452. *The Effect of Structure of Diacyl Peroxides on their Radical-induced Decomposition in Vinyl Monomers.*

By W. Cooper.

Polymerisation data have been used to calculate the rates of reaction of radicals derived from a monomer with the diacyl peroxides used as catalysts. The results have been expressed as transfer coefficients, which for substituted dibenzoyl peroxides in styrene increase with increasing negativity of the substituent. Nitro-substituted peroxides gave anomalous results, and it is suggested that in these cases a resonance-stabilised peroxide–radical complex is formed, which can participate in a termination reaction.

Aliphatic diacyl peroxides have small radical-induced decomposition reactions except when they contain conjugated double bonds. In these cases there is a marked increase. Comparison of the polymerisation data with the overall rates of decomposition shows that with aliphatic diacyl peroxides some of the peroxide decomposes without taking part in the polymerisation.

The behaviour of several peroxides in different monomers indicates that the magnitude of the radical-induced decomposition is not determined solely by the reactivity of the monomer radical.

It is well established that when diacyl peroxides decompose in solution some of the free radicals formed react with the peroxide (Cass, *J. Amer. Chem. Soc.*, 1947, **69**, 500; Bartlett and Nozaki, *ibid.*, 1946, **68**, 1686). The rate of this radical-induced decomposition is greatly dependent on the structure of the radicals derived from the solvent and this partly explains the wide variations in rate of decomposition of a peroxide in different solvents. In some cases the radical-induced reaction can be repressed by the use of reactive solvents or by the presence of certain polymerisation inhibitors (Swain, Stockmayer, and Clarke, *ibid.*, 1950, **72**, 5426). Qualitative observations by Swain *et al.* (*loc. cit.*) and by Blomquist and Buselli (*ibid.*, 1951, **73**, 3883) have shown that negative substituents in dibenzoyl peroxide increase the rate of the radical-induced decomposition, but there has been no systematic study of the influence of peroxide structure on this reaction.

When a peroxide decomposes in a polymerisable monomer, its radical-induced decomposition, which is a transfer reaction, does not influence the rate of polymerisation, but reduces the chain length of the polymer formed. It is readily shown that if the radicals from the peroxide are highly active the transfer coefficient of the peroxide $C_p(= k_{tr}/k_p$, where k_{tr} and k_p are the velocity constants for the radical-induced and chain propagation reactions respectively), which is a convenient way of expressing the magnitude of the radical-induced reaction, is given by

$$C_p = M/C[(1/\bar{P}_n - C_m) - KR_c]$$

for the initial stages of the polymerisation. $C_m(= k_t'/k_p$, where k_t' is the velocity constant for the reaction between growing polymer chains and the monomer) is the monomer transfer constant; $\bar{P}_n$ is the number average degree of polymerisation; M and C are the concentrations of monomer and catalyst respectively; R_c is the rate of the catalysed polymerisation (the effect of the thermal polymerisation has been ignored); $K = fk_t/k_p^2M^2$, where k_t is the velocity constant for chain termination. The value of f is $\frac{1}{2}$ if deactivation occurs by combination and 1 if the growing polymer chains are disproportionated.

It would be possible to calculate C_p directly from the above equation if an accurate value of K could be obtained from other data. This is as yet not possible since there is agreement neither as to the value of k_p^2/k_t nor as to the way in which the chains deactivate one-another (Matheson, Auer, Bevilacqua, and Hart, *ibid.*, p. 1701; Mayo, Gregg, and Matheson, *ibid.*, p. 1691). Moreover, it is obvious that as C_p is obtained by the difference of two numbers of comparable magnitude its value will be greatly affected by the value assigned to K. However, C_p has been determined for dibenzoyl peroxide by an independent method (Mayo *et al.*, *loc. cit.*), and this may be used for calculation of K. In this way dibenzoyl peroxide is the reference compound for the whole series and the effect of changes in structure may readily be seen.

