387. *Arylazotriarylmethanes and Tetra-arylsuccinic Dinitriles as Catalysts in Addition Polymerisation.*

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Experiments are described on the polymerisation of styrene in which *p*-chloro- and *p*-bromo-phenylazotriphenylmethane, phenylazotri-*p*-methoxyphenylmethane and tetra-*p*-methoxyphenylsuccinic dinitrile are used as catalysts. For the substituted phenylazotriphenylmethanes there is evidence that both the aryl and the triarylmethyl radicals are incorporated in the polymer. The radicals derived from the substituted tetraphenylsuccinic dinitrile also become incorporated in the polymer.

Although the fundamental principles of the free-radical theory of addition polymerisation, which is supported by both chemical and kinetic evidence, are now firmly established, there remains a number of points on which further information is desirable. The present communication describes the results of experimental work designed to make a further contribution to the subject from the chemical standpoint. Investigations carried out by one of us fifteen years ago (Grieve and Hey, *J.*, 1934, 1797; Hey, *J.*, 1934, 1966 and subsequent papers) revealed the possibility of the occurrence of free radicals as transient intermediates in a number of organic reactions in solution and thus indicated the types of compound which might be active as catalysts for the initiation of addition polymerisation. The function of benzoyl peroxide in this respect was suggested by Hey and Waters (*Chem. Reviews*, 1937, **21**, 201), and the subsequent identification of fragments of the catalyst in the polymer molecule confirmed the hypothesis. By the use of *p*-bromobenzoyl peroxide, *p*-methoxybenzoyl peroxide, and chloroacetyl peroxide, polymers were obtained from styrene and methyl methacrylate which contained bromine, methoxyl, and chlorine, respectively (Price, Kell, and Krebs, *J. Amer. Chem. Soc.*, 1942, **64**, 1103). Similar results were later reported with 3 : 4 : 5-tribromobenzoyl peroxide (Price and Tate, *ibid.*, 1943, **65**, 517) and with *m*-bromobenzoyl peroxide (Pfann, Salley, and Mark, *ibid.*, 1944, **66**, 983). In like manner by the use of *p*-bromobenzenediazo hydroxide (Price and Durham, *ibid.*, 1942, **64**, 2508) and of substituted nitrosoacetanilides (Blomquist, Johnson, and Sykes, *ibid.*, 1943, **65**, 2446), polymers were again obtained in the molecules of which fragments of the catalyst were incorporated.

When a catalyst is employed which can be considered to give rise in solution to two different free radicals it would be reasonable to suppose that the more reactive radicals would play the predominant role in the initiation of the polymerisation process. The peroxides of organic acids can be regarded as sources of two types of radical because, provided that the temperature is not high, the peroxide can give both a hydrocarbon radical and an acid radical, thus :

$$(\mathrm{R{\cdot}CO_2})_2 \longrightarrow \mathrm{R{\cdot}} + \mathrm{R{\cdot}CO{\cdot}O{\cdot}} + \mathrm{CO_2}$$

In agreement with this view Bartlett and Cohen (*ibid.*, 1943, **65**, 543) have shown that, when styrene is polymerised in the presence of *p*-bromobenzoyl peroxide, the polystyrene contains both *p*-bromophenyl and *p*-bromobenzoyloxy-groups. The groups are not, however, found in equal amounts and a differential activity is revealed since some 64% of the bromine in the polymer is present as *p*-bromobenzoyloxy- and some 36% as *p*-bromophenyl groups. The proportions in which the two different end groups are found depend upon the experimental conditions used. Similar results were recorded for the polymerisation of allyl acetate with *p*-chlorobenzoyl peroxide (Bartlett and Altschul, *ibid.*, 1945, **67**, 812). These results may be due in part to a step-wise decomposition of the catalyst, *e.g.*,

$$(\mathrm{R{\cdot}CO_2})_2 \longrightarrow 2\mathrm{R{\cdot}CO{\cdot}O{\cdot}}$$
$$2\mathrm{R{\cdot}CO{\cdot}O{\cdot}} \longrightarrow \mathrm{R{\cdot}CO{\cdot}O{\cdot}} + \mathrm{R{\cdot}} + \mathrm{CO_2}$$

