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Rates of Initiation and Chain Transfer Constants in the Polymerization of Methyl Acrylate II

BY

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ABSTRACT

A study of the bulk polymerization of methyl acrylate at 60°C to 80°C with 2,2′ Azobisisobutyronitrile, (Azo), 1,1′ Azobiscyclohexanecarbonitrile (HAzo), Hydrogen peroxide (H_2O_2), Benzoyl peroxide (Bz_2O_2), and Methyl ethyl ketone peroxide (MEKP) in 20 per cent ethyl acetate as a diluent, has been made. Rates of (a) initiation of polymerization, (b) chain transfer constants for the monomer and the catalyst have been evaluated. Catalyst efficiencies have been calculated. Certain aspects polymerization of methyl acrylate have been compared with styrene and methyl methacrylate.

In our previous publications (V. Mahadevan and M. Santappa 1955), the general nature of polymerization of methyl acrylate at 55°C to 75°C, using various initiators in 50 per cent ethyl acetate as a diluent and a non-transfering solvent was reported. The catalysts tried were Benzoyl peroxide, Methyl ethyl ketone peroxide, Ditertiary butyl peroxide and Tertiary butyl hydro peroxide. A small thermal rate and auto acceleration were also noticed under the experimental conditions. In this paper, results of polymerization with 20 per cent ethyl acetate in which thermal rate and auto acceleration are completely suppressed, are reported. Azo, HAzo, H_2O_2, Bz_2O_2 and MEKP have been used as initiators. Rates of initiation of polymerization, rates of transfer constants for the monomer and catalysts with the growing polymethylacrylate radical chain and the activation energies for these rates have been evaluated. The dependence of monomer concentration on rates has been studied and correlated to catalyst efficiencies.

The theoretical scheme relevant to this work has already been given in the first of the series of the papers (V. Mahadevan and M. Santappa 1955). For the sake of understanding of this paper, we reproduce below the three important relationships. The total overall rate R_{pt} is given by

$$R_{pt} = R_{pth} + R_p \sim \; R_p = [k_p (k_{df})^{1/2} / (k_{tc} + k_{td})^{1/2}] M [Cat]^{1/2} = KM[Cat]^{1/2} \quad \ldots (1)$$

where R_{pth} is thermal rate and R_p represents catalysed rate. k_p, k_{tc}, k_{td}, k_d represent the specific rate constants for propogation, termination by combination, termination by disproportionation and specific rate constant for spontaneous decomposition of the catalyst [Cat] respectively; f is catalyst efficiency and M represents monomer concentration.

The second relationship connecting reciprocal degree of polymerization $1/P_n$ and various rates of polymer formation by transfer with monomer C_M and rate of polymer formation by transfer with catalyst C_{cat} is given by

$$1/Pn = (ktc + 2\,ktd)\;Rp/Kp^2M^2 + CM + C_{cat}[(Cat]/(M)] \quad \ldots (2\text{-a})$$

$$1/P_n = A'Rp/M^2 + CM + C_{cat}[cat)/(M)] \quad \ldots (2\text{-b})$$

$$1/P_n = A\,Rp + CM + C_{cat}[(cat)/(M)] \quad \ldots (2\text{-c})$$

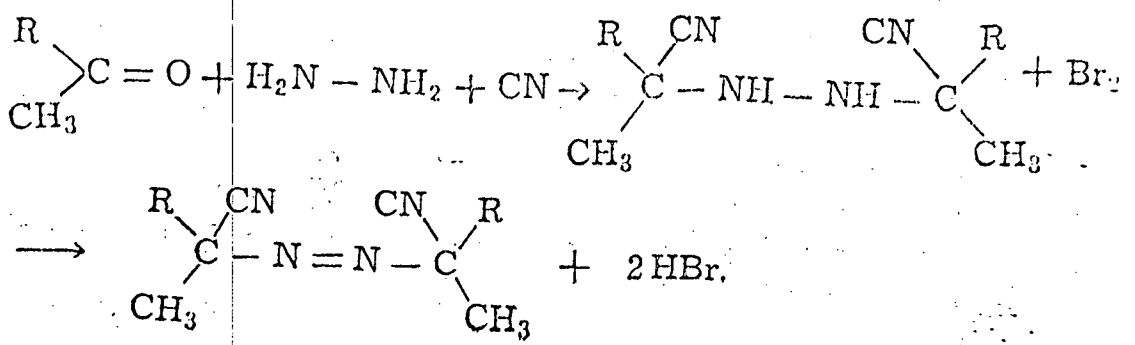
It is easy to deduce the rate of initiation of polymerization R_i as

$$Ri\;(1+x)/[cat] = R_i/[cat] = 2kdf\,(1+x) = 2K^2A'$$

$$\text{where } x = k_{td}/(k_{td}+k_{tc}). \quad \ldots (3)$$

From the two simple measurements of overall rates of polymerization and degrees of polymerization at these overall rates, rates of initiation, rate of transfer with monomer and rate of transfer with catalyst have been evaluated. With the known values of k_d an approximate value of catalyst efficiency and therefore the relative importance of the type of termination reaction has been arrived at.

Experimental: The method of purification and estimation of the monomer and the catalysts Bz_2O_2 and MEKP were the same as reported previously (V. Mahadevan and M. Santappa 1955). The catalysts Azo and HAzo have been prepared by the method of Thiele and Heuser (1896) as adapted by C. G. Overberger etal (1949). The general scheme of the reaction is as follows:



where R stands for any alkyl or aromatic group except in the case of cyclohexanone where the whole group composed of R and CH_3 is replaced by the cyclohexylring. The appropriate quantities of the ketone, hydrazine sulphate and sodium cyanide in water were shaken for two days and the substituted hydrazine compound obtained, was purified. This was then oxidised with a solution of bromine in absolute ethyl alcohol (4 gms in 100 cc). The hydrazine compound was dissolved in ethanol saturated with pure dry HCl. The bromine solution was added till absorption of bromine became very slow. The mixture was then poured into a large volume of ice water and the precipitated Azo-compound filtered and purified by repeated recrystallisation.

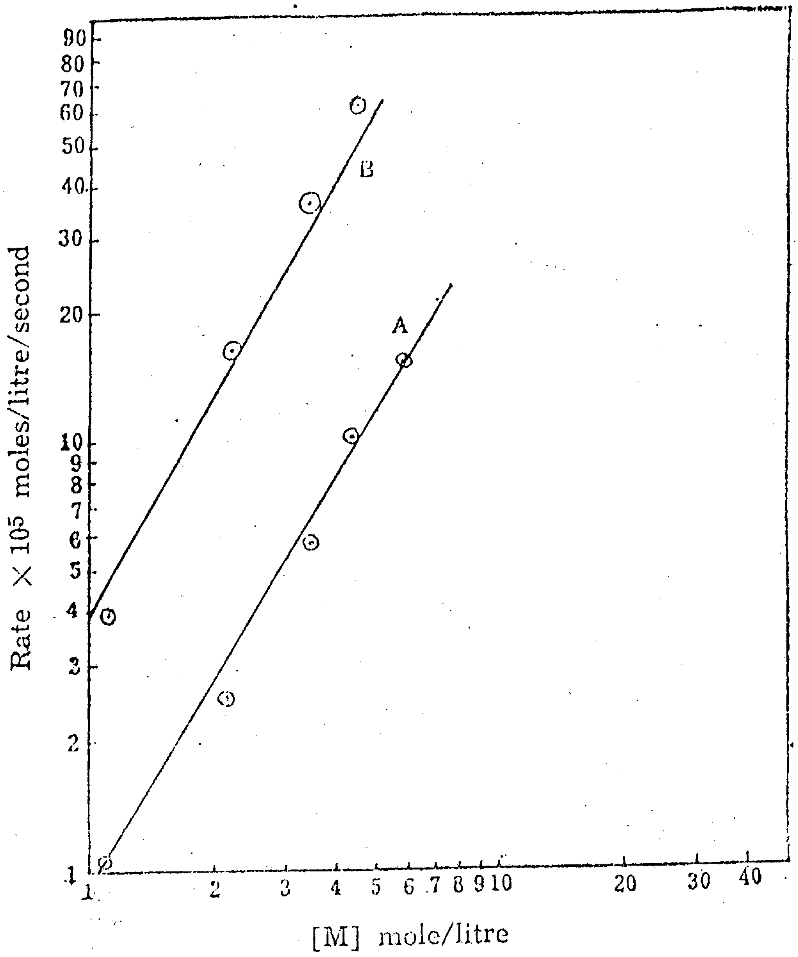


Fig. I. Plot A gives the relationship between log R_p and log M in the polymerization of methyl acrylate with Bz_2O_2 as initiator at 60°C in ethyl acetate solution. The values are plotted on the Logarithmic Scale. Plot B gives the same relationship with Azo as initiator at 70°C in ethyl acetate.

The standard solution of H_2O_2 in ethyl acetate was prepared by shaking B.D.H. H_2O_2 (~ 60 vols.) in water, with pure AR ethyl acetate, extracting the ethyl acetate layer, drying it over anhydrous sodium sulphate, and estimating the H_2O_2 content by iodometry. This solution was then diluted to the required strength.

The details about the method of carrying out the polymerization experiments and evaluating the overall rates and degrees of polymerization have been dealt with in the previous publication (V. Mahadevan and M. Santappa 1955).