The following data on the polymerisation of styrene at 70°, with dibenzoyl peroxide as catalyst, were used for determination of K: $C_p = 0{\cdot}075$; $C_m = 0{\cdot}85 \times 10^{-4}$, calculated from values given by Mayo *et al.* (*loc. cit.*) on the assumption that $E_{tr} - E_p = 3{\cdot}5$ kcal./mole and $E_t' - E_p = 7{\cdot}7$ kcal./mole [the values for the activation energies were obtained from the data of Bartlett and Nozaki (*loc. cit.*) and Bamford and Dewar (*Discuss. Faraday Soc.*, 1947, **2**, 311)]; $R_c = 1{\cdot}265 \times 10^{-4}$ mole l.$^{-1}$ sec.$^{-1}$; $\bar{P}_n = 970$ (from $[\eta] = 0{\cdot}69$, by use of the relation $\bar{P}_n = 1610[\eta]^{1{\cdot}37}$; Mayo *et al.*, *loc. cit.*); $M = 8{\cdot}28$ mole/l.; and $C = 0{\cdot}014$ mole/l.

Substitution of these values gives $K = 6{\cdot}5$ mole^{-1} l. sec., which will be used throughout.

The principal errors in using the equation are likely to be in the calculation of $\bar{P}_n$. Small amounts of impurities in the peroxide, or a rapid rate of decomposition, will make the value of $\bar{P}_n$ rather dependent on the degree of conversion. However, its utility may be shown by calculating C_p for dibenzoyl peroxide at 70° over a range of catalyst concentrations. The agreement between the results shown in Table 1 is reasonable, an acceptable figure from the five values being 0·07 ± 0·02. The accuracy of the relation would be better with larger values of C_p, but for very small values its accuracy will fall off greatly.

TABLE 1.

C	10^4R_c	$[\eta]$	$\bar{P}_n$	C_p	C	10^4R_c	$[\eta]$	$\bar{P}_n$	C_p
0·0070	0·903	0·90	1390	0·070	0·0550	2·49	0·38	435	0·089
0·0209	1·54	0·59	800	0·057	0·0950	3·48	0·28	315	0·066
0·0415	2·17	0·45	550	0·073					

Substituted Diacyl Peroxides.—In Table 2, *p*- and *m*-substituents are listed in order of increasing negativity, and it is seen that there is a corresponding increase in the values of C_p.

The trend is in the reverse direction to that found for the rates of the primary decomposition (Cooper, *J.*, 1951, 3106; Swain *et al.*, *loc. cit.*). Where special resonance stabilisation may occur, as discussed below, the radical-induced reaction may be very large, but in all cases withdrawal of electron density from the region of the carbonyl group and peroxide link increases the rate of the reaction. It is very difficult to give an adequate explanation for this effect. The most probable site for attack on the peroxide would be at the carbonyl group. Davison (*J.*, 1951, 2456), however, has shown from infra-red examination of the peroxides that the strength of the carbonyl group is increased by negative substituents. From this it appears that polarity alone does not determine the magnitude of the radical-induced reaction; this is further discussed in the case of the nitro-substituted peroxides.

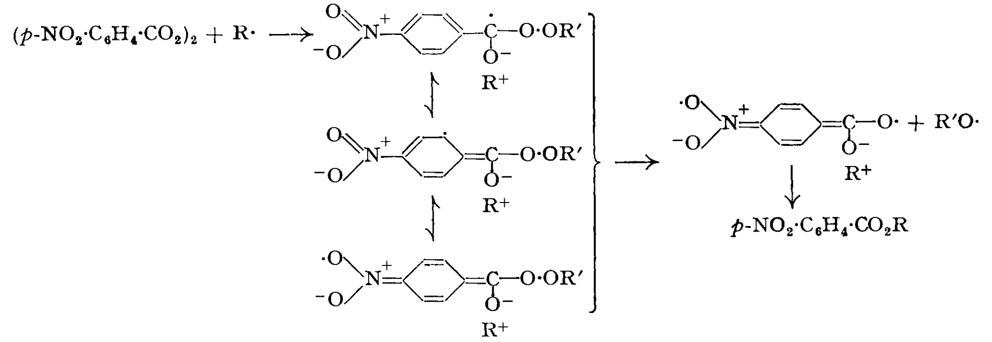
TABLE 2.

