417. *The Mechanisms of Inhibition and Retardation in Radical Polymerizations. Part V.* The Effects of Picric Acid and* m-*Dinitrobenzene on the Sensitized Polymerization of Styrene.*

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The effects of picric acid and *m*-dinitrobenzene on the sensitized radical polymerization of styrene have been examined The former acts as a rather inefficient inhibitor and is converted into a substance which is a retarder for the subsequent polymerization; *m*-dinitrobenzene is a retarder. ^{14}C-labelled specimens of the nitro-compounds have been used to determine the amounts incorporated in the polymers. The effects of the nitro-compounds on the average number of initiator fragments in each polymer molecule have been studied by using labelled initiator. Treatment of polymers with trifluoroacetic anhydride reduces the molecular weight and removes combined nitro-compound from the polymer. A reaction scheme is suggested which satisfies the observations.

MANY aromatic nitro-compounds act as chain terminators for radical polymerizations but the mechanisms by which they exert their effects are uncertain. It has been suggested[1] that the polymer radical becomes attached directly to the aromatic nucleus of the nitro-compound, but other authors[2] suppose that the attack is on the nitro-group itself. The products of the interaction of 1-cyano-1-methylethyl radicals and various nitro-compounds have recently been identified;[3] this work is of significance in connection with the effects of

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* Part IV, Bevington and Ghanem, *J.*, 1958, 2254.

[1] Price and Durham, *J. Amer. Chem. Soc.*, 1943, **65**, 757.

[2] Bartlett, Hammond, and Kwart, *Discuss. Faraday Soc.*, 1947, **2**, 342.

[3] Inamoto and Simamura, *J. Org. Chem.*, 1958, **23**, 408.

nitro-compounds on radical polymerizations. In this paper a study of the effects of picric acid and *m*-dinitrobenzene on the polymerization of styrene is reported; it involved the use of labelled nitro-compounds and labelled azoisobutyronitrile as initiator.

Previous tracer studies of the effects of retarders of various types have given useful information on the natures of the reactions involved.[4] The experimental work has been directed chiefly to determination of the numbers of molecules of retarder and fragments of initiator incorporated on the average in each polymer molecule for reactions carried out under various conditions. In some cases it has been possible to discover the way in which the retarder is linked in the polymer by examining the effects of chemical treatment upon the specific activities of polymers prepared by using labelled reagents.

EXPERIMENTAL

Descriptions have already been published for the various experimental procedures.[4] Standard methods were used for the preparation of [^{14}C]*m*-dinitrobenzene from [^{14}C]benzene. The product was recrystallized from ethanol; its specific activity was about 11 μcuries/g. of carbon. The labelled picric acid was an intermediate in the preparation of [^{14}C]diphenylpicrylhydrazine and the corresponding hydrazyl.[5] It was purified by recrystallization from aqueous ethanol; its specific activity was about 25 μcuries/g. of carbon.

Results.—Separation tests. Blank experiments with labelled contaminants showed that all traces of uncombined picric acid and *m*-dinitrobenzene could be removed from polystyrene by two precipitations of the polymer from benzene, methanol being used as precipitant.

Experiments with picric acid. Polymerizations of styrene in bulk at 60° were initiated by azoisobutyronitrile at a concentration close to 0·300 g./l. The concentration of picric acid ranged from 0 to about 0·1 g./l. Results are summarized in Table 1, and typical conversion–time curves are shown in Fig. 1. Reactions were carried to 5% conversion.

Experiments with [^{14}C]picric acid showed that appreciable quantities were incorporated in the polymer. On use of [^{14}C]picric acid giving a counting rate of 177,000 counts/min., polymers 3 and 4 gave counting rates of 44 and 56 counts/min., respectively. From the counting rates of the polymers and the original picric acid and the molecular weights of the polymers, it is calculated that for both polymers just over 0·5 molecule of picric acid was combined on the average in each polymer molecule. Polymer 4 was treated with diethyl ether and its counting rate was reduced to 7 counts/min., showing that a large proportion of the combined picric acid was contained in polymer of comparatively low molecular weight.

TABLE 1.

