

202. *The Nitration of Polystyrene.*

By H. ZENFTMAN.

Polystyrene has been nitrated with mixtures of nitric and sulphuric acids. By regulating the conditions of nitration, products with degrees of substitution between 1.0 and 2.0 (nitrogen content, 9.4—14.4%) could be obtained, but attempts to obtain higher substitution were unsuccessful. Oxidative fission of nitropolystyrenes produced *p*-nitrobenzoic and 2 : 4-dinitrobenzoic acids. During nitration some degradation of the original polystyrene chain took place, but could be controlled under suitable conditions. The properties of various nitropolystyrenes have been determined.

IN the first recorded nitration of polystyrene Blyth and Hofmann (*Annalen*, 1845, **53**, 316) boiled a glassy polymer of styrene with fuming nitric acid and obtained a product of 10.6% nitrogen content which they called "nitrometastylol." This product was soluble in nitric acid and sulphuric acid, but insoluble in most other solvents. Elementary analysis of this product led these authors to incorrect formulations for styrene and nitrostyrene. Bachman *et al.* (*J. Org. Chem.*, 1947, **12**, 108) nitrated polystyrene with fuming nitric acid in a similar way at 50° and 150° and obtained products with 10.0 and 11.22% of nitrogen, respectively. They were unable to obtain dinitropolystyrene. Recent knowledge of high polymers suggested that a range of nitropolystyrenes differing in chain length and degree of nitration, and consequently in solubility and solution viscosity, should be accessible by suitable choice of starting material and nitration conditions.

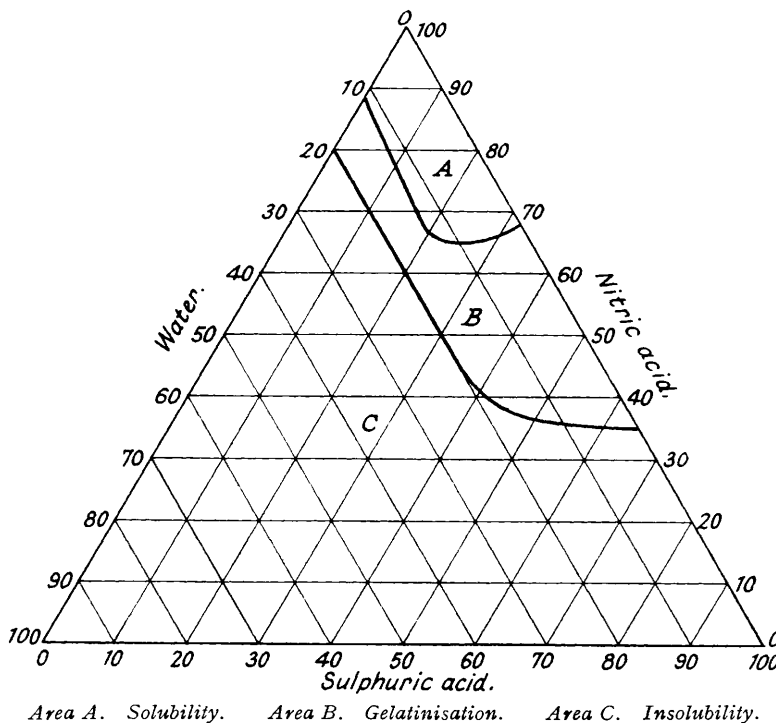
Preliminary experiments showed that nitration of polystyrene in a non-solvent medium merely gave a negligible surface reaction. When the nitrating medium caused swelling of the granules the nitration was more pronounced, but the product was not uniform and unchanged polymer still persisted. It was, therefore, essential to use a nitrating medium capable of completely dissolving the polystyrene. Mixtures of nitric and sulphuric acids were found to be the most suitable nitrating agents for this work. Investigation of the solubility of polystyrene after two hours at 20° in variants of the system nitric acid-sulphuric acid-water gave the results summarised in the triangular diagram.

