2. Azonitriles as Initiators for Polymerization of Methyl Methacrylate.

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The polymerization of methyl methacrylate, both homogeneous and in toluene and ethyl acetate, has been initiated with six azonitriles at 60°. The kinetic order with respect to initiator concentration is 0·5, and to monomer concentration 1·1 and 1·0 in toluene and ethyl acetate respectively. A mean value of 8·32 is obtained for δ (60°) from bulk-polymerization experiments with all six azonitriles.

The rates of initiation of all the azonitriles are about the same except that of azo*cyclo*hexane-1 : 1'-dicarbonitrile which is slightly lower. Efficiencies are all about 82% in bulk and decrease on dilution to about 50%.

The chain-transfer coefficients for monomer (C_M), initiator (C_I), and solvents (C_S) were determined. C_M is $1·0 \times 10^{-5}$ whereas C_I is very close to zero in all cases. The chain-transfer coefficients for two solvents were also determined by using four of these catalysts and the results agree well with the literature values.

AZONITRILES decompose more cleanly, without complicating side effects,[1] than benzoyl peroxides previously used[2] to polymerize methyl methacrylate. We now report polymerizations initiated with six azonitriles at 60°.

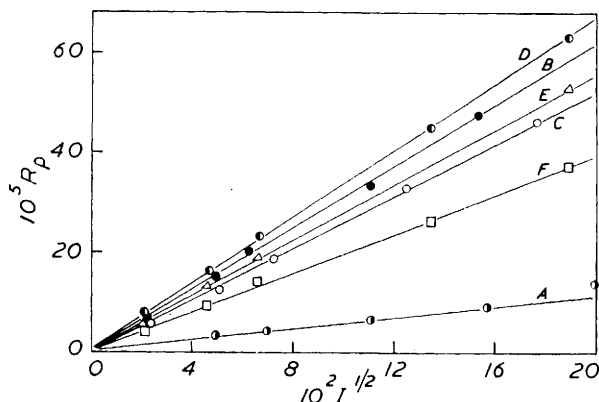*Dependence of the Rate of Polymerization, R_p, on Catalyst Concentration.*—Table 1 and

[1] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686; Bartlett and Nozaki, *ibid.*, 1947, **69**, 2299; Cass, *ibid.*, 1946, **68**, 1976.
[2] (*a*) Saha, Nandi, and Palit; *J.*, 1956, **85**, 427; (*b*) Palit, *Proc. Nat. Acad. Sci.*, 1954, **23**, *A*, 11.

the Figure show that in all cases R_p is proportional to $I^{\frac{1}{2}}$ in agreement with the usual equation

$$R_p = K I^{\frac{1}{2}} M^n \qquad \ldots \ldots \ldots \ldots \quad (1)$$

where I and M are the initiator and monomer concentrations respectively, and K is a constant. The straight lines pass through the origin, showing that there is practically no inhibition period and very little superimposed thermal reaction, and termination is

Dependence of rate of polymerization R_p on the initiator concentration. For catalysts, see Table 1.

TABLE 1. *Polymerization of methyl methacrylate in bulk (9·29 moles l.$^{-1}$) in presence of catalysts at 60°.*

