was obtained as colorless needles; m. p. 129.5–130.5°; yield, 3.67 g. (89%). Distillation at 170° at 0.01 mm. followed by two recrystallizations from benzene-petroleum ether and one from dilute acetic acid, raised the melting point to 131.5–132.5°. There appears to be a lack of agreement in regard to the melting point of this acid. Values of 128–129° (Mayer[6]), 137° (Sieglitz and Jassoy[6]), and 138–139° (Wislicenus and Eble[6]) have been reported.

Summary

Methods are described whereby 2- and 9-fluoreneacetic acid can be obtained readily and in good yields.

The synthesis of the new 4-fluoreneacetic acid is described.

ANN ARBOR, MICHIGAN RECEIVED JULY 15, 1940

[CONTRIBUTION FROM RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS LTD.]

Macropolymerization; the Mechanism of Activation

BY ERNEST P. IRANY

The formal definition of macropolymerization as a chain reaction[1]

$$\begin{array}{lll} M \longrightarrow M^* & & \text{(Activation)} \\ M^* + M & \longrightarrow M_2^* & \text{(Chain propagation)} \\ M_r^* + M & \longrightarrow M_{r+1}^* & \\ M_r^* + M_s^* & \longrightarrow M_{r+s} & \text{(Termination)} \end{array}$$

does not attempt a specific description of the state of activation which is presumed to be transmitted through the reaction sequence. That this state is distinguished by a higher energy content than that possessed by the average molecule is obvious and, for general considerations of kinetics, sufficient. However, our understanding of the chemical mechanism of the process remains incomplete unless it be possible to interpret the enhanced energy content of the activated molecule in terms of chemical reactivity and, hence, in some distinctive concept of structure.

The usual assumption with respect to activation is that of the "opening double bond"[2]

$$M = CH_2{=}CHX \qquad M^* = —CH_2—CHX—$$

which is preferred because the moderate energy increase attributed to this transformation seems to be in accord with the energy of activation observed for the whole polymerization process. A small number of monomeric molecules are supposed to initiate the state M* and, thereupon, to initiate chain propagation in two directions

$$\begin{array}{ccc} —CH_2—CHX— & —(CH_2—CHX)^*— & —CH_2—CHX— \\ \text{Addend molecule} & \text{Initially activated} & \text{Addend molecule} \\ \longleftarrow \text{Propagation} & & \text{Propagation} \longrightarrow \end{array}$$

This conception of macropolymerization encounters various difficulties, several of which are discussed in the following.

(a) Termination cannot be explained satisfactorily.—The state of activation resides in two separate portions of the growing macromolecule which, with increasing length of the interposed chain, must become entirely independent of each other, so that they may be regarded as two disconnected monovalent radicals

$$—(CH_2 \ldots\ldots CHX)—$$

Such a structure cannot come to rest as a stable molecule[3] except through the saturation of both terminal valences. How this is to occur in the absence of independent monovalent radicals cannot be explained; the free end valences are definitely paired and, though it may be possible to account for the eventual stabilization of individual molecules through "transfer" of their state of activation to new monomeric centers,[4] it is impossible to explain the termination of the process as such. For this reason, some subsidiary mechanism must be assumed which can only be based on dissociation into monovalent radicals, disproportionation, internal stabilization through "mesomerization," or cyclization. The first two possibilities are excluded by excessive energy requirements, and the latter by their statistical improbability. Resonance between the terminal groups as well as their union becomes practically inconceivable once the saturated main structure of the chain has achieved a certain length; if these possibilities existed, low polymer products would predominate, but they are usually entirely absent.[5]

(b) The opening double bond mechanism is

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[1] Chalmers, *Can. J. Research*, **7**, 113, 472 (1932); H. Mark, "IX Congr. Chim.," Madrid, 1934; Dostal and Mark, *Z. physik. Chem.*, **B29**, 299 (1935); Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936), etc.

[2] Staudinger, *Ber.*, **59**, 3035 (1926); Flory, THIS JOURNAL, **59**, 241 (1937).

[3] Staudinger, *Ber.*, **59**, 3035 (1926); Taylor and Vernon, THIS JOURNAL, **53**, 2527 (1931).

[4] Flory, *ibid.*, **59**, 241 (1937).

[5] Chalmers, *ibid.*, **56**, 912 (1934).

common to most ethenoid substances, but only relatively few among this large group are capable of macropolymerization. By its very nature, the latter indicates that the actual number of initially activated molecules must be extremely small; their occurrence evidently is limited by a much lower probability than the activation of the opening double bond.

(c) The catalysts particularly effective in macropolymerization, *e. g.*, peroxides, do not induce other reactions involving the opening double bond mechanism.

(d) No traces of stable six-membered cyclic derivatives can be found in the polymerization products of simple vinyl compounds.

(e) The "material chain" of macropolymerization leaves in its path but one single molecule which has assimilated all of the reactant. This is a very special case among chain reactions. The original concept of the chain mechanism refers to systems of two reacting substances (*e. g.*, hydrogen + chlorine) and each chain cycle consists of two alternating reactions involving two kinds of radicals (hydrogen atom and chlorine atom, respectively). It cannot be said that the omission of this feature of alternation is at all compatible with the concept of a reaction "chain"; it rather seems that the idea of a reaction impulse maintaining itself on a perfectly level crest of activation is a departure from sound premises.

