

molecular weight mercaptans through the aqueous phase is a controlling factor in determining

the rate of regulator reaction.

PASSAIC, NEW JERSEY

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[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

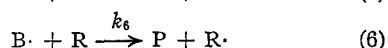
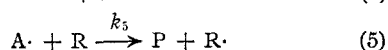
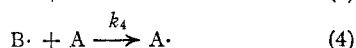
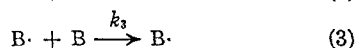
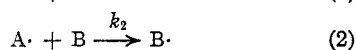
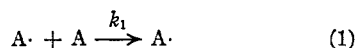
Regulator Theory in Emulsion Polymerization. III. Regulator Reaction in Copolymerizing Systems

By W. V. SMITH

The relative rates of reaction of two monomers during copolymerization have been discussed from both a theoretical and experimental standpoint.¹ The rate of reaction of a transfer agent or regulator in the polymerization of a single monomer has been discussed by Mayo.² It is the purpose of this paper to combine these two treatments and thus obtain the law governing the rate of reaction of a regulator during the copolymerization of two monomers. While the theory should apply either to oil-phase polymerization or to emulsion polymerization, the experimental portion is confined to emulsion polymerization.

Theory

The following elementary reactions are assumed to account for chain propagation and chain transfer in a system in which the monomers A and B are copolymerizing in the presence of the regulator R



In the above system of reactions $A\cdot$ and $B\cdot$ designate growing polymer free radicals in which only the active ends are specified, since it is assumed that the nature of the rest of the free radical will have a negligible effect on the specific reaction rate constants involving the free radical. R is regulator, $R\cdot$ is the free radical derived from the regulator by chain transfer, and P is inactive polymer. The specific reaction rate constants for the six reactions considered are k_1 to k_6 . Certain ratios of these rate constants can be measured by analytical methods, these are

$$\begin{aligned} k_1/k_2 &= \sigma; \quad k_3/k_4 = \mu \\ k_5/k_1 &= C_A; \quad k_6/k_3 = C_B \end{aligned}$$

(1) (a) F. R. Mayo and F. M. Lewis, *THIS JOURNAL*, **66**, 1594 (1944); (b) F. M. Lewis, F. R. Mayo and W. F. Hulse, *ibid.*, **67**, 1701 (1945); (c) F. T. Wall, *ibid.*, **66**, 2050 (1944); (d) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944); (e) R. Simha and H. Branson, *ibid.*, **12**, 253 (1944).

(2) F. R. Mayo, *THIS JOURNAL*, **65**, 2324 (1943).

The symbols are those used by Mayo in his treatment of copolymerization^{1a} and of transfer constants.²

By reactions (5) and (6) the rate of regulator disappearance is given by

$$d \ln R/dt = k_5(A\cdot) + k_6(B\cdot) \quad (1)$$

Letting (A) and (B) represent the molal concentrations of the two monomers, the rate of disappearance of monomer by reactions 1 to 4 is

$$d((A) + (B))/dt = k_1(A)(A\cdot) + k_2(B)(A\cdot) + k_3(B)(B\cdot) + k_4(A)(B\cdot) \quad (2)$$

By using the steady state assumption of Mayo

$$k_2(B)(A\cdot) = k_4(A)(B\cdot) \quad (3)$$

and replacing the individual k 's by the ratios given above, equations 1 and 2 give

$$\frac{d \ln R}{d((A) + (B))} = \frac{\sigma(A)C_A + \mu(B)C_B}{\sigma(A)^2 + 2(A)(B) + \mu(B)^2} \quad (4)$$

This can be put into a form which is in some respects more convenient to use by making the substitutions

$$\frac{(A)}{(A) + (B)} = A \text{ and } \frac{(B)}{(A) + (B)} = B$$

where A and B are the mole fractions of each unreacted monomer expressed on the basis of total unreacted monomer so that $A + B$ is 1 at all times. Then

$$\frac{d \ln R}{d \ln ((A) + (B))} = \frac{\sigma A C_A + \mu B C_B}{\sigma A^2 + 2AB + \mu B^2} \quad (5)$$