and the possibility of similar considerations arising with catalysts which provide free radicals with liberation of nitrogen must not be overlooked. An even greater differential effect was revealed in the work of Blomquist, Johnson, and Sykes (*loc. cit.*), who used as catalysts a series of substituted nitrosoacylanilides, which can also give two types of radical, thus :

$$\mathrm{Ar{\cdot}N(NO){\cdot}COR} \rightleftarrows \mathrm{Ar{\cdot}N{:}N{\cdot}O{\cdot}COR} \longrightarrow \mathrm{Ar{\cdot}} + \mathrm{R{\cdot}CO{\cdot}O{\cdot}} + \mathrm{N_2}$$

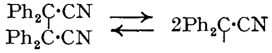
The results obtained indicated that only the active free aryl radical, Ar•, becomes incorporated in the polymer molecule and that the free acyloxy-radical, R•CO•O•, appears not to be involved. The contrast with the behaviour of the peroxides, which also yield an aryl and an acyloxy-radical, was unexpected, but may be attributed in part to the fact that the experiments with the peroxides made use mainly of aromatic acyloxy-radicals, whereas, in the experiments with the nitrosoacylarylamines, only aliphatic acyloxy-radicals were used. A recent re-examination of the use of nitrosoacylarylamines containing aromatic acyloxy-groups (Hey and Misra, *Faraday Soc. Discussion*, 1947, **2**, 279) provided some indication that both aryl and acyloxy-groups were incoporated into the polymer molecules, although under these conditions the aryl radicals still appeared to be the more active.

In order to obtain further information on the differential incorporation of catalyst fragments in polymer molecules attention has now been directed to the use of substituted phenylazotriphenylmethanes, which on heating can give two free radicals of markedly different stability, thus :

$$R{\cdot}N{:}N{\cdot}CR'_3 \longrightarrow R{\cdot} + R'_3C{\cdot} + N_2$$

The use of the unsubstituted phenylazotriphenylmethane as a catalyst in the polymerisation of styrene was first reported by Schulz (*Naturwiss.*, 1939, **27**, 659), but there appear to be no records of the use of substituted phenylazotriphenylmethanes and in the absence of a substituent atom or group, which can be qualitatively identified, the incorporation of either or both radicals into the polymer cannot be readily observed. Experiments have now been carried out with phenylazotriphenylmethanes as catalysts for the polymerisation of styrene and methyl methacrylate in which either (*a*) the single phenyl group carries a chlorine or bromine atom at the *para*-position or (*b*) the triphenylmethyl group is replaced by the tri-*p*-methoxyphenylmethyl group. Analysis of the purified polymers for either halogen or methoxyl showed that both types of radical can become incorporated into the polymer molecules, and it is possible that, whereas the more active aryl radicals play the dominant role in initiating the polymerisation process, the much more stable triarylmethyl radicals act as retarders and cause chain termination. It is known that free radicals of the triarylmethyl type are able to add to certain ethylenic systems (Conant and Scherp, *J. Amer. Chem. Soc.*, 1931, **53**, 1941; Conant and Chow, *ibid.*, 1933, **55**, 3475; Marvel, Dec, and Corner, *ibid.*, 1945, **67**, 1855), and, with styrene, triphenylmethyl gives rise to a 1 : 2-adduct. Mayo and Gregg (*ibid.*, 1948, **70**, 1284) have suggested that with a radical of the stability associated with triphenylmethyl almost as many chains may be stopped as started, and that its function as catalyst or inhibitor is not clear-cut. On the other hand, Schulz (*loc. cit.*) considers that both the aryl and triarylmethyl radicals act as initiators and has suggested that in the polymerisation of styrene with phenylazotriphenylmethane the termination of the chain reaction is less likely to arise from dimerisation and that with relatively high concentrations of the catalyst the termination process may be due to combination with a free radical from the catalyst. It may be noted that experiments designed to place *different* labelled end-groups at either end of polystyrene molecules have already been reported by Price and Read (*J. Polymer Res.*, 1946, **1**, 44).