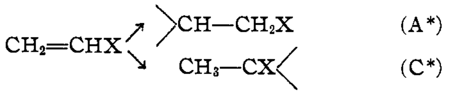
In order to avoid the enumerated inconsistencies, a formulation of the reaction mechanism of macropolymerization should be in accord with the following principles, *viz.*: (a) Initial activation must be represented by a molecular structure different from the opening double bond type. (b) The mechanism of propagation must provide one-sided growth of the chain. (c) Termination must be explained without supplementary assumptions, as due to the mutual deactivation of two activated molecules. (d) The proposed mechanism must be in accord with the relatively low energy of activation of the over-all process. (e) The absence of low-molecular cyclic by-products must be explained. (f) Resolution of the propagation mechanism into cycles comprising two alternating reactions and involving two kinds of activated carriers would avoid undue modification of the original chain concept.

Initial Activation.—If the energy content of a polyatomic molecule is raised until it becomes capable of a reactivity which otherwise it does not possess, it may be assumed to have passed through a constitutional change; this change ought to be expressed by a modification of the valency formula conventionally assigned to its unexcited form. The open bond biradical $—CH_2—CHX—$ is one valency interpretation of the activated state but it is by no means the only one possible. It also is not necessary to consider the actual transformation of the ethenoid structure into a genuine biradical, as indicated by the open bond formula, or to connect activation with any such valency formula in a literal sense. The biradical formula may merely indicate the tendency of constitutional change which brings about activation and reactivity may be attained at some intermediate stage of the transition

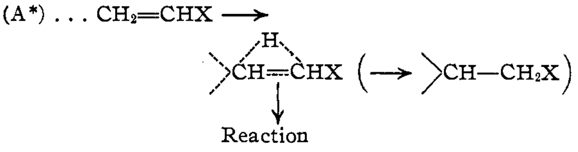
$$CH_2{=}CHX \longrightarrow \cdots CH_2{=}CHX\cdots \longrightarrow —CH_2—CHX—$$

Here the dotted lines represent valences in the process of redisposition (in a condition of resonance) between the definite forms of the normal molecule and the open bond radical. Of course, this transitional state may be expressed in other terms, such as atomic distances, the "order" of the bond,[6] odd or fractional numbers of shared electrons, etc.

As suggested in the foregoing, the originally activated molecule must be able to initiate the chain reaction into one single direction; in other words, it must possess asymmetric reactivity which may be formulated as a definitely polar mesomeric state. Such states or structures may be conceived as transitory toward biradical forms which involve the intramolecular shift of a hydrogen atom



as distinct from the open bond radical $—CH_2—CHX—$ (B*). The reactive intermediary form may be symbolized by, *e. g.*



The supposed mobility of the hydrogen atom would be due to the presence of the electro-negative substituent X and the shift would be in the sense of (A*) rather than that of (C*), so that the latter type of activation may be disregarded.

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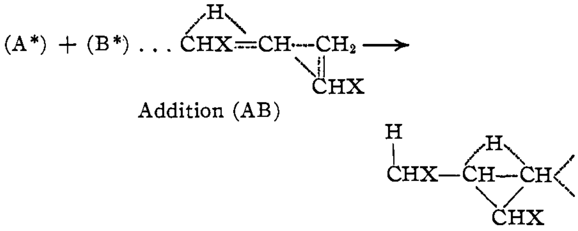
[6] Lennard-Jones and Coulson, *Trans. Faraday Soc.*, **35**, 811 (1939); Evans, *ibid.*, **35**, 824 (1939); Carothers, THIS JOURNAL, **46**, 2226 (1924).

This is very well in agreement with the fact that only compounds containing the unsubstituted terminal methylene group $CH_2=$ are capable of typical macropolymerization.[7]

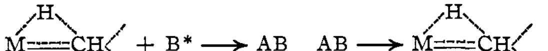
Propagation.—The continuity of addition requires that the initial state of activation be reconstructed in every chain cycle prior to the addition of one molecule of the monomer; *i. e.*, the terminal grouping . . . CHX—CH< of (A*) must appear in identical form in each reaction step. This condition can only be fulfilled by assuming that the addend molecule is activated in the sense of the opening double bond radical (B*). One complete addition cycle would consist of two distinct phases



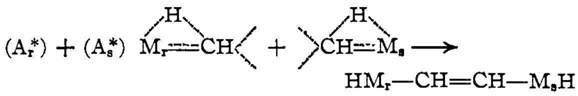
Addition (AB)

Re-activation (A_2^*)

The state of activation (A*) would be transmitted in only one direction while the other end of the chain would rest in the fully deactivated original molecular unit. The mechanism of the reaction would follow a rigorous rule of alternation between addition of one monomer and subsequent re-activation true to type, involving two different carriers, (A*) and (B*)



Termination by mutual deactivation of two active chains is very simply accounted for without recourse to further assumptions



The polymeric molecule at rest contains regularly aligned . . . CH_2—CHX . . . members in "head to tail" arrangement which is supported by experimental evidence[8]; the end groups are CH_2X . . . and the molecule has a single structural discontinuity with a double bond

$$CH_2X—(CH_2—CHX)_r—CH=CH—(CHX—CH_2)_s—CH_2X$$
$$r + s + 2 = n$$

The whole chain process which, in the above form, satisfies the premises of macropolymerization far better than the open-bond concept, can be formulated as follows.

