86–87% dechlorination, points are obtained which are higher than expected for an extrapolation of the smooth rate curve. This additional halogen removal may be resulting from the utilization of isolated chlorine atoms for the formation of larger rings. Because of entropy effects, one would expect the rate of ring formation to decrease with increasing ring size. Experimentally one finds that as the vinyl chloride content of a copolymer decreases, thereby requiring a greater degree of larger ring formation to reach 87% dehalogenation, the rates of dehalogenation fall rapidly to a point where, for very low vinyl chloride contents, no reaction is observed within 400 hours. Thus we feel that the normal zinc dehalogenation reaction consists of rapid random removal of 1,3-chlorines and this is followed by the 1,5, etc. reactions at correspondingly lower rates. Superimposed on the normal zinc reaction are complicating factors such as the removal of acetate in the case of the vinyl chloride/vinyl acetate copolymers and loss of hydrogen chloride by vinyl chloride/methyl methacrylate copolymers.

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[CONTRIBUTION NO. 273 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Kinetics of the Polymerization of Methyl Methacrylate with Aliphatic Azobisnitriles as Initiators[1]

BY L. M. ARNETT

Methyl methacrylate has been polymerized in bulk and in benzene solution with each of three aliphatic azobisnitriles which have decomposition rates in a range whose extremes differ by a factor of 100. The initial rate of polymerization is found to be proportional to the square root of the initiator concentration, to the square root of the specific rate constant for initiator decomposition, and to the first power of the monomer concentration. The relationship between the number average molecular weight and the initiator concentration indicates that approximately one-half of the radicals generated by decomposition of the initiator start polymer chains. It is also indicated that the termination reaction is combination of two growing chains.

In studies of the mechanism of vinyl polymerization, several investigators have related the rate of initiation of growing polymer chains to the rate of decomposition of benzoyl peroxide used as initiator.[2–4] Their results show that, although the decomposition of this peroxide appears to be a first order reaction under a given set of conditions, the rate constant calculated for a first order reaction varies widely with changes in reaction medium and peroxide concentration.[2–5] This deviation from a true first order reaction is generally attributed to free radical attack on undecomposed peroxide to produce induced decomposition which makes no contribution to the sum total of initiating radicals.[4] As a result, the rate of generation of free radicals from decomposing peroxide is always less by an uncertain amount than the rate of decomposition of the peroxide.

The discovery that certain aliphatic azobisnitriles are excellent initiators of vinyl polymerization[6] prompted an investigation of the decomposition of typical azobisnitriles. This work indicated that the aliphatic azobisnitriles decompose thermally in solution by a true first order reaction not influenced by solvent or concentration. This conclusion is in agreement with that of other workers as reported recently in the literature.[7–9] It is therefore to be expected that when azobisnitriles are used as vinyl polymerization initiators, the rate of generation of free radicals may be set equal to the rate of decomposition of the initiator. This ideal behavior of the azobisnitrile initiators has been used in this investigation to obtain evidence concerning the mechanism of the polymerization of methyl methacrylate.

Experimental Methods

Decomposition of Azobisnitriles.—The azobisnitriles used in this study were prepared by the method of Thiele and Heuser.[10] The decomposition of the azobisnitrile was carried out in solution in a glass vessel immersed in a vapor-bath or water thermostat. The reaction medium was brought to the temperature of the bath, and the gas space swept out with purified nitrogen (less than 20 p.p.m. O_2). A known weight of azobisnitrile was added to the liquid, and the vessel was closed and agitated to bring about solution. The evolved nitrogen was collected in a gas buret, and the volume noted as a function of time.

Monomer Purification.—Methyl methacrylate monomer containing phenols as polymerization inhibitors was washed with 5% sodium hydroxide solution and then with distilled water. The monomer was dried with Drierite and then fractionated in a stream of purified nitrogen at 100 mm. in a 12-inch column packed with Fenske rings. The middle fraction boiling at 46° was stored under purified nitrogen in a glass bottle at 0–5°. This monomer polymerized at 70° with benzoyl peroxide at a rate in good agreement with that

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[1] Presented orally at the Division of High Polymer Chemistry, American Chemical Society, Cleveland, Ohio, April 9, 1951.

