85. *Peroxides as Initiators of Polymerization of Methyl Methacrylate.*

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The polymerisation of methyl methacrylate, both homogeneous and in benzene, toluene, and ethyl acetate, has been initiated with nine diacyl peroxides at 60°. The kinetic order of the reaction with respect to the initiators and the monomer is found to be $\frac{1}{2}$ and $\frac{3}{2}$, respectively, in all cases. The value of δ (Table 1) for methyl methacrylate at 60° has been determined at different monomer concentrations initiated by each peroxide and a mean value of 7·60 is obtained.

The initiation constants of all the diacyl peroxides have been determined by two independent methods (rate, and degree of polymerisation) which give similar results, the constants being increased by electron-releasing groups in the benzene ring.

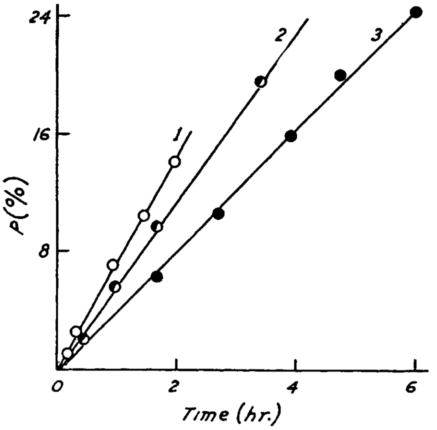
The chain-transfer coefficients for monomer (C_M), initiator (C_I), and solvents (C_S) have also been determined by various methods. The value of C_M is 1×10^{-5}; an attempt has been made to correlate values of C_I with the structure of the peroxides. The chain-transfer coefficients for solvents could be determined very accurately (in agreement with recorded values) in the presence of any type of peroxide from the known values of C_M and C_I with the help of the general equation for degree of polymerisation.

WE have polymerised methyl methacrylate with diacyl peroxides both in bulk and in solution and have determined various kinetic constants, especially the chain-transfer coefficients for monomer (C_M), initiators (C_I), and solvents (C_S). The influence of substituents in the benzene ring of the peroxide on initiation and on catalyst-transfer reaction has also been studied, and the results are compared with those reported by Cooper [1] for the polymerization of styrene.

Yield Curves.—Methyl methacrylate was polymerized with varying concentrations of catalyst (0·0006—0·14 mole/l.) in bulk and in solutions in ethyl acetate and toluene at 60°. Some typical yield curves are represented in Fig. 1. They are good straight lines passing through the origin, thus showing that there is practically no inhibition period under any conditions, so in subsequent experiments the rate of polymerization was calculated from the yield of a single tube.

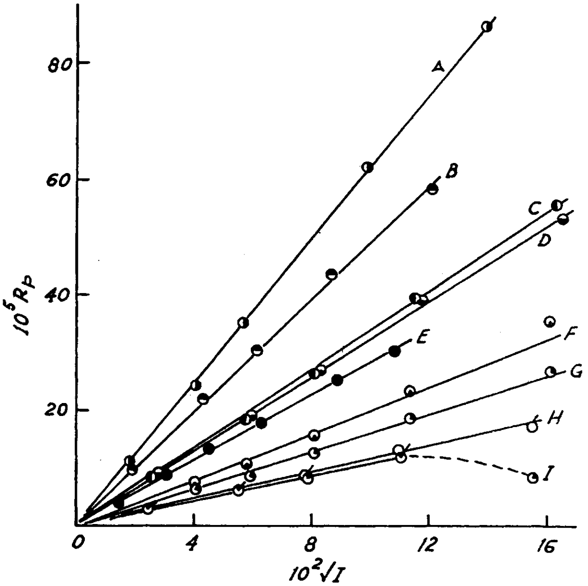
Dependence of the Rate of Polymerization, R_p, on Catalyst Concentration.—The relation between the initiator concentration and the rate of polymerization was studied at different monomer concentrations with nine diacyl peroxides at 60°. The results are shown in Tables 1 and 2 and Fig. 2. Thomas and Pellon [2] have shown recently that in the bulk polymerization of acrylonitrile with benzoyl peroxide R_p is proportional to $I^{0\cdot75}$ but in all cases studied by us we find it to be proportional to the square root of the catalyst concentration, in agreement with the usual equation [3]

FIG. 1. *Determination of inhibition period in catalyzed polymerization at* 60°.



1, *o*-Methylbenzoyl peroxide in bulk.
2, *o*-Methylbenzoyl peroxide in ethyl acetate (4·645M).
3, *o*-Chlorobenzoyl peroxide in toluene.