$$\begin{array}{lll} M \longrightarrow A_1^* & \text{Initial activation} & \\ A_1^* + (M \longrightarrow B^*) \longrightarrow A_1B & \text{Addition} & \left.\right\} \\ \quad A_1B \longrightarrow A_2^* & \text{Re-activation} & \text{Propagation} \\ A_r^* + (M \longrightarrow B^*) \longrightarrow A_rB & \text{Addition} & \\ \quad A_rB \longrightarrow A^*_{r+1} & \text{Re-activation} & \\ A_r^* + A_s^* \longrightarrow P_{r+s=n} & \text{Termination} & \end{array}$$

where M are normal monomeric molecules, P_n a polymer at rest composed of *n* monomeric units; A_r^* are propagating chain molecules carrying the structure and energy of initial activation, composed of *r* monomeric units.

Discussion

Direct experimental proof of the proposed mechanism of activation is, for obvious reasons, as difficult as to disprove it. As a chemical process, macropolymerization is a singular phenomenon and calls for an explanation of reactivity which must be applicable to it alone; the proposed mechanism would lose its significance if it were proved to occur in other more common reactions of the parent substance. For this reason it is necessary to inquire into the formation of low-molecular by-products which, in some cases, accompany macropolymerization. It must be shown that these are due to a different and independent mechanism of activation.

Dimerization.—No low-molecular by-products are formed in the polymerization of the simple vinyl derivatives. Thus, various dimers of styrene are known[9] but none of them are produced under polymerization conditions. The absence of trimeric substituted cyclohexanes which would be bound to appear among the reaction products if activation took the form of the open-bond radical (B*), is very well explained by the assumed form of propagation

$$CH_2X—CH_2—CHX—CH_2—CHX—CH<$$

which does not allow for resonance between the chain ends.

The thermal polymerization of the dienes is accompanied by the formation of cyclic dimers. The current explanations assume the occurrence of these bodies as due to the interception of a polymerization chain in its dimeric stage and cyclization of the open chain addition product. According to the view proposed above, this explanation

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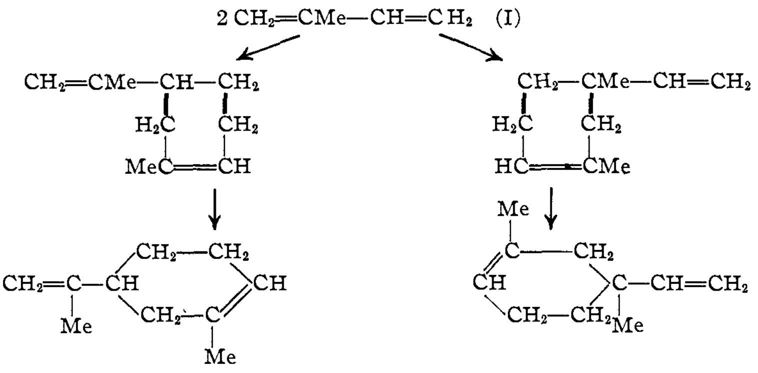
[7] In vinyl alcohol, $CH_2=CH\cdot OH$, the hydrogen atom seems to shift in the sense of (C*); this does not initiate polymerization to polyvinyl alcohol but leads to stable acetaldehyde.

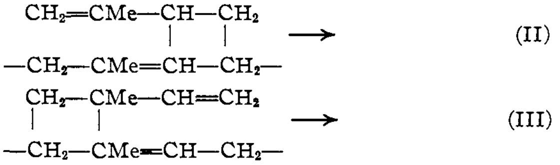
[8] Marvel and co-workers, THIS JOURNAL, **60**, 280, 1045 (1938); **61**, 3241, 3244 (1939); Flory, *ibid.*, **61**, 1518 (1939).

[9] Risi and Gauvin, *Can. J. Research*, **B14**, 255 (1936).

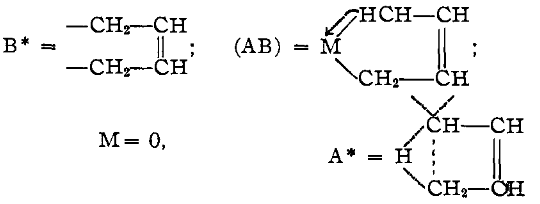
must be wrong. Macropolymerization must be considered as following a rigorous and unique mechanism initiated and sustained by a specific type of activation and its course must not admit of alternatives. Actually, it can be shown *e. g.*, in the case of isoprene (I), that the dimers formed, dipentene (II) and 1,3-dimethyl-3-vinylcyclohexene-6 (III),[10] would derive from different open-chain dimers ("head to head" and "head to tail," respectively) and that, therefore, different original forms of activation must be involved in any case. The two dimers can be explained directly by assuming two different types of monomeric activation, both open-bond and as such incapable of sustaining macropolymerization,



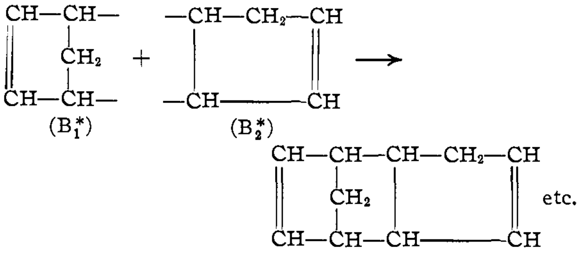
(II) (III)