The use of tetraphenylsuccinic dinitrile as a catalyst for the polymerisation of styrene and methyl methacrylate was reported by Schulz and Wittig (*Naturwiss.*, 1939, **27**, 387; *Kunstoffe*, 1943, **33**, 224). Its function as a catalyst presumably results from its dissociation into two diphenylcyanomethyl radicals, thus :



$$\begin{array}{c}Ph_2C{\cdot}CN\\ |\\ Ph_2C{\cdot}CN\end{array} \rightleftarrows 2Ph_2\overset{|}{C}{\cdot}CN$$

The incorporation of fragments of this catalyst into polymers prepared from styrene is shown by the presence of nitrogen, but in order to confirm the presence of the free-radical catalyst experiments have now been carried out with tetra-*p*-methoxyphenylsuccinic dinitrile and styrene using solutions in dioxan in order to favour the formation of polymers of low molecular weight. The use of this substituted tetraphenylsuccinic dinitrile has the further advantage that, according to Löwenbein and Gagarin (*Ber.*, 1925, **58**, 2643), tetra-*p*-methoxyphenylsuccinic dinitrile dissociates into two di-*p*-methoxyphenylcyanomethyl radicals at temperatures between 60° and 80° with the production of a rose-red colour, whereas a temperature of 140° is required for the production of a similar colour with tetraphenylsuccinic dinitrile (cf. Wittig *et al.*, *Annalen*, 1934, **513**, 26; *Ber.*, 1936, **69**, 790). In spite of these observations it was found that at temperatures below 97° the effect of any di-*p*-methoxyphenylcyanomethyl radicals so formed was negligible, and that the resulting polymers, when purified by precipitation from ethyl acetate solution, did not contain methoxyl groups. In polymerisation experiments carried out at 97—98° the rose-red colour due to the free radicals disappeared within fifteen minutes, but, if the polymerisation was stopped at this stage, again no methoxyl groups were found in the purified polymers and a considerable quantity of the adduct of styrene with the dinitrile, which was removed by its comparative insolubility in cold ethyl acetate, was isolated. If, however heating was continued for at least a further fifteen minutes after the disappearance of the colour, the polymers thus formed were found to contain fragments of the catalyst. With high concentrations of the catalyst the main product consisted of the adduct. Schulz and Wittig (*loc. cit.*) had reported the formation of a similar adduct in their experiments with tetraphenylsuccinic dinitrile. The polymerisation of styrene with a chlorinated tetraphenylsuccinic dinitrile has been studied by Raff, but no experimental details are available (see Abere, Goldfinger, Mark, and Naidus, *Ann. N.Y. Acad. Sci.*, 1943, **44**, 293).

EXPERIMENTAL.

Preparation of Materials.

Styrene and Methyl Methacrylate.—The sample of styrene was left in contact with solid potassium hydroxide to remove quinol and, after decantation, distilled under reduced pressure, the middle fraction alone being used. The methyl methacrylate was purified similarly.

Phenylazotriphenylmethane, p-*Chlorophenylazotriphenylmethane, and Phenylazotri*-p-*methoxyphenylmethane.*—These compounds were prepared by the method of Wieland, Popper, and Seefried (*Ber.*, 1922, **55**, 1816). Phenyl- and *p*-chlorophenyl-hydrazotriphenylmethane were oxidised by potassium ferricyanide as described by Wieland, vom Hove, and Börner (*Annalen*, 1926, **446**, 31), but for the oxidation of phenylhydrazotri-*p*-methoxyphenylmethane silver oxide was used.

p-*Bromophenylazotriphenylmethane.*—A mixture of triphenylchloromethane (5 g.) and *p*-bromophenylhydrazine (7·62 g.) in absolute ether (100 c.c.) was boiled under reflux for 4 hours. After the mixture had been kept overnight the precipitated *p*-bromophenylhydrazine hydrochloride was filtered off and the filtrate, made up to 250 c.c. with ether, was oxidised with an aqueous alkaline solution of potassium ferricyanide (26 g. in 80 c.c.). The ethereal layer was separated, washed several times with water, and finally dried ($CaCl_2$). After removal of the ether under reduced pressure, p-*bromophenylazotriphenylmethane* (4·8 g.) was obtained, which after crystallisation from benzene–alcohol melted at 110° (Found : C, 70·0; H, 4·6. $C_{25}H_{19}N_2Br$ requires C, 70·25; H, 4·5%).