FIG. 2. *Determination of the order of reaction with respect to initiator concentration in bulk.*



A, *o*-Chlorobenzoyl peroxide; *B*, *o*-methylbenzoyl peroxide; *C*, anisoyl peroxide; *D*, cinnamoyl peroxide; *E*, palmitoyl peroxide; *F*, *G*, *p*-, *m*-chlorobenzoyl peroxide; *H*, *I*, *m*-, *p*-nitrobenzoyl peroxide.

$$R_p = (k_p/k_t^{\frac{1}{2}})k_i^{\frac{1}{2}}M^{\frac{3}{2}}I^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I and M are the initiator and monomer concentrations respectively, and k_p, k_i, and k_t are the rate constants for propagation, initiation, and termination processes respectively. The straight lines pass through the origin, again showing that there is no inhibition period and very little superimposed thermal reaction, and termination is probably by a bimolecular free-radical interaction. Nitrobenzoyl peroxides, especially the *para*-substituted one, show abnormal behaviour, the rate decreasing with increasing catalyst concentration. This is attributed to the inhibiting effect of nitro-compounds on polymerization, which is confirmed by the failure to follow the square-root relation ($I^{\frac{1}{2}}$).

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[1] Cooper, *J.*, 1951, 3106; 1952, 2408.
[2] Thomas and Pellon, *J. Polymer Sci.*, 1954, **13**, 329.
[3] Bawn, "Chemistry of High Polymers," Interscience Publ. Inc., p. 67.

TABLE 1. *Polymerization of methyl methacrylate in bulk* (9·29 *moles/l.*) *in presence of catalysts at* 60°.

$10^3 I/M$	$10^5 R_p$ *	$10^5/\bar{P}$	
Catalyst : *o*-Chlorobenzoyl peroxide.			
2·08	86·40	62·13	$10^6 R_p^2/I$ = 36·73
1·04	62·20	42·76	$10^6 k_i$ = 2·64, 2·84 †
0·35	35·50	25·17	δ = 7·55
0·17	24·40	17·80	C_I = 0·02
0·03	11·20	8·16	$10^5 C_M$ = 0·90
Catalyst : *p*-Methoxybenzoyl peroxide.			
2·84	55·62	42·76	$10^6 R_p^2/I$ = 12·26
1·42	39·45	24·98	$10^6 k_i$ = 0·88, 0·62
0·71	26·41	18·20	δ = 7·22
0·35	18·32	12·57	C_I = 0·04
0·07	8·94	7·01	$10^5 C_M$ = 1·00
Catalyst : palmitoyl peroxide.			
1·26	30·61	25·37	$10^6 R_p^2/I$ = 8·40
0·84	25·31	20·65	$10^6 k_i$ = 0·60, 0·61
0·42	18·16	16·14	δ = 8·25
0·21	13·49	11·03	$C_I = \sim 0$
0·10	9·04	8·53	$10^5 C_M$ = 0·97
0·02	4·17	4·14	
Catalyst : *m*-Chlorobenzoyl peroxide.			
2·77	27·20	14·54	$10^6 R_p^2/I$ = 2·25
1·38	18·51	11·64	$10^6 k_i$ = 0·16, —
0·69	12·80	8·31	δ = 8·12
0·34	8·91	6·44	C_I = 0·003
0·17	6·12	5·18	$10^5 C_M$ = 1·00
Catalyst : *p*-Nitrobenzoyl peroxide.			
2·56	8·80	48·98	$10^6 R_p^2/I$ = 1·21
1·28	12·56	27·98	$10^6 k_i$ = 0·09, 0·09
0·64	8·75	15·51	δ = 7·66
0·32	6·41	9·37	C_I = 0·144
0·06	2·69	4·32	$10^5 C_M$ = 1·05

$10^3 I/M$	$10^5 R_p$ *	$10^5/\bar{P}$	
Catalyst : *o*-Methylbenzoyl peroxide.			
1·59	58·05	46·66	$10^6 R_p^2/I$ = 25·0
0·80	43·58	31·39	$10^6 k_i$ = 1·79, 1·73
0·40	30·86	21·04	δ = 7·22
0·20	22·40	16·50	C_I = 0·05
0·04	9·77	7·01	$10^5 C_M$ = 1·10
Catalyst : Cinnamoyl peroxide.			
2·93	53·29	42·76	$10^6 R_p^2/I$ = 10·56
1·46	39·50	31·39	$10^6 k_i$ = 0·76, 0·79
0·73	27·45	22·65	δ = 7·95
0·36	19·10	15·50	C_I = 0·009
0·07	9·43	9·46	$10^5 C_M$ = 1·01
Catalyst : *p*-Chlorobenzoyl peroxide.			
2·77	35·32	13·77	$10^6 R_p^2/I$ = 4·00
1·38	24·13	11·32	$10^6 k_i$ = 0·29 —
0·69	15·75	8·42	δ = 7·80
0·34	10·84	6·49	C_I = 0·009
0·17	6·91	5·56	$10^5 C_M$ = 1·03
Catalyst : *m*-Nitrobenzoyl peroxide.			
2·56	17·86	17·80	$10^6 R_p^2/I$ = 1·40
1·28	13·34	11·45	$10^6 k_i$ = 0·10, 0·11
0·64	9·00	7·48	δ = 7·55
0·32	6·72	5·69	C_I = 0·012
0·06	2·89	3·51	$10^5 C_M$ = 1·20

* R_p is given in mole l.$^{-1}$ sec.$^{-1}$.

† In all these entries for $10^6 k_i$ the first number is that determined by the R_p method, and the second that by the degree of polymerization method.