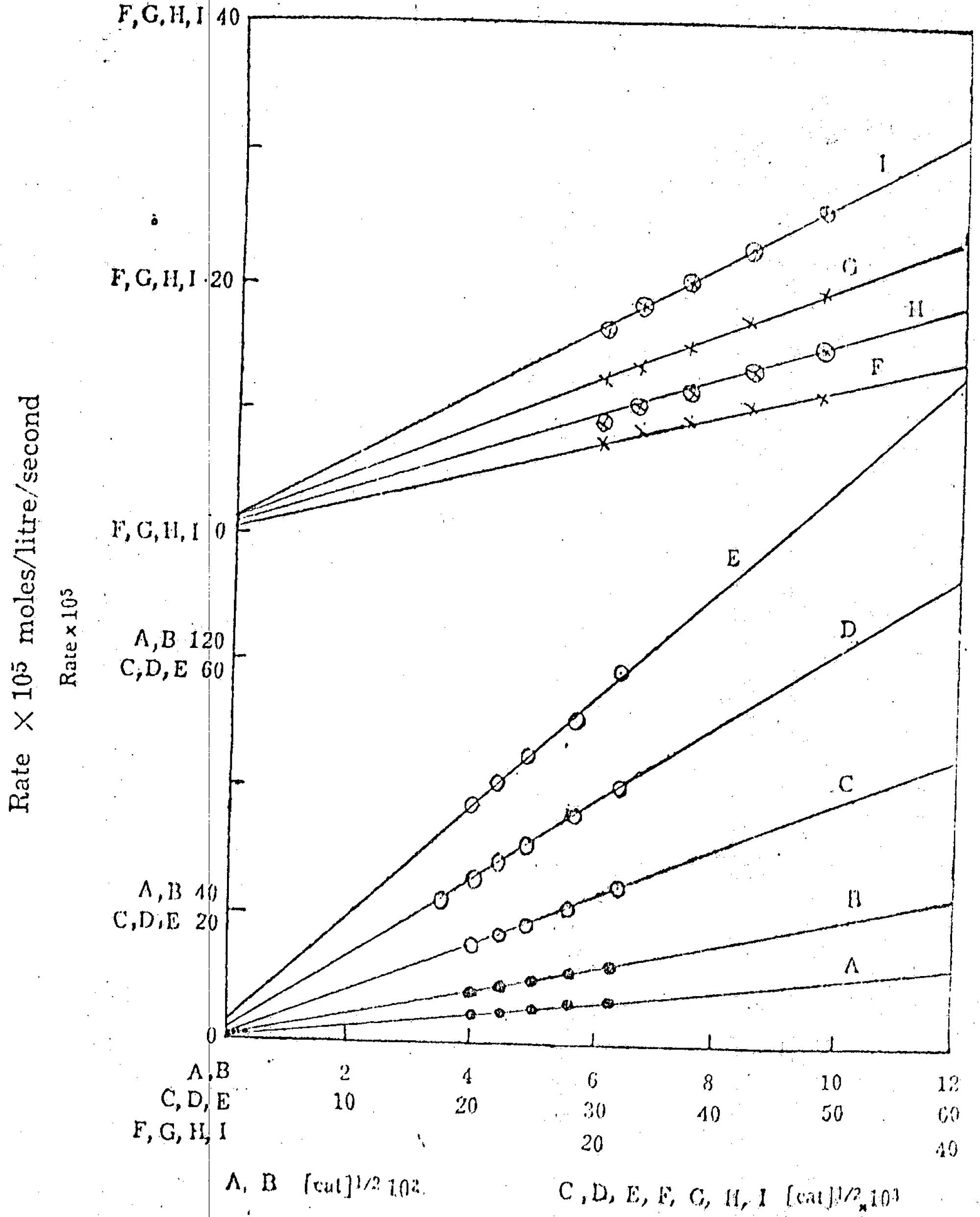


FIG. II. Plots A & B give the relationship between R_p and (Cat)½ in the polymerization of methyl acrylate with HAzo as initiator at 70°C and 80°C respectively, with a 20 per cent solution of the monomer in ethyl acetate. Plots C, D & E give the same relationship with Azo as initiator at 60°C, 70°C and 80°C respectively, with a 20 per cent solution of the monomer in ethyl acetate.

Plots F & G give the same relationship with H_2O_2 as initiator at 70°C and 80°C respectively at the same monomer concentration.

Plots H & I refer to Bz_2O_2 as initiator at 60°C and 70°C respectively at the same monomer concentration.

Table 1

Rates of Initiation and Chain Transfer Constants in the Polymerization of Methyl Acrylate

Catalyst	Temp.	K	A′	Ri′/(Cat)	C cat	
Azo	60°C	$3\cdot182 \times 10^{-3}$	$2\cdot48$	$5\cdot203 \times 10^{-5}$	$8\cdot065 \times 10^{-3}$	$12\cdot75 \times 10^{-5}$
	70°C	$6\cdot046 \times 10^{-3}$	$1\cdot94$	$14\cdot18 \times 10^{-5}$	$1\cdot724 \times 10^{-2}$	15×10^{-5}
	80°C	$11\cdot35 \times 10^{-3}$	$1\cdot21$	$31\cdot26 \times 10^{-5}$	$3\cdot125 \times 10^{-2}$	$17\cdot5 \times 10^{-5}$
		$3\cdot981 \times 10^{8}$ exp (-17100/RT)	$2\cdot692 \times 10^{-6}$ exp (9154/RT)	$6\cdot918 \times 10^{12}$ exp (-26200/RT)	$8\cdot511 \times 10^{9}$ exp (-18330/RT)	$\cdot1256$ exp (-4583/RT)
HAzo	70°C	$9\cdot09 \times 10^{-4}$	$1\cdot936$	$3\cdot2 \times 10^{-6}$	4×10^{-3}	22×10^{-5}
	80°C	$1\cdot728 \times 10^{-3}$	$1\cdot2$	$7\cdot16 \times 10^{-6}$	8×10^{-3}	24×10^{-5}
		$4\cdot365 \times 10^{8}$ exp (-18310/RT)	$2\cdot864 \times 10^{-6}$ exp (9154/RT)	$1\cdot096 \times 10^{12}$ exp (-27500/RT)	30548×10^{8} exp (-17190/RT)	$\cdot182$ exp (-4583/RT)
H_2O_2	70°C	$1\cdot363 \times 10^{-3}$	$10\cdot75$	$3\cdot998 \times 10^{-5}$	$6\cdot579 \times 10^{-3}$	$8\cdot3 \times 10^{-5}$
	80°C	$2\cdot728 \times 10^{-3}$	$7\cdot259$	$10\cdot8 \times 10^{-5}$	$1\cdot921 \times 10^{-2}$	$10\cdot75 \times 10^{-5}$
		$6\cdot457 \times 10^{8}$ exp (-18310/RT)	$1\cdot585 \times 10^{-6}$ exp (9154/RT)	$1\cdot479 \times 10^{11}$ exp (-24400/RT)	$2\cdot188 \times 10^{15}$ exp (-27500/RT)	$1\cdot991$ exp (-6875/RT)

Table 2

Comparison of values of rates of initiation and other constants at 5·5 molar and 2·2 molar Concentration of Methyl Acrylate

(a) K, (b) A′, (c) Ri/(Cat), (d) C cat, (e) C

Catalyst	Temp		5·5 molar			2·2 molar
Bz_2O_2	60°C	(a)	$1{\cdot}963 \times 10^{-3}$		(a)	$2{\cdot}182 \times 10^{-3}$
		(b)	$2{\cdot}52$		(b)	$2{\cdot}419$
		(c)	$1{\cdot}943 \times 10^{-5}$		(c)	$2{\cdot}308 \times 10^{-5}$
		(d)	$2{\cdot}46 \times 10^{-2}$		(d)	$2\ 941 \times 10^{-2}$
		(e)	$3{\cdot}25 \times 10^{-5}$		(e)	$3{\cdot}5 \times 10^{-5}$
	70°C	(a)	$3{\cdot}472 \times 10^{-3}$		(a)	$3{\cdot}637 \times 10^{-3}$
		(b)	$1{\cdot}97$		(b)	$1{\cdot}936$
		(c)	$4{\cdot}8 \times 10^{-5}$		(c)	$5{\cdot}12 \times 10^{-5}$
		(d)	5×10^{-2}		(d)	$5{\cdot}5 \times 10^{-2}$
		(e)	$4{\cdot}05 \times 10^{-5}$		(e)	5×10^{-5}
MEKP	65°C	(a)	$1{\cdot}325 \times 10^{-3}$	Ref. 8.	(a)	$1{\cdot}386 \times 10^{-3}$
		(b)	$9{\cdot}456$		(b)	$9{\cdot}679$
		(c)	$3{\cdot}322 \times 10^{-5}$		(c)	$3{\cdot}715 \times 10^{-5}$
		(d)	5×10^{-2}		(d)	2×10^{-2}
		(e)	$1{\cdot}1 \times 10^{-5}$		(e)	$6{\cdot}8 \times 10^{-5}$
	75°C	(a)	$2{\cdot}909 \times 10^{-3}$		(a)	$2{\cdot}728 \times 10^{-3}$
		(b)	$6{\cdot}554$		(b)	$6{\cdot}437$
		(c)	$11{\cdot}19 \times 10^{-5}$		(c)	$9{\cdot}579 \times 10^{-5}$
		(d)	$11\ 3 \times 10^{-2}$		(d)	$3{\cdot}3 \times 10^{-2}$
		(e)	$2{\cdot}5 \times 10^{-5}$		(e)	$11{\cdot}8 \times 10^{-5}$

Results and Discussions:

Polymerization conditions with 20 per cent methyl acrylate monomer in ethyl acetate solution were ideal inasmuch as the thermal rate and the phase of autoacceleration were totally absent. With Bz_2O_2 as well as Azo as catalysts, it was found (Fig. I) that the rate was dependent on 3/2 powers of monomer concentration. This indicated that the catalyst efficiencies in these cases were dependent upon monomer concentration.

Polymerization experiments were conducted with the catalysts HAzo, Azo, H_2O_2, Bz_2O_2 and MEKP at temperatures ranging from 60°C to 80°C. Plots of Rate vs. $(Cat)^{1/2}$ (Fig. II) with all these catalysts were linear and passed through the origin which indicated the absence of any superimposing or disturbing reactions. The slope of each plot gave KM (Eqn 1) from which K values were evaluated. These values at various temperatures with the various catalysts with their exponential forms appear in Tables 1 and 2. An activation energy of $\sim$ 18 K cals for K would give a value of $\sim$ 26 K cals for rate of initiation with all these catalysts. The value for the frequency factor was $\sim 10^8$. If Matheson's frequency factors (Matheson etal 1951) for k_p ($\sim 10^8$) and k_t ($\sim 10^{10}$) are taken into account, a frequency factor of $\sim 10^{10}$ would be obtained for initiation.

