the subsequent reaction of the alkoxy benzonitriles with alcohols, has been extended to its, apparent, limit.

Possible mechanisms for the somewhat obscure reactions involved are suggested.

CHAPEL HILL, N. C. RECEIVED AUGUST 16, 1943

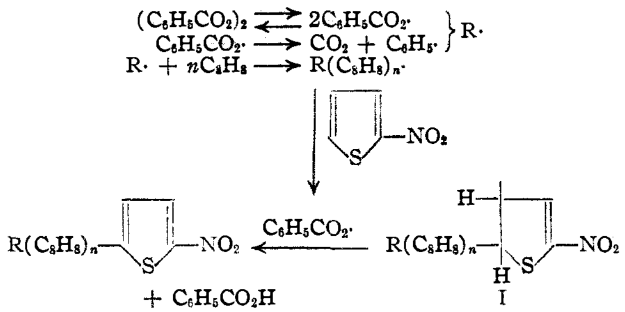
[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Polymerization of Styrene in the Presence of Nitrothiophene and Chloranil

BY CHARLES C. PRICE

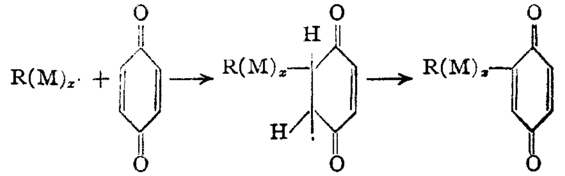
Since thiophene analogs of aromatic compounds are frequently of similar character but considerably more reactive, it was of some interest to compare the effect on free-radical addition polymerization of nitro derivatives of the two classes. Actually, the retardation of the polymerization of styrene in the presence of nitrothiophene was indeed much more pronounced than in the presence of nitrobenzene.[1]

Furthermore, polystyrene formed in the presence of nitrothiophene was found to contain the elements of the retarder in the proper amount for one nitrothienyl residue per polymer chain. Since the retardation is due to coupling of the growing free-radical polymer chain with the nitro compound, these results would indicate that the thiophene ring is more reactive toward free radical attack than the benzene ring. The radical is believed to attack the open α-position since this is the reactive position in thiophene and also reaction in this manner will enable the nitro group to lend resonance stability to the adduct.

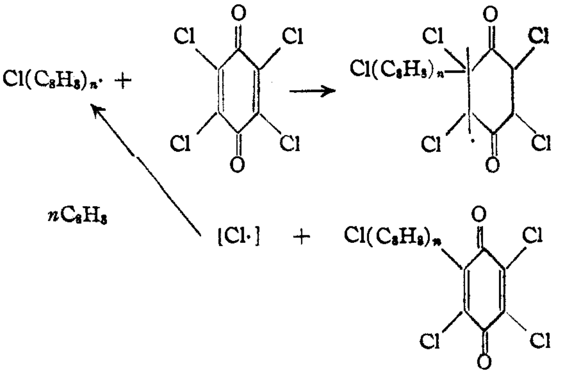


It is this stabilizing influence of the nitro group in the adduct I which evidently prevents it from reacting further with monomer molecules. Reaction of the growing chains with nitrothiophene thus serves to deactivate them thereby retarding the progress of the polymerization. The free radical adduct I, although stabilized toward reaction with monomer, will, of course, undergo disproportionation with another radical, such as, *e. g.*, the benzoxy radical.

The ease with which free radicals attack quinones to yield substitution products[2] has suggested that, in this case also, retardation or inhibition may be due to coupling of free radical chains with the quinone. (The symbol *M* is used to represent monomer units.)



Since chloranil is a quinone with no hydrogen to displace in this manner an investigation of its effect on free-radical addition polymerization was undertaken. Polystyrene prepared in the presence of chloranil was found to contain the elements of the added reagent in the proper proportion for one chloranil residue per polymer molecule. However, this compound did not appear to act as a retarding agent since the yield of polymer was not markedly decreased as is the case for a retarder or inhibitor. The action is more nearly analogous to that of carbon tetrachloride,[3] which appears to involve *transfer* of the activity of the growing chain through chlorine atoms rather than destruction of the activity.



To confirm the chemical nature of the union of chloranil with polystyrene prepared in its presence, a sample of polystyrene of about the same molecular weight as that formed in the presence of chloranil was mixed with chloranil. The procedure used for isolating polystyrene led to a practically quantitative separation of the two

---

(1) Price and Durham, THIS JOURNAL, **65**, 757 (1943).

(2) Fieser and Chang, *ibid.*, **64**, 2043 (1942); Fieser and Oxford, *ibid.*, 2060.

(3) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

components in one reprecipitation and the recovered polystyrene was found to contain less than 0.05% chlorine.

Since anthraquinones are also quinones with no quinoid hydrogen to displace, polymerization of styrene was carried out in the presence of β-chloroanthraquinone. The reaction appeared to proceed without retardation. The quinone was recovered unchanged and the polystyrene, obtained in good yield, had the same molecular weight as a blank[1] and contained chlorine equivalent to only one atom for each seven polymer molecules.