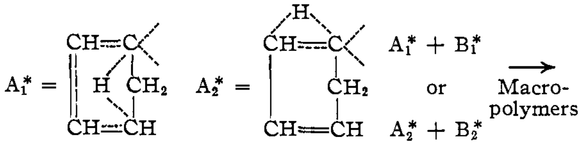
In considering the possibility of macropolymerization, $A^* + B^*$, an initial activation form A^* can be computed for each open-bond reactivity B^* if the latter is either known or deduced from the structure of simple addition compounds; *e. g.*, for butadiene



Analogous types of initial activation can be recognized in the cyclic polymers of all dienes. That these products are not formed within the chain of macropolymerization is particularly clear in the case of cyclopentadiene, which has been thoroughly studied.[11] Thermal polymerization of this substance produces not only a dimer, but, in decreasing quantities, a complete series up to the pentamer. None of these well-identified compounds which evidently are formed in successive reactions, can be induced into macropolymerization. The true chain polymers have only a transitory existence as radicals. As in the case of isoprene, the cyclic polymers derive from two open bond radicals, joined in 1–4 and 1–2 positions respective to the conjugated system. Hence, these forms must be excluded as initiators of macropolymerization. Assuming, however, that one or the other of these open-bond radicals may represent the addend molecule, two corresponding forms of initial activation can be deduced



Cyclic polymers



The smoothness and variety of the Diels-Alder reactions prove the tendency of dienes and of substances containing the grouping $C{=}C{-}CH{=}O$ toward open-bond activation. However, dienes enter into macropolymerization with the similarly constituted vinyl ketones[12] as well as with styrene and acrylic nitrile; there is no evidence of "adduct" formation.

Even a single C—H valence can be activated into an open bond. This is evident in many reactions of acetylene, *e. g.*, the dimerization to

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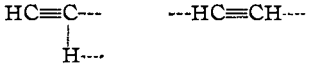
(10) Levedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249 (1913); Aschan, *Ann.*, **439**, 221 (1924).

(11) Staudinger and Bruson, *ibid.*, **447**, 97 (1926); Alder and Stein, *ibid.*, **485**, 223 (1931).

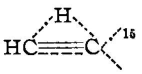
(12) U. S. P. 1,901,354 (1930), 1,973,000 (1930), to I. G. Farbenind, A.-G.

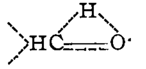
vinylacetylene, the formation of ethynyl carbinols with aldehydes and ketones,[13] the trimerization to divinylacetylene, dipropargyl, 3-methylpentadiene-1,4 and benzene. All these limited addition reactions[14] can be derived from two activated forms, both of the open-bond type

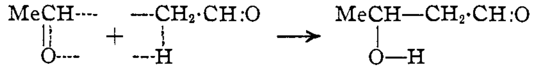


(B_1^*) (B_2^*)

Macropolymerization of acetylene, leading to high-polymer bodies like cuprene, can only be initiated by one form

(A*)  [15]

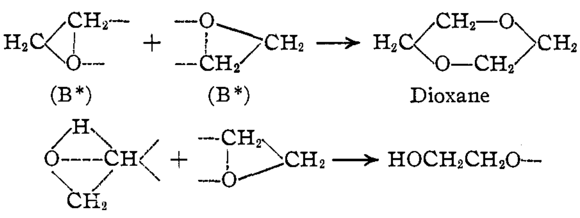
The activation of the C═O double bond follows analogous rules. Macropolymerization occurs where the C atom holds two H atoms, *i. e.*, in the case of formaldehyde, $H_2C{=}O$ (paraformaldehyde and polyoxymethylene). The initiating A* form must be  Acetaldehyde, CH_3—CH═O, is not capable of macropolymerization; its numerous addition reactions depend on open-bond type activation, for example



(B_1^*) (B_2^*) Acetaldol

$3B_1^* \longrightarrow$ Paraldehyde

Polymerization of ethylene oxide leads to the cyclic dimer dioxane, or it takes the course of macropolymerization. The respective activation types are



(B*) (B*) Dioxane

(A*) (B*) Macropolymer

The principle demonstrated in the above examples may be defined as follows:

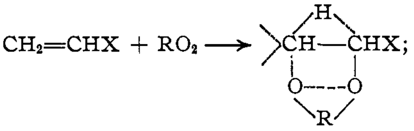
(*1*) *Macropolymerization is initiated by a form of the monomer whose state of activation is concentrated in one particular atom* (*in terms of a valence formula, represented by two potential free valences on one atom*). *This state is attained through a virtual shift of a hydrogen atom away from its normal position on the activated atom* (*prototropic radical*).

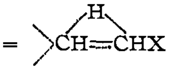
(*2*) *Activation of a bond between two atoms of the molecule without virtual dislocation of a hydrogen atom, to the effect that both bonded atoms partake of the state of activation* (*open-bond radical*), *promotes cyclization.*

(*3*) *Macropolymerization is propagated by a mechanism based on addition of an open-bond type radical* (*B**) *to a prototropic type radical* (*A**).