Reciprocal degrees of polymerization versus overall rates (Fig. III A to F) were plotted after conducting polymerization of methyl acrylate with all the abovementioned catalysts. From the equations (2—a to 2—c) in the theoretical section it is obvious that the intercepts on the ordinates of these plots represent the rates of transfer of the polymethylacrylate radical chain with a monomer molecule (CM, Method 1). It was found that such a transfer did take place. It could be concluded that the specific rate of transfer with monomer was approximately 10^{-5} times as efficient as for propogation. Transfer with the monomer was highest when HAzo was the catalyst and lowest when TBHP was used (Table 3). From the slopes of the plots in Fig. III, A' values were evaluated. These values with their exponential forms are to be found in Tables 1 and 2.

Using Matheson's values for $k_p = 2000$ and $2\,k_t = \cdot 85 \times 10^7$ in the polymerization of methyl acrylate, a value of $2\cdot125$ for $A = \dfrac{2k_t}{k_p{}^2}$ at 60°C could be obtained. Our values with Azo, and

Table 3

CM Values as obtained from the intercepts of the I/Pn vs. Rp Plot as well as [(1/Pn) — ARp] vs. [Cat]/[M] Plot

Catalyst	Temp.	Intercept of 1/Pn vs. Rp Plot		Intercept of [(1/Pn) — ARp] vs. Cat/M Plot	
Bz_2O_2	55°C	$2\cdot8 \times 10^{-5}$	Ref. 8 & 11	$2\cdot75 \times 10^{-5}$	Ref. 8 & 11
	60°C	$3\cdot25 \times 10^{-5}$		$3\cdot2 \times 10^{-5}$	
	65°C	4×10^{-5}		$3\cdot7 \times 10^{-5}$	
	70°C	$4\cdot2 \times 10^{-5}$		$4\cdot05 \times 10^{-5}$	
MEKP	65°C	$1\cdot1 \times 10^{-5}$	Ref. 8	1×10^{-5}	Ref. 8
	70°C	2×10^{-5}		$1\cdot8 \times 10^{-5}$	
	75°C	$2\cdot7 \times 10^{-5}$		$2\cdot5 \times 10^{-5}$	
Azo	60°C	13×10^{-5}		$12\cdot75 \times 10^{-5}$	
	70°C	16×10^{-5}		15×10^{-5}	
	80°C	19×10^{-5}		$17\cdot5 \times 10^{-5}$	
DTBP	65°C	$1\ 25 \times 10^{-5}$	Ref. 8	1×10^{-5}	Ref. 8
	70°C	$1\cdot8 \times 10^{-5}$		$1\cdot6 \times 10^{-5}$	
	75°C	$2\cdot75 \times 10^{-5}$		$2\cdot24 \times 10^{-5}$	
TBHP	60°C	$\cdot5 \times 10^{-5}$	Ref. 8	$\cdot36 \times 10^{-5}$	Ref. 8
	70°C	$1\cdot25 \times 10^{-5}$		$\cdot72 \times 10^{-5}$	
HAzo	70°C	$22\ 1 \times 10^{-5}$		22×10^{-5}	
	80°C	24×10^{-5}		24×10^{-5}	
H_2O_2	70°C	$8\cdot5 \times 10^{-5}$		$8\cdot3 \times 10^{-5}$	
	80°C	$11\cdot5 \times 10^{-5}$		$10\cdot75 \times 10^{-5}$	

Bz_2O_2 at this temperature were 2·48 and 2·41 respectively. A value of ~ 1·9 for A′ at 70°C was also observed with Azo, HAzo and Bz_2O_2. Wide variation in the values of A′ with H_2O_2 and other catalysts (V. Mahadevan and M. Santappa 1955) remain inexplicable at present. An activation energy of ~ 9 K cals for A′ was obtained and it was quite normal. Fig. IV (Plots A, B, C and D) represents variation of A′ with temperature when Azo, Bz_2O_2, DTBP and MEKP were used as catalysts.

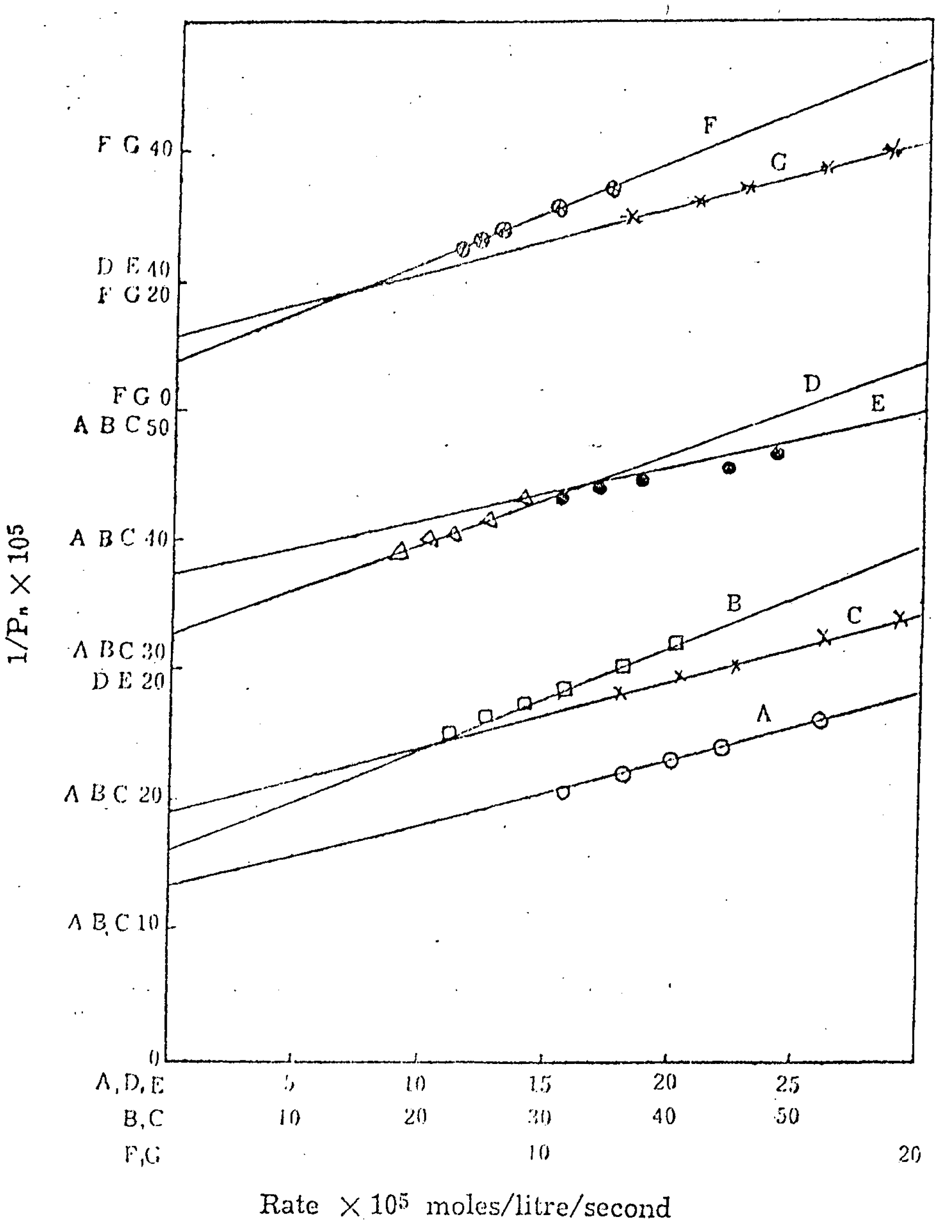


FIG. III. Plots A, B & C give the relationship $1/P_n$ vs. R_p with Azo as initiator at 60°C, 70°C and 80°C (2·2 molar monomer).

Plots D & E refer to the same relationship with HAzo at 70°C and 80°C respectively at the same monomer concentration.

Plots F & G refer to H_2O_2 at 70°C and 80°C respectively.

Making use of the slopes in the Figures II and III, it was possible to evaluate rates of initiation of polymerization with all the catalysts under consideration at 60°C to 80°C (Eqn. 3). The $R'_i/[Cat]$ values at 70°C with Azo, HAzo, Bz_2O_2 and H_2O_2 were $14{\cdot}18 \times 10^{-5}$, $3{\cdot}2 \times 10^{-6}$, $5{\cdot}12 \times 10^{-5}$ and $3{\cdot}99 \times 10^{-5}$ respectively which indicated that Azo and Bz_2O_2 were the most efficient initiators. Further, it was found that our values for rate of initiation of methyl acrylate with Azo were much higher than the values with methyl methacrylate and styrene, the values being $5{\cdot}023 \times 10^{-5}$, $1{\cdot}48 \times 10^{-5}$ and $1{\cdot}77 \times 10^{-5}$ respectively at 60°C (Tobolsky and coworkers 1952 and 1953). This was in agreement with the finding by Arnett and Peterson (1952) that the rate of initiation depended upon the monomer used and not the same as had been claimed by Tobolsky and Baysal (1953). Variation of rate of initiation with temperature with the catalysts DTBP, MEKP, Bz_2O_2 and Azo are given in Fig. V. Values of initiation at various temperatures with the various catalysts with their exponential forms are given in Tables 1 and 2.