[2] S. G. Cohen, THIS JOURNAL, **67**, 17 (1945).

[3] P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

[4] K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946); *ibid.*, **68**, 1686 (1946).

[5] D. P. Brown, *ibid.*, **62**, 2657 (1940).

[6] Madison Hunt (to du Pont) U. S. Patent 2,471,959 (5/31/49).

[7] F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

[8] C. Walling, *ibid.*, **71**, 1930 (1949).

[9] C. G. Overberger, M. T. O'Shaughnessy and Harold Shalit, *ibid.*, **71**, 2661 (1949).

[10] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

observed by Schulz and Blaschke.[11] Samples removed from this supply during the period of a month after purification gave no indications of altered polymerization behavior.

Benzene.—Baker and Adamson thiophene-free, reagent-grade benzene was used.

Rate of Polymerization.—Rates of polymerization were determined by heating samples of monomer in bulk or in benzene solution with initiator for a known length of time and then isolating and weighing the polymer. Sample tubes were made of 19-mm. diameter Pyrex glass tubing. The tube was constricted at about 12 cm. from the bottom and was sealed to a Ŧ joint at the top. These tubes were washed with acid dichromate solution and then with 12 portions of distilled water. They were drained and attached by the Ŧ joint to a vacuum manifold which was evacuated to less than 10^{-3} mm. by a trapped mercury diffusion pump backed by a Cenco Hyvac pump. The polymerization tubes were flamed while the vacuum pumps were in operation, cooled and used immediately.

A sample of azobisnitrile or of a solution of azobisnitrile in benzene was weighed into a sample tube and the tube again attached to the vacuum manifold. A sample of methyl methacrylate monomer was placed in a separate reservoir attached to the manifold. All liquid samples were outgassed by the following method. The reservoir was immersed in liquid nitrogen to freeze the liquid in the bottom of its reservoir. The manifold was opened to the pumps and outgassed. The manifold was then shut off from the pumps and the liquid melted with the resultant evolution of dissolved gases. The liquid was then refrozen in liquid nitrogen and the pumping operation repeated. This outgassing step was usually repeated three times since it was shown that further repetitions did not alter polymerization rates. After the materials were thoroughly outgassed, connection was made between the monomer reservoir and the tube containing the initiator. The desired amount of monomer was distilled into the tube by cooling the tube in liquid nitrogen and maintaining the monomer reservoir at room temperature. The polymerization sample was given one final outgassing by the above-described method and then sealed at the constriction. Sample size was in the range of 12 to 18 ml. The monomer content was determined by weight increase of the polymerization tube. The sample was melted in an ice-water-bath and shaken to assure homogeneity.

The samples were placed in a water thermostat controlled to ±0.1° for a measured length of time and then cooled again in an ice-water-bath. The tubes were opened and the polymer-containing sirups washed out with benzene and poured into 500–600 ml. of methanol stirred in a Waring Blendor. The polymers were obtained in the form of a finely-divided, flocculent precipitate. The polymers were filtered into stainless steel crucibles with sintered bottoms and thoroughly washed with methanol. The samples were dried at room temperature for at least four hours and then to constant weight at 60–65°.

In agreement with other workers, it was found that the extent of polymerization up to at least 12–15% conversion is proportional to time so that the initial rate of polymerization can be calculated from only one polymerization sample.

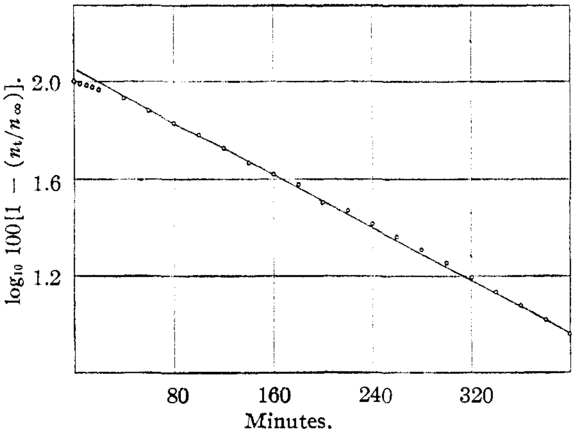

Fig. 1.—Decomposition of α,α'-azobisisobutyronitrile in xylene at 77°.

