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]

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[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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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).

bath. The capsule was opened, and the contents were washed into a suitable precipitant stirred vigorously in a laboratory mixer. The polymer was collected in a stainless steel crucible with sintered bottom and dried to constant weight at 60°. The last traces of uncombined initiator and initiator fragments were removed by repeated solution and precipitation of the polymer. Proper choice of solvent and precipitant permitted this removal to be accomplished in three to four repetitions as judged by the constancy of the radioactive counts on the polymer. Specific systems are discussed in detail below.

Polymethyl Methacrylate.—This polymer was purified by solution in benzene and precipitation in methanol.

The extent to which possible loss of low molecular weight fractions in the precipitation procedure may affect the results has been considered in the following fashion. Denbigh's equation[4] for molecular weight distribution has been used since it is derived for low conversion of vinyl polymers with termination by combination. The weight fraction W_r of molecules containing r monomer units is given by

$$W_r = ar(r - 1)/b^{r+1}$$

where

$$a = 4/(DP - 2)^3$$

and

$$b = DP/(DP - 2)$$

DP being the number average degree of polymerization. If it is assumed that all fractions with $r < 300$ are removed from a polyethyl methacrylate with a $DP = 3000$, then integration shows that 0.12% of the weight of the polymer is lost or that 1.76% of all molecules are lost. This is less than the experimental error, and the possible loss is without effect on the experimental results.

Polystyrene.—The polymer was originally precipitated in methanol and then redissolved in chloroform and precipitated in methanol.

Polyacrylonitrile.—This polymer was precipitated in methanol, redissolved in dimethylformamide, and precipitated in methanol.

Polyvinyl Acetate.—This polymer was originally precipitated in a 25/75 by volume methanol/water mixture, redissolved in acetone, and precipitated in n-hexane.

Polyvinyl Chloride.—This polymer was precipitated in methanol, redissolved in cyclohexanone and precipitated in methanol.

Radioactivity Assay.—Activity measurements in all cases were made directly on thin polymer films supported on 18-mm. diameter circular glass discs. The films were deposited directly on the glass discs by evaporation of dilute solutions of the polymers to give deposits ranging in thickness from about 4 to 10 mg. per square cm. In order to obtain good adhesion of the polymer to the glass, the discs were given a finely roughened surface by grinding with a water paste of Number 600 Carborundum powder. All counts were made with an end-window type counter having a window thickness of 3.1 mg. per square cm.

Self-absorption correction curves were obtained for several different polymers deposited as described above. Samples of inactive polymers containing varying known amounts of the tagged aliphatic azobisnitrile were used as standards which were counted at the same time as the unknowns. Several series of standards were used covering the activity range of the unknowns. Thus direct comparison between knowns and unknowns was made at comparable levels of activity so as to eliminate coincidence and counter performance corrections.

The following data for the first polystyrene sample in Table I give an indication of the accuracy obtained in the radioactivity assay. The values are tabulated as per cent. by weight of initiator in the polymer. Each value listed is the average of at least 4 counts on a different counting sample compared to a standard of equal thickness.

	First precipitation	Second precipitation	Third precipitation
	0.129	0.111	0.111
	.129	.114	.109
	.134	.108	.108
	.129	.110	.107
	.135	.114	.110
Average	0.131	0.111	0.109

The assay would have been 4.07% if all the initiator had been retained in the polymer. Thus, it is seen that the extraction of uncombined initiator is essentially complete in the first precipitation. It is seen from the above data that the probable error of the mean of five determinations is of the order of 1%. Thus, the accuracy of the calculated efficiencies is determined not by the error in the radioactivity assays but by uncertainties in the extraction of uncombined initiator and in the values of the decomposition constant for initiator. It is seen from Table II of the previous paper[2] that the error in the decomposition constant may easily be as great as 10%. For example, if the decomposition constant of Overberger, O'Shaughnessy and Shalit is used to calculate the efficiency in the methyl methacrylate sample polymerized at 77°, the efficiency is 0.55 rather than 0.63 as given in Table I.

Results and Discussion

The experimental results on all monomers are given in Table I. The results on polymethyl methacrylate are discussed in detail to illustrate the calculation methods.

TABLE I

POLYMERIZATION OF VINYL MONOMERS AT 50° WITH α,α'-AZOBISISOBUTYRONITRILE CONTAINING C^{14}

Monomer and concentration	Original azo-nitrile, g.	Decomposed azo-nitrile, g × 10^4	Combined azo-nitrile, g × 10^4	Efficiency
Methyl methacrylate				
Bulk	0.2096	13.6	7.07	0.52
52% in benzene	.1997	19.2	11.3	.59
Bulk, 77°	.0127	12.8	8.05	.63
Styrene				
Bulk	0.0475	20.0	13.2	0.66
Bulk	.0395	5.59	4.14	.74
Bulk, 66°	.0146	11.2	8.51	.76
Bulk, 66°	.0148	7.77	6.29	.81
Bulk, 66°	.0147	3.87	3.17	.82
Acrylonitrile				
75% in ethanol	0.00606	0.947	0.966	1.02
75% in ethanol	.00604	.713	.717	1.02
75% in ethanol	.00607	.577	.606	1.05
Vinyl acetate				
Bulk	0.0455	1.41	1.17	0.83
54% in ethanol	.0592	11.1	7.52	.68
54% in ethanol	.0592	7.09	4.89	.69
54% in ethanol	.0575	3.88	2.64	.68
Vinyl chloride				
67% in acetone	0.0103	2.92	2.25	0.77
52% in acetone	.0102	1.71	1.20	.70