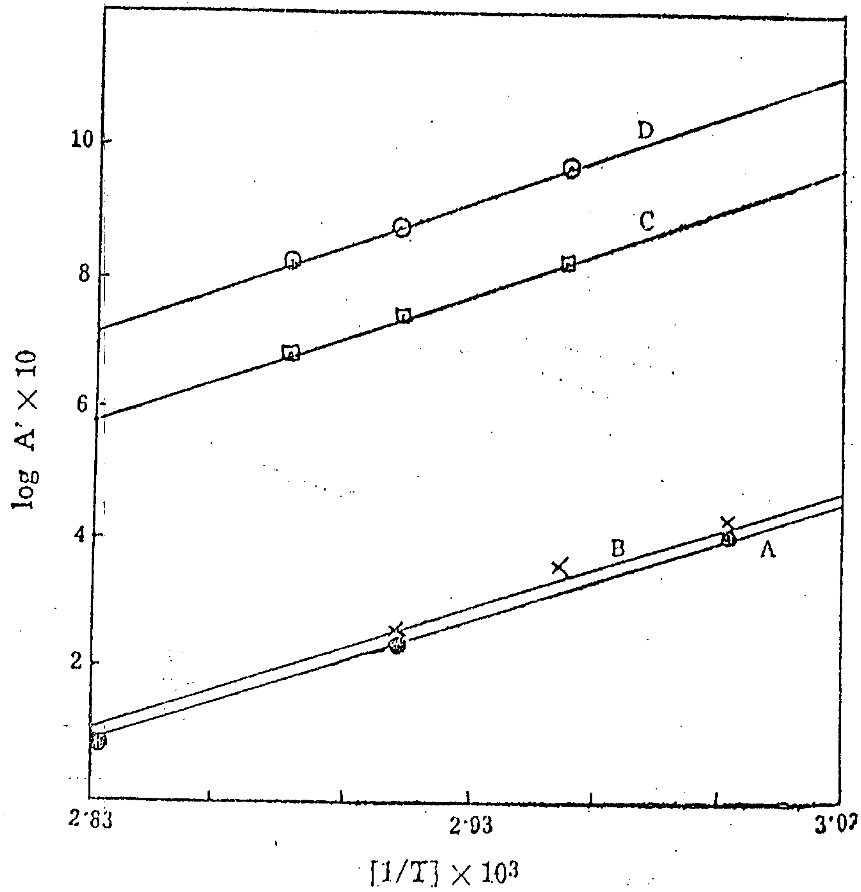


FIG. IV. Plot A log A' vs. 1/T with Azo.
Plot B log A' vs. 1/T with Bz_2O_2.
Plot C log A' vs. 1/T with DTBP.
Plot D log A' vs. 1/T with MEKP.

The specific rate constants for the spontaneous decomposition of the catalysts (k_d) Azo ($\cdot 0001533 \times sec^{-1}$) and HAzo ($4 \cdot 7 \times 10^{-6}$) (F. M. Lewis and M. S. Matheson 1949) being known, it was possible to calculate the catalyst efficiencies (f′) in both these cases (Eqn. 3). A catalyst efficiency of nearly 1 was obtained for Azo and approximately ·8 for HAzo. From these values, it appeared as though that termination by combination was more predominant in methyl acrylate polymerization and the monomer conformed to methyl methacrylate rather than styrene in the type of termination in its polymerization.

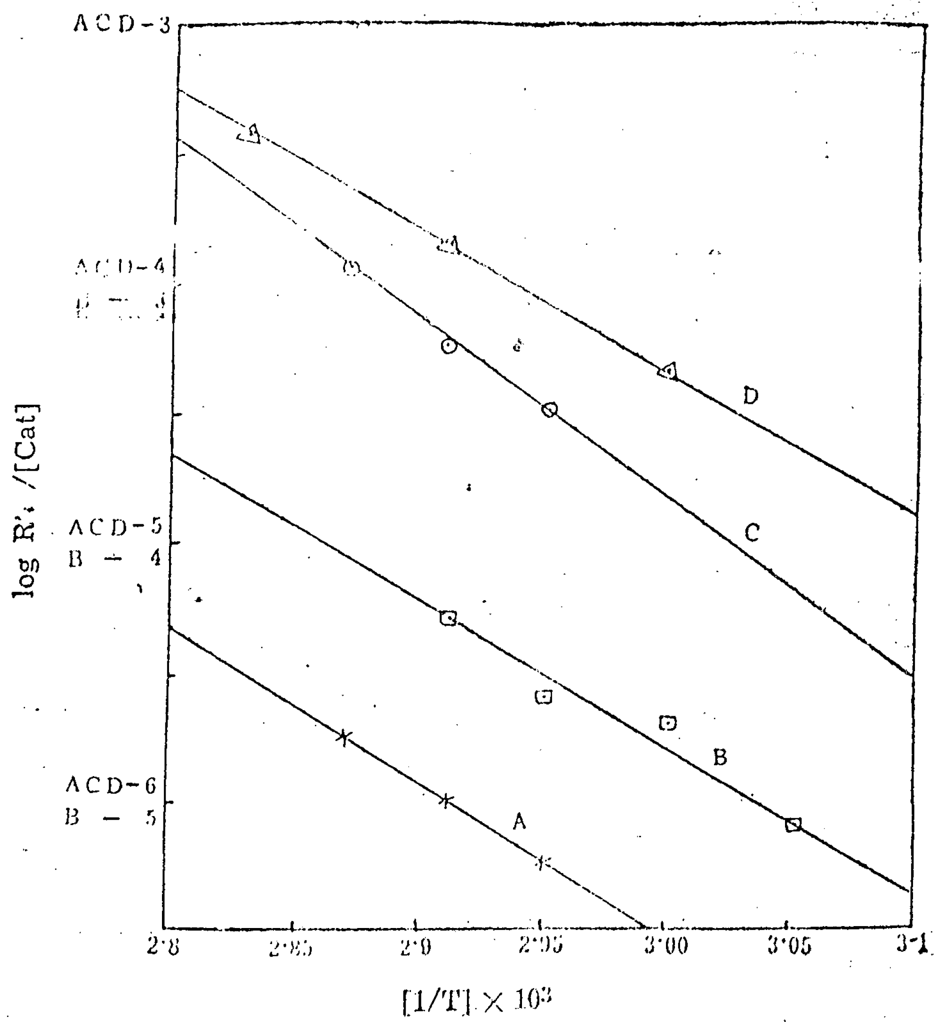


FIG. V. Plots A, B, C & D refer to the variation of R'_i/[Cat] with temperature when DTBP, Bz_2O_2, MEKP and Azo respectively were used us initiators.

Values of $[(1/Pn) - AR_p]$ were plotted against [Cat]/[M] (Eqn. 2—c) and from the slope and the intercept of these plots were evaluated rates of transfer of the chain radical with the catalyst C_{cat} and with monomer C_M (Method 2) respectively. C_{cat} values for all the catalysts were $\sim 10^{-2}$ to 10^{-3}. These values with their exponential forms for all the catalysts are given in Tables 1 and 2. It was interesting to observe that in all cases catalyst was more efficient by hundred to thousand times than monomer for transfer. Further, wherever transfer was more efficient with catalyst, transfer with monomer in the same reaction was comparably less efficient.

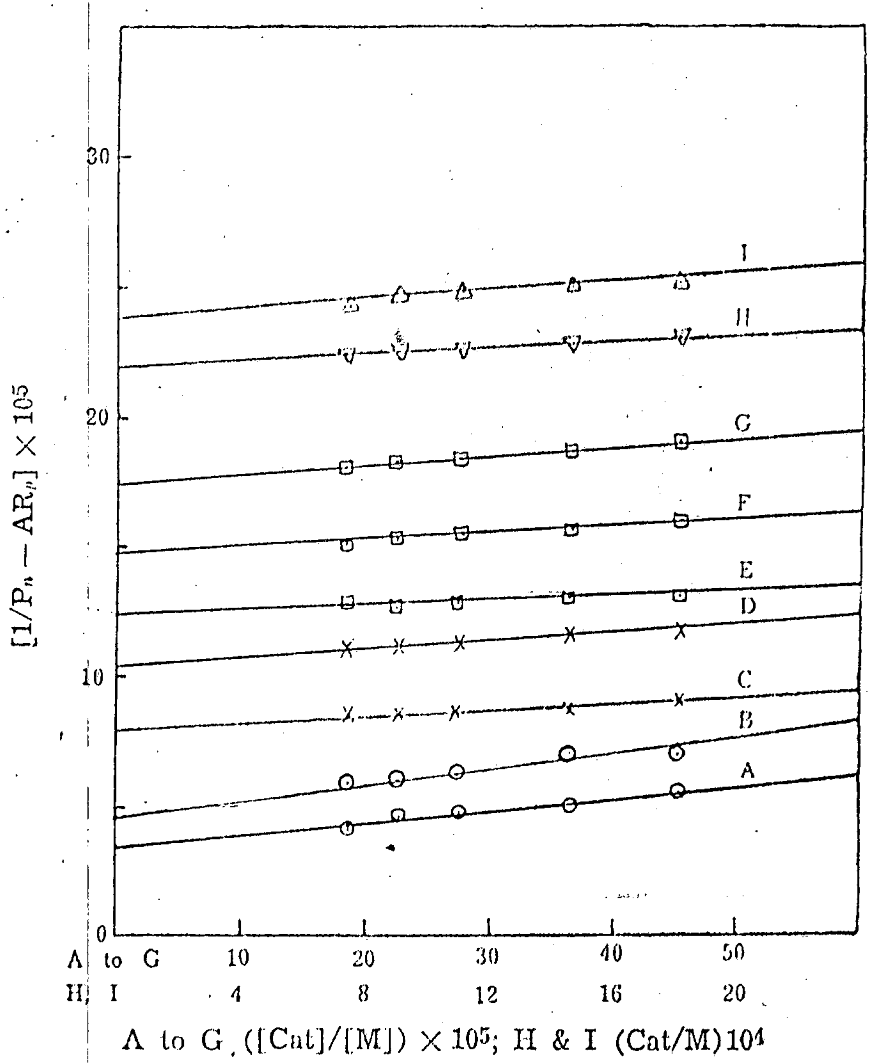


FIG. VI. All the Plots give the variation of $[(1/P_n) - AR_p]$ with [Cat]/[M] in the polymerization of methyl acrylate with a 20 per cent solution in ethyl acetate.

Plots A & B refer to Bz_2O_2 at 60°C and 70°C.
Plots C & D refer to H_2O_2 at 70°C and 80°C.
Plots E, F & G refer to Azo at 60°C, 70°C and 80°C respectively.
Plots H & I refer to HAzo at 70°C and 80°C.