Tetraphenylsuccinic Dinitrile.—Diphenylacetonitrile, prepared by the method of Wittig and Petri (*Annalen*, 1934, **513**, 39) from diphenylchoromethane, was converted into tetraphenylsuccinic dinitrile by the action of iodine in sodium ethoxide solution (Auwers and Meyer, *Ber.*, 1889, **22**, 1228).

Tetra-p-*methoxyphenylsuccinic Dinitrile.*—Di-*p*-methoxyphenylacetonitrile was prepared from *p*-methoxymandelonitrile and an excess of anisole in presence of concentrated sulphuric acid (Bistrzycki, Paulus, and Perrin, *Ber.*, 1911, **44**, 2606). The action of alkaline potassium ferricyanide on di-*p*-methoxyphenylacetonitrile afforded tetra-*p*-methoxyphenylsuccinic dinitrile in 57% yield. The substance melts indefinitely at 220° (with red coloration) (cf. Löwenbein and Gagarin, *loc. cit.*).

Tetra-p-*methoxyphenylsuccinic Dinitrile–Styrene Adduct.*—Tetra-*p*-methoxyphenylsuccinic dinitrile (1 g.) was aded to boiling styrene (5 c.c.), and the mixture heated under reflux for a few minutes until the rose colour which appeared at the beginning faded to a straw-yellow. The mixture was cooled and the precipitated solid was crystallised from ethyl acetate. The *adduct* (0·56 g.) separated in hexagonal plates, m. p. 213—214° (Found : C, 78·6; H, 5·95. $C_{40}H_{36}O_4N_2$ requires C, 78·9; H, 6·0%).

Polymerisation Studies.

For the determination of the molecular weight of purified samples of polystyrene, viscosities were measured with an Ostwald viscometer, and the revised equation of Kemp and Peters (*Ind. Eng. Chem.*, 1942, **34**, 1097), *viz.*, $M = \log \eta_r \times K_{\text{cm.}}/C$, where $K_{\text{cm.}} = 0{\cdot}45 \times 10^4$ for polystyrene in benzene and η_r is the relative viscosity, has been used. To calculate the molecular weights of samples of polymerised methyl methacrylate, the original Staudinger equation, $M = \eta_{\text{sp.}}/CK_m$, where $K_m = 1{\cdot}7 \times 10^{-4}$ for methyl methacrylate in benzene and $\eta_{\text{sp.}}$ is the specific viscosity, was used. Typical approximate formulæ are ascribed, where possible, to the polymers formed based on the observed molecular weight ±500.

(1) A mixture of styrene (9·07 g.) and phenylazotriphenylmethane (1 g.) was heated on the boiling water-bath for 18 hours. The crude polystyrene was dissolved in dioxan and precipitated by pouring into methyl alcohol. The polymer (8 g.) was purified by three such reprecipitations (Found : C, 89·8; H, 7·4%; *M*, 23,560).

(2) A mixture of styrene (18·15 g.), *p*-bromophenylazotriphenylmethane (3 g.), and benzene (80 c.c.) was heated under reflux on a water-bath for 5 hours. The crude polystyrene was purified as described above and weighed 0·50 g. after one purification [Found : C, 88·8; H, 7·3; Br, 2·5%; *M*, 12,810. $C_6H_4Br{\cdot}(C_8H_8)_{120}{\cdot}C_6H_4Br$ requires C, 91·2; H, 7·6; Br, 1·25%; *M*, 12,792].

(3) A mixture of styrene (5·21 g.) and *p*-bromophenylazotriphenylmethane (0·62 g.) was heated in a sealed ampoule at 78° for 48 hours. The reaction was then brought to an abrupt end by chilling The crude polymer (4·5 g.), obtained by dissolving the reaction mixture in dioxan and pouring this into an excess of methyl alcohol, was purified three times in this way. The purified polymer weighed 3·75 g. [Found : C, 90·4; H, 7·4; Br, 1·8%; *M*, 15,080. $C_6H_4Br{\cdot}(C_8H_8)_{140}{\cdot}C_6H_4Br$ requires C, 91·4; H, 7·6; Br, 1·1%; *M*, 14,872].