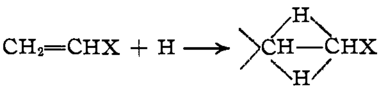
Co-polymerization is possible between components which are able to substitute for one another in all functions of the chain mechanism. The lowest energy of initial or A* type activation must be higher than the maximum energy of addend or B* type activation among the molecular species. There are systems where one substance can be incorporated into the chain of another one without being polymerizable by itself. The open-chain mechanism offers no explanation for this behavior; on the base of dual type activation it can be understood as incapacity of the inducible substance to form an initial A* type radical of its own.

Catalysts.—If catalysts are effective in promoting the presumably unique mechanism of macropolymerization,[16] they must possess the capacity of either inducing the formation of A* molecules, or of forming compounds with the monomer (probably B*) which have the characteristic A* constitution. Thus, peroxides may initiate vinyl polymerization by forming the addition complexes



A* = 

which simulate A* activation very closely. Initiation by radicals, *e. g.*, H atoms, may be formulated similarly



These compounds may again liberate the monomer in the form A*, or they may split off the catalyst during the first propagation step.

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[13] Nef, *Ann.*, **308**, 264 (1899); Scheibler and Fischer, *Ber.* **55**, 2903 (1922).

[14] The above reactions are usually explained by disproportionation. The activation form B_1^* represents reactivity in the same sense without, however, assuming complete release of the H atom.

[15] Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931), ascribe the dimerization of acetylene and its derivatives to the radical —C═CH_2 and inter-molecular H migration.

[16] There is no evidence that initiation by different agencies yields macropolymers of a different nature.

Kinetics of Macropolymerization.—The concept of a dual mechanism of activation calls for the separate evaluation of the activation energies of the two types of reactivity and of the reaction constants which govern the various phases of the chain process. This may be based on the following assumptions.

1. The state of initial activation, A*, exists in statistical energy distribution among the molecules of the monomer

$$c_A^* = k_A c \quad k_A = e^{-E_A/RT} \quad (A_A = 1) \qquad (1)$$

where c is the concentration of the monomer, c^* that of molecules of type A* activation; k_A, E_A, A_A are, respectively, the velocity constant, activation energy and non-exponential factor of the process of initiation.

2. The continuity of the chain propagation suggests that the activated molecule A* is capable of reacting with all monomeric molecules in its path. The energy E_B required to activate the addend (to open its double bond to the point of reactivity) may be accounted for through collision with, or induction by A*, so that the effective concentration of B* is that of the monomer, c, and E_B may be considered the activation energy involved in the formation of the addition complex (AB). The latter must be exothermic; the heat evolved must be sufficient to re-activate (AB) into an enlarged biradical of type A*. This reaction sequence is responsible for the consumption of the monomer

$$\begin{aligned}(\mathrm{d}c/\mathrm{d}t) &= -k_P c_A^* c \quad k_P = A_P e^{-E_B/RT} \qquad (2)\\ &= -k_A k_P c^2\end{aligned}$$

3. The termination reaction, consisting of the union of two A* type molecules, does not require further activation

$$(\mathrm{d}c_A^*/\mathrm{d}t) = -k_T(c_A^*)^2 \quad k_T = A_T \quad (E_T = 0) \qquad (3)$$

The chain length, n, is given by the quotient of the rate of propagation and that of termination

$$n = \frac{-k_P c_A^* c}{-k_T (c_A^*)^2} = \frac{k_P c}{k_T c_A^*} \qquad (4)$$

Estimated according to Staudinger's rule, n remains constant during the reaction.[17] Inserting c_A^* from (4) into (2) and integrating

$$\begin{aligned}\frac{c}{c_0} &= \frac{1}{1 + Kc_0 t}\\ K &= \frac{k_P^2}{k_T n} = k_A k_P \qquad (5)\end{aligned}$$

c_0 is the original concentration of monomer and t time; K is the over-all reaction constant

$$\begin{aligned}K &= Ae^{-E/RT} \quad E = E_A + E_B\\ A &= A_A A_P = A_P \qquad (6)\end{aligned}$$

The constancy of K is very well confirmed in the values calculated from the most reliable data available for styrene and vinyl acetate (Tables I and IV, Fig. 1). For styrene the total energy of activation is E = 22,100 cal./mole and $A_P = 10^{7.75 \pm 0.02}$. By inserting k_P from (2) and k_T from (3), the term for K in (5) yields

$$K = \frac{A^2{}_P}{A_T n} e^{-2E_B/RT} \qquad (7)$$

Equating K from (6) and K from (7), gives E_A = 13,700 cal./mole and E_B = 8400 cal./mole; $A_T = 10^{7.58 \pm 0.02}$.

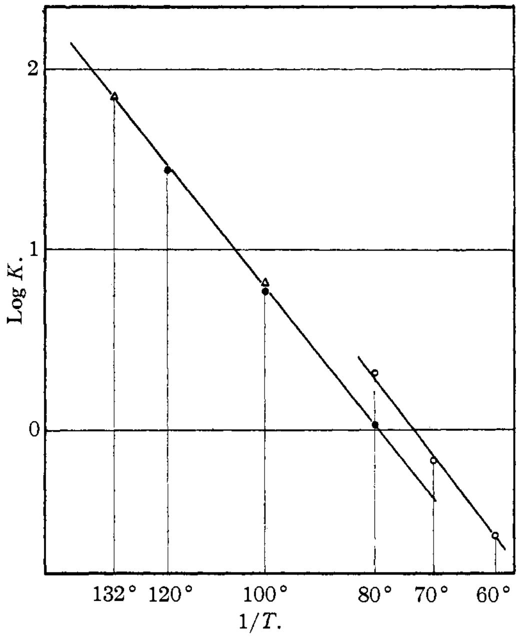

Fig. 1.—Reaction constants of styrene polymerization: △, Schulz and Husemann; ●, Suess, Pilch and Rudorfer; ○, Mark and Raff.