Expt. no.	Concn. of initiator (g./l.)	Concn. of picric acid (g./l.)	Time to reach steady rate (hr.)	Steady rate (%/hr.)	Molecular weight of polymer
1	0·300	0	0	1·37	264,000
2	0·297	0·049	7	0·99	169,000
3	0·292	0·050	7	1·06	169,000
4	0·294	0·073	9	0·84	126,000
5	0·303	0·099	11	0·70	114,000

Polymers 2 and 5 were prepared by using ^{14}C-initiator and unlabelled picric acid; the average number of initiator fragments per polymer molecule for these polymers was close to 1·5. In polymer 1, prepared in the absence of picric acid, there were 2·0 initiator fragments per polymer molecule. A specimen of polymer 2 was treated with diethyl ether; about 20% of the polymer was soluble in the ether and the counting rate of the insoluble portion was 123 counts/min. compared with 228 counts/min. for the whole polymer.

Polymer 2 was treated with trifluoroacetic anhydride reagent; its average molecular weight fell to 140,000 but there were no significant changes in the total weight of the specimen or its counting rate. Similar treatment of polymer 3, containing labelled picric acid, reduced its counting rate to 12 counts/min., and isotope dilution analysis showed that about 70% of the labelled groups lost from the polymer appeared as picric acid.

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[4] Bevington, Ghanem, and Melville, *J.*, 1955, 2822.
[5] Bevington, *J.*, 1956, 1127.

A solution of [^{14}C]azoisobutyronitrile (17·0 mg.) and picric acid (20·6 mg.) in benzene (3·5 c.c.) was degassed and kept at 60° for 17½ hr. By isotope dilution analysis, it was found that 1·6 mg. of tetramethylsuccinodinitrile and 0·3 mg. of isobutyronitrile were produced; in a similar experiment in the absence of picric acid, the weights of these products were 3·2 mg. and 1·4 mg., respectively.

Experiments with m-*dinitrobenzene.* Polymerizations of styrene at 60° with a fixed concentration of azoisobutyronitrile (close to 0·300 g./l.) and various concentrations of *m*-dinitrobenzene are referred to in Fig. 2 and Table 2; reactions were allowed to proceed to 6% conversion. As indicated in Table 2, some experiments involved ^{14}C-retarder and others ^{14}C-initiator; the results of experiment 1 are included for comparison. The average numbers of retarder molecules or initiator fragments incorporated in the polymer molecules are shown in Table 2.

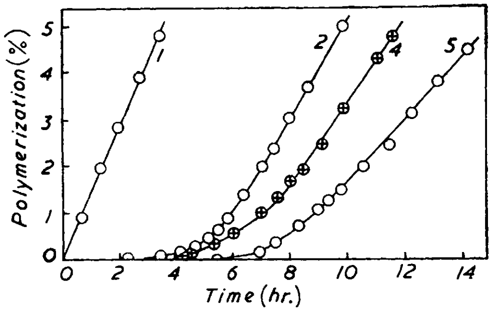


Fig. 1. *Conversion–time plots for the polymerization of styrene at* 60° (*curves labelled with experiment numbers as in Table* 1).

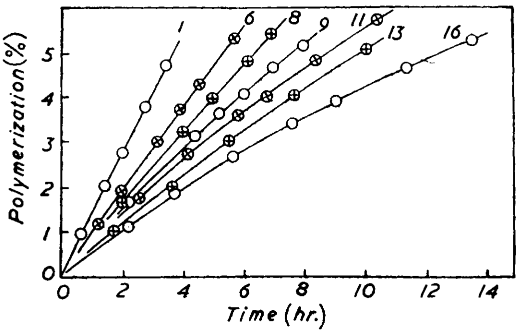


Fig. 2. *Conversion–time plots for polymerization of styrene at* 60° (*curves labelled with experiment numbers as in Table* 2).

Table 2.

Expt. no.	Concn. of retarder (g./l.)	Molecular weight of polymer	Counting rate for polymer (counts/min.)	No. of initiator fragments per molecule	No. of retarder molecules per molecule
1	0	264,000	197 ^{a}	2·00	—
6	0·203	187,000	220 ^{a}	1·58	—
7	0·251	177,000	16	—	0·5
8	0·319	151,000	288 ^{a}	1·67	—
9	0·404	126,000	20	—	0·4
10	0·500	111,000	24	—	0·4
11	0·504	114,000	330 ^{a}	1·44	—
12	0·698	99,000	41	—	0·6
13	0·690	97,000	110 ^{b}	1·25	—
14 ^{c}	0·704	94,000	105 ^{b}	1·15	—
15	0·989	75,000	54	—	0·7

^{a} Counts/min. for initiator = 500,000. ^{b} Counts/min. for initiator = 165,000; counts/min. for retarder = 76,000. ^{c} Polymerization carried to 3% conversion only.

