TABLE I

INFRARED ABSORPTION BANDS OF Ar—N—O—C(CH₃)₂ IN THE 7.5-12 μ REGION OF THE SPECTRUM[a,b,c]

$$NC—C(CH_3)_2CN$$

Ar Wave lengths, μ, →	7.5–8.0	8.0–8.5	8.5–9.0	9.0–9.5	9.5–10.0	10.0–10.5	10.5–11.0	11.0–12.0
o-Nitrophenyl	7.72w	8.22m	8.62s	9.19w	9.58w	10.25w	10.6m	11.23w
	7.84w	8.33m	8.73m		9.82w	10.42w	10.96w	11.45m
		8.43m						11.74m
m-Nitrophenyl[14]	7.63w	8.16m	8.55s	9.23m	9.80w	10.42m	10.55w	11.14m
	7.85w	8.24m	8.63s		9.98w		10.74w	11.48w
		8.34m						11.72m
p-Nitrophenyl	7.63m	8.15m	8.58s	9.05s	9.82w	10.25w	10.70w	11.38s
	7.76w	8.20m	8.67s		9.95w	10.37m	11.00w	11.56m
		8.38m				10.42m		11.73s
								11.95*w*
2-[2-(Cyano-2-propoxy)-4-nitrophenyl]	7.68m	8.28s	8.67s	9.20m	9.82w	10.20m	10.72w	11.09w
	7.98s		8.92m			10.45m		11.32m
								11.46m
								11.95w
3,5-Dinitrophenyl	7.55m	8.04w	8.55s	9.04w	9.69w	10.08w	10.50w	11.10w
		8.12w	8.62s	9.25m		10.16m	10.58w	11.40w
		8.30w				10.45w	10.81m	11.80w
		8.42w					10.94s	

[a] w = weak absorption, m = moderate absorption, s = strong absorption. [b] The first four compounds were prepared for infrared scanning using the pressed KBr window technique. The last compound, Ar = 3,5-dinitrophenyl, was prepared as a Nujol mull. [c] The first four compounds showed an extremely weak C≡N absorption at 4.5 μ but the last compound showed none at all.

The products were isolated in the same manner as in the reaction of II with hydrobromic acid. The first material to come off the chromatographic column was 0.087 g. (24% yield) of 4-bromo-2-nitroaniline, m.p. 111–112° (lit.[17] m.p. 111.5°). Next came 0.074 g. (32% yield) of o-nitroaniline 68–70°. Recrystallization from hot water raised the melting point to 70–71°. A mixture melting point with an authentic sample of o-nitroaniline (m.p. 70–71°) did not show depression. There were additional small quantities of material on the column, but no attempt was made to isolate and identify these.

Reductive Acetylation of N-(p-Nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II).—Two grams of zinc dust and 0.27 g. (0.00093 mole) of II were added to 20 ml. of acetic anhydride. The mixture was heated to reflux for 10 min., and then filtered. The excess acetic anhydride was removed by distillation at 0.1 mm. pressure. The residue was washed with water and filtered. The solid residue

was recrystallized from ethanol to give about 5 mg. of diacetyl-p-phenylenediamine, m.p. 300–301°. A mixture melting point with an authentic sample of diacetyl-p-phenylenediamine (m.p. 303–304°) showed no depression.

Infrared Spectra.—Waters[6] published infrared absorption data on a number of di- and trisubstituted hydroxylamines. He was unable to assign any particular band as being diagnostic of the hydroxylamine group but noticed that there were four sharply defined bands in the 8–9 μ region and grouped bands in the 9.5–11.5 μ region. These are regions where the N–O bond of hydroxylamine might be expected to absorb. In Table I are listed infrared absorption bands in the 7.5 to 12 μ region of five additional trisubstituted hydroxylamines. There are certain similarities in the pattern of absorptions in Table I and Waters'[6] compilation. No speculations will be made here regarding assignments of bands to specific bonds.

The samples were prepared and the infrared absorption spectra determined by Dr. Allen L. Olsen of this Laboratory.

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(17) F. D. Chattaway, K. J. P. Orton and R. C. T. Evans, *Ber.*, **33**, 3057 (1900).