Polymethyl Methacrylate.—A polymerization sample consisting of 15.45 g. of monomer and 0.2096 g. of azobisnitrile was heated at 50° for 55 minutes. The yield of polymer was 1.6826 g. This sample analyzed for 0.042% or 7.07 × 10^{-4} g. of azobisnitrile. The amount of azobisnitrile decomposed under these conditions is given by the equation

$$C_0 - C = C_0(1 - e^{-kt}) \quad (1)$$

where C_0 and C are the initial and final concentrations of azobisnitrile, t is time in minutes, and k is the first order rate constant for azobisnitrile decomposition given by[2]

$$\log_{10} k\ (\text{min.}^{-1}) = (-7019/T) + 17.806 \quad (2)$$

For $T = 323$, $k = 1.2 \times 10^{-4}$ min.$^{-1}$. Substitu-

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(4) K. G. Denbigh, *Trans. Faraday Soc.*, **43**, 648 (1947).

tion of these values in equation (1) gives $C_0 - C = 13.7 \times 10^{-4}$ g. The efficiency is then calculated as $7.07 \times 10^{-4}/13.7 \times 10^{-4} = 0.52$.

The kinetic study[2] showed that the initiation reaction with this azobisnitrile is practically independent of the monomer concentration. This observation can be true only if essentially 100% of the available initiating radicals start chains. Thus, the efficiency of 52% obtained in this investigation substantiates the previous conclusion that only one type radical from the azobisnitrile is utilized and that this type is highly efficient.

Two additional polymethyl methacrylate samples were prepared under the conditions listed in Table I. These experiments show that the efficiency is essentially independent of monomer concentration and temperature.

The number average molecular weight of the polymer prepared in bulk at 50° as calculated from osmotic pressure measurements was found to be 390,000. Table II shows the comparison of this value with that calculated from radioactivity analysis, assuming one initiator fragment for each end of the polymer chain, and with the value expected from initiator concentration as given by the equation

$$1/MW = 8.54 \times 10^{-6} C_0^{1/2} + 3.8 \times 10^{-7}$$

obtained in the previous kinetic study.[2]

TABLE II

MOLECULAR WEIGHT OF POLYMETHYL METHACRYLATE PREPARED WITH RADIOACTIVE AZOBISNITRILE

Basis of calculation	Molecular weight
Radioactive content	390,500
Osmotic pressure	390,000
Initiator concentration	363,000

These molecular weight values are in excellent agreement and substantiate the conclusion that the termination reaction in methyl methacrylate polymerization is combination of growing chains.

Polystyrene.—Styrene was polymerized in bulk at 50° and at 60° with the radioactive azobisnitrile initiator. The data show that the initiator efficiency is appreciably greater with this monomer than with methyl methacrylate. Since the fraction utilized is greater than one half, at least some of each type radical A* and A—N═N* is capable of initiating polymerization. The results are in essential agreement with those of other investigators who have studied styrene polymerization. Tobolsky[5] reports that his kinetic data on the polymerization of styrene at 60° with α,α'-azobisisobutyronitrile indicate that the initiator efficiency would be about 80% if it is assumed that termination is by combination. Inasmuch as the initiator efficiency measured in this study is 80%, the assumption of termination by combination is substantiated. Cohen[6] reports that the initiator efficiencies in styrene polymerized at 110 and 100° with 1,1′-azobis-1-phenylpropane are, respectively, 77 and 80%.

Polyacrylonitrile.—Three samples of polyacrylonitrile were prepared at 50° in absolute ethanol solution of monomer. The initiator efficiency with this monomer was essentially 100%.

Polyvinyl Acetate.—Samples of polyvinyl acetate were prepared at 50° both in bulk and in ethanol solution. The initiator efficiency with this monomer ranged from 68 to 83%. It is noted that when the monomer concentration was reduced, the efficiency dropped as would be expected when the efficiency is less than 100% in bulk monomer.

Polyvinyl Chloride.—Two samples of polyvinyl chloride were prepared at 50° from monomer solution in acetone. As with vinyl acetate, a decrease in monomer concentration lowered the efficiency.

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(5) A. V. Tobolsky, Oral Presentation at 118th National Meeting of American Chemical Society, Chicago, Ill., September, 1950.

(6) S. G. Cohen, Oral Presentation at 118th National Meeting of American Chemical Society, Chicago, Ill., September, 1950.