The C_M values evaluated by the methods (1 and 2) indicated above are compared in Table 3. It was found that the values differed very little when either of the methods was used for calculating this quantity. It was further found that the values of K, A′, R_i'/[cat], C_{cat} and C_M differed very little when either 5·5 molar monomer or 2·2 molar monomer was used for polymerisation. These

Table 4

Rates of Initiation in the Polymerization of Methyl Acrylate, Methyl Methacrylate and Styrene

(a) K, (b) A′, (c) R′i/(Cat), (d) C_{cat}, (e) CM

Monomer		Azo			HAzo			MEKP	
Methyl acrylate	(a)	$3{\cdot}182 \times 10^{-3}$	at 60°C	(a)	$1{\cdot}728 \times 10^{-3}$	at 80°C	(a)	$1{\cdot}447 \times 10^{-3}$	at 70°C Ref. 8
	(b)	$2{\cdot}48$		(b)	$1{\cdot}2$		(b)	$7{\cdot}563$	
	(c)	$5{\cdot}023 \times 10^{-5}$		(c)	$7{\cdot}164 \times 10^{-6}$		(c)	$5{\cdot}733 \times 10^{-5}$	
	(d)	$8{\cdot}065 \times 10^{-3}$		(d)	8×10^{-3}		(d)	$7{\cdot}698 \times 10^{-2}$	
	(e)	$12{\cdot}75 \times 10^{-5}$		(e)	24×10^{-5}		(e)	18×10^{-6}	
Styrene	(a)	$8{\cdot}61 \times 10^{-5}$	at 60°C Ref. 4	(a)	$1{\cdot}17 \times 10^{-5}$	at 80·3°C Ref. 4	(a)	$5{\cdot}909 \times 10^{-4}$	at 70°C Ref. 13
	(b)	900 & 861		(b)	399		(b)	1085	
	(c)	$1{\cdot}77 \times 10^{-5}$		(c)	$1{\cdot}08 \times 10^{-7}$		(c)	$10{\cdot}68 \times 10^{-6}$	
	(d)	0		(d)	No data		(d)	$21{\cdot}714 \times 10^{-2}$	
	(e)	6×10^{-5}		(e)	No data		(e)	No data	
Methyl methacrylate	(a)	$3{\cdot}28 \times 10^{-4}$	at 60°C Ref. 4	(a)	$2{\cdot}9 \times 10^{-4}$	at 77°C Ref. 4	(a)	$1{\cdot}086 \times 10^{-4}$	at 70°C Ref. 5
	(b)	$67{\cdot}3$		(b)	No data		(b)	$103{\cdot}3$	
	(c)	$1{\cdot}48 \times 10^{-5}$		(c)	$5{\cdot}57 \times 10^{-6}$		(c)	$2{\cdot}44 \times 10^{-6}$	
	(d)	0		(d)	No data		(d)	5×10^{-3}	
	(e)	1×10^{-5}		(e)	No data		(e)	2×10^{-5}	

various values for the catalysts Bz_2O_2 and MEKP are given in Table 2. All these values for methyl acrylate with Azo, HAzo and MEKP are also compared with the values for methyl methacrylate and styrene polymerizations with the same catalysts (Table 4). From a glance at these values, it is obvious that methyl acrylate conforms to the other normal monomers for polymerization in spite of its abnormal tendency for autoacceleration.

REFERENCES

Arnett, L. M. (1952) Kinetics of the polymerisation of methyl methacrylate with aliphatic azobisnitriles as initiators. *J. Amer. chem. Soc.* 74: 2027.

Arnett, L. M. & Peterson, J. H. (1952) Vinyl polymerisation with radioactive aliphatic azobisnitriles as initiators. *J. Amer. chem. Soc.* 74: 2031.

Baysal, B. & Tobolsky, A. V. (1952) Rates of initiation in vinyl polymerisation Methyl methacrylate. *J. Polym. Sci.* 8: 529.

Baysal, B. & Tobolsky, A. V. (1953) A Review of Rates of Initiation *J. Polym. Sci.* 11: 471.

Gopalan, M. R. & Santappa, M. (1956) Methyl ethyl ketone peroxide as initiator in the polymerisation of methyl methacrylate. *J. Madras. Univ.* (In press).

Johnson, D. H. & Tobolsky, A. V. (1952) Monoradical and Diradical Polymerisation of styrene. *J. Amer. chem. Soc.* 74: 938.

Lewis, F. M. & Matheson, M. S. (1949) Decomposition of Aliphatic Azo compounds" *J. Amer. chem. Soc.* 71: 747

Mahadevan, V. & Santappa, M. (1955) Rates of initiation and chain transfer constants in the polymerisation of methyl acrylate. *Makromol. chem.* 16: 119.

Matheson, M. S., Auer, E. E., Bevilacqua, E. B. & Hart, E. J. (1951) Rate constants in freeradical polymerisation. IV. Methyl acrylate. *J. Amer. chem. Soc.*, 73: 5395.

Overberger, C. G, O'Shaughnessy, M. T., & Shalit, H. (1949) Preparation of Aliphatic Azobisnitriles *J. Amer. chem. Soc.*, 71: 2661.

Santappa, M. & Mahadeva Ayyar, V. (1955) Rates of initiation in the polymerisation of methyl acrylate. *Curr. Sci.* 24: 173.

Thiele, J. & Heuser, K. (1896) Ueber Hydrazinderivate der Isobuttersaure *Liebigs, Ann.* 290: 1.

Vaidhyanathan, V. S. (1956) M. Sc. Thesis to the University of Madras January, 1956.

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Methyl Ethyl Ketone Peroxide as an Initiator in the Polymerization of Methyl Methacrylate

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ABSTRACT

Methyl Ethyl Ketone Peroxide was employed to catalyse the polymerization of methyl methacrylate in the range 65-80°C in bulk as well as in solution. From two simple measurements of overall rates and degrees of polymerization under various conditions it was possible to evaluate (i) the ratio of the propagation constant to the termination constant raised to half power (ii) transfer coefficient for the monomer (iii) transfer coefficient for the catalyst (iv) transfer coefficient for the solvent (v) Rates of initiation etc. The specific rate transfer constants for the monomer and the catalyst in solution appeared to differ slightly from those in bulk.

Methyl ethyl ketone peroxide (MEKP) has not been extensively employed as an initiator of vinyl polymerizations. Vaidhyanathan and Santappa (1955) and Mahadevan and Santappa (1955) have briefly reported polymerization of styrene and methyl acrylate with this catalyst. A systematic investigation of kinetics of vinyl polymerization with MEKP as initiator was undertaken. A few results in the polymerization of methylmethacrylate at 65°-80°C are briefly reported here.

Theoretical: Various rate equations and equations relating to degrees of polymerizations under a variety of conditions have been explained in great detail in the previous publications by Santappa et al (1955). The following relationships which are relevant to our present work are being reproduced.

Catalysed overall rate R, is given by

$$R = \frac{k_p\, k_d^{1/2} f^{1/2} [\mathrm{Cat}]^{1/2} [\mathrm{M}]}{[k_{tc} + k_{td}]^{1/2}} = K[\mathrm{Cat}]^{1/2} \quad .. \quad (1)$$

where k_p, k_{tc} and k_{td} are the rate constants for propagation, termination by combination and disproportionation respectively in the polymerization of monomer (M), k_d, f are the rate constant for the spontaneous decomposition of the catalyst (Cat) and catalyst efficiency respectively. The latter, according to definition by Matheson (1945) is

$$f = \frac{k_a[\mathrm{M}]}{\{k_a[\mathrm{M}] + k_b\}} \qquad .. \quad (2)$$

k_a and k_b are the rate constants for the initiation and irreversible association respectively of the primary radicals.

Further, the reciprocal of the degree of polymerization P_n is given by

$$1/P_n = AR + C_M + C_{cat}\frac{R^2}{K^2[\mathrm{M}]^3} + C_s\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad .. \quad (3)$$

C_M C_{cat}, C_s are transfer coefficients for monomer, catalyst and solvent respectively; A is $[k_{tc} + 2k_{td}]/k_p^2[\mathrm{M}]^2$. The third term in the R.H.S. of equation (3) may be replaced by $C_{cat}\dfrac{(\mathrm{Cat})}{(\mathrm{M})}$.

Experimental: Methyl methacrylate, a Rohm and Haas product, was purified by repeated distillation in oxygen free nitrogen under reduced pressure and was always stored in a refrigerator. Methyl ethyl Ketone peroxide was supplied as 60% solution by Laporte Chemicals. Details of estimation and purity of the monomer and catalyst as well as deaeration of the system are reported in previous publications. (Santappa et al)

Polymerization of methyl methacrylate was carried out in a glass ampoule (8 cms. long and 1 cm. diameter) well cleansed and flamed before use. After deaeration of the monomer catalyst system with nitrogen for about half hour, the ampoule was sealed and heated in a thermostat bath at the desired temperature till the monomer was converted to ca. ten percent, found by few trial experiments. The time for polymerization was usually one to two hours. Afterwards the ampoule was taken out of the thermostat and chilled in a beaker containing ice. The fused capillary of the ampoule was then broken open and the contents were dissolved in small quantities of acetone and quantitatively transferred to a beaker. Addition of methanol precipitated the polymer which was transferred to a weighed sintered glass crucible, washed with methanol and dried to a constant weight at 70°C. From the weight of the polymer, rate of monomer disappearance was evaluated. The degrees of polymerization of the polymers were determined by measuring the viscosities of 0·1 percent polymer solutions in benzene in B.S. No. 1 Ostwald Viscometer and using the well known Staudinger's relationship $n = k[\eta]^{\alpha}$, the values of $k = 2 \cdot 8 \times 10^{3}$ and $\alpha = 1 \cdot 32$ having been determined by Baxendale, Bywater and Evans for polymethyl methacrylate, (1946).