(4) A mixture of styrene (4·54 g.), *p*-chlorophenylazotriphenylmethane (2 g.), and dioxan (25 c.c.) was boiled under reflux for 5 hours under nitrogen. The crude polymer (0·5 g.) was purified three times as above by reprecipitation [Found : C, 90·6; H, 7·3; Cl, 1·5%; *M*, 2,980. $C_6H_4Cl{\cdot}(C_8H_8)_{26}{\cdot}C(C_6H_4)_3$ requires C, 91·4; H, 7·4; Cl, 1·2%; *M*, 3,058. $C_6H_4Cl{\cdot}(C_8H_8)_{25}{\cdot}C_8H_9$ requires C, 91·2; H, 7·5; Cl, 1·3%; *M*, 2,816].

(5) A mixture of styrene (5·44 g.) and *p*-chlorophenylazotriphenylmethane (1 g.) was heated in a sealed ampoule at 65° for 48 hours. The crude polymer (1·2 g.), obtained by dissolving the reaction mixture in dioxan and pouring the solution into an excess of methyl alcohol, was purified three times by

reprecipitation [Found: C, 91·3; H, 7·5; Cl, 0·9%; *M*, 4,700. $C_6H_4Cl\cdot(C_8H_8)_{42}\cdot C(C_6H_5)_3$ requires C, 91·7; H, 7·5; Cl, 0·75%; *M*, 4,723. $C_6H_4Cl\cdot(C_8H_8)_{43}\cdot C_8H_9$ requires C, 91·7; H, 7·6; Cl, 0·8%; *M*, 4,688].

(6) A mixture of styrene (4·91 g.) and *p*-chlorophenylazotriphenylmethane (1 g.) was heated in a sealed ampoule at 85° for 22 hours. The polymer, isolated and purified as in the previous case, weighed 2·2 g. [Found: C, 9·18; H, 7·9; Cl, 0·9%; *M*, 8,240. $C_6H_4Cl\cdot(C_8H_8)_{76}\cdot C(C_6H_5)_3$ requires C, 92·0; H, 7·6; Cl, 0·4%; *M*, 8,260. $C_6H_4Cl\cdot(C_8H_8)_{78}\cdot C_6H_4Cl$ requires C, 91·6; H, 7·6; Cl, 0·85%; *M*, 8,336].

(7) A mixture of styrene (5·44 g.) and *p*-chlorophenylazotriphenylmethane (0·996 g.) was heated in a sealed ampoule at 95° for 22 hours. The polymer, isolated and purified as in experiment (5), weighed 2·5 g. [Found: C, 90·55; H, 8·7; Cl, 0·3%; *M*, 17,740. $C_6H_4Cl\cdot(C_8H_8)_{169}\cdot C_8H_9$ requires C, 92·1; H, 7·7; Cl, 0·2%; *M*, 17,792].

(8) A mixture of styrene (4·54 g.) and *p*-chlorophenylazotriphenylmethane (0·993 g.) was sealed in an ampoule and maintained at 100° for 18 hours. The crude polymer was purified three times in the usual way and weighed 2·5 g. [Found: C, 91·2; H, 7·7; Cl, 0·6%; *M*, 16,480. $C_6H_4Cl\cdot(C_8H_8)_{156}\cdot C_6H_4Cl$ requires C, 91·9; H, 7·6; Cl, 0·4%; *M*, 16,447].

(9) A mixture of *p*-chlorophenylazotriphenylmethane (1 g.), styrene (4·537 g.), and dioxan (10 c.c.) was heated in a sealed ampoule at 80° for 5 hours. The contents were poured into methyl alcohol, but no precipitate was formed. On addition of water, globules of an oily liquid separated. The mixture was shaken with ether and cooled. The ethereal layer was then poured into an excess of ice-cold methyl alcohol. A powdery polymer separated which was again purified in the same way (Found: Cl, 1·0%).