TABLE 2. *Polymerization of methyl methacrylate in solution in presence of catalyst at* 60°.

Catalyst : *o*-Methylbenzoyl peroxide. Solvent : Toluene. $10^5 C_S$ (uncatalyzed) = 2·00.

$10^3\sqrt{I/M}$	S/M	$10^5 R_p$ *	$10^5/\bar{P}$	$10^5 C_S$ † (1)	$10^5 C_S$ † (2)
19·95	1·005	10·70	40·83		
13·91	,,	7·64	27·98	1·73	2·35
6·30	,,	3·10	14·26		
19·95	2·345	4·90	44·77		
13·91	,,	3·50	31·20	1·70	1·80
6·30	,,	1·50	16·88		
19·95	4·020	2·10	49·00		
13·91	,,	1·50	36·66	1·90	2·20
6·30	,,	0·60	20·84		

Catalyst : Palmitoyl peroxide. Solvent : Ethyl acetate. $10^5 C_S$ (uncatalysed) = 1·30.

$10^3\sqrt{I/M}$	S/M	$10^5 R_p$ *	$10^5/\bar{P}$	$10^5 C_S$ † (1)	$10^5 C_S$ † (2)
29·04	1·112	5·42	27·77		
20·05	,,	4·38	23·50		
14·50	,,	3·25	16·38	1·32	1·36
10·27	,,	2·28	11·84		
4·56	,,	,,	6·15		

Catalyst : Palmitoyl peroxide. Solvent : Ethyl acetate. $10^5 C_S$ (uncatalyzed) = 1·30.

$10^3\sqrt{I/M}$	S/M	$10^5 R_p$ *	$10^5/\bar{P}$	$10^5 C_S$ † (1)	$10^5 C_S$ † (2)
29·04	2·594	3·12	31·38		
20·05	,,	2·10	26·27		
14·50	,,	1·90	19·63	1·00	1·20
10·27	,,	0·88	14·43		
4·56	,,	—	7·21		
29·04	4·448	0·89	39·72		
20·05	,,	0·70	30·81		
14·50	,,	0·31	21·23	1·00	1·33
10·27	,,	0·09	16·62		
4·56	,,	—	7·69		
29·04	10·008	0·30	53·95		
20·05	,,	0·13	40·36	1·00	1·41
14·50	,,	—	29·58		
10·27	,,	—	17·94		

* R_p in mole l.$^{-1}$ sec.$^{-1}$.

† From intercept of curve of $(1/\bar{P} - C_I I/M)$ against (1) $\sqrt{I/M}$ and (2) R_p.

Dependence of R_p on M.—Since the kinetic order of $\frac{3}{2}$ with respect to monomer concentration (eqn. 1) is not always followed, we have determined the kinetic order with respect to monomer with all the catalysts at various concentrations in both the solvents. It can be easily shown that the theoretical slope of the plot of log R_p against log M should be $(n + \frac{1}{2})$ at constant values of I/M, where n is the actual kinetic order. From Fig. 3, with the data given in Tables 1 and 2, it is seen that in all cases studied the order is $\frac{3}{2}$ with respect to monomer concentration, so the bimolecular initiation mechanism which we have assumed in the methyl methacrylate-catalysed polymerization[4] is followed. Andréconix and Smets[5] have reported the reaction to be of first order with respect to monomer concentration in the polymerization of methyl methacrylate in benzene solution and of somewhat higher order in *tert.*-butylbenzene. They attributed the difference to the influence of the solvent molecules on the induced rate of decomposition of the peroxide, as well as to a

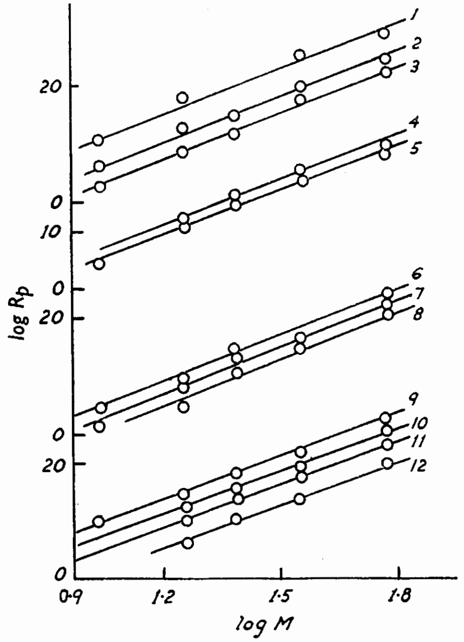

FIG. 3. *Determination of the order of reaction with respect to monomer concentration in ethyl acetate.*

1, Anisoyl peroxide.
2, 3, Cinnamoyl peroxide.
4, 5, *o*-Methylbenzoyl peroxide.
6, 7, 8, Palmitoyl peroxide.
9—12, *o*-Chlorobenzoyl peroxide.