Area *A* included all nitrating media of practical importance, and the curved boundary of area *C* indicated the approximate minimum degree of dilution required to precipitate the product. Table II summarises the effects of times from 1 to 24 hours and temperatures from 10° to 50° on using various nitrating acids having compositions lying within area *A*.

It was found that polystyrene was nitrated by every nitric or nitric-sulphuric acid

composition capable of dissolving it. The lowest nitrogen content of nitropolystyrene obtained from clear solutions was approximately 9.4%, corresponding to one nitro-group per styrene unit, whereas the highest nitrogen content obtained was 14.4%, corresponding to two nitro-groups per styrene unit. Any intermediate substitution could be obtained by controlling the composition of the nitrating acid, the temperature, and the time of nitration. The molecular weight of the initial polystyrene (as indicated by the viscosity data in Table IV) was found to have little influence on the nitrogen content of the final product. The introduction of the first nitro-group was rapid and appeared to accompany the dissolution of the polystyrene. The rate of mononitration could be regulated by modifying the rate of dissolution of polystyrene in the nitrating acid, *e.g.*, by variation of the particle size. Introduction of the second group took place at a slower rate which was dependent on the dilution of the nitrating acid and the temperature of nitration. Addition of polystyrene to nitrating acid was always accompanied by evolution of heat, and efficient stirring and cooling were necessary to control the nitration. It was observed, however, during renitration of nitropolystyrene (9.8% nitrogen content) to a higher nitrogen content (14.1%) that it dissolved in the nitric-sulphuric acid quickly but without significant evolution of heat. For each nitrating acid composition and temperature of nitration there was a limiting degree of substitution which, as a rule, was attained more rapidly the higher the temperature. Attempts were made to obtain nitropolystyrene of a higher degree of substitution than 2.0 by carrying out nitration in sealed tubes at high temperatures (120° and 150°), but these met with no success. The nitrogen contents of the products were determined by the Dumas method. Elementary analyses of a few samples of nitropolystyrene of various nitrogen contents were consistent with the expected empirical formula $C_8H_{8-n}(NO_2)_n$, where n represents the degree of substitution calculated from the equation $n = 104N/(1400 - 45N)$ (where $N = \%$ of nitrogen).

Solubility of polystyrene in nitric acid-sulphuric acid-water mixtures.



The positions of the nitro-groups in the polymeric chain were determined by oxidative fission of nitropolystyrenes. Aromatic nitro-compounds with an aliphatic side chain are readily oxidised to the corresponding nitrobenzoic acids. Bigelow (*J. Amer. Chem. Soc.*, 1919, **41**, 1575) obtained good yields of mononitrobenzoic acids from mononitrotoluenes by using potassium permanganate in alkaline solutions. For the same purpose Feldman *et al.* (*J. Gen. Chem. Russia*, 1945, **15**, 962) used manganese dioxide and concentrated sulphuric acid. Dinitro-

toluenes were oxidised to dinitrobenzoic acids by Sirks (*Rec. Trav. chim.*, 1908, **27**, 221), using nitric acid or potassium permanganate, and by Buehler and Calfee (*Anal. Chem.*, 1934, **6**, 351), using chromic acid.

Oxidation of nitropolystyrenes to nitrobenzoic acids was found to be difficult, and all methods gave large amounts of unchanged nitropolystyrene. The best results were obtained by using manganese dioxide in concentrated sulphuric acid. Only *p*-nitrobenzoic and 2:4-dinitrobenzoic acids could be isolated. Nitropolystyrene of a nitrogen content 9.4% (degree of substitution 1.0) gave on oxidation only *p*-nitrobenzoic acid, but nitropolystyrenes with a degree of substitution between 1 and 2 always gave both *p*-nitrobenzoic and 2:4-dinitrobenzoic acids. All attempts to isolate mononitrobenzoic acids from the oxidation of a nitropolystyrene of a degree of substitution approximately 2.0 were unsuccessful, and this suggested the absence of nitro-groups in the aliphatic chain.