(10) A mixture of phenylazotri-*p*-methoxyphenylmethane (0·50 g.), styrene (9·074 g.), and dioxan (10 c.c.) was boiled under reflux for 3 hours under nitrogen. The crude polymer, obtained by pouring the dioxan solution into methyl alcohol, was purified three times in the usual way and afforded 1 g. of pure polystyrene [Found: C, 92·1; H, 7·9; OMe, 0·7%; *M*, 11,770. $C_6H_5\cdot(C_8H_8)_{110}\cdot C(C_6H_4\cdot OCH_3)_3$ requires C, 91·9; H, 7·6; OMe, 0·8%; *M*, 11,850].

(11) A mixture of phenylazotri-*p*-methoxyphenylmethane (0·50 g.) and styrene (4·537 g.) was maintained at 100° under nitrogen for 2 hours. The crude polystyrene (2·3 g.) was purified several times by reprecipitation [Found: C, 91·4; H, 7·7; OMe, 0%; *M*, 13,520. $C_6H_5\cdot(C_8H_8)_{128}\cdot C_6H_5$ requires C, 92·3; H, 7·7; *M*, 13,466].

(12) A mixture of phenylazotri-*p*-methoxyphenylmethane (0·50 g.), styrene (4·54 g.), and dioxan (10 c.c.) was heated in a sealed ampoule at 80° for 6 hours. The mixture was poured into an excess of methyl alcohol, and the crude polymer (0·50 g.) which separated was purified three times by reprecipitation [Found: C, 89·7; H, 7·3; OMe, 1·6%; *M*, 12,900. $C_6H_5\cdot(C_8H_8)_{120}\cdot C(C_6H_4\cdot OCH_3)_3$ requires C, 92·0; H, 7·6; OMe, 0·7%; *M*, 12,890. $(CH_3O\cdot C_6H_4)_3C\cdot(C_8H_8)_{116}\cdot C(C_6H_4\cdot OCH_3)_3$ requires C, 91·6; H, 7·6; OMe, 1·5%; *M*, 12,730].

(13) A mixture of *p*-chlorophenylazotriphenylmethane (2·001 g.) and methyl methacrylate (10·681 g.) was sealed in an ampoule and heated at 65° for 24 hours. The crude polymer (2·5 g.), obtained by dissolving the reaction mixture in dioxan and pouring into an excess of methyl alcohol, was purified three times by reprecipitation and weighed 1·5 g. [Found: C, 59·4; H, 7·6; Cl, 0·8%; *M*, 7,303. $C_6H_4Cl\cdot(C_5H_8O_2)_{71}\cdot C_5H_9O_2$ requires C, 60·1; H, 7·9; Cl, 0·5%; *M*, 7,312].

(14) A mixture of tetraphenylsuccinic dinitrile (1 g.), styrene (4 c.c.), and dioxan (20 c.c.) was heated under reflux for 3 hours under nitrogen. The crude polystyrene (2·5 g.), obtained by pouring the reaction mixture into an excess of methyl alcohol, was dissolved in ethyl acetate. A small portion of the solid which did not dissolve was found to be the adduct of styrene and the dinitrile, m. p. 224°. The polystyrene was then obtained by pouring the filtrate into methyl alcohol. It was purified three times in this way [Found: C, 91·3; H, 7·3; N, 1·8%; *M*, 9,888. $(C_6H_5)_2(CN)C\cdot(C_8H_8)_{90}\cdot C(CN)(C_6H_5)_2$ requires C, 92·1; H, 7·6; N, 0·6%; *M*, 9,744].

(15) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (0·50 g.), styrene (4·54 g.), and dioxan (15 c.c.) was heated in a sealed ampoule at 80° for 6 hours. The crude polymer, obtained by pouring the dioxan mixture into methyl alcohol, was dissolved in ethyl acetate. A small portion of the solid remained undissolved and was identified as the adduct of styrene with the dinitrile, m. p. 212—214°. The polymer was precipitated on pouring the filtrate into methyl alcohol and was further purified by two more precipitations (Found: C, 90·7; H, 7·6%; OMe, 0; *M*, 17,420).