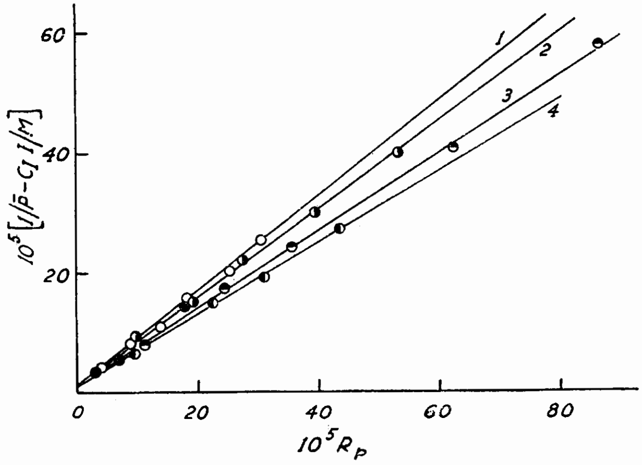

FIG. 4. *Determination of δ for methyl methacrylate at* 60°.

1, Palmitoyl peroxide.
2, Cinnamoyl peroxide.
3, *o*-Chlorobenzoyl peroxide.
4, *o*-Methylbenzoyl peroxide.

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[4] Basu, Sen, and Palit, *Proc. Roy. Soc.*, 1950, *A*, **202**, 485; 1952, *A*, **214**, 247.

[5] Andréconix and Smets, *J. Polymer Sci.*, 1953, **10**, 525.

"cage effect." It is, however, well known that solvent plays an important part in the decomposition of peroxides, which in turn affects the initiation reaction, so the above change may be due to a change in the initiation reaction.

The Value of δ for Methyl Methacrylate.—The ratio of the square root of the termination constant to the propagation constant, $k_t^{\frac{1}{2}}/k_p = \delta$, is of fundamental importance in the determination of kinetic constants in polymerization. Reported values vary,[6] so we have calculated its value from our results, with the help of the general equation for the degree of polymerization : [6d, 7]

$$1/\overline{P} = C_{\mathrm{M}} + C_{\mathrm{S}}(S/M) + C_{\mathrm{I}}(I/M) + R_p\delta^2/M^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to this equation the plot of $[(1/\overline{P} - C_{\mathrm{I}}(I/M)]$ against R_p at constant monomer concentration should give a straight line from the slope of which the value of δ can be calculated. The value of C_{I} was determined for different peroxides by an independent method (see Table 1). For bulk polymerization the above plot, with the data in Table 1, gives straight lines shown in Fig. 4. From the slopes of these straight lines, the value of δ obtained (Table 1) seems to vary slightly with the peroxide used. For palmitoyl peroxide, for which the value of C_{I} is zero, δ, calculated directly from the slope of the plot of $1/P$ against R_p, is 8·25, in good agreement with the values of 8·33 and 8·43 reported by Matheson *et al.*[6c] and Nandi and Palit [6f] respectively. Moreover, it is noteworthy (Table 4) that variation in the monomer concentration or in the nature of the solvent has no marked effect on its value. However, in order that the kinetic constants for the different initiators

TABLE 3. *Polymerization of methyl methacrylate in toluene in presence of catalyst at* 60°.

				10^5C_{S} †						10^5C_{S} †	
$10^3I/M$	S/M	10^5R_p *	$10^5/\overline{P}$	(1)	(2)	$10^3I/M$	S/M	10^5R_p *	$10^5/\overline{P}$	(1)	(2)
Catalyst : *p*-Methoxybenzoyl peroxide.											
26·66	1·005	11·22	33·57		2·10	26·66	4·020	1·89	44·45	4·00	1·90
,,	2·345	—	37·56	4·00	—	,,	9·045	0·37	64·18	4·00	—
Catalyst : Cinnamoyl peroxide											
27·04	1·005	10·95	33·52		2·20	19·13	1·005	6·40	26·54		
,,	2·345	3·12	40·36	5·00	—	,,	2·345	1·52	30·00	2·50	—
,,	4·020	1·86	46·66		3·00	,,	4·020	0·73	34·98		
,,	9·045	0·40	73·01		—	,,	9·045	0·18	47·00		
Catalyst : *m*-Nitrobenzoyl peroxide.											
25·39	1·005	—	9·18			12·75	1·005	—	7·10		
,,	2·345	—	12·54	2·70	—	,,	2·345	—	10·58	2·00	—
,,	4·020	—	18·20			,,	4·020	—	13·45		
,,	9·045	—	32·00								

* In mole l.$^{-1}$ sec.$^{-1}$.

† C_{S} obtained from (1) slope of curve of $1/\overline{P}$ against S/M; (2) equation (4). 10^5C_{S} (uncatalyzed) = 2·00 throughout.

TABLE 4. *Values of initiation constant* (k_i) *and* δ *at different monomer concentrations.*

	10^6k_i		
Monomer concn. (mole/l.)	*o*-Methylbenzoyl peroxide in toluene	Palmitoyl peroxide in ethyl acetate	δ
9·290	1·79	0·61	7·22
4·645	5·54	1·31	8·30
2·790	6·20	1·66	7·67
1·858	6·92	2·45	7·68
0·929	—	3·86	—

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[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] Palit, Nandi, and Saha, *ibid.*, 1954, **14**, 295.

used may be compared with each other the mean value of 7·60 for δ has been used in the present study.