$10^3(I/M)$	$10^5 R_p$ (moles l.$^{-1}$ sec.$^{-1}$)	$10^5/\bar{P}$		$10^3(I/M)$	$10^5 R_p$ (moles l.$^{-1}$ sec.$^{-1}$)	$10^5/\bar{P}$	
Azo*cyclo*hexane-1 : 1'-dicarbonitrile (A)				αα'-Azo-α-methylvaleronitrile (D)			
4·30	13·5	11·86	$10^4 R_p/I^{\frac{1}{2}} = 7·0$	3·90	62·5	52·02	$10^3 R_p/I^{\frac{1}{2}} = 3·33$
2·65	9·0	8·17	$\delta = 8·32$	1·95	44·5	38·08	$\delta = 8·32$
1·33	6·6	5·69	$10^7 R_i/I = 7·86$	0·48	23·0	21·04	$10^6 R_i/I = 17·79$
0·53	4·2	4·33	$C_I = \sim 0$	0·24	16·2	15·15	$C_I = \sim 0$
0·27	3·2	3·65	$10^4 C_M = 1·0$	0·05	7·5	6·00	$10^5 C_M = 1·0$
αα'-Azo*iso*butyronitrile (B)				αα'-Azo-αββ-trimethylbutyronitrile (E)			
2·62	47·3	38·62	$10^3 R_p/I^{\frac{1}{2}} = 3·0$	3·90	52·5	44·10	$10^3 R_p/I^{\frac{1}{2}} = 2·8$
1·31	33·2	27·98	$\delta = 8·32$	0·48	19·0	17·00	$\delta = 8·32$
0·52	20·4	17·00	$10^6 R_i/I = 14·44$	0·24	13·3	12·57	$10^6 R_i/I = 12·57$
0·26	14·8	12·96	$C_I = \sim 0$	0·05	6·0	4·89	$C_I = \sim 0$
0·05	6·5	6·13	$10^5 C_M = 1·0$				$10^5 C_M = 1·0$
αα'-Azo-α-methylbutyronitrile (C)				αα'-Azo-α-ethylbutyronitrile (F)			
3·35	46·0	37·56	$10^3 R_p/I^{\frac{1}{2}} = 2·5$	3·90	37·1	31·39	$10^3 R_p/I^{\frac{1}{2}} = 2·0$
1·68	32·9	27·37	$\delta = 8·32$	1·95	26·2	22·82	$\delta = 8·32$
0·56	18·9	16·50	$10^6 R_i/I = 10·02$	0·48	13·8	11·99	$10^6 R_i/I = 6·42$
0·28	12·5	9·50	$C_I = \sim 0$	0·24	9·2	7·48	$C_I = \sim 0$
0·06	6·1	5·46	$10^5 C_M = 1·0$	0·05	4·6	4·26	$10^5 C_M = 1·0$

probably by a bimolecular free-radical interaction. This behaviour was observed by Overberger, Fram, and Alfrey [3] in the polymerization of styrene by αα'-azo*iso*butyronitrile and azo*cyclo*hexane-1 : 1'-dicarbonitrile and by Arnett [4] in αα'-azo*iso*butyronitrile-initiated polymerization of methyl methacrylate. However, Thomas and Pellon [5a] found R_p to be proportional to $I^{0·75}$ in the benzoyl peroxide-initiated bulk polymerization of

[3] Overberger, Fram, and Alfrey, *J. Polymer Sci.*, 1951, **6**, 539.
[4] Arnett, *J. Amer. Chem. Soc.*, 1952, **74**, 2027.
[5] (a) Thomas and Pellon, *J. Polymer Sci.*, 1954, **13**, 329; (b) Andreconix and Smets, *ibid.*, 1953, **10**, 525; (c) Horikx and Hermans, *ibid.*, 1953, **11**, 325.

acrylonitrile. This unusual behaviour might be due to the separation of phase in acrylonitrile polymerization. With substituted benzoyl peroxides [2] and hydrogen peroxide [6f] we found R_p to be proportional to $I^{0.5}$.

Dependence of R_p on Monomer Concentration.—Since the expected kinetic order of 3/2 with respect to monomer concentration is often not obtained [3, 4, 5a, 5b, 6f] we determined the kinetic order with respect to monomer with different azonitriles in solutions of ethyl acetate and toluene. Eqn. (1) can be reduced to the form

$$R_p = K(I/M)^{\frac{1}{2}} M^{(n + \frac{1}{2})} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where n is the order of the reaction with respect to the monomer. By plotting $\log R_p$ against $\log M$ at constant I/M, n was found (Table 2). In toluene n is 1·1 and 1·0 with

TABLE 2. *Dependence of R_p on monomer concentration at* $60°$.