Reaction constants for the thermal polymerization of styrene in the absence of solvents and catalysts, as computed from the above values, are given in Table II.

The ratio k_P/k_A is of the order 10^{10}, which agrees with an empirical estimate by Schulz and Husemann.[18] Melville, Jones and Tuckett[19] concluded from observations on the photo-sensitized polymerization of vinyl acetate that k_T must be of

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[17] Staudinger and Frost, *Ber.*, **68**, 2351 (1935); Staudinger, *Trans. Faraday Soc.*, **32**, 97 (1936).

[18] Schulz and Husemann, *Z. physik. Chem.*, **B34**, 187 (1936).

[19] Melville, Jones and Tuckett, *J. Soc. Chem. Ind.*, **59**, 267 (1940).

a much higher magnitude than k_A; this is very well confirmed in the above results.

TABLE I

THERMAL POLYMERIZATION OF STYRENE (NO SOLVENT, NO CATALYST)

t, hr.	Temp., °C.	Conversion, %	n	K	Observer
1	80	0.35	2980	...	a
2	80	.67	2730	...	
4	80	1.61	2950	1.14 10^{-6}	
7.5	80	3.10	2860	1.18	
15.5	80	6.47	2710	1.24	
24	80	9.97	2660	1.28	
0.5	100	0.9	..	...	a
1	100	2.05	..	5.82 10^{-6}	
2	100	4.02	1920	5.81	
3	100	6.3	1950	6.22	
5	100	10.60	..	6.59	
7	100	15.15	..	7.08	
9	100	18.02	..	6.77	
12	100	23.51	..	7.11	
1	120	9.26	1400	28.4 10^{-6}	a
2	120	17.06	1410	28.6	
3	120	24.25	1420	29.6	
4.6	120	34.50	1410	31.8	
6	120	43.11	1430	35.1	
No. of measmts.			n (mean)	K (mean)	
12	60		..	0.26 10^{-6}	b
24	70		..	.82	b
5	100.5		1910	6.60	c
4	132		1380	72.5	c

[a] Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937).

[b] Mark and Raff, *ibid.*, **B31**, 275 (1935).

[c] Schulz and Husemann, *ibid.*, **B36**, 184 (1937).

TABLE II

	80°	100°	120°		Eq.
k_A	3.1	9.4	20.7	10^{-9}	(1)
k_P	1.7	3.1	6.9	10^{+2}	(2)
k_T	3.8	3.8	3.8	10^{+7}	(3)

Solvents.—The constants calculated from rate measurements of the polymerization of styrene in various solvents (Table III) show appreciable differences from the above; they vary with the nature and the concentration of the solvent. According to the premises, neither initial activation nor the mechanism of propagation can be affected by the presence of third substances; the latter can, however, interfere by deactivating A* type molecules.

Assuming a bimolecular reaction between solvent and A*, the denominator in (4) must be extended by a term representing the deactivating effect of the solvent

$$n = \frac{-k_P c c_A^*}{-k_T (c_A^*)^2 - k_S(1 - c)c_A^*}$$

$$k_S = \frac{k_P c}{1 - c}\left(\frac{1}{n} - \frac{1}{n_0}\right) \qquad (8)$$

k_S must depend on the nature but not on the concentration of the solvent; n is the degree of polymerization observed in the presence of the solvent,

TABLE III

THERMAL POLYMERIZATION OF STYRENE (SOLVENTS; NO CATALYSTS)

Solvent	Temp., °C.	c_0 (Styrene), mole	Measmts.	n	$K \times 10^6$	Observer
None	80	8.70	4[c]	2815	1.07[d]	a
	100	8.70	7[c]	1935	5.70[d]	a
	120	8.70	5[c]	1415	27.7[d]	a
Benzene	80	0.5	2	1390	0.86 ± 0.02	b
	80	1.0	1	1870	.98	b
	80	3.0	2	2360	1.08 ± .03	b
	100	0.5	2	700	3.02 ± .00	b
	100	1.0	1	1100	3.91	b
	100	3.0	2	1540	4.63 ± .12	b
	100	5.0	2	1770	5.51 ± .09	b
Toluene	80	2.32	5	2030	1.14 ± .02	a
	80	4.39	2	2500	1.26 ± .03	a
	100	0.53	3	570	7.48 ± .4	a
	100	1.04	5	810	5.80 ± .2	a
	100	1.82	2	1160	6.71 ± .1	a
	100	2.32	3	1300	6.48 ± .25	a
	100	3.07	3	1470	7.48 ± 1.25	a
	100	4.52	3	1740	7.85 ± 0.5	a
	120	1.04	3	430	19.4 ± .7	a
	120	2.32	3	890	23.4 ± .5	a
	120	4.59	2	1160	22.4 ± 2	a
Ethylbenzene	80	0.5	2	530	1.07 ± 0.03	b
	80	2.5	2	1270	1.01 ± .04	b
	100	0.5	3	380	5.00 ± .05	b
	100	1.5	3	640	7.25 ± .5	b
	100	2.5	3	940	5.70 ± .3	b
	100	4.0	3	1200	6.92 ± .2	b
	100	5.5	2	1460	6.14 ± .1	b
	120	1.5	2	450	29.25 ± .1	b
	120	4.0	2	820	30.60 ± .1	b
	120	5.5	2	1040	28.65 ± .1	b
Heptane	100	1.5	2	1000	3.77 ± .07	b
	100	3.0	3	1390	4.04 ± .2	b
	100	5.0	2	1720	4.60 ± .14	b
Carbon tetrachloride	80	4.0	4	95	0.59 ± .03	a
	80	5.5	3	150	.76 ± .13	a
	80	7.0	4	265	.92 ± .04	a
	100	2.0	2	60	4.1 ± .1	a
	100	3.0	3	65	3.8 ± .0	a
	100	4.0	4	85	4.4 ± .5	a
	100	5.5	3	135	4.5 ± .2	a
	100	7.0	4	230	6.3 ± .4	a
Ethylene dichloride	100	3.0	2	630	6.28 ± .15	b
	100	6.0	2	1270	9.94 ± .06	b
Tetrachloroethane	100	3.0	2	380	2.30 ± .01	b
	100	6.0	2	910	3.98 ± .03	b
Chlorobenzene	100	1.0	5	960	6.53 ± .4	a
	100	3.0	4	1700	6.44 ± .3	a
	100	6.0	4	1750	7.25 ± .4	a

