3. *The Effect of Temperature on Azonitriles as Initiators in the Polymerization of Styrene.*

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Kinetic constants of the polymerization of styrene were studied from 30° to 117°. The rate of polymerization, R_p, is proportional to $I^{0.5}$. The rates of initiation for all the azonitriles are about the same; the corresponding energies of activation and frequency factors have been compared with literature values. The efficiency factor is near 0·6 and is little affected by change of initiator or temperature.

The values of δ, C_M and C_I have been evaluated with six azonitriles and equations are given: $C_I \simeq 0$. The chain-transfer coefficient for toluene has also been determined with one azonitrile; results agree with those in the literature.

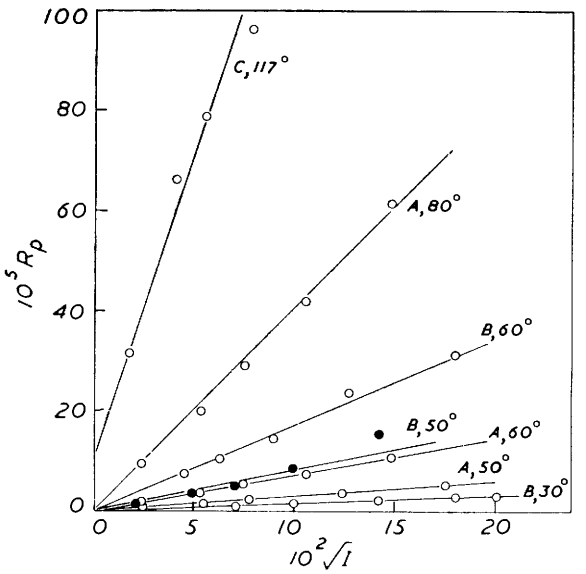
SIX azonitriles, similar to those used in the preceding paper [1] to polymerize methyl methacrylate, have been applied to styrene, with special emphasis on the effect of temperature. The symbols, equations, and methods are those of the preceding paper.[1]

Effect of Initiator Concentration on the Rate of Polymerization.—Fig. 1 shows plots of R_p versus $I^{\frac{1}{2}}$ for the bulk polymerization of styrene over the range 30—117°. They are linear, as with methyl methacrylate [1,2] and styrene with other initiators and may indicate that the termination reaction is of second order.

Evaluation of δ.—We have evaluated δ from the slope of the plot of $1/\bar{P}$ against R_p (Fig. 2) as previously.[1] Results are in Table 1. The temperature variation of δ and hence the corresponding energy of activation $E_p - \frac{1}{2}E_t$ were calculated. Table 2 and Fig. 3 contain our results and values for δ from the literature.[3-9] Our value for $E_p - \frac{1}{2}E_t$ agrees well with most of the literature values, which are about 5 kcal. mole^{-1}, except for one very high value of 19·34 kcal. mole^{-1} (Baysal and Tobolsky [7]). Our value of 28·6 for δ at 60° agrees fairly well with 29·39 by Baysal and Tobolsky [7] and 25·0 by Bonsal *et al.*[6] but Baysal and Tobolsky's [7] value of 122·0 for δ at 47·8° seems to be high. In Fig. 3 the straight-line

[1] Saha, Nandi, and Palit, *J.*, 1956, **85**, 427; and preceding paper.
[2] Nandi and Palit, *J. Polymer Sci.*, 1955, **17**, 65.
[3] Melville and Valentine, *Trans. Faraday Soc.*, 1950, **46**, 210; *Proc. Roy. Soc.*, 1950, *A*, **200**, 337.
[4] Bamford and Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192**, 309.
[5] Burnett, *Trans. Faraday Soc.*, 1950, **46**, 1772.
[6] Bonsal, Valentine, and Melville, *ibid.*, 1952, **48**, 763.
[7] Baysal and Tobolsky, *J. Polymer Sci.*, 1952, **8**, 529.
[8] Matheson, Auer, Bevilacqua, and Hart, *J. Amer. Chem. Soc.*, 1951, **73**, 1700.
[9] Tobolsky and Baysal, *J. Polymer Sci.*, 1953, **11**, 471.