Substituent	10^4R_c	$[\eta]$	$\bar{P}_n$	C_p	Substituent	10^4R_c	$[\eta]$	$\bar{P}_n$	C_p
p-Bu^t	1·695	0·64	870	~0	*m*-F	0·910	0·66	910	0·246
p-OMe	2·050	0·51	640	0·074	*m*-I	0·910	0·65	890	0·262
p-Me	1·570	0·65	890	0·003	*m*-Cl	0·910	0·59	790	0·346
3 : 4-Benzo	1·330	0·60	800	0·178	*m*-Br	0·925	0·53	675	0·465
(H)	1·265	0·69	970	0·075	*p*-CN	0·900	0·42	490	0·804
p-O·CO$_2$Me	1·163	0·62	840	0·208	*m*-NO$_2$	0·380	0·125	93	6·2
p-OAc	1·200	0·63	850	0·187	*p*-NO$_2$	0·215	0·11	79	7·4
p-F	1·100	0·63	850	0·219					
p-Cl	1·110	0·63	850	0·216	*o*-Me	2·515	0·42	490	0·175
p-Br	1·090	0·65	890	0·193	*o*-F	1·520	0·46	565	0·40
p-I	1·110	0·58	765	0·293	*o*-Cl	2·580	0·22	200	1·91
					o-Br	4·420	0·18	150	2·17

ortho-Substituents lead to a substantial increase in the value of C_p, but when this is compared with the increased rate of primary decomposition it is seen that the fraction of peroxide decomposing by the radical-induced reaction is not greatly different from that of the *p*- or *m*-isomers.

In the determination of C_p by this method it is important to note that reliable results are obtained only if the rate of reaction of the radicals from the peroxide with the monomer (k_p') is equal to or greater than that of the chain propagation reaction (k_p). That this is so for most of these catalysts is shown by the fact that they give linear relations between R_c and $\sqrt{C}$ in vinyl monomers, including vinyl acetate for which k_p is large. It follows therefore that the peroxide radicals are highly active and that k_p' is very large. Moreover, it may be calculated, following Ri and Eyring (*J. Chem. Physics*, 1940, **8**, 433), that the polarisation effect of a substituent would have a negligible effect on the activation energy for the reaction of a free radical with styrene (the fractional electronic charge on the β-carbon atom of styrene is not greater than $0·1 \times 10^{-10}$ e.s.u.; hence the energy change brought about by a substituent on an attacking radical will be very small).

It was not found possible to obtain satisfactory results with the nitro-substituted peroxides. The reaction rates were abnormally small and, therefore, the calculated transfer constants were too large. It is of some interest to consider the manner by which these compounds inhibit the polymerisation. There is no doubt but that nitro-substituted aryl or acyloxy-radicals are of fairly high activity. They can attack relatively inert aromatic solvents such as benzene (Hey and Walker, *J.*, 1948, 2213) and it is difficult to visualise any way in which the nitro-group could stabilise free radicals of this type by resonance effects. It is necessary to assume that the radicals produced in the induced decomposition are of low activity or that there is a rapid termination reaction between the monomer and peroxide radicals. As regards the first suggestion, free-radical attack on the nucleus to give stable radicals could occur in the way suggested by Price (*Ann. N.Y. Acad. Sci.*, 1943, **44**, 367), since Wheland's calculations (*J. Amer. Chem. Soc.*, 1942, **64**, 900) show that a nitro-group activates *meta*-positions in the nucleus to attack by a free radical. Alternatively, reaction could occur at the carbonyl groups in the peroxide with resonance stabilisation of the intermediate complex. For example, with di-*p*-nitrobenzoyl peroxide the following reaction is suggested.



R· is a styrene polymer radical, and R′ = p-NO_2·C_6H_4·CO.

Attack may be facilitated by favourable energy contributions from the R^+ ion in the way suggested by Walling and Mayo (*Discuss. Faraday Soc.*, 1947, **2**, 295) and may account for the specific character of the radical-induced reaction. An interesting feature of this scheme is that an oxygen atom from the peroxide link is the carbonyl oxygen atom in the ester molecule formed.

The fact that di-*m*-nitrobenzoyl peroxide decomposes more rapidly in styrene than in benzene, notwithstanding the usual inhibiting effect of styrene on such reactions (Swain *et al.*, *loc. cit.*), suggests that some such interaction occurs. Moreover, when this peroxide was decomposed in styrene no less than 77% was isolated as *m*-nitrobenzoic acid and most of this (83%) was combined with the polymer.