These results indicated that during nitration of polystyrene only nuclear substitution occurred, a maximum of two nitro-groups entering each benzene ring. The first group entered the *p*-position, the second being randomly distributed along the polymer chain entirely or predominantly in the *o*-position. It was not possible, however, to state definitely that substitution was entirely limited to the *o*- and the *p*-positions on account of the low yields of nitrobenzoic acids calculated on unrecovered nitropolystyrene (usually less than 40%).

Degradation of the chain length of the polystyrene during nitration was estimated approximately by measuring the viscosities of the nitrated products and the original polystyrene. Viscosities were measured in dilute cyclohexanone solutions at such concentration that $\eta_{rel.}$ had values between 1.1 and 1.2, and were applied to the following approximation of Staudinger's expression: Degree of polymerisation = $k(\eta_{rel.} - 1)/C$; k for nitropolystyrene was unknown, but may be taken as constant in the range of nitrogen contents under consideration.

It is, moreover, considered unlikely that k for polystyrene will be halved when the material is nitrated, so that the results in Table III indicate that under all conditions of nitration some degradation of the polymer chain occurred. However, by carrying out the nitration under strict conditions of temperature and time, it could to a large extent be controlled. Degradation was most rapid during the first stages of nitration and then continued more slowly. High nitration temperatures favoured degradation. Table IV also shows that the decrease in degree of polymerisation of polystyrene with higher initial molecular weight was relatively greater.

Nitropolystyrenes of 9.4% to 14.4% nitrogen content were amorphous, pale cream-coloured to light yellow solids which darkened on exposure to daylight. When heated to 300°, nitropolystyrenes decomposed without melting, at a rate increasing with nitrogen content, and evolved greyish-yellow gases leaving a black residue. Nitropolystyrenes were soluble in a restricted range of solvents to form viscous solutions.

Solubility increased with nitrogen content (Table I). In some solvents nitropolystyrene underwent limited swelling, forming gels.

TABLE I.

Solubility of nitropolystyrenes of different nitrogen contents in various solvents at 20°.

Solvent.	Nitrogen content of nitropolystyrene, %.						
	9.8.	11.7.	12.4.	13.0.	13.4.	13.8.	14.4.
Nitric acid, 90%	S	S	S	S	S	S	S
Ethylene dinitrate	S	S	S	S	S	S	S
Nitroglycerol	S	S	S	S	S	S	S
Furfuraldehyde	G	S	S	S	S	S	S
cycloPentanone	SW	S	S	S	S	S	S
cycloHexanone	SW	G	S	S	S	S	S
Dinitrotoluene (liquid mixture)	G	S	S	S	S	S	S
Mononitrotoluene (mixture)	SW	G	G	S	S	S	S
Nitrobenzene	G	S	S	S	S	S	S
Nitromethane	SW	G	G	G	G	G	G
Acetone	I	I	I	I	SW	SW	SW

S = soluble at 20°. S = requires heating to facilitate dissolution, remains in solution when cooled to 20°. G = gelatinised. G = gelatinised when heated. SW = swelling observed. I = no visible reaction.

EXPERIMENTAL.

Nitration of Polystyrene.—Nitration was carried out by adding granular polystyrene to a 10–20-fold weight of nitrating acid with vigorous stirring. The initial temperature of the acid was about -10° , and the whole of the polystyrene was added within 2–3 minutes. The temperature increased immediately after addition of polystyrene but effective cooling prevented it from exceeding 20° . After approximately