Results and Discussion

Decomposition of Azobisnitrile Initiator.—After a short induction period, the rate of evolution of nitrogen from the decomposing azobisnitrile corresponds to a first order reaction. The amount of nitrogen evolved at a given time is considered to be a measure of the extent of reaction. The rate constants were calculated from the slope of the straight line portion of a plot of $\log_{10} 100(1 - (N_t/N_\infty))$ against time, where N_t and N_∞ are the volumes of nitrogen at times t and infinity, respectively. Figure 1 is a plot of typical data for the decomposition of α,α'-azobisisobutyronitrile in xylene at 77°.

It is difficult to determine whether the apparent induction period observed in the evolution of nitrogen is a characteristic of the experimental method or of the decomposition reaction. It was observed in this study in agreement with Overberger[9] that exclusion of molecular oxygen from the decomposition reaction shortens but never entirely eliminates the induction period. If it is reasonably assumed that nitrogen is produced by two consecutive first order reactions

$$\text{A—N=N—A} \xrightarrow{k_1} \text{A—N=N}^* + \text{A}^*$$

$$\text{A—N=N}^* \xrightarrow{k_2} \text{A}^* + \text{N}_2$$

then an apparent induction period is to be expected.[12] If k_2 is large compared to k_1, the apparent induction period is approximately $1/k_2$. In this connection, it might be pointed out that no induction periods were ever observed when the azobisnitrile was used as an initiator of methyl methacrylate polymerization. The data of Table IV show that this is true for polymerization periods as short as 20 minutes at 50°. This is consistent with the hypotheses of the several workers[7,9] that the measured rate constant is for the decomposition of azobisnitrile into free radicals.

Effect of Initial Azobisnitrile Concentration on Rate of Decomposition.—α,α'-Azobisisobutyronitrile was decomposed at 77° at six initial concentrations from 0.715 to 7.007 g./100 ml. of xylene. The values of the rate constant (k_1) varied in the range 0.0055–0.0060 min.$^{-1}$ with no apparent correlation with concentration. This is in agreement with the results of Overberger.[9]

Effect of Medium on Rate of Decomposition.—The rate of decomposition of α,α'-azobisisobutyronitrile has been determined at 82° in a variety of

TABLE I

DECOMPOSITION OF α,α'-AZOBISISOBUTYRONITRILE IN VARIOUS SOLVENTS AT 82°

Solvent	k_1, min.$^{-1}$
Xylene	0.0087
n-Butyl alcohol	.0093
Acetic acid	.0090
Cyclohexanone	.0086
1-Nitrobutane	.0087
Isobutyl alcohol	.0100

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[11] G. V. Schulz and F. Blaschke, *Z. physik. Chem.*, **B51**, 75 (1942).

[12] Samuel Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y. 1940, p. 1055.

liquid media (Table I). These data show that under the conditions studied the solvent is essentially without effect on the decomposition rate in agreement with the conclusions of other workers.[7,9]

The absence of effect of either of the variables, initial concentration and solvent, upon the rate of decomposition of α,α′-azobisisobutyronitrile indicates that the reaction is strictly first order and therefore the rate of generation of free radicals may be set equal to the rate of decomposition.