The abnormal relation between the rate of polymerisation and catalyst concentration would also be explained by the presence of a stable intermediate complex which could participate in a termination reaction with growing polymer chains. The total free-radical concentration and, therefore, the reaction rate, would be greatly reduced. The retarding effect would be dependent on the relative velocities of unimolecular breakdown into a free radical and an ester molecule and termination with a polymer radical. In extreme cases the rate of polymerisation would be almost independent of the catalyst concentration as is found, for example, in the case of di-*m*-nitrobenzoyl peroxide (Cooper, *Nature*, 1948, **162**, 927). An alternative explanation which cannot be excluded is a rapid "crossed" termination reaction between the polymer radicals and catalyst radicals (Arlman, Melville, and Valentine *Rec. Trav. chim.*, 1949, **68**, 945). This type of reaction would also cause a marked decrease in the rate of polymerisation.

Determination of C_p at different temperatures should give its temperature coefficient. It should be relatively small, however, since E_{tr} is not greatly different from E_p ($EC_p = E_{tr} - E_p$). The results given for dibenzoyl peroxide at various temperatures in Table 3 bear this out. The appropriate values for C_m and K at the different temperatures were calculated from $E_t' = 14$ kcal./mole, $E_p = 6{\cdot}5$ kcal./mole, and $E_t = 2{\cdot}8$ kcal./mole (Bamford and Dewar, *loc. cit.*); $C = 0{\cdot}014$ mole/l. in all cases.

TABLE 3.

Temp.	10^4R_c	$[\eta]$	$\bar{P}_n$[a]	C_p
40°	0·063	1·59	3040	0·075
50	0·180	1·18	2030	0·091
60	0·480	0·87	1330	0·125
70°	1·265	0·69	970	0·075
80	3·00	0·50	616	0·166

[a] The same $[\eta]$–$\bar{P}_n$ relation has been assumed for all temperatures.

There is a definite tendency for C_p to increase slightly with rise in temperature, but the results are insufficiently accurate for an estimate to be made of the energy of activation of C_p, which would only be of the order of 2—3 kcal./mole.

Aliphatic Diacyl Peroxides.—Straight-chain, saturated diacyl peroxides have similar values of C_p, although there is an increase as the series is ascended.

The results for dioctanoyl peroxide may be taken as an example : $10^4 R_c = 2{\cdot}17$; $[\eta] = 0{\cdot}48$; $\bar{P}_n = 595$; $C_p = 0{\cdot}098$.

The values for the other peroxides in this group were :

Carbon atoms in chain	2	4	6	12	14	16	18
C_p	~0	0·018	0·166	0·024	0·116	0·142	0·154

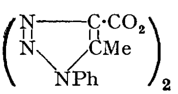
Unsaturation distant from the carbonyl group was without effect; for example, for dioleoyl peroxide $C_p = 0{\cdot}154$, and for dihendec-10-enoyl peroxide $C_p = 0{\cdot}065$. When conjugated groupings were present the effects were very pronounced.

Conjugation of an ethylenic bond with the carbonyl group has a small effect, but two double bonds in the side chain considerably increase the transfer constant. The increase is more marked when there is conjugation with a benzene ring, as in dicinnamoyl peroxide. [Reduction of the aliphatic double bond, to give bis-β-phenylpropionyl peroxide, reduces the transfer constant to that of a normal, short-chain, saturated acyl peroxide ($C_p \sim 0$).] Further conjugation, in bis-5-phenylpenta-2 : 4-dienoyl peroxide, gives very high values, although here the rate of polymerisation appears to be anomalously low. The results are summarised in the following Table :

Peroxide	C_p	Peroxide	C_p
Dibut-2-enoyl	0·146	Dicinnamoyl	1·10
Dihexa-2 : 4-dienoyl	1·19	Bis-5-phenylpenta-2 : 4-dienoyl	5·24

The effects of unsaturated groupings are observed in other types of peroxides. For example, β-carbo-*tert.*-butoxyacryloyl peroxide gave the expectedly high value of $C_p = 1{\cdot}52$, typical of an unsaturated acyl grouping. On the other hand the not dissimilarly constituted *o*-carbo-*tert.*-butoxybenzoyl peroxide gave $C_p = 0{\cdot}018$, which is what might be expected for the aromatic grouping.