30 minutes the temperature was kept steady at the desired point, and maintained there by either cooling or heating. The viscosity of the mixture increased and the rate of stirring was reduced. Rapid addition of polystyrene to acid at low temperature was a necessary condition for obtaining a product with consistent properties. If the addition was carried out slowly at a constant temperature the rise of viscosity hindered the immersion and dispersion of further portions of polystyrene and caused local overheating of the particles. This was indicated by the appearance of brown fumes, and also by an excessively degraded product. When the nitration was finished, the mixture formed a clear, straw-coloured or brown, viscous liquid. Nitropolystyrene was precipitated from the solution by running the liquid in one or many very thin streams into gently stirred cold water. The precipitated product formed coils of threads which gradually became brittle and finally broke up into easily handled elongated granules which were sufficiently porous to permit washing out of the last traces of acid. When mechanical losses were avoided the weight of product as a percentage of the weight of initial polystyrene, approximated to the theoretical value of $100 + 100N/(31.11 - N) \%$ ($N = \%$ of nitrogen).

A typical nitration was carried out as follows: Mixed acid (300 ml.; composition: HNO_3 , 73.2; H_2SO_4 , 26.3; HNO_2 , 0.1; H_2O , 0.4%) was cooled to -10° in a wide-necked conical flask. Polystyrene (125 g.; M , 210,000; particle size, 16–30 B.S. gauge) was added during two minutes, the temperature rising to 18° . Cooling with ice-salt and effective stirring during the first 30 minutes were required to prevent a further rise of temperature. After 30 minutes the temperature settled at 20° . After 1 hour from the start the whole of polystyrene had dissolved. Slow stirring was maintained for a further 3 hours at 20° , and the solution was then run from a dropping-funnel during 40 minutes into slowly stirred water (4–5 l.). The thread-like product was broken up into short lengths, washed five times by decantation, filtered off, washed on the filter, and steeped in water overnight. The filtered product was ground for 16 hours in a porcelain ball-mill with water (approx. 5 parts). Filtration, washing with water at 90 – 95° until the washings were neutral to methyl-orange, and drying to constant weight gave a product (42 g.) containing N, 13.4% (by Dumas's method). The degree of substitution was found to be 1.75, and ultimate analysis gave C, 51.9; H, 3.1% [Calc. for $\text{C}_8\text{H}_6.25(\text{NO}_2)_{1.75}$: C, 52.5; H, 3.4%].

TABLE II.

Influence of conditions of nitration on nitrogen content of nitropolystyrene.

Nitrating acid composition, %.				Temp. of nitration.	Time of nitration (hrs.).	Nitrogen content of nitropolystyrene (%).	Degree of substitution (η).
HNO_3 .	H_2SO_4 .	HNO_2 .	H_2O .				
72.73	28.09	0.24	—1.06	10°	1	12.4	1.53
"	"	"	"	"	2	12.8	1.62
"	"	"	"	"	3	13.2	1.70
"	"	"	"	"	5	13.3	1.73
"	"	"	"	"	7	13.4	1.75
"	"	"	"	"	24	13.4	1.75
"	"	"	"	20	1	12.8	1.62
"	"	"	"	"	2	13.3	1.73
"	"	"	"	"	3	13.4	1.75
"	"	"	"	"	4	13.4	1.75
"	"	"	"	"	5	13.6	1.80
"	"	"	"	30	1	13.1	1.68
"	"	"	"	"	3	13.7	1.82
"	"	"	"	"	4	14.1	1.92
"	"	"	"	"	6	14.1	1.92
"	"	"	"	40	1	13.3	1.73
"	"	"	"	"	2	13.8	1.84
"	"	"	"	"	4	14.3	1.97
"	"	"	"	50	1	13.7	1.82
"	"	"	"	"	2	14.2	1.94
"	"	"	"	"	3	14.4	2.00
72.98	22.29	0.25	4.48	20	1	11.7	1.39
"	"	"	"	"	3	12.0	1.45
"	"	"	"	"	4	12.8	1.62
"	"	"	"	"	5	13.1	1.68
"	"	"	"	"	6	13.3	1.73
76.75	15.30	0.10	7.85	20	1	10.0	1.09
"	"	"	"	"	3	11.6	1.37
"	"	"	"	"	4	11.8	1.41
"	"	"	"	"	6	12.1	1.47
66.40	20.30	0.10	13.20	20	2	9.5	1.02
"	"	"	"	"	4	9.7	1.05
"	"	"	"	"	6	9.8	1.06

Molecular weight of polystyrene used, 210,000.