It is of interest to point out that, for the low molecular weight polymers we have investigated, the yield of solid polymer isolated is a much more sensitive indication of retardation than the molecular weight of the product. Since the reprecipitation procedure will tend to discard the very low molecular weight fractions, a much larger proportion of the product may be thus lost from a retarded polymerization than from a parallel unretarded experiment; the average molecular weight of the portions actually isolated may differ only slightly.

As has been observed frequently before, the samples of polymers obtained all contained "extra" oxygen atoms for which no structural assignment can yet be made. The source and functional nature of this oxygen will be the subject of further investigation.

Experimental

Polystyrene in the Presence of α-Nitrothiophene.—A mixture of 5 g. of benzoyl peroxide, 5 g. of α-nitrothiophene and 25 cc. of styrene was warmed on a steam-bath. The solution turned dark red and the temperature rose to slightly above 100° and then subsided to 90° within an hour. The cooled mixture was diluted with ether and poured into ice-cold alcohol. Reprecipitation of the dark red oil thus obtained yielded 3.3 g. (15%) of orange-tan powder. Reprecipitation of 2.0 g. of this material from 10 cc. of ether by pouring into 50 cc. of ice-cold 95% ethanol yielded 1.4 g. of buff powder which gave strong positive tests for nitrogen and sulfur on sodium fusion.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{10}C_4H_2SNO_2 \cdot O_4$: C, 80.67; H, 6.47; N, 1.03; S, 2.36; mol. wt., 1350. Found: C, 80.60; H, 6.08; N, 1.36; S, 2.28; mol. wt., 1350.[4]

In an experiment parallel to the above except that only 2 g. of nitrothiophene was used, the reaction was considerably more vigorous, the temperature rising to 140°. The product weighed 6.0 g. (30%) and reprecipitation of a 2.0-g. sample yielded 1.45 g. of pale buff powder.

Anal. Calcd. for $C_6H_5CO_2(C_8H_8)_{16}C_4H_2SNO_2 \cdot O_4$: C, 84.33; H, 6.87; N, 0.72; S, 1.61; mol. wt., 1980. Found: C, 84.49; H, 7.07; N, 0.86; S, 1.00; mol. wt., 1950.[4]

Polystyrene in the Presence of Chloranil.—A mixture of 5 g. of benzoyl peroxide and 4 g. of chloranil in 25 cc. of styrene was heated on the steam-bath. The dark orange-red solution faded markedly as the temperature rose to 155°. After cooling, the viscous residue was dissolved in ether and precipitated with alcohol, yielding 15.7 g. (80%) of very pale yellow powder. A 2.0-g. sample was reprecipitated from 10 cc. of ether by pouring into 50 cc. of ice-cold alcohol; yield, 1.7 g. of creamy-white powder (I). A second 3.0-g. sample was reprecipitated in the same manner five times to yield 1.7 g. (II).

Anal. Calcd. for $Cl(C_8H_8)_{10}C_6Cl_3O_2 \cdot O_3$: C, 77.17; H, 6.04; Cl, 10.62; mol. wt., 1350. Found (I): C, 76.86; H, 6.24; Cl, 10.66; mol. wt., 1300.[4] Found (II): C, 77.48; H, 5.80; Cl, 11.04; mol. wt., 1550.[4]

Separation of Polystyrene and Chloranil.—A mixture of 5.0 g. of polystyrene (mol. wt., 1400) and 2.0 g. of chloranil was shaken in 30 cc. of ether. The polymer dissolved completely, leaving 2.0 g. of crystalline chloranil which was collected by filtration. The mother liquor was poured into 100 cc. of ice-cold alcohol, yielding 4.6 g. of creamy-white powder. A qualitative test for halogen by sodium fusion was negative. Quantitative analysis by Parr bomb showed 0.00 and 0.06% Cl.

Polystyrene in the Presence of β-Chloroanthraquinone.—A mixture of 5 g. of benzoyl peroxide, 5 g. of β-chloroanthraquinone and 25 cc. of styrene was heated on a steam-bath. The temperature rose gradually to 100°, then rapidly to 165°. As the solution cooled the quinone crystallized from the viscous polymer. The polymer was dissolved in 100 cc. of ether leaving 4.5 g. of pale yellow crystalline β-chloroanthraquinone, m. p. 206–207° (uncor.). The ethereal solution was poured into cold alcohol, yielding 12.0 g. of pale yellow powdery polymer. A 2.0-g. sample was twice reprecipitated, yielding 1.75 g. of analytical sample.

Anal. Found: C, 89.51; H, 7.51; Cl, 0.26; mol. wt., 1850.[4]

Summary

Analysis of samples of polystyrene prepared in the presence of α-nitrothiophene and chloranil has demonstrated the presence of the elements of these substances in the polymer. Nitrothiophene acts as a retarder; chloranil appears to act merely as a chain-transfer agent.

URBANA, ILLINOIS RECEIVED AUGUST 5, 1943

---

[4] Viscometrically, using the constant of Kemp and Peters (*Ind. Eng. Chem.*, **34**, 1097 (1942)) which has been found[1] to give satisfactory results for low molecular weight polystyrene.