Effect of Temperature on the Rate of Decomposition.—The rate of decomposition of α,α′-azobisisobutyronitrile was determined at temperatures in the range 56–88° in which the azobisnitrile is conveniently employed as a polymerization initiator. The dependence of k_1 upon temperature is given by

$$\log_{10} k_1 = -(7019/T) + 17.807 \qquad (1)$$

The values given by this equation at 77 and 50° have been used in this study. Table II shows a comparison of these values and those calculated from the data of Overberger[9] and of Lewis and Matheson.[7]

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF α,α′-AZOBISISOBUTYRONITRILE

	k_1, min.$^{-1}$		
°C.	This study	Overberger, O'Shaughnessy and Shalit[9]	Lewis and Matheson[7]
50	1.2×10^{-4}	1.1×10^{-4}	1.5×10^{-4}
77	5.7×10^{-3}	6.5×10^{-3}	6.3×10^{-3}

Rates of Decomposition of Other Aliphatic Azobisnitriles.—Table III lists the specific rate constants for decomposition of other aliphatic azobisnitriles which have been employed in this investigation.

TABLE III

RATE CONSTANTS FOR DECOMPOSITION OF ALIPHATIC AZOBISNITRILES AT 77° IN XYLENE

	Azobisnitrile	k_1, min.$^{-1}$
(I)	α,α′-Azobis-(α,γ-dimethylvaleronitrile)	0.0348
(II)	α,α′-Azobisisobutyronitrile	.0057
(III)	1,1′-Azobiscyclohexanecarbonitrile	.00032

Effect of Initiator Concentration on Rate of Polymerization of Methyl Methacrylate.—Methyl methacrylate was polymerized at 50° with concentrations of the initiator, α,α′-azobisisobutyronitrile (II) ranging from 0.47×10^{-2} to 21.06×10^{-2} mole/liter. Table IV lists the results of 12 such determinations. The constancy of $R/C^{1/2}$ in the last column demonstrates that the initial rate of polymerization is proportional to the square root of the initiator concentration. This observation is in agreement with results on this monomer with benzoyl peroxide as initiator.[11] This is interpreted in the usual manner to mean that the termination reaction is second order with respect to growing chains and initiation is first order with respect to the initiator concentration.[13]

Effect of Rate Constant for Initiator Decomposition on Rate of Polymerization.—Methyl methacrylate was polymerized at 77° with the three initiators listed in Table III. Table V gives the rate data and shows that the ratio $R/(k_1C)^{1/2}$ is essentially constant within the experimental accuracy.

TABLE IV

POLYMERIZATION OF METHYL METHACRYLATE AT 50° WITH α,α′-AZOBISISOBUTYRONITRILE AS INITIATOR

Initiator concentration, $C \times 10^2$ moles/liter	Time of polymerization, min.	Polymerization, %	Rate of polymerization, $R \times 10^3$ moles/liter/min.	$R/C^{1/2}$
0.47	135	6.53	4.66	0.068
0.62	113	6.69	5.54	.070
1.15	95	7.48	7.37	.069
1.27	80	6.77	7.92	.070
1.83	67	6.66	9.30	.069
2.56	57	6.94	11.40	.071
3.70	48	6.61	13.31	.069
5.21	40	6.67	15.60	.069
7.45	34	6.84	18.84	.069
10.77	28	6.71	22.45	.068
14.82	24	6.77	26.40	.069
21.06	20	6.75	31.61	.069

TABLE V

POLYMERIZATION OF METHYL METHACRYLATE AT 77° WITH SEVERAL ALIPHATIC AZOBISNITRILES

Azobisnitrile	k_1, min.$^{-1}$	$R/C^{1/2}$	$R/(k_1C)^{1/2}$
I	0.0348	1.81	9.71
II	.0057	0.76	10.07
III	.00032	0.16	8.93

These data show that the rate of polymerization is proportional to the square root of the rate of initiator decomposition.

When the usual assumption of a steady-state concentration of growing chains with a bimolecular termination reaction is made, the rate of polymerization is proportional to the square root of the rate of initiation, which in turn is proportional to the rate of decomposition of the individual azobisnitrile. This leads directly to the conclusion that within experimental error the same fraction of free radicals produced from decomposition of these three azobisnitriles are effective in starting polymer chains.

Effect of Monomer Concentration on Rate of Polymerization of Methyl Methacrylate.—Methyl methacrylate was polymerized in benzene solution at 77° with the monomer concentration in the range of 2.07 to 9.04 moles/liter. These data are shown in Table VI. The constancy of the quantity $R/C^{1/2}M$ in the last column of Table VI indicates that the initial rate of polymerization is proportional to the first power of the monomer concentration.