[a] Suess, Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937). [b] Suess and Springer, *ibid.*, **A181**, 81 (1937). [c] See Table I. [d] Extrapolated to zero reaction.

TABLE IV

POLYMERIZATION OF VINYL ACETATE[b]

70 parts by weight of vinyl acetate; 30 parts by weight of toluene; 0.07 part by weight of benzoyl peroxide; temperature, 76 ± 0.2°

t, min.	Conversion, %	n^a	$K\ 10^6$
74	17.7	4.78	48.5
134	29.8	4.83	54.5
194	38.8	4.73	54.6
251	46.4	4.71	57.5
314	52.6	4.71	58.9
404	59.5	4.74	60.6
528	65.8	4.48	60.7
584	67.9	4.57	60.4
644	68.3	4.46	55.8
704	69.4	4.57	53.7

[a] Viscosity in 8.60% (molar) benzene solution at 20°.
[b] Blaikie and Crozier, Shawinigan Chemicals Ltd., unpublished data.

TABLE V

THERMAL POLYMERIZATION OF STYRENE (EFFECT OF SOLVENTS)

Solvent	c_0 (Mol. % styrene)	k_S (Eq. 8) 80°	100°	120°	E_S cal./mole	A_S
Benzene	0.5	0.0039	0.017	..		
	1.0	.0041	.016	..	18,800	$10^{9.24}$
	3.0	....	.021	..		
Toluene	1.04	....	.030	0.15		
	2.32	.0087	.028	.10	18,400	$10^{9.33}$
	4.5	.0079	.019	.11		
Ethylbenzene	0.5	.016	.040	..		
	1.5	....	.086	.22		
	2.5	.030	.068	..	18,850	$10^{9.96}$
	4.0	....	.083	.30		
	5.5	....	.089	.30		
Heptane	1.5	....	.031	..		
	3.0	....	.033	..		
	5.0	....	.026	..		
Ethylene dichloride	3.0	....	.174	..		
	6.0	....	.186	..		
Tetrachloroethane	3.0	....	.344	..		
	6.0	....	.401	..		
Chlorobenzene	1.0	....	.021	..		
	3.0	....	.011	..		
	6.0	....	.040	..		
Carbon tetrachloride (2nd order)	2.0	....	.150	..		
	3.0	....	.243	..		
	4.0	1.50	.342	..		
	5.5	1.88	.367	..		
	7.0	2.44	.693	..		
Carbon tetrachloride (3rd order) Eq. (9)	2.0	....	1.50×10^9	..		
	3.0	....	1.58×10^9	..		
	4.0	2.03×10^9	1.49×10^9	..		
	5.5	1.79×10^9	1.43×10^9	..		
	7.0	2.57×10^9	1.40×10^9	..		

n_0 in its absence, at the same temperature. Table V shows the actual constancy of k_S computed according to (8). For benzene, toluene and ethylbenzene, the activation energy E_S of the interfering termination process is found nearly equal, 18,700 cal./mole; since the energy content of A* is 13,700 cal./mole, the remainder, 5000 cal./mole, is carried by the reactive solvent molecule. The value of $A_S = 10^{9.5}$ is in agreement with a bimolecular reaction.

The effect of carbon tetrachloride is quite different from that of the other solvents. The degree of polymerization is extremely low and k_S for a second order reaction increases sharply with concentration. However, the data are in very good accord with a trimolecular reaction, $CCl_4 + 2\,A^*$, for which

$$k_S = \frac{k_T}{1-c}\left(\frac{n_0}{n} - 1\right) \qquad (9)$$

As in other trimolecular reactions, the temperature coefficient is negative.