Results and Discussion:

Percentage conversion against time (Fig. 1) was studied in the polymerization of methyl methacrylate catalysed by MEKP

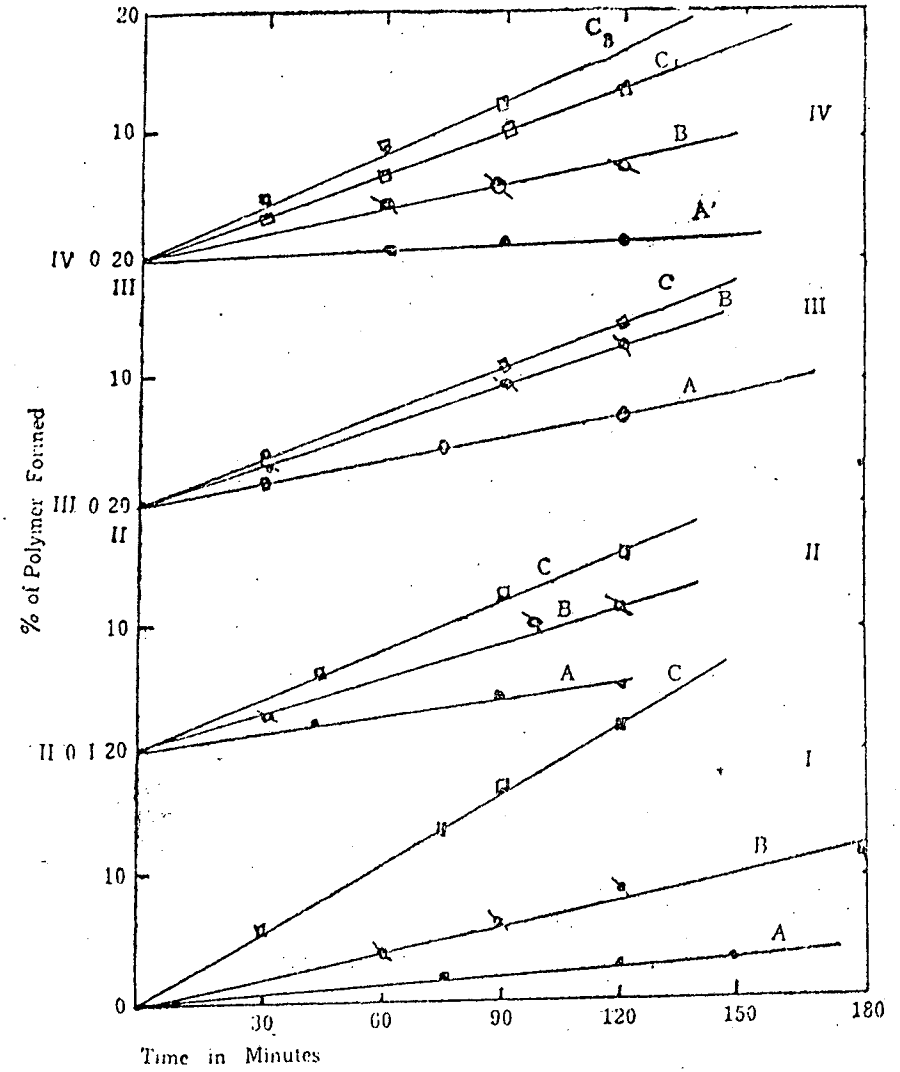

FIG. 1. Percentage Polymer formed vs. Time in bulk and in solutions. Catalyst concentration were: $A' = 10^{-3}$; $A = 10^{-2}$; $B = 5 \times 10^{-2}$ $C = 10^{-1}$.

Set I Bulk; II Ethyle Acetate; III Benzene; IV A' and C_1 Toluene; IV B and C_8 Methyl Ethyl Ketone.

both in bulk (monomer M 9·2 molar) and in solution (M = 4·6 molar). It was found that all the lines in the Fig. 1 passed through origin. This indicated the absence of period of induction and suitability of the catalyst in the further studies of polymerization.

Employing a hundred fold variation of concentration of MEKP the order of reaction with respect to catalyst was studied. As with radical initiated vinyl polymerizations and in conformity with equation (1) above, plots of Rate vs (Cat)½ were all linear (Fig 2)

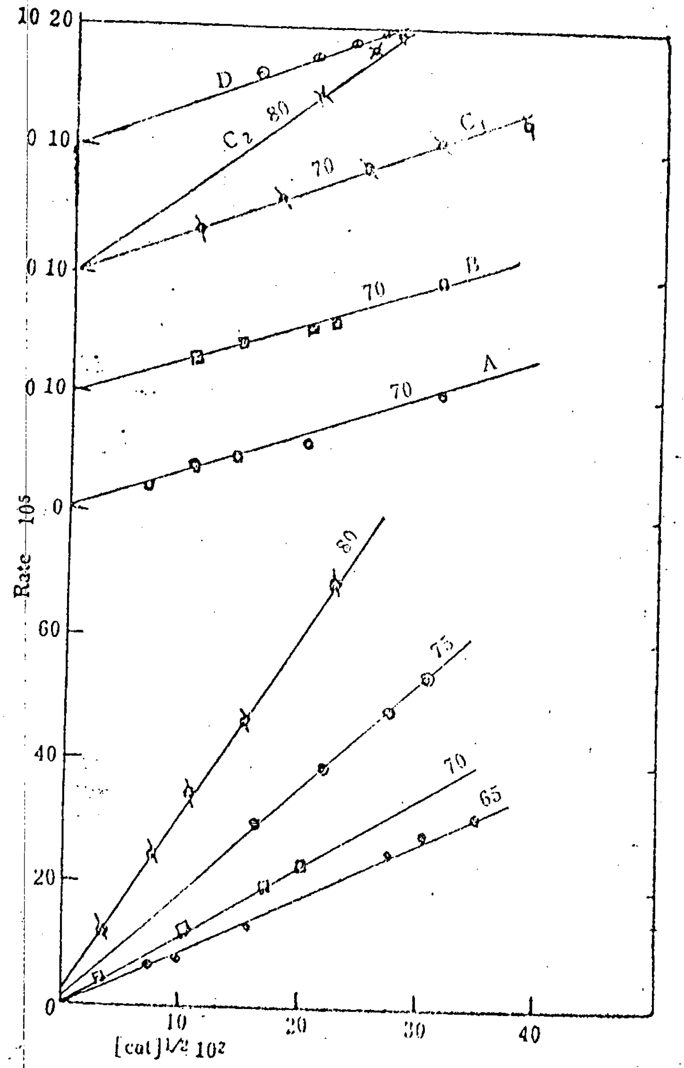

FIG. 2. Rate vs. (Cat)½ in Bulk at temperatures 65°, 70°, 75 and 80°C from below and in solution (4·6 molar).
A Benzene, B Ethyl Acetate, C_1 Toluene D Methyl Ethyl Ketone at 70°C and C_2 Toluene at 80°C.

both in bulk and in solution. The absence of any intercept on the ordinates of the plots indicated that the thermal rate did not make any contribution. The slopes of the plots in bulk gave the values of $K \times 10^3$ as 0·83, 1·0, 1·7, 2·89 and the values for the constant

$K' = \frac{k_p (k_d f)^{1/2}}{k_t^{1/2}}$ as $0 \cdot 9053 \times 10^{-4}$, $1 \cdot 086 \times 10^{-4}$, $1 \cdot 848 \times 10^{-4}$, $3 \cdot 142 \times 10^{-4}$ at 65°, 70° and 80°C respectively and $K' = 1 \cdot 936 \times 10^{3}$, exp (−9065/RT for temperatures 65° to 70°C and $K' = 4 \cdot 43 \times 10^{6}$, exp (−16760/RT) for 65-75°C. Values of $K \times 10^3$ in benzene, toluene, ethyl acetate and methyl ethyl ketone solvents ($M = 4 \cdot 6$ molar) at 70° C were 0·3, 0·318, 0·3 and 0·4 respectively and for toluene $K = 2 \cdot 79 \times 10^{9}$ ex (−20440/RT) was found. The values of activation energy for overall rate thus varied within wide limits. A value of ca 10 ± 3 K Cals was reported for the overall activation energy in bulk by Flory (1937). This value was supported recently by Umasankar Nandi and S. R. Palit (1955) in the homogeneous polymerization of methyl methacrylate catalysed by hydrogen peroxide. The latter authors have given divergent values for overall activation energy in solution polymerization. A calculation of the activation energies from values of K by various authors given in the paper by Tobalsky (1953) indicated the divergent nature of the values and therefore in our opinion a great uncertainty appeared to be attached for the accuracy of those values.

The relationship between the degree of polymerization and rate has been studied both in bulk and in solution in the four solvents mentioned above. It may be pointed out at the outset that equation (3) given under theoretical above, generally obeyed for bulk and solution polymerizations though it must be admitted that methyl ethyl ketone peroxide conformed to the same behaviour as Tertiery Butyl Hydroperoxide and Cumene hydroperoxide, which exhibit certain curvature in the plots of $1/P_n$ vs Rates. From studies of $1/P_n$ vs Rates both in bulk and solution it was possible to evaluate $A (= k_t/k_p^2[M]^2)$, transfer constants for monomer, catalysts and solvent. In bulk and at very low concentration MEKP ($\sim 10^{-3}$) it was presumed that the transfer of growing polymethyl methacrylate chain with the catalyst was negligible and from plots of $1/P_n$ vs Rates (Fig. 3) the slopes gave A and the intercepts gave C_M The A values at 65, 70, 75 and 80°C were 1·5, 1·22, 0·895 and 0·3 respectively. Values of $k_p/k_t^{1/2}$ obtained from A at 65, 70, 75 and 80°C were $8 \cdot 87 \times 10^{2}$, $9 \cdot 84 \times 10^{-2}$ $11 \cdot 62 \times 10^{-2}$ and $19 \cdot 85 \times 10^{-2}$ respectively and $k_p/k_t^{1/2} = 1 \cdot 69 \times 10^{4}$ exp (—5112/RT). The C_M values from the intercepts at 65, 70, 75 and 80°C were 2×10^{-5}, 3×10^{-5}, $3 \cdot 3 \times 10^{-5}$ and 4×10^{-5} respectively. With C_M values so obtained two methods of evaluating C_{cat} values in bulk were conceived. The first method was to plot $\{(1/P_n) - C_M\}/R$ against R at high catalyst concen-

