NITRATION OF POLYSTYRENE—PART II

EFFECT OF NITRATING MEDIUM ON NITRATION

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Polystyrene has been nitrated in mixtures of anhydrous nitric and sulphuric acid (70 : 30 and 80 : 20 by volume). Degree of substitution of nitro group per benzene ring varies from 1 to 2 depending on the time, temperature and composition of the nitrating media. Effect of polar and non-polar solvents on nitration has been studied by nitrating the polymer in (*i*) fuming nitric acid and (*ii*) mixture of nitric and sulphuric acid in presence of dimethyl formamide (DMF) and carbon tetrachloride (CCl_4). MF increases the rate of nitration in fuming nitric acid whereas the rate of nitration is lowered in the presence of DMF in the nitrating mixtures. In the case of CCl_4, however, the effect is just the opposite to that observed in DMF. The results have been explained from the

mechanism of the formation of '*nitronium ion, $NO_2{}^+$*' in various nitrating media. Degradation of the polymer has been found to be comparatively less in the presence of the organic solvents used in the study.

In our earlier communication[1] (Part I), it was shown that nitration of polystyrene in fuming nitric acid resulted in a mono-substituted product and that molecular weight of the polymer had no marked influence on the degree of substitution of nitro group per mono-mer unit in the polymer chain. Bachman *et al*[2] could not produce *di*-nitropolystyrene by nitrating the polymer in fuming nitric acid even under very drastic condition. Zenftman[3] was the first to establish the condition for preparing *di*-nitropolystyrene by nitrating the polymer in a mixture of anhydrous nitric and sulphuric acid and had shown the importance of solubility of the polymer in the nitrating mixture in getting an uniformly nitrated product.

Although there are a few reports on the nitration of polystyrene in mixtures of nitric and sulphuric acid in literature[3,4,5], there appears to have been no work on nitration of the polymer in presence of organic solvents. The work reported in this paper was undertaken with a view to studying the influence of various nitrating media on nitration and degradation associated with nitration.

EXPERIMENTAL PROCEDURE

Material used—Polystyrene used in the study was prepared by bulk polymerization of monomeric styrene using benzoyl peroxide as initiator. The unfractionated polymer sample was powdered in an iron pestle and mortar and the material having particle size between B.S.S. 32–52 was used in the nitration experiments.

(*a*) *Nitration with nitrating mixture*—Nitric acid (Sp gr 1·51) and fuming sulphuric acid (Sp. gr. 1·84) were mixed in definite proportions (Table 1) for the nitration experiments. Powdered polystyrene sample (1 gm) was added slowly to the nitrating mixture (20 ml) in a 250 ml conical flask fitted with calcium chloride guard tube on the top to avoid contact with moisture. The mixture was vigorously stirred by means of a magnetic stirrer. The initial temperature during addition of polystyrene was kept below 10°C

TABLE 1

NITRATION OF POLYSTYRENE IN A MIXTURE OF NITRIC ACID AND SULPHURIC ACID

Composition of nitrating mixture		Temperature of nitration	Duration of nitration	Nitrogen	Degree of nitration	Intrinsic viscosity in cyclohexa-none [η]
Nitric acid, Sp gr 1·51	Sulphuric acid, Sp gr 1·84					
(ml)	(ml)	(°C)	(hr)	(%)	(n)	(dl/g)
70	30	20	4	10·70	1·21	..
70	30	40	1	12·72	1·59	0·35
70 (with mercuric nitrate)	30	40	1	12·55	1·36	0·39
70	30	50	3	13·60	1·79	..
80	20	50	3	14·26	1·96	0·13

Acid to polystyrene ratio = 20 : 1 ; Mol. Wt. of Polystryene = 2,27,000; [η] for polystyrene = 0·98 in cyclo-hexanone

and the time of addition was limited to 3 to 5 minutes. When the mixture became homogeneous, the temperature was raised and heating continued for definite periods (Table 1) in a thermostat. At the end of the reaction, a reddish yellow coloured viscous liquid was obtained. It was poured into ice-cold water and stirred. After sometime a straw yellow coloured solid precipitate was obtained which was thoroughly washed several times with warm water till it was free from acid. The sample was then dried in a vacuum oven at 60°C for 12 hours.

(b) *Nitration in presence of mercuric nitrate*—The procedure was essentially the same as in (a) except that 1% mercuric nitrate (on the weight of polystyrene) was added to the nitrating mixture before adding polystyrene.

(c) *Nitration in presence of organic solvents*—In this method, instead of adding the polystyrene powder, a 5% solution of the polymer in dimethylformamide (DMF) or carbon tetrachloride (CCl_4) was slowly added to the fuming nitric acid or nitrating mixture with stirring. The rest of the method is similar to that described in (a).