From the polymerizations involving ^{14}C-initiator, average kinetic chain lengths were calculated, and thence average rates and efficiencies of initiation. In these calculations, the average rates of polymerization over the whole reactions were used. In some cases, appreciable decomposition of the initiator occurred during the reaction and the mean of the initial and final concentrations was used in calculating the efficiencies; for calculation of the final concentration, k_d was taken as $1{\cdot}30 \times 10^{-5}$ sec.$^{-1}$. The results of these calculations are summarized in Table 3.

A solution of azoisobutyronitrile (10·9 mg.) and [^{14}C]*m*-dinitrobenzene (10·2 mg.) in benzene (2·5 c.c.) was degassed and sealed in vacuum. After 16 hr. at 60°, no *m*-nitronitrosobenzene could be detected in the reaction mixture by isotope dilution analysis.

Refluxing polymers 7 and 9 with trifluoroacetic anhydride reagent for 10 and 15 hr. respectively caused the counting rates of the polymers to fall to about 8 counts/min. Isotope dilution

TABLE 3.

Expt. no.	Rate of polym. $\times 10^5$ (mole $l.^{-1}$ sec.$^{-1}$)	Average concn. of initiator (g./l.)	Kinetic chain length	Rate of initn. $\times 10^8$ (mole $l.^{-1}$ sec.$^{-1}$)	Efficiency of initiation (%)
1	3·18	0·29	1270	2·51	54·6
6	2·13	0·26	1136	1·88	45·6
8	1·76	0·26	868	2·03	49·2
11	1·37	0·24	833	1·64	43·1
13	1·11	0·23	750	1·48	40·6
14	1·28	0·27	786	1·63	38·1

analysis for *m*-dinitrobenzene produced during treatment of polymer 9 showed that a small amount was liberated. The counting rates of the materials in the experiments were so low that the analysis was qualitative only.

DISCUSSION

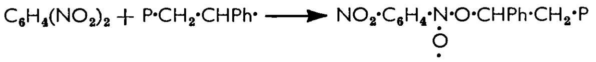
Picric acid is not an ideal inhibitor for the radical polymerization of styrene since polymerization is not suppressed completely; the rate gradually rises to a steady value and the induction period does not end abruptly. The steady rate falls as the initial concentration of picric acid is raised; the effect is too large to be accounted for by the consumption of initiator during the early stages of the reaction. The concentrations of initiator remaining when the steady rates were first attained in experiments 2—5 have been calculated; rates of polymerization corresponding to these concentrations have been calculated by taking experiment 1 as standard and assuming an order of 0·5 with respect to initiator. The rates thus calculated for experiments 2, 3, 4, and 5 are respectively 1·16, 1·15, 1·13, and 1·05%/hr.; these rates are respectively 1·17, 1·08, 1·35, and 1·50 times the observed rates. The discrepancy between observed and calculated rates increases with rising concentration of picric acid, suggesting that during the early stages the picric acid is converted into a retarder, the amount of which increases as the initial concentration of the acid is raised. This conclusion is confirmed by the differences between the molecular weights of the polymers in this series.

The incorporation of picric acid in the polymer disproves certain of the mechanisms suggested for the interaction of polymer radicals and nitro-compounds. The effect of trifluoroacetic anhydride upon the molecular weight of a polymer prepared in the presence of picric acid shows that the polymers contain linkages sensitive to the reagent; it is likely that the picric acid combined in the polymer is not held by carbon–carbon bonds since most of the combined acid can be eliminated from the polymer by treatment with the reagent. Most of the picric acid eliminated from the polymer appears as such, suggesting that the picric acid unit is intact in the polymer.

It is likely that one of the nitro-groups in the molecule of picric acid is involved in the first stages of the reaction, and that the unused nitro-groups are concerned in the subsequent retardation process. No significance can be attached to the relative numbers of initiator fragments and picric acid molecules combined in the polymers, since the picric acid acts in two distinct ways during the course of the polymerization. The results of the experiments involving diethyl ether show that the polymers contain much material of fairly low molecular weight, so that some fractionation may well occur during recovery of the polymers.

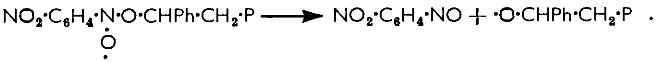
m-Dinitrobenzene retards the polymerization of styrene but it also interferes in the initiation step since its presence reduces the efficiency of initiation. The continuous decrease in rate during the course of a retarded polymerization (see Fig. 2) can be accounted for by the consumption of initiator; at the end of experiment 13, for example, the concentration of initiator had fallen to about 55% of its original value. Part, at least, of the *m*-dinitrobenzene included in the polymer is not held by carbon–carbon bonds since much of it can be removed by treatment with trifluoroacetic anhydride.