Oxidation of Vinyl Monomers[1]

BY ELIZABETH DYER, STEWART C. BROWN AND ROBERT W. MEDEIROS

The rates of absorption of oxygen by acrylonitrile and by methacrylonitrile at 50° and atmospheric pressure in chlorobenzene and bromobenzene solutions are dependent on the first power of the monomer concentration and the one-half power of the concentration of the azo initiator, 2,2'-azobis-(2-methylpropionitrile). The initial rates of oxidation of several other α-alkylacrylonitriles have been determined. Relatively stable 1:1 copolymers of the α-alkylacrylonitriles with oxygen have been characterized.

Recently there have been extensive studies by Mayo and co-workers[2–5] on the action of oxygen on

various unsaturated compounds, from the point of view of both products and mechanisms. This paper reports a continuation of our work,[6] chiefly on the nitrile monomers. Studies have been made

(1) From the Ph.D. thesis of Stewart C. Brown, 1957, and the M.S. thesis of Robert W. Medeiros, 1957.

(2) A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956).

(3) F. R. Mayo and A. A. Miller, *ibid.*, **78**, 1023 (1956).

(4) G. A. Russell, *ibid.*, **78**, 1035 (1956).

(5) F. R. Mayo and co-workers, *ibid.*, **80**, (a) 2465, (b) 2480, (c) 2493, (d) 2497, (e) 2500 (1958).

(6) (a) K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952); (b) E. Dyer, O. A. Pickett, Jr., S. F. Strause and H. E. Worrell, Jr., *ibid.*, **78**, 3384 (1956); (c) S. F. Strause and E. Dyer, *ibid.*, **78**, 136 (1956).

on rates and products of oxidation in non-aqueous solutions, usually with 2,2'-azobis-(2-methylpropionitrile), hereafter called ABN, as initiator. Most of the work was done on acrylonitrile and on its α-methyl, ethyl, n-propyl, isopropyl and n-amyl homologs; limited comparative data were obtained on methyl vinyl ketone and methyl isopropenyl ketone.

Experimental and Results

Materials.—Acrylonitrile[6b] and methacrylonitrile[6c,7] were purified as previously described. Methyl vinyl ketone[8] was dried and distilled immediately before use; b.p. 81.5°, $n^{25}D$ 1.4210. Methyl isopropenyl ketone[9] was distilled, b.p. 98°, $n^{25}D$ 1.4210. ABN was recrystallized from ethanol. Bis-(o-chlorobenzoyl) peroxide was prepared according to the method of Blomquist and Buselli.[10] Solvents were dried and distilled.

α-Alkylacrylonitriles.—These compounds, all prepared by pyrolysis of the acetate esters of the appropriate ketones by the method described by Bailey, Naylor and Hewitt,[11] had the following constants: α-ethylacrylonitrile,[11] b.p. 113°, $n^{20}D$ 1.4133; α-isopropylacrylonitrile,[12] b.p. 126–127°, $n^{20}D$ 1.4159 (the absence of carbonyl was shown by infrared spectrum; a lower index was reported[12] on a slightly impure specimen prepared in a different way); α-n-propylacrylonitrile,[11,13] b.p. 137°, $n^{20}D$ 1.4224; α-n-amylacrylonitrile,[13] b.p. 57–60° at 10 mm., $n^{24}D$ 1.4331.

Procedure for Kinetic Experiments.—The reactions were done in a flask immersed in a water-bath at 50 ± 0.1°. The flask was connected to equipment arranged for measuring the volume of dry oxygen absorbed at constant pressure.[6b,14] Stirring was maintained at 2500 r.p.m. The capacity of the flask was 500 ml. for most of the experiments done in solution at a volume of 100 ml.; for experiments with 25 ml. of undiluted monomer a 100-ml. flask was used.

To the flask was added an accurately weighed portion of initiator and known quantities of monomer and solvent. After flushing the reaction flask with oxygen, the system was closed and allowed to come to equilibrium for 10 to 15 minutes. Then the reaction was set for measurement of oxygen absorbed, with observations over periods of 8 hours. Initial slopes of the straight-line graphs of oxygen consumption *versus* time were calculated by the method of least squares.