Determination of Initiation Constant (k_i).—The rates of initiation were determined by two different independent methods. The results are summarized in Table 1.

Overall rate (R_p) *method.* In this process, we have determined the value of k_i from the values of R_p with the help of equation (1), in which $k_p/k_t^{\frac{1}{2}}$ has been replaced by δ:

$$k_i = \delta^2 R_p^2 / M^3 I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The value of R_p^2/I, which is different for different peroxides, has been taken from Table 1.

Degree of polymerization method. The initiation constants of both bulk and solution polymerization have also been determined from the general equation (2) for the average degree of polymerization. Equation (2) can be transformed into the form:

$$\left\{\frac{1}{\overline{P}} - C_{\mathrm{I}}\frac{I}{M}\right\} = C_{\mathrm{M}} + C_{\mathrm{S}}\frac{S}{M} + \frac{k_t^{\frac{1}{2}}}{k_p} \cdot k_i^{\frac{1}{2}}\left\{\frac{I}{M}\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

According to this equation the plot of $[1/\overline{P} - C_{\mathrm{I}}(I/M)]$ against $(1/M)^{\frac{1}{2}}$ at constant monomer concentration gives a straight line (Fig. 5) from the slope of which k_i has been calculated. The values of C_{I} for different peroxides have been taken from Table 1, and from this Table it is evident that the agreement between the values of k_i, determined by these two methods, is satisfactory within our experimental accuracy. Our values of k_i are comparable with those reported by Cooper,[1] and our results (Table 5) also indicate that the electron-releasing groups in the *meta*- and the *para*-position in dibenzoyl peroxides increase the rate of initiation in methyl methacrylate also. *o*-Chlorobenzoyl peroxide has a higher value for k_i than those of its *meta*- and *para*-isomers. The order of peroxides, according to their power on initiation in the polymerization studied is: *o*-Cl > *o*-Me > *p*-OMe > Cinnamoyl > Palmitoyl > *p*-Cl > *m*-Cl > *m*-NO_2 > *p*-NO_2. The different effect of the *meta*- and the *para*-position for chloro- and for nitro-substituents is noteworthy. The very low value of k_i for nitro-substituted peroxides may be due to the formation of stabilized radicals with the monomer itself, and this is more likely in the case of *p*-nitrobenzoyl peroxide. This is confirmed by the retarding effect of *p*-nitrobenzoyl peroxide on polymerization, which is evident from the non-linearity of the plot of R_p against $I^{\frac{1}{2}}$ (Fig. 2).

TABLE 5. *Comparison of initiation and transfer constants of styrene with those of methyl methacrylate.*

Peroxide	Styrene * at 70° $10^6 k_i$	C_{I}	Methyl meth-acrylate at 60° $10^6 k_i$	C_{I}
o-Chlorobenzoyl ...	28·20	1·91	2·64	0·019
o-Methylbenzoyl ...	27·80	0·18	1·79	0·046
p-Methoxybenzoyl	18·50	0·07	0·88	0·037
Cinnamoyl	16·20	—	0·76	0·009
Palmitoyl	15·60	—	0·60	~0
p-Chlorobenzoyl ...	5·40	0·22	0·29	0·009
m-Chlorobenzoyl ...	3·60	0·35	0·16	0·003
m-Nitrobenzoyl ...	0·70	6·20	0·10	0·012
p-Nitrobenzoyl ...	0·20	7·40	0·09	0·144

* Cooper's values (*J.*, 1951, 3106; 1952, 2408).

Our investigations also indicate that the value of k_i (Table 4) changes with the monomer concentration, tending to increase with dilution. Swain *et al.*[8] similarly found that the value of k_i in dioxan solution is higher than that in bulk polymerization. Nandi and Palit [6f] found the same trend in the hydrogen peroxide-initiated polymerization of methyl methacrylate, although at a very high dilution of the monomer the value again decreased, but was still higher than that for bulk. This may be attributed to the fact that in solution the peroxide decomposes more rapidly and so is able to initiate more polymer chains.

Chain-transfer Coefficients.—(1) *To monomer.* The chain-transfer coefficient (C_{M}) of

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[8] Swain *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

growing methyl methacrylate radical to monomer has been calculated from equation (2). For bulk polymerization the equation reduces to

$$1/\bar{P} = C_{\mathrm{M}} + C_{\mathrm{I}}(I/M) + \delta^2 R_p/M^2 \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

and the plot of $1/\bar{P}$ against R_p should give a straight line for those catalysts which have no chain-transfer reaction. From Fig. 6 it is evident that this plot is a straight line only for