Catalyst	Solvent					
B	Toluene	$\{$	$10^4 I/M$	13·12	6·56	3·28	0·66
			n	1·1	1·2	1·1	1·1
A	Toluene	$\{$	$10^4 I/M$	44·00	22·00	11·00	
			n	1·0	1·0	1·05	
B	Ethyl acetate	$\{$	$10^4 I/M$	13·12	6·56	3·28	0·66
			n	1·1	1·1	1·1	1·1

αα-azo*iso*butyronitrile and azo*cyclo*hexane-1 : 1′-dicarbonitrile respectively. In ethyl acetate with αα-azo*iso*butyronitrile the order is 1·0. Arnett [4] found n to be unity in benzene in the polymerization of methyl methacrylate by αα′-azo*iso*butyronitrile whereas Overberger, Fram, and Alfrey [3] report 1·2 for styrene in toluene with αα′-azo*iso*butyronitrile and azo*cyclo*hexane-1 : 1′-dicarbonitrile as catalysts.

Value of $\delta (= k_t^{\frac{1}{2}}/k_p)$.—For methyl methacrylate many different values of δ have been obtained.[2, 6] The general equation [2b, 6d] for the average degree of polymerization is

$$1/\overline{P} = \sum C_X \cdot X/M = C_M + C_I(I/M) + C_S(S/M) + R_p(\delta^2/M^2) \qquad . \qquad . \qquad (3)$$

With all azonitriles (see later) C_I is consistently near zero. For bulk conditions, eqn. (3) becomes

$$1/\overline{P} = C_M + (\delta^2/M^2)R_p \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

Hence a plot of $1/\overline{P}$ against R_p should be a straight line from whose slope δ can be evaluated. For the six azonitriles we found a mean value of 8·32 (Table 1) for δ for methyl methacrylate at 60° [cf. 8·43 (Nandi and Palit [6f]), 8·3 (obtained from the absolute values of k_p and k_t (Matheson *et al.*[6c]), and 8·3 (Baysal and Tobolsky [6d])]. We conclude that the correct value of δ lies between 8·3 and 8·4.

Rates of Initiation.—At the steady state during polymerization [6d, 7]

$$R_i = 2 k_t(M^*)^2 = 2(k_t/k_p^2)(R_p^2/M^2) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

$$R_i/I = 2(k_t/k_p^2)(R_p^2/I)(1/M^2) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

$$= (2 \delta^2/M^2)(R_p^2/I) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

Since R_p^2/I is constant, R_i/I should be constant for a particular monomer concentration. R_p^2/I has been taken from Table 1 and values of R_i/I are listed in Table 3, which shows that the specific initiation rates for all the azonitriles are of the same order of magnitude. Thus

[6] (a) Bonsal, Valentine, and Melville, *Trans. Faraday Soc.*, 1952, **48**, 765; (b) Bamford and Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 310; (c) Matheson, Auer, Bevilacqua, and Hart, *J. Amer. Chem. Soc.*, 1949, **71**, 497; (d) Baysal and Tobolsky, *J. Polymer Sci.*, 1952, **8**, 529; (e) Melville and Burnett, *ibid.*, 1954, **13**, 417; (f) Nandi and Palit, *ibid.*, 1955, **17**, 65.
[7] Tobolsky and Baysal, *J. Polymer Sci.*, 1953, **11**, 471.

the reactivities of the radicals formed are all about the same. The slightly lower rate of initiation observed with azo*cyclo*hexane-1 : 1′-dicarbonitrile may be due to the cyclic structure of the radical reducing the number of effective collisions bringing about initiation.