The influence of heterocyclic groupings is not readily predicted. Difuroyl peroxide is a very inefficient polymerisation catalyst (Frank, Blegen, and Deutschmann, *J. Polymer Sci.*, 1948, **3**, 58); the heterocyclic peroxide (I) is of high activity ($C_p = 0{\cdot}23$ at $C = 0{\cdot}0025$ mole/l.).



(I)

It is necessary to examine these unsaturated peroxides in more detail, as it is possible that they may act as co-monomers in addition to being polymerisation catalysts. If this is so, their chain-terminating effect may be due to the formation of end groups which are inefficient in attacking further monomer molecules. This could result in complications of chain branching and in other chain-termination reactions. The effect of changes of catalyst concentration and temperature on reaction rate and chain length were studied for dicinnamoyl and bis-5-phenylpenta-2 : 4-dienoyl peroxides, and, for comparison, dibenzoyl peroxide (Figs. 1*a* and *b* and 2*a* and *b*). Dicinnamoyl peroxide initiates the polymerisation normally but bis-5-phenylpenta-2 : 4-dienoyl peroxide gives a non-linear relation; the overall activation energy of the polymerisation, however, does not vary appreciably with the three peroxides.

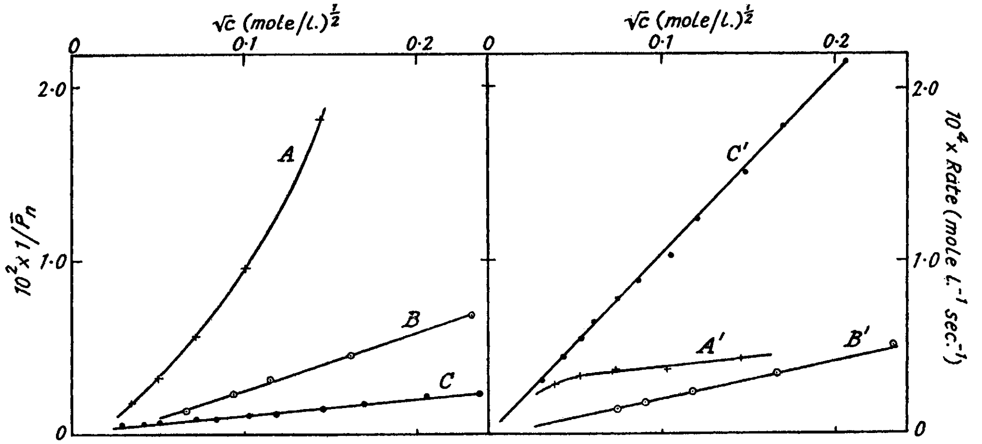
The effect on chain length is more marked, and deviation from linearity for the two unsaturated peroxides is evidence of the radical-induced decomposition. With these two peroxides the small effect of change of temperature on the chain length compared with the normal case of dibenzoyl peroxide shows the chain-termination step to have low activation energy. It is considered that, in the case of bis-5-phenylpenta-2 : 4-dienoyl peroxide, resonance stabilisation of the peroxide facilitates attack by the monomer radicals, giving intermediate complexes which terminate growing chains. The behaviour of the peroxide in other ways in the polymerisation appears to be quite normal. Mr. C. E. Kendall has carried out an ultra-violet spectroscopic examination of the polymer catalysed by this peroxide. Maxima at 302 and 325 mμ show that the polymer contains hydrocarbon and ester end groups derived from the peroxide. Hydrolysis of the polymer removes the ester absorption (the identity of this absorption was proved by comparison with ethyl

5-phenylpenta-2 : 4-dienoate). The extinction coefficients, by comparison with the pure reference compounds, show that the ester groups predominate over the hydrocarbon end groups (in the ratio of 1·6 : 1) as would be expected from the large radical-induced reaction, and that there is one end group to 34 styrene units. Viscosity measurements on the same polymer give 40 monomer units to each end group.

Further information can be derived by comparing the catalyst taking part in the polymerisation with that actually decomposing (k_d). The total amount of peroxide taking part in the polymerisation, when expressed as a "first-order" velocity constant, is given by $k_i + C_pk_p\sqrt{2k_iC/k_t}$.* Values of k_i were taken from the rates of polymerisation (Cooper, *loc. cit.*) and $k_p/\sqrt{k_t}$ from Bamford and Dewar's data (*loc. cit.*). The results given below are at $C = 0{\cdot}014$ mole/l. and, except where stated, at 70°. It is seen that with the aliphatic diacyl peroxides there is a considerable difference between the values for peroxide

FIG. 1.