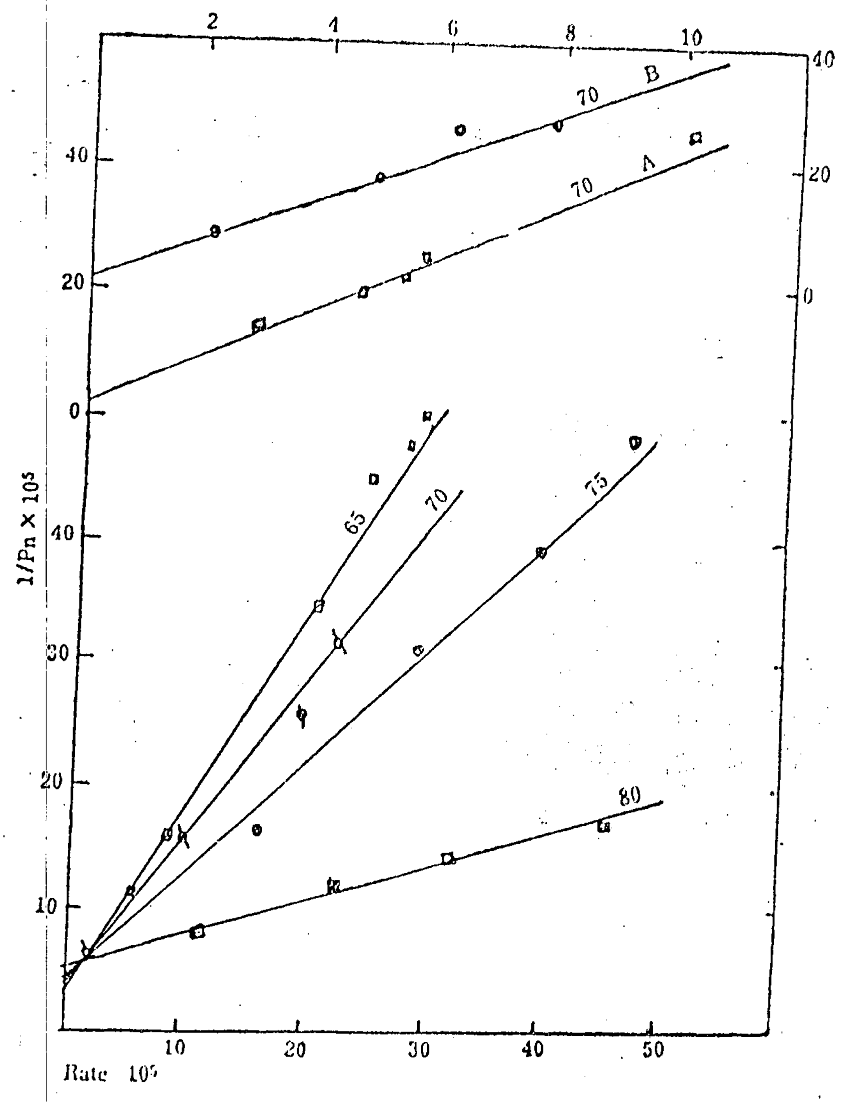

FIG. 3. Rate vs. 1/Pn in Bulk at 80°, 75°, 70 and 65°C from below and in solution. A Ethyl Acetate, B Benzene at 70°C.

trations (~ 10^{-1} to 10^{-2}) and evaluating C_{cat} from the slope, $C_{cat}/K^2[M]^3$. The second method was to plot $\left\{\frac{1}{P_n} - AR\right\}$ against (Cat)/(M) and evaluating C_{cat} from the slope. Both the methods gave more or less identical values for C_{cat}. Since small variations in the slope produced large divergences in the C_{cat} values by the first method it was discarded and therefore the second method was resorted to for the accurate evaluation of the constant. The values for the C_{cat} at 65, 70, 75 and 80°C were all in the neighbourhood of ~ 5×10^{-3} showing surprisingly very little variation with temperature. From the values of K and A it was possible to evaluate by methods described previously (Santappa et al 1955) the rate of initiation R_i in the bulk polymerization of methyl methacrylate catalysed by MEKP. The values for Ri/cat at 65, 70, 75 and 80°C were $2 \cdot 08 \times 10^{-6}$, $2 \cdot 44 \times 10^{-6}$, $5 \cdot 17 \times 10^{-6}$, 5×10^{-6}, respectively and an activation energy of ~ 30 Kcals for initiation was obtained;

$$R_i'/\text{cat} = 5 \cdot 608 \times 10^{13} \times \exp\ (-30700/RT)$$

Polymerization experiments at 70°C in the four solvents indicated above were also conducted and all the constants K, A, C_{cat}, C_M C_S and R_i'/Cat were evaluated. Values of K′ in the four solvents ranged from 6 to 8×10^{-5} indicating approximately 40 to 20 per cent decrease of the constant from the bulk value. The decrease in the value of K′ in solution may be attributed either to increase in k_t or decrease in k_p or $k_d f$. Probably increase of k_t and f were responsible.

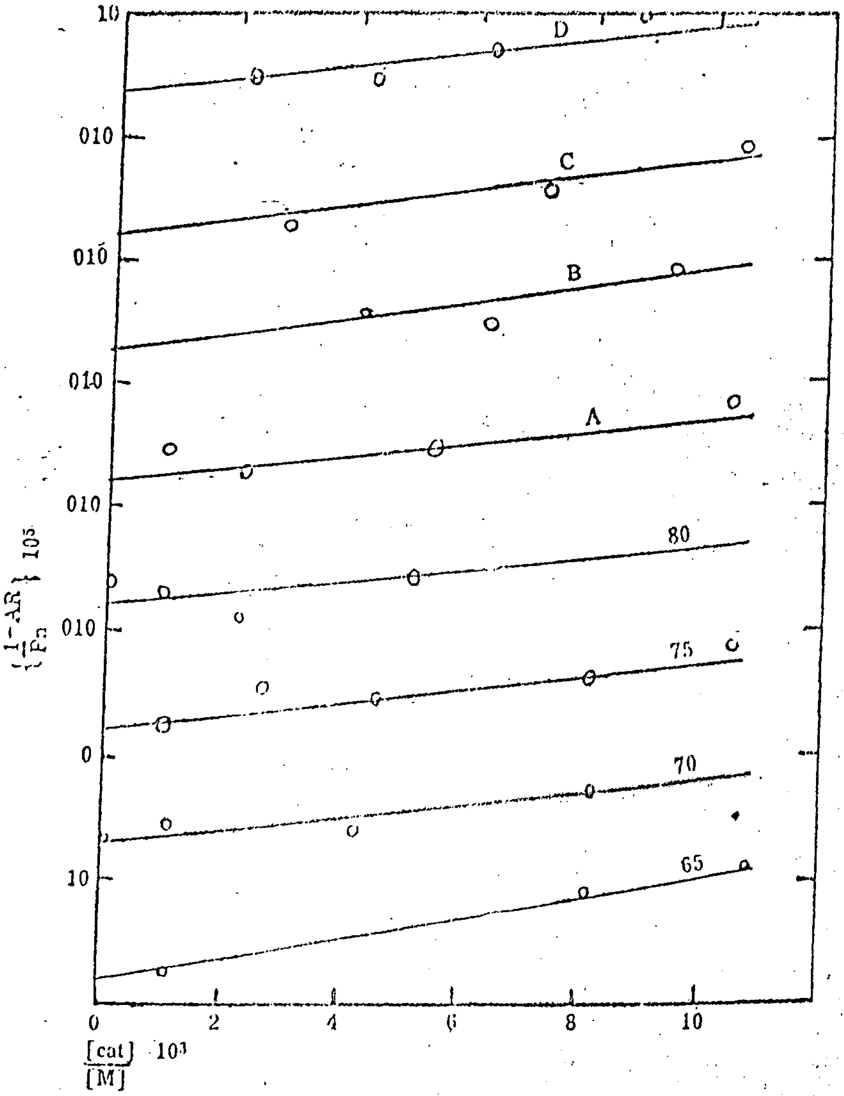

FIG. 4. {(1/P$_n$) − AR} vs. [Cat]/[M] in Bulk at temperatures 65°, 70°, 75° and 80°C and in solution A (Ethylacetate), B (Benzene), C (Toluene), D Methyl Ethyl Ketone at 70°C.

Evaluation of A, C_{cat}, C_M values in solution was also possible. From the slopes of the plots I/P$_n$ vs R (Fig. 3) in the four solvents at 70°C the A value was ~ 4 and $k_p/k_t^{1/2}$ value was ~ $11 \cdot 9 \times 10^{-2}$. The values of $k_p/k_t^{\frac{1}{2}}$ in solution appeared to be in better agreement than these in bulk with the value calculated from Matheson's et al (1949) values for k_p and k_t. The A′ values got by plotting $1/P_n$ vs $R/[M]^2$ in solution at different monomer concentrations was used to plot $\left\{\frac{1}{P_n} - \frac{A'R}{[M]^2}\right\}$ against [S]/[M] at constant [Cat]/[M]. {Method (i) in the Table 1} (Fig. 5) From the slopes of the linear plots values for C_s at 70° were evaluated. From the intercept given by ($C_M + C_{cat}$ Cat/M) it was also possible