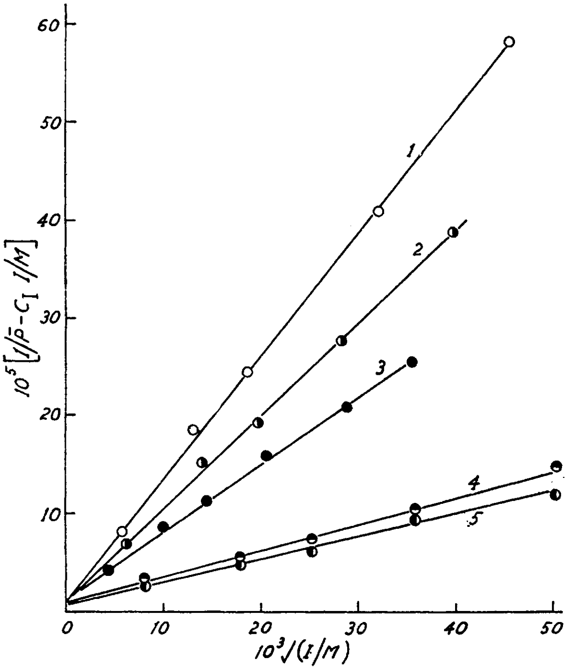

FIG. 5. *Determination of the initiation constant by the degree of polymerization method.*

1, *o*-Chlorobenzoyl peroxide.
2, *o*-Methylbenzoyl peroxide.
3, Palmitoyl peroxide.
4, *m*-Nitrobenzoyl peroxide.
5, *p*-Nitrobenzoyl peroxide.

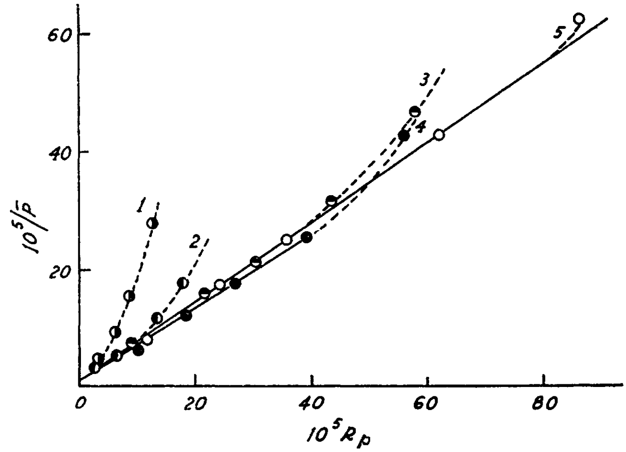

FIG. 6. *Determination of* C_{M} *at* 60°.

1, *p*-Nitrobenzoyl peroxide.
2, *m*-Nitrobenzoyl peroxide.
3, *o*-Methylbenzoyl peroxide.
4, *p*-Methoxybenzoyl peroxide.
5, *o*-Chlorobenzoyl peroxide.

palmitoyl peroxide, being curved for the other peroxides. The intercept of the straight line for palmitoyl peroxide should give the value of C_{M}. For the other peroxides C_{M} was determined from the intercept of the linear part of the curve of the plot at low concentration of the catalyst. The results are included in Table 1. The mean value of C_{M} obtained is $1{\cdot}03 \times 10^{-5}$, in agreement with the value of $1{\cdot}00 \times 10^{-5}$ reported by Baysal and Tobolsky [6d] and by Nandi *et al.*[9]

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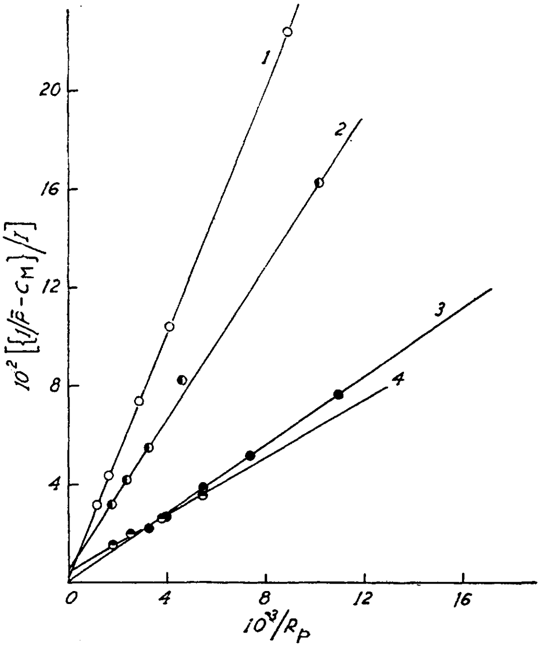
[9] Nandi *et al.*, Proceedings of International Symposium on Macromolecules, Milan, 1954, published in *Ricerca Sci.*

(2) *To catalyst.* The substituents in the benzene ring of the diacyl peroxide have a general inductive effect,[8] depending on their electro-positive or -negative character, on the radical-induced decomposition of the peroxide in solution. Cooper[1] studied the radical-induced decomposition of different diacyl peroxides in styrene and concluded that this decomposition, termed chain-transfer reaction, increases with increasing negativity of the substituents. We have carried out similar experiments to determine the radical-induced decompositions of various peroxides in methyl methacrylate at 60°. Chain-transfer coefficients with catalysts have been determined according to equation (6) from the measured value of $1/\bar{P}$ and R_p at different catalyst concentrations and from the value of C_M just determined :