(d) *Determination of intrinsic viscosity*—Viscosities of polystyrene and nitro-polystyrene were determined in cyclohexanone and DMF in an Ostwald capillary viscometer at 35°C (±0·02°C) and intrinsic viscosity was obtained as the intercept of the linear plot η_{sp}/C vs. η_{sp} according to Schulz & Blaschke's equation[6].

$$\eta_{sp}/C = [\eta] + k [\eta] \eta_{sp}$$

where η_{sp} = specific viscosity, C = concentration in gm/dl and k is the interaction constant.

For the estimation of nitrogen and calculation of degree of substitution (n), methods as described in Part *I*, were followed

RESULTS AND DISCUSSION

Solubility of polystyrene in the nitrating medium is an essential condition for getting a uniformly nitrated product. A non-solvent medium merely results in a surface reaction. Two compositions of nitric acid and sulphuric acid (70 : 30 and 80 : 20 by volume) were found suitable for the purpose. The results of nitration experiments in these media are given in Table 1. By adjusting the temperature and duration of nitration, it is possible to get products with desired degree of substitution from 1 to 2. In one experiment, a product with nitrogen content $14·26\%$ ($n = 1·95$) was obtained in a single step nitration. Renitration of a monosubstituted product with 80 : 20 nitrating mixture resulted in a *di*-substituted product (nitrogen content $14·4\%$). A crossed-linked polystyrene sample kept in the nitrating mixture at $50°C$ for more than 24 hours resulted only in surface reaction and the polymer remained insoluble in the nitration mixture. Particle size of the starting material also plays an important part in reducing the time of dissolution of the polymer in the nitrating medium. The smaller the particle size the quicker it goes into solution and more efficient is the nitration. It was, however, not possible to introduce more than two nitro groups per monomer unit even under very drastic conditions of nitration.

Effect of mercuric nitrate—Catalytic activity of mercury and mercury salts in the nitration of aromatic compounds has been reported by many workers[7-10]. It was, therefore, thought of interest to study the effect of mercuric nitrate on the nitration of polystyrene in the nitrating mixture. Results of our experiment, however, indicate (Table 1) that the rate of nitration as evidenced from the nitrogen content of the product, remains practically unaffected in the presence of mercuric nitrate. Intrinsic viscosity of the nitrated product in cyclohexanone is slightly higher in this case than the polymer of similar nitrogen content and prepared under identical conditions in the absence of mercuric nitrate. This probably indicates that the degradation of the polymer chain is less pronounced in the presence of mercuric nitrate.

Effect of organic solvents—In the nitration of polystyrene, the polymer is generally added to the nitrating medium in the form of granules or powder. In order to study the effect of organic solvents on nitration, we have added to the nitrating mixture a solution of the polymer in the organic solvents to the nitrating mixture. Dimethylformamide, a polar solvent and carbon tetrachloride, and a non-polar solvent were selected as they do not form nitrated products with the nitrating media. Polystyrene is soluble in both these solvents but the nitrated polymer is soluble in dimethylformamide and not in carbon tetrachloride. Moreover, DMF forms a homogeneous solution in fuming nitric acid and in the nitrating mixture whereas carbon tetrachloride is immiscible in both the nitrating media. It will be evident from Table 2, that the rate of nitration is higher (nitrogen content in the product $11·84\%$) in fuming nitric acid in presence of dimethylformamide than in the presence of carbon tetrachloride (nitrogen content in the product $8·83\%$). This can be explained from the mechanism of the formation of '*nitronium ion*' responsible for aromatic nitration as postulated by Ingold et al[11]. In nitric acid medium, '*nitronium ion*' is produced by the following mechanism :
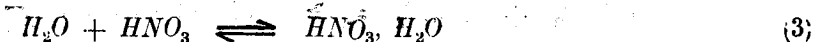
$$HNO_3 + HNO_3 \rightleftharpoons H_2NO_3{}^+ + NO_3{}^- \tag{1}$$

$$H_2NO_3{}^+ \rightleftharpoons NO_2{}^+ + H_2O \tag{2}$$

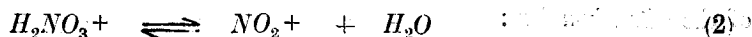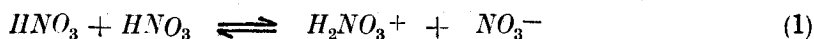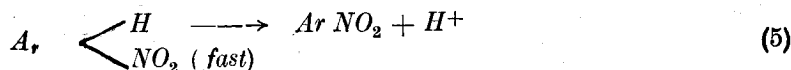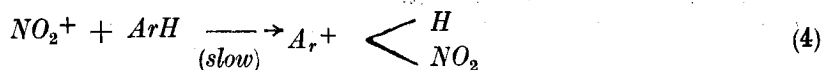$$H_2O + HNO_3 \rightleftharpoons HNO_3, H_2O \tag{3}$$