The results of Inamoto and Simamura[3] indicate that the first stage in the interaction of a polymer radical with *m*-dinitrobenzene is likely to be



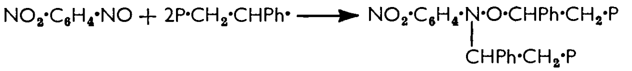
$$C_6H_4(NO_2)_2 + P{\cdot}CH_2{\cdot}CHPh{\cdot} \longrightarrow NO_2{\cdot}C_6H_4{\cdot}\underset{\underset{\bullet}{O}}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P \quad \ldots\ldots \quad (1)$$

where P represents a polystyrene chain with a terminal initiator fragment. According to the suggestion of these authors, the next stage is the formation of the nitroso-compound



$$NO_2{\cdot}C_6H_4{\cdot}\underset{\underset{\bullet}{O}}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P \longrightarrow NO_2{\cdot}C_6H_4{\cdot}NO + {\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P \quad \ldots\ldots \quad (2)$$

The products of this reaction might react as follows:

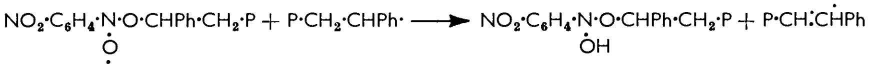


$$NO_2{\cdot}C_6H_4{\cdot}NO + 2P{\cdot}CH_2{\cdot}CHPh{\cdot} \longrightarrow NO_2{\cdot}C_6H_4{\cdot}\underset{CHPh{\cdot}CH_2{\cdot}P}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P \quad \ldots\ldots \quad (3)$$

$$P{\cdot}CH_2{\cdot}CHPh{\cdot}O{\cdot} + P{\cdot}CH_2{\cdot}CHPh{\cdot} \longrightarrow P{\cdot}CH_2{\cdot}CHPh{\cdot}OH + P{\cdot}CH{:}CHPh \quad \ldots \quad (4)$$

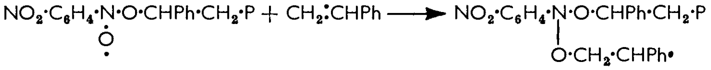
If these processes were the sole terminating reactions, the average numbers of initiator fragments and retarder molecules per polymer molecule would be 1·33 and 0·33, respectively. If reaction (3) did not occur, the number of initiator fragments would be 1·00, but no retarder would be incorporated in the polymer, contrary to the observations made in this work; further, no *m*-nitronitrosobenzene could be detected in the products of the interaction of 1-cyano-1-methylethyl radicals with *m*-dinitrobenzene. If mutual termination occurred at the same time as the termination involving the nitro-compound, the average number of combined initiator fragments would be greater than 1·33 and that of combined retarder molecules less than 0·33.

An alternative to reactions (2), (3), and (4) is reaction (5):



$$NO_2{\cdot}C_6H_4{\cdot}\underset{\underset{\bullet}{O}}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P + P{\cdot}CH_2{\cdot}CHPh{\cdot} \longrightarrow NO_2{\cdot}C_6H_4{\cdot}\underset{OH}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P + P{\cdot}CH{:}\dot{C}HPh \quad . \quad (5)$$

At high concentrations of retarder, when mutual termination is suppressed, this would lead on the average to 1 initiator fragment and 0·5 retarder molecule combined in each polymer molecule. The amount of combined retarder was a little greater than this in experiments 12 and 15; this may indicate that the radical formed in (1) occasionally reacts with monomer to give a type of copolymerization as shown:



$$NO_2{\cdot}C_6H_4{\cdot}\underset{\underset{\bullet}{O}}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P + CH_2{:}CHPh \longrightarrow NO_2{\cdot}C_6H_4{\cdot}\underset{O{\cdot}CH_2{\cdot}CHPh{\bullet}}{N}{\cdot}O{\cdot}CHPh{\cdot}CH_2{\cdot}P \quad \ldots \quad (6)$$

which could lead to more than 0·5 molecule of retarder on the average in each polymer molecule. This type of behaviour was observered when *p*-benzoquinone was used as a retarder.[4] If the nitro-compound enters the polymer in the way suggested here, it could be removed subsequently by treatment with trifluoroacetic anhydride. Similar considerations can be applied to the mechanisms by which picric acid interferes in radical polymerizations.

The authors thank Sir Harry Melville, F.R.S., for his interest, and the University of Birmingham for a University Research Fellowship (to N. A. G.).

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