Kinetic Data Using ABN.—Tables I and II give data on oxygen absorbed by acrylonitrile and methacrylonitrile at various initiator concentrations, at a total pressure of one atmosphere. Table III shows the rates of absorption of oxygen by various α-alkylacrylonitriles at a single concen-

TABLE I
RATES OF ABSORPTION OF OXYGEN BY ACRYLONITRILE IN CHLOROBENZENE[a] AT 50° WITH ABN INITIATOR

[ACN],[b] M	[ABN],[c] M	$R_0{}^d \times 10^2$ mole/l./hr.	Rate/ [ACN][ABN]$^{1/2}$
4.00	0.010	0.421	0.0105
2.00	.010	.210	.0105
1.50	.010	.137	.0092
1.50	.005	.093	.0088
1.50	.015	.162	.0088
1.50	.025	.221	.0093
0.75	.010	.069	.0092

[a] Volume of solution 100 ml. [b] Acrylonitrile concentration. [c] Azobis-(2-methylpropionitrile). [d] Rate of absorption of oxygen.

(7) Kindly supplied by the Shell Development Co.

(8) Kindly furnished by the C. S. Pfizer Co.

(9) Kindly supplied by the Celanese Corporation.

(10) A. T. Blomquist and A. J. Buselli, THIS JOURNAL, **73**, 3883 (1951).

(11) W. J. Bailey, F. E. Naylor and J. J. Hewitt, *J. Org. Chem.*, **22**, 1076 (1957).

(12) C. S. Marvel, W. R. Miller and L. C. Chou, THIS JOURNAL, **72**, 5408 (1950).

(13) A. Vermeulen and L. Adriaens, *Bull. soc. chim. Belg.*, **38**, 301 (1929).

(14) L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1251 (1949).

TABLE II
RATES OF ABSORPTION OF OXYGEN BY METHACRYLONITRILE AT 50° WITH ABN INITIATOR

[MACN],[a] M	[ABN], M	$R_0{}^d \times 10^2$, moles/l./hr.	Rate [MACN] [ABN]$^{1/2}$
		Bromobenzene solution[b]	
11.95[c]	0.0026	2.45	0.039
11.95[c]	.0102	4.67	.039
11.95[c]	.0410	8.77	.041
5.98	.0102	2.38	.040
4.05	.0100	1.58	.039
3.50	.0100	1.38	.039
2.50	.0100	0.98	.039
2.39	.0102	.98	.036
1.50	.0100	.51	.034
0.75	.0100	.22	.030
		Chlorobenzene solution[e]	
3.44	0.0100	1.25	0.036
2.98		1.05	.035
2.38		0.78	.033
1.94		.62	.032
1.50		.46	.031
0.75		.21	.028
0.375		.088	.023

[a] Methacrylonitrile concentration. [b] Volume of reaction mixture 25 ml. except as specified. [c] Undiluted monomer. [d] Rate of absorption of oxygen. [e] Volume of reaction mixture 100 ml.

TABLE III
RATES OF ABSORPTION OF OXYGEN BY $CH_2=CXY$ WITH 0.01 M ABN AT 50°

Monomer X	Monomer Y	$R_0{}^a \times 10^2$, moles/l./hr.	Reactivity,[b] $100k$
		Monomer concn. 0.75 M in chlorobenzene	
H	CN	0.069	0.092
CH_3	CN	.210	.28
C_2H_5	CN	.173	.23
n-C_3H_7	CN	.150	.20
i-C_3H_7	CN	.128	.17
n-C_5H_{11}	CN	.123	.16
		Undiluted monomer	
H[c]	CN	1.8	0.10
C_2H_5	CN	3.60	.36
H	$COCH_3$	1.20	.096
CH_3	$COCH_3$	1.60	.15
CH_3	$OCOCH_3$	0.15	.017

[a] Rate of absorption of oxygen. [b] Reactivity factor, k, is R_0/molar concn. of monomer. [c] Data of Mayo and co-workers.[5a]

tration of monomer and initiator, and also comparative data for undiluted monomers. Monomer vapor pressure has been neglected.

Kinetic Data on Acrylonitrile with a Peroxide Initiator.—The absorption of oxygen by acrylonitrile in bromobenzene solution using a peroxide initiator is shown in Table IV. A blank test showed that no oxygen was absorbed by solvent and initiator in the absence of monomer. Good straight lines were obtained for the graphs of oxygen absorbed *versus* time over 8-hour periods.

Preparation of Polymeric Peroxides.—A rapid stream of dry carbon dioxide-free oxygen was introduced through a gas dispersion tube into a solution of ABN in monomer, which was agitated by a magnetic stirrer in an air-bath kept at 50 ± 2° by an infrared lamp. The reaction flask was always covered by aluminum foil. The exit gases were passed through a 50-cm. Graham condenser into a trap for formaldehyde.