(16) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (0·50 g.), styrene (4.54 g.), and dioxan (10 c.c.) was heated in a sealed ampoule at 80° for 6 hours. The crude polymer was purified three times by dissolving it in ethyl acetate and pouring into an excess of ice-cold methyl alcohol (Found: C, 91·2; H, 7·8%; OMe, 0; *M*, 20,250).

(17) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (0·50 g.), styrene (13·61 g.), and dioxan (60 c.c.), was heated under reflux under nitrogen for 1 hour The rose-red colour disappeared in about 10 minutes. The crude polymer was purified as in the previous examples [Found: C, 91·4; H, 7·4; OMe, 2·1%; *M*, 8,702. $(CH_3O\cdot C_6H_4)_2(CN)C\cdot(C_8H_8)_{74}\cdot C(CN)(C_6H_4\cdot OCH_3)_2$ requires C, 91·3; H, 7·6; OMe, 1·5%; *M*, 8,100].

(18) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (1·00 g.), styrene (9·074 g.), and dioxan (15 c.c.) was heated at 90° for 2 hours. When the mixture was poured into ice-cold methyl alcohol, the crude polymer (0·70 g.) separated. It was purified twice by precipitation from ethyl acetate (Found: C, 90·9; H, 7·5%; OMe, 0; *M*, 15,720). From the first filtrate some adduct was obtained.

(19) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (0·50 g.), styrene (9·074 g.), and dioxan (20 c.c.) was heated at 95° for 2 hours. The crude polymer (0·70 g.), obtained by pouring the mixture into ice-cold methyl alcohol, was purified twice by precipitation from ethyl acetate (Found: C, 91·5; H 7·65%; OMe, 0; *M*, 18,890). As before, some adduct was obtained.

(20) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (1 g.), styrene (9·074 g.), and dioxan (50 c.c.) was heated under reflux under nitrogen for ½ hour. The bulk of the dioxan was evaporated under reduced pressure, and the crude polymer (2 g.) was purified three times by precipitation from ethyl acetate [Found: C, 90·05; H, 7·6; OMe, 1·6%; *M*, 5,274. $(CH_3O\cdot C_6H_4)_2(CN)C\cdot(C_8H_8)_{46}\cdot C(CN)(C_6H_4\cdot OCH_3)_2$ requires C, 90·8; H, 7·5; OMe, 2·35%; *M*, 5,288].

(21) A mixture of tetra-*p*-methoxyphenylsuccinic dinitrile (1·20 g.), styrene (9.074 g.), and dioxan (60 c.c.) was heated under reflux under nitrogen for 16 minutes. The reaction was stopped as soon as the pink colour disappeared. A small quantity of the crude polymer was obtained and purified as described above (Found : C, 86·9 ; H, 7·5% ; OMe, 0 ; *M*, 8,017).

(22) A mixture of styrene (9·074 g.), dioxan (50 c.c.), and tetra-*p*-methoxyphenylsuccinic dinitrile (1 g.) was heated under reflux for 15 minutes under nitrogen. The crude polystyrene was purified as described above (Found : C, 90·6 ; H, 7·5% ; OMe, 0).

(23) A mixture of styrene (9·074 g.) and dioxan (50 c.c.) was heated under reflux for 15 minutes under nitrogen. The crude product (0·70 g.), obtained by taking off the bulk of dioxan under reduced pressure and pouring the residue into methyl alcohol, was purified by precipitation from ethyl acetate (Found : *M*, 9,949).

(24) A mixture of styrene (9·074 g.), dioxan (50 c.c.), and tetra-*p*-methoxyphenylsuccinic dinitrile (1 g.) was heated under reflux under nitrogen for ¾ hour. The crude polymer (1·3 g.) was purified three times by precipitation from ethyl acetate [Found : C, 90·95 ; H, 7·6 ; OMe, 0·4% ; *M*, 11,360. $(CH_3O\cdot C_6H_4)_2(CN)C\cdot(C_8H_8)_{105}\cdot C_8H_9$ requires C, 90·0 ; H, 7·7 ; OMe, 0·55% ; *M*, 11,276].

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