Mechanism of Polymerization.—The effect of rate of initiator decomposition and of monomer concentration on the initial rate of methyl methacrylate polymerization can be expressed in equation form as

$$R = K(k_1C)^{1/2}M \qquad (2)$$

Equation (2) is of the form usually written for polymerizations in which the rate of initiation is independent of monomer concentration.[13]

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[13] J. Abere, G. Goldfinger, H. Mark and H. Naidus, *Ann. N. Y. Acad. Sci.*, **44**, Art. **4**, 267 (1943).

Several workers[14–15] have proposed rate equations of the form

$$R = K_1C^{1/2}M[M/(M + \alpha)]^{1/2} \qquad (3)$$

to account for those cases in which the polymerization rate is dependent upon monomer concentration to a power greater than unity.

Matheson has considered $M/(M + \alpha)$ to represent the efficiency with which radicals from the initiator are used in starting polymer chains rather than being lost by side reactions. Equation (3) may be rearranged to give

$$\frac{M^2C}{R^2} = \frac{1}{K^2}\left(1 + \frac{\alpha}{M}\right) \qquad (4)$$

Thus, a plot of M^2C/R^2 against $1/M$ should yield a straight line with an intercept of $1/K^2$ and a slope of α/K^2. A least squares fit of the data of Table VI to this equation gives values of $1/K^2 = 142.9$ and $\alpha/K^2 = 11.67$ with a probable error of the latter $= \pm 17.58$. These values correspond to an $\alpha = 0.082$ and efficiencies in pure monomer and in 2.07 moles/liter of 99.1 and 96.2%, respectively. If the error is taken in the positive direction, $\alpha = 0.211$ and the efficiencies drop to 96.8 and 90.7%, respectively. Thus, these data indicate that essentially all radicals capable of initiating chains are utilized in the concentration range studied.

TABLE VI

POLYMERIZATION OF METHYL METHACRYLATE IN BENZENE SOLUTION AT 77° WITH α,α'-AZOBISISOBUTYRONITRILE

M-Monomer concentration, moles/liter	Azonitrile concentration $C \times 10^4$ moles/liter	Rate of polymerization, $R \times 10^5$ moles/liter/min.	$R/C^{1/2}$	$R/C^{1/2}M$
9.04	2.35	11.61	0.75	0.084
8.63	2.06	10.20	.71	.082
7.19	2.55	9.92	.62	.086
6.13	2.28	7.75	.51	.084
4.96	3.13	7.31	.41	.083
4.75	1.92	5.62	.41	.085
4.22	2.30	5.20	.34	.081
4.17	5.81	7.81	.32	.078
3.26	2.45	4.29	.27	.084
2.07	2.11	2.49	.17	.083

Identity of the Initiating Radical.—The above conclusion concerning the efficiency of utilization of free radicals does not include evidence as to whether both radicals (A—N=N* and A*) or only one are consumed in initiation. The rate equation for polymerization is now written in the usual form[13]

$$R = \frac{k_p}{k_t^{1/2}}(Fk_1C)^{1/2}M \qquad (5)$$

where the constant F is the number of free radicals, either 1 or 2, per initiator molecule which start chains.

The relationship between number average degree of polymerization (DP) and initiator concentration is used to obtain evidence concerning the value of F. The DP is given by the relationship[11]

$$\frac{1}{DP} = \frac{1}{DP_k} + k^1 \qquad (6)$$

where k^1 is the transfer constant for growing chains with monomer and DP_k is the degree of polymerization if there were no transfer. DP_k is equal to

$$DP_k = TR/Fk_1C \qquad (7)$$

where T is 1 or 2 depending on whether the termination reaction is disproportionation or combination of two growing chains. Substitution of (7) in (6) gives

$$\frac{1}{DP} = \frac{(F)}{(T)}\frac{(k_1C)}{(R)} + k' \qquad (8)$$

Since $C^{1/2}/R$ is a constant, $1/DP$ is a linear function of $C^{1/2}$ with a slope of $(F)(k_1C^{1/2})/(T)(R)$ and an intercept of k'.