TABLE 2

NITRATION OF POLYSTYRENE IN PRESENCE OF DIMETHYLFORMAMIDE AND CARBON TETRACHLORIDE

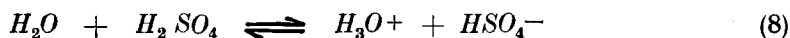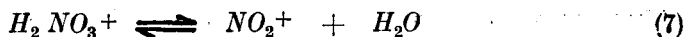| Solvent used	Nitrating acid	Nitrogen	Degree of substitution	Intrinsic viscosity in DMF
		%	(n)	[η] in dl/g
DMF	Fuming HNO_3	11·84	1·42	0·32
CCl$_4$	Fuming HNO_3	8·83	0·92	0·33
DMF	$HNO_3 + H_2SO_4$ (70 : 30)	4·99	0·43	0·36
DMF	$HNO_3 + H_2SO_4$ (80 : 20)	7·30	0·71	0·38
CCl$_4$	$HNO_3 + H_2SO_4$ (70 : 30)	8·86	0·92	0·38
CCl$_4$	$HNO_3 + H_2SO_4$ (80 : 20)	12·37	1·52	0·24

Time of nitration for all samples = 1 hour. Intrinsic viscosity of the polystyrene used = 0·32 in DMF.

'*Nitronium ion*' produced in (2) attacks the aromatic nucleus to produce the nitrated product :

$$NO_2^+ + ArH \xrightarrow[(slow)]{} A_r^+ < \begin{matrix} H \\ NO_2 \end{matrix} \tag{4}$$

$$A_r < \begin{matrix} H \\ NO_2 \, (fast) \end{matrix} \longrightarrow Ar\,NO_2 + H^+ \tag{5}$$

The process of formation of *nitronium ion*, NO_2^+, will be accelerated in the presence of dimethylformamide by the increased solvation forces of the polar molecules and hence the higher rate of nitration. Carbon tetrachloride being non-polar cannot exert such influence on the formation of *nitronium ion*. Moreover, being insoluble in the nitrating medium it acts as a protecting layer from the attack of *nitronium ion*, which probably explains the lower rate of nitration in the presence of carbon tetrachloride. Presence of dimethylformamide, however, lowers the rate of nitration in both the nitrating mixtures of nitric and sulphuric acid as will be evident from the lower nitrogen content of the product. In both the nitrating media, carbon tetrachloride solution of the polymer on nitration gave products with higher percentage of nitrogen than those obtained by nitrating in dimethylformamide solution. This lowering of the rate of nitration in presence of dimethylformamide can be explained if we consider the part played by sulphuric acid in the formation of the *nitronium ion* :

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^- \tag{6}$$

$$H_2 NO_3^+ \rightleftharpoons NO_2^+ + H_2O \qquad (7)$$

$$H_2O + H_2 SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (8)$$

Westheimer and Kharasch[12] in their study of aromatic nitration found that the main factor influencing the rate of nitration was the acidity of the reaction medium. The acidity was optimum in their experiments when the concentration of sulphuric acid was 90%. While determining the rate constant for nitration of nitrobenzene in sulphuric acid they found that these constants increased with a drop in sulphuric acid concentration from 95·6 to 90%. On further decrease of sulphuric acid concentration there was a sharp fall in the rate constant, which at 80% sulphuric acid is diminished 3,000 times as compared to 90% sulphuric acid. They also found that substances which did not alter the acidity of the medium (e.g., di-nitrobenzene and phosphoric anhydride) did not affect the rate of reaction. The addition of potassium bisulphate, which is basic in relation to sulphuric acid affects the rate of nitration differently depending on the acidity of the medium. Dimethylformamide which acts as a base in presence of sulphuric acid removes the proton from the protonated nitric acid in (6) thus retarding the formation of *nitronium ion* in (7) which probably can explain the lower rate of nitration in the nitrating mixtures.

Degradation of the polymer during nitration—In earlier study (Part I) we have shown that degradation of the polymer is dependent on the molecular weight of the polymer used in nitration : higher the molecular weight of the polymer, more is its degradation. Intrinsic viscosities of the polymers before and after nitration were determined in cyclohexanone and dimethylformamide in order to have a qualitative idea about the degradation of polymeric chain associated with nitration. It will be evident from Table 1 that higher temperature and prolonged time of nitration results in more degradation and consequently lower values of intrinsic viscosity. Degradation is, however, comparatively less pronounced when the polymer is nitrated in presence of dimethylformamide and carbon tetrachloride (Table 2).

ACKNOWLEDGEMENT

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