TABLE IV

OXYGEN ABSORPTION BY ACRYLONITRILE IN BROMOBENZENE
WITH BIS-(o-CHLOROBENZOYL) PEROXIDE AT 50°

[ACN], M	[Peroxide] $\times 10$, M	$R_0 \times 10^3$, mole/l./hr.	Rate [ACN]$^{1.6}$[peroxide]$^{0.6}$
0.36	0.74	0.121	2.96
.48	.74	.196	3.02
.62	.74	.272	2.79
.75	.74	.404	3.06
.75	.52	.340	3.20
.75	.35	.264	3.12
.75	.18	.147	2.91

should be multiplied by a factor of 1.2 (deduced from Table VI) and (2) that all of the formaldehyde formed was swept out of the reaction mixture and precipitated in the trap, it was estimated that 0.017 mole of peroxide was formed per 0.00059 mole of formaldehyde, or approximately 30 moles of peroxide for every mole of formaldehyde during the first four hours of oxidation. From the data of Table II for pure monomer the oxygen absorbed during four hours with 0.015 M ABN was calculated to be approximately 0.018 mole. Therefore even if assumption (2) above is not correct, the proportion of oxygen consumed in forming formaldehyde is probably not greater than 1 mole per 17 moles of peroxide during the first four hours.

In the preparation of the polymeric peroxide of ethacrylonitrile under the same conditions, 0.017 mole of peroxide

TABLE V

PREPARATION OF POLYMERIC PEROXIDES $[-CH_2C(CN)(R)OO-]_n$

Monomer R	Mole used	[ABN], M	Time, hr.	Yield, %	D.P.^{a,b}	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
CH$_3$	0.89	0.015	48	15.3	8–18	48.48	5.09	14.14	49.13	5.42	13.51
C$_2$H$_5$	.62	0	37	15.8	4	53.09	6.24	12.38	52.56	6.87	12.01
C$_2$H$_5$	.82	0.020	66	20.5	6				53.05	6.53	
C$_2$H$_5$	.80	.015	58	16.4	6				53.30	5.34	11.67
i-C$_3$H$_7$	.14	.015	59	8.5		56.65	7.14	11.02	56.75	6.98	10.96
n-C$_5$H$_{11}$	.45	.015	63	18.6	4	61.92	8.44	9.02	61.98	7.65	8.16

^{a} Degree of polymerization, estimated from cryoscopic molecular weight in ethylene bromide. ^{b} The explosive decomp. temp. of all the peroxides was in the range 140–160°.

The polymeric peroxide was precipitated as a heavy oil by adding petroleum ether and the oil was separated and subjected to reduced pressure at room temperature, first with a water pump and then with a high vacuum pump^{5a} in order to remove remaining solvent, monomer and other volatile products. In the case of the α-isopropyl- and α-n-amylacrylonitriles, the precipitation with petroleum ether was omitted and all non-polymeric material was removable solely by evaporation at 50° and 0.5 mm. The peroxides, which in all cases were transparent viscous materials, were stored in a refrigerator. There was no evidence of the formation of normal polymer with any of the monomers treated with oxygen under these conditions. The results of the preparation of polymeric peroxides are shown in Table V.

No effort was made to identify all the oxidation products, but it was shown that formaldehyde was produced simultaneously with the polymeric peroxide in the case of every alkylacrylonitrile. It was collected as the 2,4-dinitrophenylhydrazone, or dimedon derivative identified by mixed melting points with authentic samples.

Another oxidation product of α-ethylacrylonitrile was α-ketobutyronitrile, separated from the petroleum ether washings of the polymeric peroxide. It was identified by (a) reaction with water to give propionic acid and hydrogen cyanide and (b) hydrolysis to a mixture of α-ketobutyramide and α-ketobutyric acid by treating^{15} with concd. hydrochloric acid at 0° and then boiling for one minute. The α-ketobutyramide and α-ketobutyric acid form 2,4-dinitrophenylhydrazones, m.p. 240° and 218°, respectively, which are separable with sodium carbonate.