FIG. 1. *Dependence of R_p on catalyst concentration (for catalysts, see Table 1).*



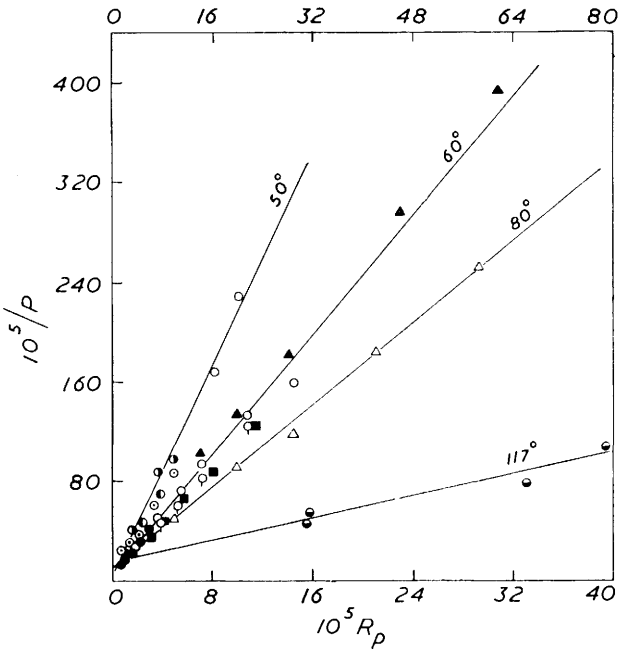


FIG. 2. *Determination of δ at different temperatures (for catalysts, see Table 1).*

○ *A*, 60°; △ *A*, 80°; ⊙ *A*, 50°; ◑ *B*, 50°; ▲ *B*, 60°; ● *C*, 60°; ◒ *C*, 117°; ⚲ *D*, 60°; ■ *E*, 60°; ◐ *F*, 50°.

TABLE 1. *Polymerization of styrene in bulk (8·63 moles l.$^{-1}$) in presence of catalysts at different temperatures.*

Temp.	$10^4 I/M$	$10^5/R_p$ (moles l.$^{-1}$ sec.$^{-1}$)	$10^5/\overline{P}$	
	αα′-Azo*iso*butyronitrile (*A*)			
50°	35·29	5·0	86·77	$10^8 R_p^2/I = 8·99$
	17·64	3·4	61·20	$10^6 R_t/I = 2·99$
	7·06	2·1	36·79	$f = 0·60$
	3·53	1·5	31·05	$\delta = 35·15$
	0·71	0·7	15·79	$10^5 C_M = 4·0$
				$C_I = \sim 0$
60	25·64	10·7	133·00	$10^7 R_p^2/I = 4·90$
	12·82	7·2	94·30	$10^5 R_t/I = 1·14$
	6·41	5·6	71·77	$f = 0·66$
	3·21	3·8	48·50	$\delta = 28·51$
	0·64	1·9	28·50	$10^5 C_M = 6·0$
				$C_I = \sim 0$
80	25·64	61·4	252·30	$10^5 R_p^2/I = 1·60$
	12·82	41·9	185·10	$10^4 R_t/I = 6·40$
	6·41	29·0	116·00	$f = 0·41$
	3·21	19·9	90·63	$\delta = 17·29$
	0·64	9·5	47·32	$10^5 C_M = 10·0$
				$C_I = \sim 0$
	αα′-Azo-αγ-dimethylvaleronitrile (*B*)			
30	46·72	2·9	90·63	$10^8 R_p^2/I = 1·77$
	37·32	2·8	73·45	$10^6 R_t/I = 1·06$
	23·36	2·1	65·60	$\delta = 47·26$
	11·68	1·5	50·06	$10^5 C_M = 2·0$
	5·84	0·9	32·30	$C_I = \sim 0$
50	23·36	10·2	228·60	$10^7 R_p^2/I = 6·4$
	11·68	8·2	168·60	$10^5 R_t/I = 2·56$
	5·84	4·9	98·17	$\delta = 38·59$
	2·92	3·6	87·90	$10^5 C_M = 4·0$
	0·58	1·7	40·68	$C_I = \sim 0$
60	37·32	31·0	393·20	$10^7 R_p^2/I = 29·38$
	18·66	23·1	294·80	$10^5 R_t/I = 7·46$
	9·33	14·3	182·20	$\delta = 30·18$
	4·67	10·3	133·40	$10^5 C_M = 6·0$
	2·33	7·2	102·00	$C_I = \sim 0$
	Azo*cyclo*hexane-1 : 1′-dicarbonitrile (*C*)			
60	38·01	2·9	40·43	$10^7 R_p^2/I = 0·24$
	14·00	2·1	29·99	$10^7 R_t/I = 5·35$
	7·00	1·6	21·85	$\delta = 28·63$
	3·50	1·5	16·52	$10^5 C_M = 6·0$
	1·75	0·8	13·06	$C_I = \sim 0$
117	7·00	96·4	130·30	$10^4 R_p^2/I = 1·0$
	3·50	78·9	107·40	$10^4 R_t/I = 2·4$
	1·75	66·2	77·00	$\delta = 9·45$
	0·35	31·6	53·14	$10^5 C_M = 14·0$
	0·18	31·2	45·76	$C_I = \sim 0$
	αα′-Azo-α-methylvaleronitrile (*D*)			
60	56·06	14·6	159·10	$10^7 R_p^2/I = 4·13$
	28·03	11·0	125·00	$10^5 R_t/I = 1·05$
	14·01	7·3	81·66	$f = 0·51$
	7·01	5·3	59·43	$\delta = 28·58$
	3·50	3·9	47·32	$10^5 C_M = 6·0$
				$C_I = \sim 0$
	αα′-Azo-α-methylbutyronitrile (*E*)			
60	48·20	11·3	124·20	$10^7 R_p^2/I = 3·03$
	24·10	8·2	84·14	$10^6 R_t/I = 6·05$
	12·05	5·7	67·54	$f = 0·50$
	6·03	4·2	48·93	$\delta = 27·29$
	3·01	3·1	37·96	$10^5 C_M = 6·0$
				$C_I = \sim 0$
	αα′-Azo-α-methyl*iso*valeronitrile (*F*)			
50	26·04	3·7	69·58	$10^8 R_p^2/I = 6·05$
	13·02	2·6	46·03	$10^5 R_t/I = 1·99$
	5·20	1·6	28·64	$\delta = 35·16$
	2·60	1·2	20·89	$10^5 C_M = 4·10$
	0·52	0·7	14·09	$C_I = \sim 0$