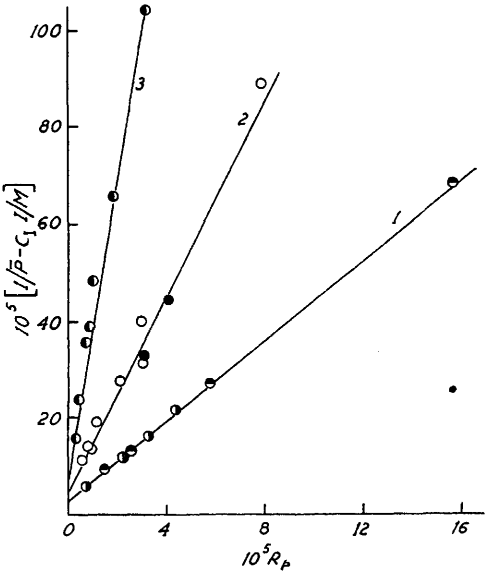
$$(1/\bar{P} - C_M)/I = C_I/M + k_i M/R_p \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

FIG. 7. *Determination of C_I at 60°.*



1, *o*-Chlorobenzoyl peroxide; 2, *o*-methylbenzoyl peroxide; 3, palmitoyl peroxide; 4, *p*-methoxybenzoyl peroxide.

FIG. 8. *Determination of C_S for ethyl acetate in polymerization catalyzed by palmitoyl peroxide.*



1, S/M = 1·112; 2, S/M = 2·594; 3, S/M = 4·448.

The results are summarized in Table 1 and represented in Fig. 7. The plot of the left-hand side of equation (6) against $1/R_p$ should give a straight line from the intercept of which the value of C_I can be calculated. The method is that used by Mayo, Gregg, and Matheson[10] for determining the value of C_I for benzoyl peroxide in the polymerization of styrene. The values of C_I thus calculated are given in Table 1, from which it is seen that the order of C_I is *o*- > *p*- > *m*- in chlorobenzoyl peroxides. Among the nitro-substituted peroxides, the *para*-isomer has an inordinately high value for C_I, in conformity with the retarding effect of the nitro-compound probably owing to the resonance stabilisation of free radicals of these peroxides. Although in the polymerisation of styrene, nitro-substituted peroxides do not follow the usual polymerization equation and abnormally high values of C_I are obtained, with methyl methacrylate the value is of normal order. A comparison of the values of C_I for methyl methacrylate and for styrene (Table 5) shows that styrene has a higher transfer constant with catalysts than methyl methacrylate.

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[10] Mayo, Gregg, and Matheson, *J. Amer. Chem. Soc.*, **1951**, **73**, 1691.

This is due to the structure of the two monomers, methyl methacrylate with an α-methyl group having a higher tendency to add than to undergo transfer reaction.

(3) *To solvent.* The monomer and catalyst transfer coefficients being known, equation (4) can be used for the determination of solvent transfer in catalyzed system. A thorough study was carried out with methyl methacrylate as monomer and ethyl acetate and toluene as solvent at 60°. The general equation (2) can be transformed into :

$$1/\bar{P} - C_I I/M = C_M + C_S S/M + \delta^2 R_p/M^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

At a constant value of S/M the plot of the left-hand side against R_p should yield a straight line from whose intercept C_S can be evaluated. From experiments with different initiators, the values of C_S so calculated agree well with that obtained from the uncatalyzed system.[4] Some typical results are represented in Figs. 8 and 9 and in Table 2.

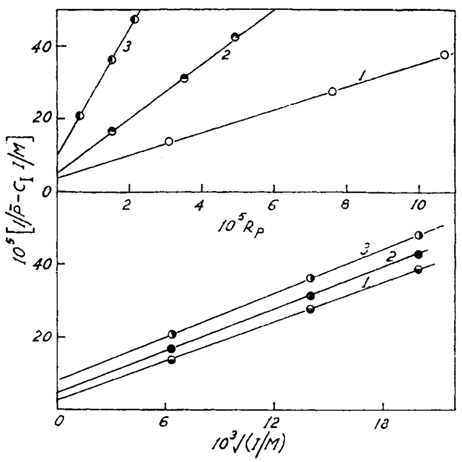

FIG. 9. *Determination of C_S for toluene in polymerization catalyzed by* o-*methylbenzoyl peroxide.*

1, S/M = 1·005; 2, S/M = 2·340; 3, S/M = 4·020.

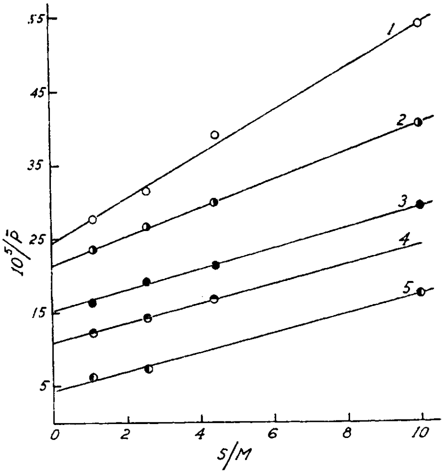

FIG. 10. *Determination of C_S for ethyl acetate in polymerization catalyzed by palmitoyl peroxide.*

$10^4 I/M$ = (1) 8·43, (2) 4·20, (3) 2·10, (4) 1·05, (5) 0·21.