The number average degree of polymerization for the polymers listed in Table IV has been determined from their viscosities in benzene by the methods of Baxendale, Bywater and Evans[16] using the equation $DP = 2.81 \times 10^3 [\eta]^{1.32}$. Table VII lists these determinations. The equation of the best straight line through the points is given by

$$1/DP = 0.0854 \times 10^{-2}\ C^{1/2} + 3.8 \times 10^{-5} \qquad (9)$$

TABLE VII

DEGREE OF POLYMERIZATION OF POLYMETHYL METHACRYLATES LISTED IN TABLE IV

Sample	Initiator concentration, $C \times 10^2$ moles/liter	$C^{1/2}$	$[\eta]$	DP	$1/DP \times 10^4$
1	0.47	0.068	2.83	11090	0.90
2	0.62	.079	2.82	11040	0.91
3	1.15	.107	2.05	7250	1.38
4	1.27	.113	2.29	8390	1.19
5	1.83	.135	1.81	6150	1.63
6	2.56	.160	2.32	8530	1.17
7	3.70	.192	1.51	4880	2.05
8	5.21	.228	1.28	3890	2.57
9	7.45	.273	1.05	3000	3.33
10	10.77	.328	0.96	2660	3.76
11	14.82	.385	1.00	2810	3.55
12	21.06	.459	0.97	2700	3.70

To determine the adequacy of the viscosity equation to give number average degrees of polymerization, osmotic pressure DP's were determined on selected samples. To provide samples of adequate size for osmotic pressure determinations, two samples were made up from equal weights of samples 5 and 6 and from 11 and 12. Table VIII lists the DP's of the separate components as calculated by equation (9), the averaged DP's as given by the equation

$$DP_{av} = \frac{2DP_1 \times DP_2}{DP_1 + DP_2} \qquad (10)$$

TABLE VIII

VISCOSITY AND OSMOTIC DEGREES OF POLYMERIZATION OF POLYMETHYL METHACRYLATE SAMPLES

Sample	Components from Table IV	Viscosity DP's from equation (9)	Average viscosity DP from equation (10)	Osmotic DP
1	5	6520		
	6	5729	6100	6435
2	11	2727		
	12	2326	2510	2560

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(14) D. Josefowitz and H. Mark, *Polymer Bulletin*, **1**, 140 (1945).

(15) M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(16) J. H. Baxendale, S. Bywater and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).

and the osmotic pressure *DP*'s. It is seen that the viscosity *DP*'s are in good agreement with the osmotic pressure values and thus the equation of Baxendale, Bywater and Evans is adequate.

From equations (8) and (9)

$$(F/T) \times \frac{k_1 C^{1/2}}{R} = 0.0854 \times 10^{-2} \qquad (11)$$

From Table IV, $C^{1/2}/R$ is a constant equal to 14.6 and from equation (1) $k_1 = 1.2 \times 10^{-4}$. Substitution of these values in (11) gives $F/T = (0.0854 \times 10^{-2})/14.6 \times 1.2 \times 10^{-4} = 0.49$. This can result only when F is equal to 1 and T is equal to 2.

These data indicate that, in the polymerization of methyl methacrylate, essentially only one type free radical from α,α'-azobisisobutyronitrile initiates polymer chains and the other type radical is consumed by some other reaction, probably by reaction with itself. The present experiments furnish no evidence to enable one to decide whether A* or A—N=N* is the initiating radical. However, if the postulated mechanism for azobisnitrile decomposition given above is correct, it is logical to assume that A—N=N* is the initiating radical; otherwise F would be 2 because the A* formed by the reaction

$$\text{A—N=N*} \longrightarrow \text{A*} + \text{N}_2$$

should not differ from the A* formed in the first step of the decomposition.