Peroxide Analysis.—In a previous paper^{6c} from this Laboratory the Nozaki method^{16} was used for analysis of the polymeric peroxide of methacrylonitrile. Because of some doubt as to the validity of the results, fresh samples of this polymer and of the polymeric peroxides from other alkylacrylonitriles were analyzed in three ways: by (a) the Nozaki method, (b) the hydriodic acid method of Miller and Mayo^2 and (c) carbon, hydrogen and nitrogen determinations. The results are shown in Table VI.

Relative Proportions of Polymeric Peroxide and of Formaldehyde.—During the preparation of polymeric peroxides formaldehyde was isolated from the exit trap as the 2,4-dinitrophenylhydrazone and peroxides were estimated by the Nozaki titration.^{16} After 4 hours of rapid passage of oxygen into 75 ml. of pure methacrylonitrile at 50° containing 0.015 M ABN, there was no precipitate of formaldehyde polymer in the condenser which preceded the trap. By assuming (1) that peroxide values from the Nozaki titration

TABLE VI

ANALYSES FOR PEROXIDIC OXYGEN IN POLYMERS $(-CH_2CR-(CN)O_2-)_n$

R	Theor. oxygen, %	Found, % N.^{a}	Found, % M.^{b}	Found, % E.^{c}
CH$_3$	32.29	26.45	32.20	31.94
C$_2$H$_5$	28.29	17.17	27.40	28.56
i-C$_3$H$_7$	25.17	21.28	24.65	25.09
n-C$_5$H$_{11}$	20.62	10.69	20.43	22.21

^{a} Nozaki method.^{16} ^{b} Method of Miller and Mayo.^{2} ^{c} By difference from elementary analysis for C, H, N.

and 0.00040 mole of formaldehyde were obtained in four hours.

The experiments on rate of oxygen absorption were carried on for eight hours in a closed system. From the above data it can be concluded that the proportion of cleavage is probably small in this period, and that therefore the difference between the total rate of oxidation and the rate of formation of peroxide was small.

Discussion

Rates of Absorption of Oxygen.—The data of Tables I and II show that in non-aqueous solution with azobis-(2-methylpropionitrile) as initiator and at concentrations of about 2 M or above, the reactions of acrylonitrile and methacrylonitrile with oxygen follow the same kinetics as for other monomers^{2,5} at atmospheric pressure. The rates are proportional to the first power of the monomer concentration and to the one-half power of the initiator concentration. These kinetics are in accord with the classical autoxidation mechanism adapted for styrene by Miller and Mayo,^{2} in which termination occurs by interaction of two peroxide radicals. Thus in non-aqueous solutions with this azo initiator the reaction of the nitrile monomers with oxygen is less complex than in the aqueous persulfate systems previously studied.^{6b,17}

(15) L. Claisen and E. Moritz, Ber., 13, 2121 (1880).
(16) K. Nozaki, Ind. Eng. Chem., Anal. Ed., 18, 583 (1946).

(17) In the aqueous systems also it is probable that the chief termination mechanism involves the interaction of two peroxide radicals. Objections to our previous postulation^{6b} of termination by other means were pointed out by Dr. Mayo in a private communication.

A close inspection of the data of Tables I and II indicates that there is a decrease in the value of the quotient rate/[monomer][ABN]$^{1/2}$ as the monomer concentration is decreased below 2 M. This effect is noticeable with methacrylonitrile, especially in the chlorobenzene solution, and probably operative with acrylonitrile in the same solvent. With ethacrylonitrile this quotient decreased from a value of 0.036 for undiluted monomer (9.96 M) to 0.023 for 0.75 M monomer in chlorobenzene.

A possible cause of the observed effect is a decrease in the efficiency of the initiator at low monomer concentrations. Bevington showed[18] that the efficiency of ABN as an initiator for the polymerization of styrene decreased when the concentration of styrene was below 1 M. At 0.5 M the initiator efficiency was about 85% as great as at 1.0 M monomer concentration. This decrease is of the same order of magnitude as the effect observed in the current work.

Jenkins has cited[19] three systems in which the rate of polymerization decreases at low monomer concentration (below 2 M) and has reviewed possible explanations based on complex formation between the initiator and monomer, a cage effect or solvent transfer (discussed by Burnett and Loan[20] and developed by Smets and Hayashi[21]). Although there are objections to each of these explanations, the data from the cases cited fit the theory of complex formation. Russell[22] has shown recently that complexes between solvents and free radicals govern the direction of free radical chlorinations and has postulated that such complexes may be important in autoxidation and polymerization reactions. The evidence from the current work is not sufficient to establish the cause of the observed effect.