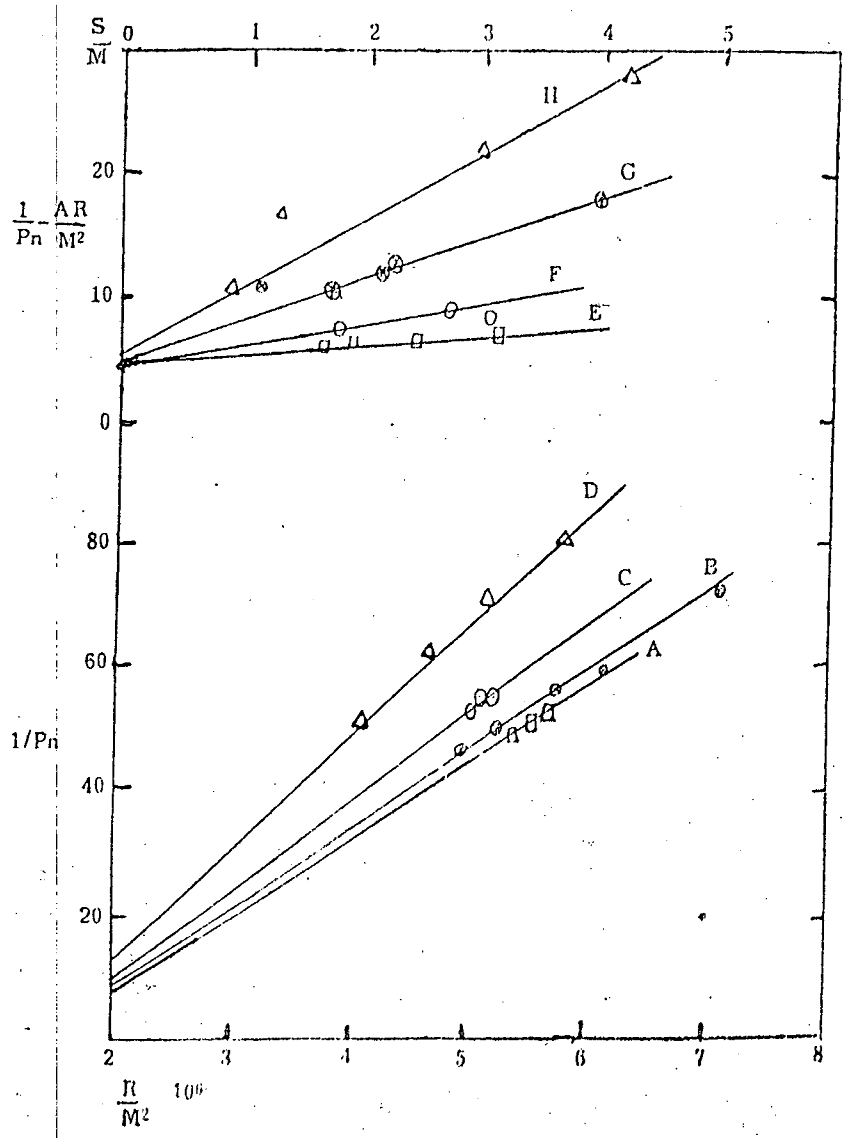

FIG. 5. $1/P_n$ vs. $R/[M]^2$ in solution at 70°C A Benzene; B Ethyl Acetate; C Methyl Ethyl Ketone; and D Toluene. (Above) $\{(1/P_n) - A'R/[M]^2\}$ vs. [S]/[M] at 70°C in E Benzene F Methyl Ethyl Ketone; G Ethyl Acetate and H Toluene.

to evaluate C_M and C_{cat}. Alternatively $\left\{\frac{1}{P_n} - AR\right\}$ vs [Cat]/[M] at constant [S]/[M] were plotted (Method (ii) Table 1) C_{cat} was given by the slope and $\left\{C_M + C_s\frac{[S]}{[M]}\right\}$ was furnished by the intercept. The values for C_s and C_M by the two methods did not differ much, the respective values are for ethylacetate $3{\cdot}3\times10^{-5}$, and 2×10^{-5}; for benzene $1{\cdot}43\times10^{-5}$, 2×10^{-5}, for toluene $5{\cdot}5\times10^{-5}$ and 0, and for methyle ethyle ketone $1{\cdot}43\times10^{-5}$ and 2×10^{-5}. The values of the transfer constants in the solvents were in the expected order (Sadan Basu, Jyotirindra Nath Sen and Santi R Palit, 1952). It was seen that C_M values for all the solvents studied were of the same order. The values for C_{cat} by method (i) and (ii) differed, though were of the same order in their powers of ten. These differences we felt were within errors accompanying the graphical evaluations. We further found that method (i) represented a more accurate and suitable evaluation because constant catalyst concentration was used and (M) was widely varied and the plots were more linear.

Values for C_{cat} in the solution were found to be generally slightly lower than in bulk for the same concentration of the catalyst. Probably specific rate transfer constant for catalyst might have decreased in the presence of solvent molecules.

Table I

C_{cat} Method	Benzene	Toluene	Ethyl Acetate	Methylethyl Ketone
(i)	$3{\cdot}3\times10^{-3}$	$3{\cdot}68\times10^{-3}$	$2{\cdot}3\times10^{-3}$	$1{\cdot}96\times10^{-3}$
(ii)	5×10^{-3}	$3{\cdot}3\times10^{-3}$	$3{\cdot}3\times10^{-3}$	4×10^{-3}

With the known values for C_{cat} and C_s it was possible to plot $\left\{\frac{1}{P_n} - C_{cat}\frac{[cat]}{[M]} - C_s\frac{[S]}{[M]}\right\}$ against R/M^2 and get more accurate values of the slope A′ referred to above. The value of the slope thus determined in ethyl acetate solution was 62·5.

With the known K′ value from Rate vs Cat½, the rate of initiation was calculated, $2K'^2\,A' = R_i/[Cat] = 5{\cdot}311\times10^{-7}$. The value for other solvents were also about the same. The low values got in solution may be due to the lowering of the rate constant for the spontaneous decomposition of the catalyst in a mixture of solvent and monomer or dependence of catalyst efficiency "f" on monomer concentration or both.

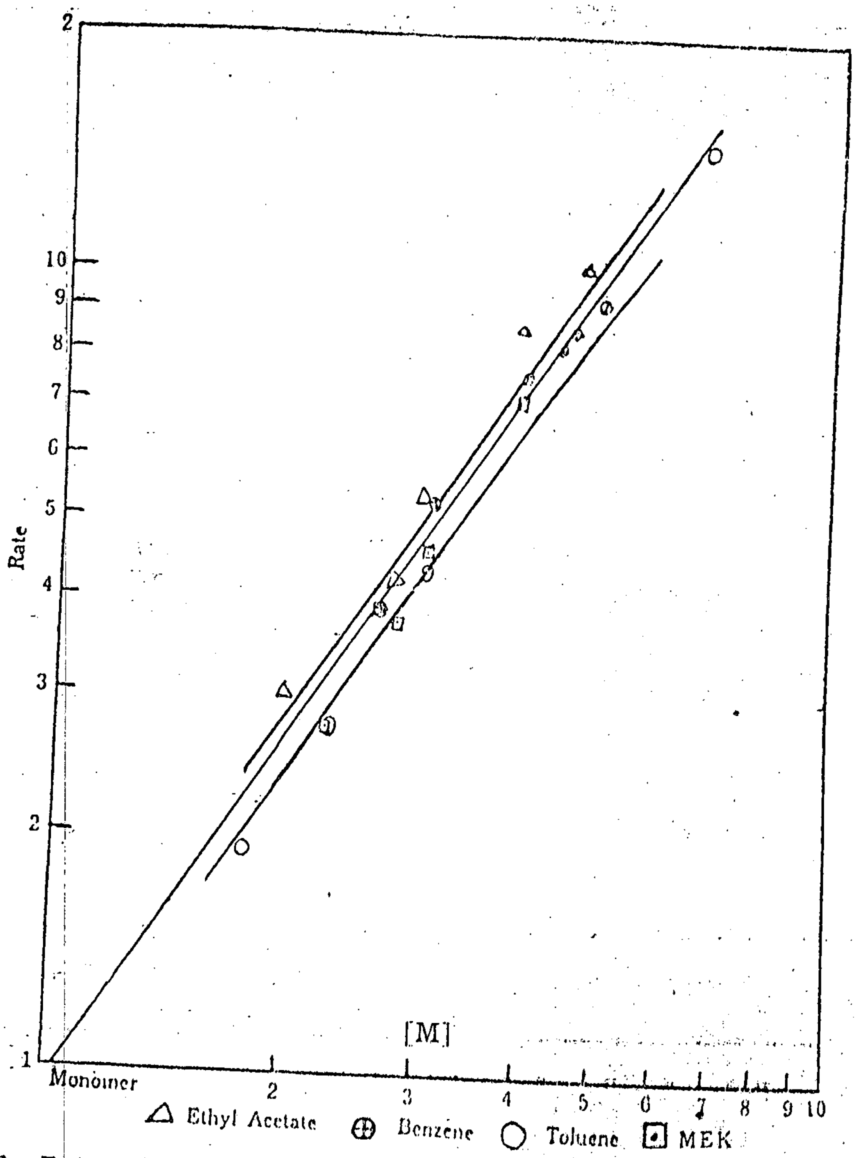

FIG. 6. Rate vs. Monomer Concentration on Logarithmic graph-slope of lines is 3/2 indicating first order reaction with respect to Monomer.

The order of the reaction with respect to monomer concentration was evaluated by carrying out polymerization at 70°C with constant catalyst concentration in the four solvents mentioned above. Log R vs Log M (Fig. 6) were plotted and the slope in all the solvents was 1·5. It could therefore be described that the reaction was of the first order with respect to monomer concentration and the other one half power of monomer concentration might be explained by the catalyst efficiency, f, being dependent on it.

REFERENCES

Baxandale, J. H., Bywaters, & Evans, M. G. (1946) *J. Polym. Sci.* 1: 237.

P. J. Flory (1937) Mechanism of Vinyl Polymerizations *J. Amer. chem. Soc.* 59: 241.

Mahadevan & Santappa (1955) Rates of Initiation and Chain transfer constants in the polymerization of methylacrylate *Makromol. Chem.* 16: 119.

Matheson et al (1949) *J. Amer. chem. Soc.* 71: 497.

Sadan Basu, Jyotirindranath Sen, & S. R. Palit, (1952) Studies in Chain Transfer, *Proc. roy. Soc.* A 214: 247

Tobalsky, A. V. & B. Baysal (1953) A Review of Rates of Initiation in Vinyl Polymerization: Styrene and Methyl Methacrylate, *J. Polym. Sci.* 11: 471-486.

Umasankar Nandi & Santi R. Palit (1955) Hydrogen Peroxide in Vinyl Polymerisation, *J. Polym. Sci.* 12: 65.

Vaidhyanathan & Santappa (1955) Chain transfer reactions and nature of initiation in the polymerization of styrene. *Makromol.* 16: 140.