Another method [7] was adopted for the determination of C_S by direct application of the general equation. Equation (2) may be written as

$$C_S = \frac{1}{S/M}\left\{\frac{1}{\bar{P}} - C_M - C_I\frac{I}{M} - \frac{\delta^2}{M^2}\cdot \quad\right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

From the values of C_M, C_I, and δ, C_S was calculated from the equation (9) and it is seen from Table 3 that it agrees well with that of the uncatalyzed one. This gives an independent check on the values of C_S as well as those of C_M and C_I determined previously.

For palmitoyl peroxide the plot of $1/\bar{P}$ against S/M at constant I/M (Fig. 10) gave good straight lines parallel to that for the uncatalyzed reaction up to a certain concentration of the peroxide, but at higher concentrations the slope tended to increase. For *m*-nitrobenzoyl and cinnamoyl peroxide, where the value of k_i is low, we again find that this plot gives the correct value of C_S (Table 3) at low concentrations of the initiator. For solvents where R_p is proportional to $M^{\frac{3}{2}}$ the general equation (2) may be transformed as follows : [7]

$$1/\bar{P} = C_M + C_S(S/M) + C_I(I/M) + \delta\sqrt{k_i}\sqrt{I/M} \quad . \quad . \quad . \quad (9)$$

At a constant value of I/M the plot of $1/\bar{P}$ against S/M for the determination of C_S, as suggested by Mayo *et al.*,[10] should give a correct value only if the last term of equation (9) is sensibly constant. Allen, Merrett, and Scanlan[11] have used the plot of $(1/\overline{P} - 1/\overline{P}_0)$ against S/M to determine C_S in the catalyzed system, instead of the conventional plot of Mayo *et al.*[10] If R_p is not proportional to $M^{\frac{3}{2}}$, or k_i varies appreciably with dilution, the term will vary with each monomer concentration and in that case Mayo's method would fail in the catalysed system.[7] Since in the present case R_p is directly proportional to $M^{\frac{3}{2}}$ at all monomer concentrations, the rise in the slope of the plot of $1/\overline{P}$ against S/M is most probably due to a large variation of the value of k_i, which has already been found to increase with dilution.

EXPERIMENTAL

Monomer.—Quinol-stabilised methyl methacrylate (National Chemical Laboratory, Poona) was purified by repeated washing with 5% aqueous sodium hydroxide followed by water. After being dried ($CaCl_2$) it was fractionally distilled twice, and the fraction of b. p. 100—100·5° collected. The purity of monomer was found to be 98—99% by the bromine addition method.[12] The absence of peroxide was ascertained by the usual iodometric method.

Solvents.—A.R. and L.R. quality samples were purified by the usual methods, dried, and fractionally distilled before use.

Preparation of Diacyl Peroxides.—All the peroxides were prepared as follows: the acid chloride (10 g.) was dissolved in chloroform (10 c.c.) and kept at 0°. To this was added a mixture of 20-vol. hydrogen peroxide (20 c.c.) and 20% aqueous sodium hydroxide (6·5 c.c.) cooled previously to 0°.[13] The peroxide was purified by repeated precipitation with methyl alcohol from chloroform solution at 0°, then dried in a vacuum desiccator at room temperature for two days. The m. p.s of the peroxides agreed with the values reported in the literature, and the purity, tested by the usual iodometric method, was 99% for most of them.

Polymerization Experiments.—Thoroughly cleaned "Pyrex"-glass ampoules of 5—8 c.c. capacity were used. Solutions of catalysts in monomer were taken in the ampoules. frozen in liquid air, and sealed under vacuum. These tubes were then suspended in an oil-thermostat at 60° (±0·05°). After about 10% of monomer conversion, the tubes were chilled, and broken open, and the polymer was freed from the monomer by double precipitation from benzene solution with alcohol. The polymer was filtered off, washed, and dried *in vacuo* to constant weight. The constancy of the results given below is typical of the reproducibility.

	Cinnamoyl peroxide (0·0272 mole/l.)				Benzoyl peroxide (0·0037 mole/l.)			
Run	Yield (%)	Time (min.)	$R_p \times 10^5$	η	Yield (%)	Time (min.)	$R_p \times 10^5$	η
I	13·08	38	53·29	0·87	7·97	40	30·86	1·50
II	13·13	38	53·30	0·86	7·90	40	30·60	1·50
III	12·9	38	52·80	0·87	7·88	40	30·10	1·505

The degree of polymerization (n) was determined from the relation $n = k[\eta]^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, and K and α are constants equal to $2·81 \times 10^{-3}$ and 1·32 respectively in benzene solution.[14] The viscosity measurements were done in benzene solution at 35° by means of Ostwald capillary viscometers, with a flow time for benzene equal to 224·3 sec. and 132·5 sec.

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[12] Kauffmann and Hartweg, *Ber.*, 1937, **70**, 2554.
[13] Hey and Walker, *J.*, 1948, 2213.
[14] Baxendale *et al.*, *J. Polymer Sci.*, 1946, **1**, 273.