness of acetyl peroxide over Porofor N, as initiator, may be significant in this connection. In the absence of data for other initiators and of any chemical evidence for a molecular initiation reaction with acetyl peroxide, these remarks must be considered as speculation. Clearly more experimental work will be required to explain these kinetic data.

The inhibition of the polymerization by ethanol may be accounted for by reasonable assumptions. The rapid decomposition of the peroxide in ethanol is almost certainly the result of induced decomposition so rapid that in ethanol the sequence of reactions:

$$(a) \qquad R\cdot \text{ (from peroxide)} + SH \text{ (Et OH)} \longrightarrow RH + S\cdot$$

$$(b) \qquad S\cdot + P \longrightarrow R\cdot + \text{products}$$

proceeds as a chain reaction of considerable length. When ethanol or a solvent of similar behavior is present in an attempted polymerization we must consider reactions (*a*) and (*b*) along with the usual reactions:

$$(c) \qquad R\cdot \text{ (from peroxide)} + M \longrightarrow RM\cdot$$

$$(d) \qquad RM\cdot + M\cdot \longrightarrow \longrightarrow RM_x\cdot$$

and the following reactions as well:

$$(e) \qquad RM_x\cdot + SH \longrightarrow RM_x H + S\cdot$$

$$(f) \qquad S\cdot + M \longrightarrow SM\cdot$$

Reactions (*a*) and (*b*) may be so rapid relative to (*c*) and (*f*) that few polymer radicals are formed, or (*a*) may dominate (*c*) less completely but (*e*) be fast enough to interrupt quickly any polymerization chains begun by (*c*). The key assumption is that the radical S·, while strongly reactive toward peroxide, is unreactive toward monomer.

Swain, Stockmayer, and Clarke[18] have found that, when styrene or a substituted styrene is introduced into a solution of benzoyl peroxide in dioxane, in which the induced decomposition is extensive, it is the induced decomposition of the peroxide rather than the polymerization which is suppressed as the outcome of the competition among the possible radical reactions. However, the chemical nature of the monomer is so considerably different in the present case that a complete reversal of the outcome of this competition is not to be ruled out *a priori.*

It is possible that the low rates of polymerization in hexane and cyclohexane are the result of a similar mechanism of retardation, operating less effectively.

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Synopsis

An exploratory investigation of the kinetics of the polymerization of chlorotrifluoroethylene (I) has been made. Experiments were conducted in bulk, in solution in several solvents, and in the presence of several comonomers. Acetyl peroxide (II) was found to be the most effective of common initiators and was used in most of the experiments. The sealed ampoule technique was employed. The bulk polymerization of I is zero order to 60–80% conversion; the rate varies as the 0.7 to 0.8 power of the acetyl peroxide concentration, and the over-all activation energy is 17 kcal./mole. The solution polymerization in benzene appears to be first order in monomer; in other solvents the order was not ascertained. The rate and activation energy in solution are solvent dependent and there appears to be an inverse relationship between the rate of polymerization of I in a solvent and the rate of decomposition of II in that solvent. The rate of decomposition of II was measured in a number of solvents and found to vary widely and to parallel, roughly, the rate of decomposition of benzoyl peroxide. The polymerization rate of I in solution is also *c.* 0.7 order in acetyl peroxide, but was 0.5 order in Porofor N in limited experiments. From copolymerization experiments with styrene, vinyl acetate and methyl methacrylate values of Q of 0.025, 0.025 and 0.016, and of e of 1.4, 2.0, 1.4, respectively, were inferred, in the Q–e scheme of Alfrey and Price. These results above are discussed in the light of polymerization theory.

Résumé

La cinétique de polymérisation du chlorotrifluoroéthylène (I) a été étudiée. Les expériences ont été effectuées en bloc, en solution dans de nombreux solvants, et en présence de nombreux comonomères. Le peroxyde d'acétyle (II) est l'initiateur courant le plus efficace, et a été utilisé dans la plupart des expériences. La méthode aux ampoules scellées a été utilisée. La polymérisation en bloc de I est d'ordre zéro jusqu'à 60 à 80% de rendement; la vitesse varie à la puissance 0.7 à 0.8 de la concentration en peroxyde d'acétyle, et l'énergie d'activation globale s'élève à 17 kcal/mole. La polymérisation en solution dans le benzène est de premier ordre par rapport au monomère; dans les autres solvants l'ordre n'a pu être déterminé. Les vitesses et énergies d'activation sont fonctions de la nature du solvant, et il semble exister une relation inverse entre la vitesse de polymérisation de I dans un solvant déterminé et la vitesse de décomposition du peroxyde d'acétyle dans ce même solvant. La vitesse de décomposition de celui-ci a été mesurée dans plusieurs solvants; elle varie considérablement et, en première approximation, parallèlement à la vitesse de décomposition du peroxyde de benzoyle. La vitesse de polymérisation de I en solution est également d'ordre 0.7 environ par rapport à la concentration en peroxyde, mais était de l'ordre 0.5 dans certaines expériences dans le Porofor N. Aux dépens d'expériences de copolymérisation, avec le styrène, l'acétate de vinyle et le méthacrylate de méthyle, les valeurs de Q de 0.025, 0.025 et 0.016 et de e de 1.4, 2.0 et 1.4 respectivement ont été obtenues dans le cadre de la théorie d'Alfrey-Price. Ces résultats sont discutés à la lumière des théories de polymérisation.

Zusammenfassung

Es wurde eine Untersuchung der Kinetik der Polymerisation von Chlorotrifluoroäthylen (I) unternommen. Die Experimente wurden im Block, in Lösung in mehreren Lösungsmitteln und in der Gegenwart von verschiedenen Comonomeren ausgeführt. Es wurde gefunden, dass Acetylperoxyd (II) der wirksamste der üblichen Initiatoren ist und es wurde in den meisten Experimenten angewendet. Die Technik des geschlossenen Rohres wurde angewendet. Die Blockpolymerisation von I ist nullter Ordnung bis zu 60–80% Umsatz, die Geschwindigkeit variiert als die 0.7 bis 0.8 Potenz der Acetylperoxydkonzentration, und die gesamte Aktivationsenergie ist 17 kcal./Mol. Die Lösungspolymerisation in Benzol scheint erster Ordnung in Monomer zu sein; in anderen Lösungsmitteln wurde die Ordnung nicht mit Gewissheit bestimmt. Die Geschwindigkeit und die Aktivationsenergie in Lösung sind vom Lösungsmittel abhängig, und es scheine eine umgekehrte Beziehung zwischen der Polymerisationsgeschwindigkeit von I in einem Lösungsmittel und der Zersetzungsgeschwindigkeit von II in diesem Lösungsmittel zu bestehen. Die Zersetzungsgeschwindigkeit von II wurde in einer Anzahl von Lösungsmitteln gemessen und es wurde gefunden, dass sie weitgehend variierte und im grossen und ganzen parallel zu der Zersetzungsgeschwindigkeit von Benzoylperoxyd verlief. Die Polymerisationsgeschwindigkeit von I in Lösung hat auch ungefähr die Ordnung 0.7 in Acetylperoxyd, sie hat die Ordnung 0.5 in Porofor N in begrenzten Experimenten. Aus Copolymerisationsexperimenten mit Styrol, Vinylacetat und Methylmethacrylat wurden Q-Werte von 0.025, 0.025 und 0.016 und e-Werte von 1.4, 2.0 beziehungsweise 1.4 im Q-e Schema von Alfrey und Price entnommen. Diese oben gegebenen Resultate werden im Bezug auf die Polymerisationstheorie diskutiert.

Received February 19, 1953