The quantity $d \ln R/d \ln ((A) + (B))$ may be considered to define the transfer function, C , in the copolymerizing system so

$$C = \frac{\sigma A C_A + \mu B C_B}{\sigma A^2 + 2AB + \mu B^2} \quad (6)$$

In using this law, the units of R are immaterial; however, A and B must be mole fractions. The use of mole fractions in the latter case is required due to use of the steady state assumption 3. The transfer function as defined above using molal units for expressing the monomer concentrations is satisfactory for relating degrees of polymerization with rate of regulator disappearance. However, for relating regulator disappearance with molecular weight, a more convenient definition of the transfer function would be one in which the monomer concentrations were in weight units; but as this would result in an ex-

pression more complicated than 6 the above definition is preferred.

Before discussing the experimental test of equation 6, it may be worth while to mention some of the more interesting characteristics of the function on the right-hand side. In the first place, it is apparent that if $\sigma = \mu = 1$, the transfer function in a mixture of two monomers is a linear function of the composition; this may be considered the "ideal" case. However, in general, there will be departures from this "ideal" behavior. The nature of these expected departures can be discussed most easily for the case where the transfer constants are the same in the two pure monomers. Under these conditions the linear relation holds (*i.e.*, transfer function is independent of composition) if $\sigma + \mu = 2$. If $\sigma + \mu > 2$ then the curve of transfer function *vs.* composition shows positive deviations from the ideal, while, if $\sigma + \mu < 2$, the deviations are negative. If $\sigma = \mu$, the curves are symmetrical, otherwise they are not. If σ (or μ) is 0, then the transfer function in a mixture is independent of C_A (or C_B), except for infinite values of the transfer constant.

Experimental

The materials and experimental technique used in this investigation were the same as those described in Part I.³ The rapidly diffusing mercaptan, *n*-amyl mercaptan, was used in order to avoid the complications found for slowly diffusing mercaptans.⁴

The experimental results on polymer yields and mercaptan reactions in emulsion polymerization for various mixtures of methyl methacrylate and styrene are given in Table I. For these data the logarithm of the unreacted mercaptan

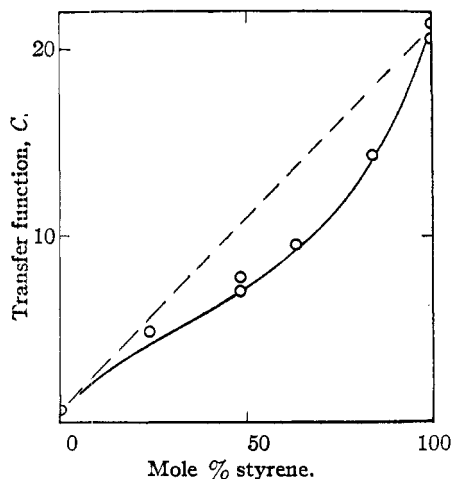


Fig. 1.—Transfer function of *n*-amyl mercaptan in the emulsion copolymerization of mixtures of styrene and methyl methacrylate: --- curve for "ideal" case ($\sigma = \mu = 1$); — theoretical curve for equation (6).

(3) W. V. Smith, *THIS JOURNAL*, **68**, 2059 (1946).

(4) W. V. Smith, *ibid.*, **68**, 2064 (1946).

was plotted against the log of the unreacted monomer; the negative slopes of the lines so obtained give the experimental transfer functions corresponding to C in equation 6. Since the molecular weights of the two monomers are so nearly the same, the weight per cent. of total unreacted monomer was used in determining the transfer function without any further correction. Also, in the case of all the mixtures, low conversions were used so that it was unnecessary to make corrections for change of composition of monomer with conversion. The experimental values of the transfer functions so obtained are given in Table II.