TABLE 3. *Rates of initiation and efficiency of catalysts in solutions at 60°.*

Solvent	Catalyst	Monomer concn. (moles l.$^{-1}$)	$10^6 R_i/I$	f	Solvent	Catalyst	Monomer concn. (moles l.$^{-1}$)	$10^6 R_i/I$	f
Nil	B	9·290	14·4	0·83	Ethyl acetate	B	4·645	10·5	0·60
							2·790	8·5	0·49
Nil	C	9·290	10·0	0·82			1·858	6·6	0·38
							0·929	6·8	0·39
Nil	D	9·290	17·8	0·87	Toluene	A	4·645	0·4	—
Toluene	B	4·675	11·5	0·60			2·790	0·4	—
		2·790	8·5	0·49			1·858	0·4	—
		1·858	6·8	0·39			0·929	0·4	—
		0·929	5·3	0·30	Toluene	C	4·645	6·9	0·56
							2·790	6·0	0·50
							1·858	6·4	0·53
							0·929	5·8	0·48

The value of $1·44 \times 10^{-5}$ for R_i/I in $\alpha\alpha'$-azo*iso*butyronitrile agrees with the value of $1·48 \times 10^{-5}$ obtained by Baysal and Tobolsky [6d] for the same catalyst and conditions.

Catalyst Efficiency (f).—The azonitriles undergo a first-order decomposition, presumably into a radical pair, at very nearly the same rate [4, 8, 9, 10] in all solvents:

$$- \, dI/dt = k_d I \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

where k_d is the specific rate constant for spontaneous homolytic cleavage. Hence the rate at which uniradical catalyst fragments are being produced by the catalyst is $2k_d I$ and the catalyst efficiency is properly defined as

$$f = R_i/(2 \, k_d I) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

The factor f represents the fraction of the free radicals, produced by the decomposition of azonitriles, initiating polymerization. The values of k_d at 60° for different catalysts were calculated from those reported by Overberger, Shaugnessy, and Shalit [8] at 80·2 and 69·8°. The values of R_i/I at 60° just obtained were used to determine f (Table 3).

The value of 0·83 for f for $\alpha\alpha'$-azo*iso*butyronitrile agrees well with Johnson and Tobolsky's value [11] (0·83), whereas Arnett and Peterson [12] obtained 0·63 at 77°.

With $\alpha\alpha'$-azo-α-methylbutyronitrile and $\alpha\alpha'$-azo-α-methylvaleronitrile f is 0·82 and 0·87 respectively, showing that the efficiency is nearly constant for all three azonitriles and substitution has little effect on it.

Using a tracer technique, Bevington [13] has concluded that in styrene polymerization the efficiency of azonitriles is independent of the monomer concentration unless the latter is too low. Our work with methyl methacrylate also shows the same constant trend in not too dilute solutions, and f increases only at very high concentration. With $\alpha\alpha'$-azo-α-methylbutyronitrile in toluene, f is constant over the whole range employed but with other azonitriles the values are scattered. At a particular monomer concentration, however, the efficiency is practically equal in both solvents, implying that the solvent has little effect on the efficiency.

[8] Overberger, O'Shaughnessy, and Shalit, *J. Amer. Chem. Soc.*, 1949, **71**, 2661.
[9] Lewis and Matheson, *J. Amer. Chem. Soc.*, 1949, **71**, 747.
[10] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.
[11] Johnson and Tobolsky, *ibid.*, 1952, **74**, 938.
[12] Arnett and Peterson, *ibid.*, p. 2031.
[13] Bevington, *Trans. Faraday Soc.*, 1955, **51**, 1392.

Though with $\alpha\alpha'$-azo-α-methylbutyronitrile the efficiency in concentrations of monomer ranging from 50% to 10% remains almost constant (0·50) it is definitely less than that for bulk (0·82).

Chain-transfer Coefficients.—Transfer with initiator (C_I). The general equation for the average degree of polymerization [eqn. (3)] for bulk can be written as

$$(1/\overline{P}) - R_p(\delta^2/M^2) = C_M + C_I(I/M) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The plot of the left-hand side against I/M will be linear and C_I can be obtained from the slope, as was done with peroxides.[2a, 14] For our azonitriles the plot was linear but parallel to the abscissa, showing that no transfer occurs. This supports the conclusion that azonitriles do not undergo induced decomposition, the cleavage of the catalyst being unimolecular.

Transfer with monomer (C_M). As C_I is practically zero, a plot of $1/\overline{P}$ against R_p [eqn. (4)] gives C_M from the intercept, as in the determination of δ.