(*a*) *Chain length.* (*b*) *Polymerisation rate.*



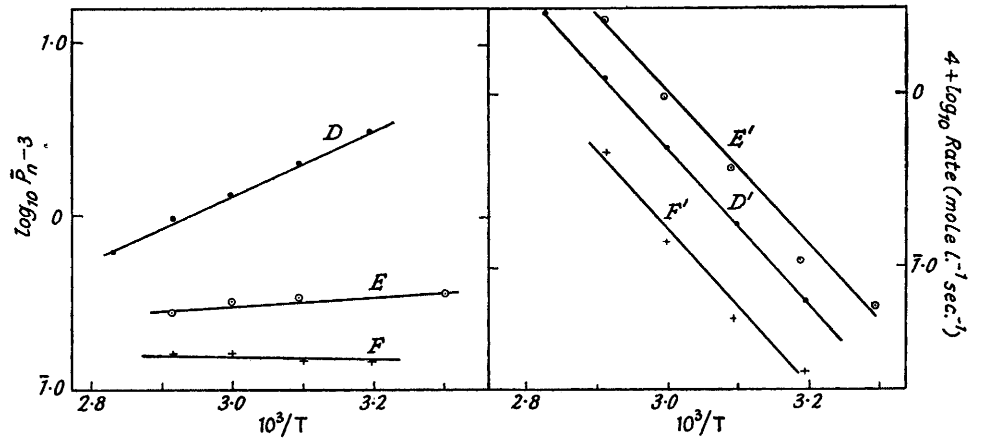


FIG. 2.

(*a*) *Chain length.* (*b*) *Polymerisation rate.*

● *Dibenzoyl peroxide.*
⊙ *Dicinnamoyl peroxide.*
+ *Bis-5-phenylpenta-2 : 4-dienoyl peroxide.*

AA' 70°; *DD'*, 0·014 *mole/l.*
BB', 50°; *EE'*, 0·025 *mole/l.*
CC', 70°; *FF'*, 0·010 *mole/l.*

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* This is an approximation, a single value being assumed for k_t. The polymerisation actually involves several termination reactions, but there is little error if the catalyst radicals are of high activity.

taking part in the polymerisation and that for peroxide decomposing. Redington (*loc. cit.*) observed this in the case of dilauroyl peroxide, using the rates of polymerisation and peroxide decomposition. His identification of the "wasted" catalyst with a radical-induced decomposition is, however, unjustified. Both reaction rate and chain-length determinations show that dilauroyl peroxide initiates polymerisation about 2·5 times as fast as dibenzoyl peroxide, whereas it decomposes about five times as fast as the latter. These results are comparative and such a large discrepancy cannot be explained by errors in experiment or in the values of the absolute velocity constants assumed for calculation, and it must be concluded that some other reaction occurs. The two most probable are ionic fission of the peroxide link and decomposition of the peroxide into inactive products in the "cage" reaction suggested by Matheson (*J. Chem. Physics*, 1945, **13**, 584).

Peroxide	$(k_i + C_p k_p \sqrt{2k_iC/k_t}) \times 10^6$, sec.$^{-1}$	$k_d \times 10^6$, sec.$^{-1}$
Dibenzoyl	8·0	9·1 (*a*)
Di-*p*-chlorobenzoyl	8·2	10·3 (*a*)
Bis-*β*-phenylpropionyl	20·5	55 (*b*)
Dilauroyl	19·2	52 (*a*)
Dicinnamoyl	41·0	167 (*b*)
,, (at 50°)	3·6	12·0 (*b*)
Bis-5-phenylpenta-2 : 4-dienoyl	(28)	218 (*b*)
Bisphenylacetyl (at 0°)	(28)	78 (*b*)

(*a*) Redington, *J. Polymer Sci.*, 1948, **3**, 503. (*b*) Author, unpublished results.