Catalysts.—Assuming that the addition compound of monomer and catalyst (see above) is reasonably stable, and that the amount of catalyst is limited, a stationary condition can be considered in which all catalyst molecules are attached to molecules of the monomer. The number of initiating centers

$$c^* = k_A c + k_C \gamma c = k'_A c \qquad (10)$$

where γ is the concentration of the catalyst and k_C the reaction constant of compound formation. Accordingly, nothing in the mechanism is changed except that k_A of the uncatalyzed reaction is raised to k'_A. From equation (5), which remains applicable

$$K' = k'_A k_P = (k_A + k_C\gamma)k_P \qquad (11)$$

k_P, the reaction constant of propagation, remains unaffected.

TABLE VI

POLYMERIZATION OF STYRENE (CATALYST, BENZOYL PEROXIDE[14])

Catalyst, mole %	$K'\ 10^6$ 27°		50°		E' cal./mole	Log A_P	E_A' cal./mole
0					22,100	7.95	13,700
0.0165	0.16	± 0.01	1.59	± 0.02	19,200	7.23	10,800
.0413	.25	.02	2.59	.06	19,500	7.64	11,100
.083	.367	.02	3.48	.03	18,800	7.29	10,400
.165	530	.003	5.85	.11	20,000	8.39	11,600
.248	.643	.008	6.70	.15	19,600	8.10	11,200
				Mean	19,400	7.73	11,000

Table VI shows values of K' calculated from the experimental data by Schulz and Husemann[20] on the polymerization of undiluted styrene in the presence of various amounts of benzoyl peroxide. K' is constant; its temperature coefficient indi-

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[20] Schulz and Husemann, *Z. physik. Chem.*, **39**, 246 (1938).

cates a very definite lowering of the over-all activation energy E', independent of the amount of catalyst, from 22,100 to 19,400 cal./mole. This difference must be due to a lower energy of initial activation; E' of the catalyst-monomer addition complex is only 11,000 cal./mole as compared with 13,700 cal./mole of the simple A* radical. The activation of the catalyst molecule itself requires $E_C = 2600$ cal./mole.

Summary

Macropolymerization is usually explained as a chain reaction which is supposed to be initiated and propagated by radicals produced by the "opening" of the double bond of the monomer. This conception is inadequate for many reasons which are discussed in the paper. It is attempted to interpret macropolymerization and the mechanism of its activation in terms of constitutional changes.

On these premises, two different states of monomeric activation are defined and formulated as virtual free radicals: the form responsible for initial activation of the chain process (prototropic or A* type) and that assumed by the addend molecules (open-bond or B* type). The latter type, without the former, can only effect cyclization. These principles are exemplified within the scope of the paper, but their general validity is implied.

The kinetics of macropolymerization is analyzed in accord with the proposed mechanism of dual activation. The activation energies of the two types of mesomeric radicals are computed from available experimental data on styrene polymerization, and the reaction constants of the main phases of the process are estimated on this basis. The effects of solvents and of catalysts are evaluated.

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The Heats of Dilution of Aqueous Solutions of Glycine and Glycolamide, and Other Thermodynamic Properties of Glycine at 25°[1,2]

BY FRANK T. GUCKER, JR., HUGH B. PICKARD AND WILLIAM L. FORD

Introduction

An investigation of the thermodynamic properties of aqueous solutions of non-electrolytes, undertaken in this Laboratory[3] indicates that the limiting slopes of the apparent molal volumes, expansibilities, heat capacities, and heat contents are linear functions of the first power of the concentration, rather than its square root, as in the case of electrolytes. This limiting law is to be expected for dipolar solutes, according to an extension of the theory of Fuoss,[4] and the slopes should be steeper the greater the dipole moment. We are testing these ideas by comparing the properties of the simple amino acids, which occur in aqueous solution chiefly as *zwitterions* with large dipole moments, and their uncharged isomers, which are much less polar.

Studies of glycine, $^{+}H_3NCH_2COO^{-}$, and the isomeric glycolamide, $CH_2OHCONH_2$, have shown[5] that the apparent molal volumes of both are linear functions of the molarity, *c*, at 25°. The apparent molal heat capacities at 5, 25 and 40° become linear in the first power of the concentration in very dilute solutions, although they are quadratic functions of the concentration over a large range. In both cases, the curves for glycine are *lower* than those for glycolamide, apparently because of greater electrostriction, and have *steeper limiting slopes*, which may be attributed to the interaction between the dipolar solute molecules. Now we have measured the heats of dilution of these isomers, which are published and compared in the present article.

Materials and Solutions.—The glycine used in this work was Eastman Kodak Co. best grade, recrystallized once from 70% alcohol. Conductivity measurements indicated about 0.02% electrolyte calculated as sodium chloride.

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[1] The material in this paper was presented before the Division of Physical and Inorganic Chemistry: the work on glycine at the Baltimore Meeting of the American Chemical Society, April 5, 1939, and that on glycolamide at the Cincinnati Meeting, April 10, 1940.

[2] This work was supported by grants from the Penrose Fund of the American Philosophical Society and from the Committee on Research of the Graduate School of Northwestern University.

[3] Gucker, *et al.* (a) THIS JOURNAL, **59**, 447 (1937); (b) **59**, 2152 (1937); (c) **60**, 2582 (1938); (d) **61**, 459 (1939); (e) **61**, 1558 (1939); (f) **62**, 1464 (1940).

[4] Fuoss, *ibid.*, **58**, 982 (1936).

[5] Gucker, Ford and Moser, *J. Phys. Chem.*, **43**, 153 (1939).