TABLE 2. *Value of C_M and δ for styrene at different temperatures.*

	δ		$E_p - \frac{1}{2}E_t$ (kcal. mole^{-1})		$10^5 C_M$		$E_{tr,M} - E_p$ (kcal. mole^{-1})	
	Present authors	Lit.	Present authors	Lit.	Present authors	Lit.	Present authors	Lit.
0°	—	308·60[8]	4·47	4·87[3]	—	1·1[4]	5·3	7·9[4]
15·0	—	80·32[5]		19·34[7]	—	1·9[5]		7·9[5]
25·0	—	71·61[3]		6·58[8]	—	3·7[4]		
		71·30[3]		5·00[3]		3·2[5]		
		110·80[8]		5·10[4]		1·1[6]		
		61·80[5]		5·35[5]				
30·0	48·93	62·43[3]			2·0	3·2[6]		
		91·37[8]						
47·8	—	122·00[7]			—	—		
50·0	35·15	—			4·0	—		
60·0	28·62	25·00[6]			6·0	6·0[14]		
		36·40[4]						
		29·39[7]						
		34·09[8]						
67·8	—	21·83[7]			—	—		
80·0	19·36	—			10·0	—		
117·0	9·45	—			14·0	—		

plot of log $(1/\delta)$ against $1/T$ fits Baysal and Tobolsky's values at 60° and 67·8° well, but not their value for 47·8°. This may account for their high value of $E_p - \frac{1}{2}E_t$.

We conclude that δ can best be represented by

$$\delta = 9{\cdot}4 \times 10^{-3} \exp(4{\cdot}4/\boldsymbol{R}T)$$

Rate of Initiation (R_i/I).—As in the preceding paper we determined R_i/I from

$$R_i/I = 2\delta^2 R_p^2/IM^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

by using values of R_p^2/I and δ from Table 1. In the present paper R_i/I was determined for the six azonitriles within temperatures ranging from 30° to 117° and results are shown

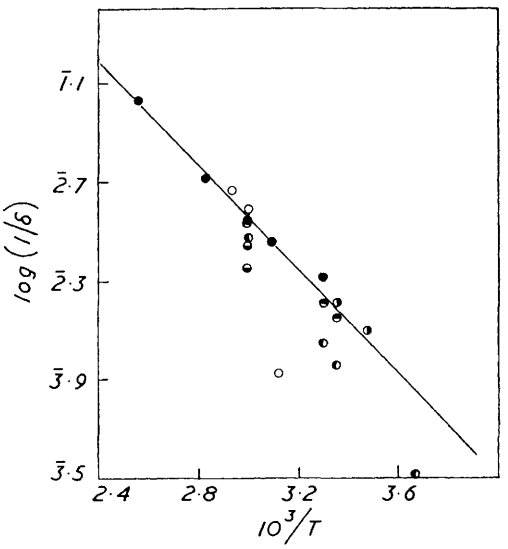


FIG. 3. *Effect of temperature on* δ.