Data on the rates of oxidation of various nitrile monomers at atmospheric pressure with 0.01 M ABN at 50° are given in Table III.

The value of "100 k" for undiluted acrylonitrile was found by Mayo, Miller and Russell[5e] to be 0.10; this is in close agreement with the value of 0.105 for 4 M or 2 M acrylonitrile (from Table I) and is slightly larger than the value of 0.092 for 0.75 M acrylonitrile in chlorobenzene. Methacrylonitrile is shown to be about three times as reactive toward oxygen as acrylonitrile; α-methylstyrene was previously found[5e] to be about twice as reactive as styrene. The α-alkylacrylonitriles are all more reactive toward oxygen than the unsubstituted acrylonitrile, presumably because these monomers are better electron donors[5e] than acrylonitrile. The slight decrease in reactivity from methyl- to n-amylacrylonitrile is to be expected because of decreasing release of electrons.

The data from Tables II and III on undiluted monomers show the following decreasing order of

reactivity toward oxygen: methacrylonitrile > ethacrylonitrile > methyl isopropenyl ketone > acrylonitrile > methyl vinyl ketone >> isopropenyl acetate. In this series the reactivity values for acrylonitrile and methyl vinyl ketone are so close as to be hardly distinguishable. In the aqueous persulfate systems previously studied[6b] the reactivity of the methyl vinyl ketone was greater than that of the acrylonitrile.

A limited amount of work on the rate of oxygen absorption by acrylonitrile in the presence of an active peroxide initiator is shown in Table IV. In bromobenzene solution with bis-o-chlorobenzoyl peroxide at 50° the following relationship was observed: $-dO_2/dt = k[ACN]^{1.6}[peroxide]^{0.6}$. The solution remained homogeneous. In the absence of a detailed study of products it is not possible to say whether the approximately three-halves dependence on monomer concentration is due to reaction of the monomer free radical with the solvent[23] or with the peroxide.[24]

Products of Oxidation.—Polymeric peroxides have been obtained from a variety of unsaturated compounds.[25] Previous work in this Laboratory[6a,c] concerned the polymeric peroxides of acrylonitrile and methacrylonitrile.

The data of Table V show that the higher α-alkylacrylonitriles form relatively stable polymeric peroxides of formulas close to $[-CH_2C(CN)(R)O_2-]_n$. In no case was there any evidence of "normal" polymer. The molecular weights were low.

Other products accompanying the polymeric peroxide were formaldehyde (identified from all monomers studied) and the cyanide-containing oxidation fragment RCOCN (isolated from methacrylonitrile and ethacrylonitrile only). Experiments have indicated that formaldehyde is produced from the very beginning of the oxidation and that the polymeric peroxides are stable under the conditions of preparation (50° in the presence of monomer and oxygen). Therefore, it is apparent that formaldehyde is a primary oxidation product of the α-alkylacrylonitriles. The concurrent formation of carbonyl products with the polymeric peroxide has been well established[2,5] for other monomers.

The current work has shown that the Nozaki method[16] of peroxide analysis is unsatisfactory for these polymeric peroxides (Table VI). Hence, the thermal decomposition method, which was reported in a previous paper[6c] to give results supporting the value from the Nozaki method, cannot be regarded as quantitative for determination of peroxide linkages. The best available method, the hydrogen iodide procedure of Miller and Mayo,[2] gave results in good agreement with those obtained from elemental analyses.

Newark, Del.

(18) J. C. Bevington, J. Polymer Sci., 29, 235 (1958).

(19) A. D. Jenkins, ibid., 29, 245 (1958).

(20) G. M. Burnett and L. D. Loan, Trans. Faraday Soc., 51, 219 (1955).

(21) G. Smets and K. Hayashi, J. Polymer Sci., 29, 257 (1958).

(22) G. A. Russell, This Journal, 80, 4987 (1958).

(23) W. M. Thomas, E. H. Gleason and J. J. Pellon, J. Polymer Sci., 17, 275 (1955).

(24) L. B. Morgan, Trans. Faraday Soc., 42, 169 (1946).

(25) Known polymeric peroxides are listed by Mayo, Miller and Russell.[5e]