It is improbable that the rate of reaction of a free radical with a peroxide is determined solely by the activity of the free radical involved. This is supported by experiments carried out in different monomers (Table 4). The results show several features of interest. Dicinnamoyl peroxide behaved as would be expected. It had a comparable catalytic activity in styrene and methyl methacrylate, but was a very inefficient catalyst for the less reactive vinyl acetate. (Dicinnamoyl peroxide has, in fact, a marked retarding effect on the polymerisation of vinyl acetate catalysed by dibenzoyl peroxide.) Di-2 : 3 : 4 : 5-tetrachlorobenzoyl peroxide, however, behaves normally in methyl methacrylate and vinyl acetate (dimyristoyl peroxide being taken as a reference compound) whereas in styrene there is a marked chain-transfer reaction. Dibut-2-enoyl peroxide initiates the polymerisation of styrene and vinyl acetate normally but terminates the reaction chains in the latter monomer; it is possible in this case that the peroxide may act as a monomer of low reactivity. These examples show clearly that generalisations concerning radical-catalyst interaction can be made only with great caution.

TABLE 4.

	Styrene [a]		Methyl methacrylate [b]		Vinyl acetate	
Peroxide	10^4R_c	$[\eta]$ *	10^4R_c	$[\eta]$ *	10^4R_c	$[\eta]$ *
Dimyristoyl	2·06	0·49	1·30	1·75	2·30	1·37
Dibut-2-enoyl	2·53	0·42	—	—	2·74	0·24
Dicinnamoyl	1·92	0·31	1·32	1·40	0·07	0·06
Di-2 : 3 : 4 : 5-tetrachlorobenzoyl	1·390	0·06	1·22 [d]	1·80	1·58 [e]	0·69

[a] At 70°; 0·014 mole/l. [b] At 60°; 0·010 mole/l. [c] At 50°; 0·005 mole/l. [d] 0·0039 mole/l. 0·0017 mole/l.

* Intrinsic viscosities determined in benzene solution.

EXPERIMENTAL

The preparation of the peroxides and the measurement of the polymerisation rates have been described previously (Cooper, *locc. cit.*).

The polymer was purified by precipitation by alcohol from a 1—2% solution in carbon tetrachloride. After filtration and washing with alcohol, it was dried at room temperature *in vacuo*, and then in an oven at 70°.

The intrinsic viscosities were obtained from the flow times of benzene solutions in Ostwald viscometers (kinetic-energy corrections were not introduced since the Reynolds numbers of the systems examined were low—*ca.* 10).

The temperature of the bath was 32·385° ± 0·005°.

The intrinsic viscosities were found graphically from plots of $(\eta_{sp}/c) - c$, $\log_e \eta_r/c - c$, and $\eta_{sp}/c - \eta_{sp}$; all gave substantially the same value for $[\eta]$ (concn. : g./100 ml.).

*Decomposition of Di-*m*-nitrobenzoyl Peroxide in Styrene.*—Di-*m*-nitrobenzoyl peroxide (2·034 g.) in styrene (100 ml.) was heated at 70° for 6 hours and then at 100° for 1 hour. *m*-Nitrobenzoic acid (0·275 g.) was obtained by extraction with potassium hydrogen carbonate solution. A further quantity of *m*-nitrobenzoic acid (1·297 g.) was obtained by hydrolysis with alcoholic potash of the polystyrene (6·873 g.; $[\eta] = 0{\cdot}046$) isolated from the styrene solution by precipitation with alcohol.

5-*Methyl*-1-*phenyl*-1 : 2 : 3-*triazole*-4-*carboxyl Peroxide.*—The acid (m. p. 151°) was obtained by Dimroth's method (*Ber.*, 1902, **35**, 1029), and the acyl chloride (m. p. 132°) was obtained from it by treatment with thionyl chloride (Found: Cl, 16·4. Calc. for $C_{10}H_8ON_3Cl$: Cl, 16·0%). The acyl chloride (1·5 g.) in ether was shaken with sodium peroxide (1·0 g.) in ice-water. The white precipitate of *peroxide* was filtered off (0·4 g.) and recrystallised from chloroform. It had m. p. 166° (decomp.) [Found (mean of several analyses by Mr. G. L. Coulter): C, 59·4; H, 4·2; N, 20·6. $C_{20}H_{16}O_4N_6$ requires C, 59·4; H, 4·0; N, 20·8%]. Its identity was proved by hydrolysis to the acid.

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Chemical Research Division,
Dunlop Research Centre, Birmingham, 24.

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