TABLE I

RATE OF REACTION OF *n*-AMYL MERCAPTAN IN THE EMULSION POLYMERIZATION OF MIXTURES OF STYRENE AND METHYLMETHACRYLATE

100% Methylmethacrylate, mercaptan 0.8 (wt. % of monomer, 50°)						
Time, min.	20	40	49	62	79	
Polymer yield, %	4.1	28.2	38.3	52.7	66.0	
Mercaptan reacted, %	8.5	24.2	37	43.8	54.5	
76 (mole) % Methylmethacrylate-24% styrene, mercaptan 0.3 (wt. % of monomer, 40°)						
Time, min.	35	50	60	81		
Polymer yield, %	3.6	6.3	7.6	13.4		
Mercaptan reacted, %	14.4	26.3	38.8	50.5		
52 (mole) % Methylmethacrylate-48% styrene, mercaptan 0.3 (wt. % of monomer, 40°)						
Time, min.	20	35	50	65	80	95
Polymer yield, %	..	3.7	5.6	10.2	12.9	16.3
Mercaptan reacted, %	18.0	35.5	50.0	61.4	72.4	80.0
Mercaptan 0.15 (wt. % of monomer, 40°)						
Time, min.	25	40	54	64	74	84
Polymer yield, %	..	7.8	12.3	15.2	19.5	22.4
Mercaptan reacted, %	11.3	50.5	62.3	75.2	80.2	85.6
37 (mole) % Methylmethacrylate-63% styrene, mercaptan 0.3 (wt. % of monomer, 40°)						
Time, min.	15	30	45	60	75	90
Polymer yield, %	0.6	3.7	7.0	11.2	16.2	23.2
Mercaptan reacted, %	17.5	45.7	59.0	72.8	84.3	93.3
16 (mole) % Methylmethacrylate-84% styrene, mercaptan 0.3, (wt. % of monomer, 40°)						
Time, min.	20	30	40	50	60	70
Polymer yield, %	2.7	5.6	8.6	11.6	17.3	22.0
Mercaptan reacted, %	41.6	59.9	76.1	87.2	93.7	97.5
100% Styrene, mercaptan 0.4% of monomer, 40° (0.5 normal amount of persulfate used)						
Time, min.	15	30	45	60		
Polymer yield, %	0.32	1.9	4.1	7.9		
Mercaptan reacted, %	28.6	50.8	70.9	84.7		

For comparing these with the values predicted by equation (6) the following were used: A = mole % styrene, B = mole % methylmethacrylate, $\sigma = 0.49$,⁵ $\mu = 0.49$,⁵ $C_A = 21$ and $C_B = 0.72$. Thus

$$C = \frac{(0.49 \times 21 \times A) + (0.49 \times 0.72 \times B)}{0.49A^2 + 2AB + 0.49B^2}$$

The curve for this equation is shown as the solid line in Fig. 1 while the experimental values are indicated by the circles. The agreement is satisfactory.

(5) These values for σ and μ are those obtained in oil-phase polymerization.^{1a} It is probable that the same values apply to emulsion polymerization since the rate of reaction of neither of the monomers should be controlled by the rate of diffusion through the aqueous phase. This relation between the emulsion and oil-phase values represents essentially the same problem as that of the relative rate of regulator and monomer reactions discussed in Part I (ref. 3) and Part II (ref. 4).

TABLE II

TRANSFER FUNCTIONS OF *n*-AMYL MERCAPTAN IN THE EMULSION COPOLYMERIZATION OF STYRENE AND METHYL-METHACRYLATE

Mole % styrene	0	23.6	48	63	84	100
Transfer Function	0.72	4.9	7.8	9.5	14.3	21.4
			7.0			20.6 ^a

^a Obtained from the data given in Part I³.

Summary

The rate of reaction of a regulator during the copolymerization of two monomers is discussed theoretically. An experimental investigation of the rate of reaction of *n*-amyl mercaptan in the emulsion copolymerization of styrene and methylmethacrylate gives satisfactory agreement with the theory.