● Present authors, ◓ Melville and Valentine,[3] ◑ Burnett,[5] ◒ Bamford and Dewar,[4] ⚲ Bonsal, Valentine, and Melville,[6] ○ Baysal and Tobolsky,[7] ◐ Matheson *et al.*[8]

therein. For αα′-azo*iso*butyronitrile, azo*cyclo*hexane-1 : 1′-dicarbonitrile, and αα′-azo-αγ-dimethylvaleronitrile R_i/I can be represented by $9{\cdot}2 \times 10^{13} \exp(-28{\cdot}5/\boldsymbol{R}T)$, $6{\cdot}82 \times 10^{11} \exp(-27{\cdot}6/\boldsymbol{R}T)$, and $8{\cdot}89 \times 10^{14} \exp(-28{\cdot}9/\boldsymbol{R}T)$ respectively. These results can be compared with $R_i/I = 6{\cdot}3 \times 10^{13} \exp(-28{\cdot}48/\boldsymbol{R}T)$ recalculated from Tobolsky and Baysal's [9] compiled data by the least-square method. They also calculated the E and A factors for several peroxides and find that E varies from 25·5 to 31·5 kcal./mole and A from 10^{11} to 10^{16}.

Efficiency, f.—The efficiency of the azonitriles was calculated from

$$f = (R_i/I)/(2kd)$$

kd for benzene as reported by Overberger *et al.*[10] being used. Table 1 shows that f lies between 0·51 and 0·66, which demonstrates the approximate constancy of the efficiency of different azonitriles. This further confirms our previous conclusion [1] that substitution has little effect on efficiency. Johnson and Tobolsky,[11] in polymerization of styrene initiated by azo*cyclo*hexane-1 : 1′-dicarbonitrile, found f to be 0·64 at 80·3°. The efficiency of azo*iso*butyronitrile has been calculated by various workers using different procedures and values vary from 0·81 to 0·66, within which range our value lies. The efficiency is almost independent of temperature (Table 1).

Monomer Transfer (C_M).—Using the same method as for δ, we determined C_M, as represented in Fig. 2 and Table 1.

[10] Overberger, Fram, and Alfrey, *J. Polymer Sci.*, 1951, **6**, 539.
[11] Johnson and Tobolsky, *J. Amer. Chem. Soc.*, 1952, **74**, 938.

Our value at 60° agrees well with those of Baysal and Tobolsky [7] and Mayo *et al.*[14] For lower temperatures Bamford and Dewar [4] and Burnett [5] give values slightly higher than ours. The temperature variation of C_M and hence the corresponding energy of activation $E_{tr,M} - E_p$ is 5·30 kcal. mole^{-1}; Bamford and Dewar [4] and Burnett [5] report

TABLE 3. *Determination of C_S for toluene in polymerization of styrene at 60° initiated by αα'-azoisobutyronitrile (uncatalysed value 2·00).*

No. of expts.	$1/\overline{P}$ *vs.* S/M	10^5C_S from slope of $\{(1/\overline{P}) - (\delta^2/M^2)R_p\}$ *vs.* S/M
3	9·0	2·2
3	7·5	2·1
3	4·3	2·1
4	2·0	2·1
		Average = 2·1

7·9 but their values were obtained at two temperatures only. The most probable value of C_M, *i.e.* the ratio $k_{tr,M}/k_p$, is given by $C_M = 16{\cdot}4 \times 10^{-2} \exp(-5{\cdot}30/\boldsymbol{R}T)$.

Transfer with Initiator (C_I).—The slope of $[(1/\overline{P}) - (\delta^2/M^2)R_p]$ against I/M, *i.e.*, C_I, is near zero. As with methyl methacrylate,[1] no induced decomposition was observed.

Transfer with Solvent (C_S).—With αα'-azo*iso*butyronitrile as initiator the chain-transfer constant for toluene in styrene at 60° has been verified with an initiator range of $7{\cdot}0 \times 10^{-4}$ to $14{\cdot}0 \times 10^{-3}$ moles l.$^{-1}$. In all cases C_S obtained from the slope of $1/\overline{P}$ *versus* S/M plots was higher than that obtained from the results for uncatalysed polymerization, but by using our modified method [15] of plotting $\{(1/\overline{P}) - R_p(\delta^2/M^2)\}$ against S/M fair agreement was found between values obtained from catalysed and uncatalysed experiments. Some typical results briefly summarised in Table 3 illustrate the point.

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[12] Arnett and Peterson, *ibid.*, p. 2031.
[13] Hammond, Sen, and Boozer, *ibid.*, 1955, **77**, 3244.
[14] Mayo, Gregg, and Matheson, *ibid.*, 1951, **73**, 1671.
[15] Palit, Nandi, and Saha, *J. Polymer Sci.*, 1954, **14**, 295.