Since T is 2, the termination reaction is shown to be the combination of two growing chains in agreement with other investigators of methyl methacrylate polymerization.[17]

The rate of polymerization of methyl methacrylate with aliphatic azobisnitriles may now be written as

$$R = \frac{k_p}{(k_t)^{1/2}} (k_1 C)^{1/2} M \qquad (12)$$

From the data of Table IV it is seen that at 50°

$$R/C^{1/2} = \frac{kp}{(k_t)^{1/2}} k_1^{1/2} M = 0.0685 \qquad (13)$$

Substitution of the values $M = 9.36$ and $k_1 = 1.2 \times 10^{-4}$ in (13) gives

$$k_p/(k_t)^{1/2} = 0.67 \qquad (14)$$

This is somewhat higher than the value of 0.52 of Schulz and Blaschke,[11] and Schulz and Harborth[17] as calculated by Matheson, *et al.*[18] From the data of Table VI, $k_p/(k_t)^{1/2}$ is calculated as equal to 1.09 at 77°. This corresponds to an activation energy $E_p - {}^1/_2E_t = 4.0$ kcal., which is lower than the value 4.9 kcal. reported by Matheson.[18]

Acknowledgment.—The author wishes to thank Dr. M. L. Ernsberger for his interest and advice during the course of this research, Dr. P. S. Pinkney for the use of his data on the decomposition of α,α'-azobisisobutyronitrile as given in Table I, Dr. J. A. Robertson for the preparation of the azobisnitriles, and Dr. J. B. Nichols for the osmotic pressure molecular weight determinations.

[17] G. V. Schulz and G. Harborth, *Die Makromoleculare Chemie*, **1**, 106 (1947).

[18] M. S. Matheson, *et al.*, This Journal, **71**, 497 (1949).

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Contribution No. 289 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company]

Vinyl Polymerization with Radioactive Aliphatic Azobisnitrile Initiators[1]

By L. M. Arnett and J. H. Peterson

Representative vinyl monomers have been polymerized with an aliphatic azobisnitrile containing C^{14} and the radioactivity of the polymer measured to determine the initiator efficiency, *i.e.*, the ratio of radicals which initiate chains to the total radicals generated by initiator decomposition. Measured efficiencies in the presence of several vinyl monomers have been found to range from about 50% for methyl methacrylate to about 100% for acrylonitrile. Comparison of the osmotic molecular weight and the amount of combined initiator fragments in a polymethyl methacrylate indicates that termination is by combination since an initiator fragment is attached to each end of the polymer molecule.

In the preceding paper[2] certain aspects of the kinetics of polymerization of methyl methacrylate with aliphatic azobisnitrile initiators were presented and discussed. The conclusion was reached that with methyl methacrylate monomer essentially only one type of radical from the decomposition of aliphatic azobisnitrile is used in initiation and that this one radical is used with 100% efficiency. In order to confirm these kinetic results by chemical methods, polymers have been prepared with an aliphatic azobisnitrile (α,α'-azobisisobutyronitrile) synthesized to contain the radioactive isotope C^{14} in the nitrile group. From the known rate of decomposition of this azobisnitrile and the radioactive content of the polymer, the efficiency of free radical usage has been directly calculated. The study has also been extended to vinyl monomers other than methyl methacrylate.

Experimental Methods

Preparation of Azobisnitrile.—The α,α'-azobisisobutyronitrile was synthesized from sodium cyanide containing the isotope C^{14} by the method of Thiele and Heuser.[3] The sodium cyanide used in this investigation was supplied by Tracerlab, Inc., on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

Preparation of Polymers.—Polymerization samples in all instances were made up by the methods described in detail in the previous paper.[2] Briefly, the polymerization sample was placed in a glass capsule of approximately 20-ml. capacity, the contents were thoroughly degassed, and the capsule sealed under a pressure of less than 10^{-3} mm. The sample was heated in a water thermostat controlled to ±0.1° for a given length of time and then cooled in an ice-

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[1] Presented orally at the Division of High Polymer Chemistry of American Chemical Society at Cleveland, Ohio, April 9, 1951.

[2] L. M. Arnett, This Journal, **74**, 2027 (1952).

[3] J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).