Table 1 gives our results for C_M, being in all cases $1·0 \times 10^{-5}$ at 60°, confirming that obtained by Saha, Nandi, and Palit [2] with benzoyl peroxides, by Nandi and Palit [6f] from hydrogen peroxide-catalysed polymerization of methyl methacrylate, and by Baysal and Tobolsky [6d] with benzoyl peroxide and $\alpha\alpha'$-azo*iso*butyronitrile, although O'Brien and Gornick [15] obtained a lower value of $0·7 \times 10^{-5}$.

Transfer with solvent (C_S). The suitability of using azonitriles for determining solvent-transfer constants has been examined in systems of few azonitriles with ethyl acetate and toluene. We saw [14,16] that Mayo's method of determining C_S from the plot of $1/\overline{P}$ against S/M is valid where R_p is proportional to M^2. For toluene and ethyl acetate, R_p is proportional to $M^{1·1}$ and M respectively and, as expected, this plot gave values of C_S increasing with the catalyst concentration, as the first column in Table 4 shows.

TABLE 4. *Determination of* C_S *in the polymerization of methyl methacrylate at* 60° *(each value the mean from four experiments).*

$10^5 C_S$ from slope of		$10^5 C_S$ from slope of	
$1/\overline{P}$ vs. S/M	$(1/\overline{P}) - R_p(\delta^2/M^2)$ vs. S/M	$1/\overline{P}$ vs. S/M	$(1/\overline{P}) - R_p(\delta^2/M^2)$ vs. S/M
Solvent, toluene; catalyst A.		Solvent, toluene; catalyst B.	
$10^5 C_S$ (uncatalysed, refs. 2a, 14, 16) = 2·0.		5·20	2·70
3·50	1·75	4·80	3·02
3·00	1·90	3·90	3·10
3·00	1·90	3·10	2·30
2·60	2·05		Average = 2·70
	Average = 1·90		
		Solvent, ethyl acetate; catalyst B.	
Solvent, toluene; catalyst D.		$10^5 C_S$ (uncatalysed, refs. 2a, 14, 16) = 1·30.	
6·60	2·00	3·10	1·25
4·20	2·00	2·80	2·00
3·50	1·90	2·00	1·25
2·00	1·40		Average = 1·50
	Average = 1·83		

Our modified method of plotting $(1/\overline{P}) - (\delta^2/M^2)R_p$ against S/M, however, gives fairly correct values for C_S as shown in the second column of Table 4, the average value being comparable with those in the literature. Hence these catalysts can be successful in the evaluation of C_S in catalysed systems.

EXPERIMENTAL

Monomer and Solvents.—Quinol-stabilized methyl methacrylate (National Chemical Laboratory) was purified by repeated washing with 5% aqueous sodium hydroxide followed by

[14] Nandi and Palit, Proceedings of International Symposium on Macromolecules, Milan, 1954, published in *Ricerca sci.*, 1954.
[15] O'Brien and Gornick, *J. Amer. Chem. Soc.*, 1955, **77**, 4757.
[16] Palit, Nandi, and Saha, *J. Polymer Sci.*, 1954, **14**, 295.

water.   After being dried (CaCl$_2$) it was fractionally distilled twice, and the fraction of b. p. 100—100·5° collected.   The monomer was 98—99% pure (bromine addition method [17]).

" AnalaR " and L. R. samples were purified by the usual methods, dried, and fractionally distilled before use.

Preparation of Azonitriles.—Azonitriles were prepared by Overberger, O'Shaughnessy, and Shalit's method [3] and repeatedly crystallized from absolute ethyl alcohol.

Polymerizations.—The procedure adopted was as previously described.[2, 6f, 16, 18]   To exclude oxygen we have taken general precautions, *e.g.*, passing nitrogen through the monomer, degassing the reaction mixtures by vacuum and nitrogen-flushing, etc.

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[17] Kauffmann and Hartweg, *Ber.*, 1937, **70**, 2554.
[18] Basu, Sen, and Palit, *Proc. Roy. Soc.*, 1950, *A*, **202**, 485.