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The Acid Catalyzed Decomposition of Diazoacetic Ester in Some Aprotic Solvents at 25°

BY ROBERT J. HARTMAN,¹ CLARENCE J. HOCHANADEL^{2,3} AND EDWARD G. BOBALEK¹

It has been suggested by Hantzsch⁴ that the comparison of the reaction rates of acid catalyzed decomposition reactions of diazoacetic ester can provide a measure of the protophilic character of different acids. Although the validity of this interpretation has been questioned in some instances,^{5,6} the general usefulness of this comparison of relative acid-strengths has been supported by rather convincing arguments.⁷

From the viewpoint of providing a criterion for measuring acidity, the interpretation of some of the earlier data^{4,6,8,9,10} was obscured by the complexity of the acid-base systems that were involved as the primary catalytic components. Such complexity is unavoidable when the acid occurs in the presence of a basic solvent or other added protophilic substances.^{11,12,13,14} The greatest simplicity can be anticipated for the reaction systems wherein the solvent medium has a minimum tendency to influence the acid-base equilibria of the reactive components, for example, in hydrocarbon solvents.^{6,7,8} In these types of systems the acid-catalysis effect should be influenced primarily by the acid-base equilibria involving only the acid catalyst and the diazoacetic ester, and it can be expected that the reaction rates should provide a less-complicated index of relative acidities for the members of a series of similar acid types. How-

ever, in view of the fact that hydrogen-bonding or similar types of association effects can occur even in aprotic solvents,¹⁵ it seemed more probable that the effective catalytic properties of any particular acid would vary considerably in different solvents of the simple aprotic class. In fact, it has been demonstrated by Weissberger and Högen⁸ that significant differences in reaction rates occurred even in solvents as simple as toluene and hexane. Consequently, it seemed to be a question of some interest to determine the influence of the anticipated solvent effects when this particular reaction-rates method is used to compare relative strengths of acids and bases, and to establish whether this procedure for measuring relative acidity provides results that are consistent with those deduced by other criteria.

Experimental

Reagents.—The diazoacetic ester was prepared according to the method of Fraenkel,¹⁶ which involved the reaction of a pure grade of glycine ethyl ester (Eastman Kodak Company) and C. P. sodium nitrite in aqueous solution, followed by an ether extraction of the diazo reaction product. After the ether extract had been dried for several days with anhydrous calcium chloride, the greater part of the ether was separated by evaporation *in vacuo* at low temperatures, and the residue of ester was purified by distillation *in vacuo* from freshly burned lime at temperatures of 50–60°. The ester was stored over barium hydroxide, and vacuum distilled again as it was required for the preparation of solutions in the various solvents. The purity of the ester was checked frequently during the course of the storage period by measuring the nitrogen yield after decomposition with acid and, in every instance, the experimental results for the material used in the experiments corresponded to the stoichiometric values calculated on the assumption that the ester contained less than 1% of non-measurable impurities. The purified diazoacetic ester and its solution in the various solvents remained stable for periods of at least several months.

The solvents used were special pure grades (Eastman Kodak Company) of toluene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, *o*-nitrotoluene and *m*-nitrotoluene. These solvents were subjected to some addi-

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(3) This paper is constructed from a dissertation presented by Clarence J. Hochenadel to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Hantzsch, *Z. Elektrochem.*, **24**, 201 (1918); **29**, 221 (1923); **30**, 194 (1926); *Z. physik. Chem.*, **125**, 251 (1927).

(5) Halban, *Z. Elektrochem.*, **29**, 434 (1923).

(6) Brönsted and Bell, *THIS JOURNAL*, **53**, 2478 (1931).

(7) Weissberger, *ibid.*, **65**, 245 (1943).

(8) Weissberger and Högen, *Z. physik. Chem.*, **A156**, 321 (1931).

(9) Bredig and Ripley, *Ber.*, **40**, 4015 (1907).

(10) Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925).

(11) Brönsted, *Rec. trav. chim.*, **42**, 718 (1923).

(12) Lowry, *Chem. Ind.*, **42**, 43 (1923).

(13) Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(14) Luder, *Chem. Rev.*, **27**, 547 (1940).

(15) S. J. O'Brien and co-workers, *THIS JOURNAL*, **61**, 2504 (1939); **62**, 1189, 2065, 3227 (1940); **63**, 2709 (1941).

(16) Fraenkel, *Z. physik. Chem.*, **60**, 202 (1907).