Ratio of acid to polystyrene, 20 : 1.

Oxidation of High-nitrogen Nitropolystyrene with Manganese Dioxide.—Finely ground nitropolystyrene (50 g.; N, 14.2%) was suspended in 96% (w/w) sulphuric acid (250 ml.) and left overnight. The liquid was heated in an oil-bath to 135° , and manganese dioxide (170 g.; MnO_2 content, 80%) was added during 16 hours in small portions at intervals of 15–20 minutes. The hot liquid was poured on crushed ice

(900 g.), and the product filtered, giving a solid residue (i) and a filtrate (ii). Residue (i) was washed with water (150 ml.), the washings being added to (ii), then suspended in water (200 ml.), made alkaline with concentrated sodium carbonate solution, heated to 85°, and filtered hot, giving a filtrate (iii) and a residue (iv). Residue (iv) was washed with hot water, separated by decantation from heavy particles of manganese dioxide, heated with diluted sulphuric acid, filtered, washed, and dried to constant weight to yield unconverted nitropolystyrene (30 g.). Filtrate (iii) was made acid (Congo-red paper) with the minimum amount of sulphuric acid (70% w/w), cooled, and filtered from traces of precipitate, giving filtrate (v).

TABLE III.

Influence of temperature and time of nitration on the viscosity of nitropolystyrene.

Nitration conditions.		Product.			
Temp.	Time (hrs.).	Nitrogen content (%).	C, g./100 ml.	$\eta_{rel.}$	$(\eta_{rel.}-1)/C$.
20°	2	13.2	0.165	1.148	0.90
"	4	13.4	0.217	1.165	0.76
"	5	13.6	0.200	1.142	0.71
30	1	13.1	0.220	1.151	0.69
"	3	13.7	0.200	1.118	0.59
"	4	14.1	0.204	1.107	0.52
40	1	13.3	0.200	1.106	0.53
"	2	13.8	0.212	1.106	0.50
"	4	14.3	0.224	1.108	0.48
50	1	13.7	0.306	1.119	0.39
"	2	14.2	0.286	1.103	0.36
"	3	14.4	0.323	1.120	0.34

The original polystyrene used in these nitrations had $(\eta_{rel.}-1)/C = 1.87$ (determined in cyclohexanone, $C = 0.060$). Nitrating acid used: HNO_3 , 72.7; H_2SO_4 , 28.1; HNO_2 , 0.2; H_2O , -1.0%.

TABLE IV.

Influence of viscosity of the polystyrene on the nitrogen content and the viscosity of nitropolystyrene.

Poly-styrene.	Nitropolystyrene.	Poly-styrene.	Nitropolystyrene.	Poly-styrene.	Nitropolystyrene.
$(\eta_{rel.}-1)/C$.	N, %.	$(\eta_{rel.}-1)/C$.	N, %.	$(\eta_{rel.}-1)/C$.	N, %.
1.05	{ 13.58 13.52	0.54	1.87	{ 13.48 13.41	0.76
				4.80	{ 13.45 13.42
					1.07

Composition of nitrating acid: HNO_3 , 72.2; H_2SO_4 , 26.4; HNO_2 , 0.2; H_2O , 1.2%. Temperature, 20°; time, 4 hours.

Filtrate (v) gave a residue (vi; 1.1 g.) on extraction with ether (100 ml.) and evaporation of the extract. Residue (vi) was dissolved in the minimum amount of hot water, and decolorised with charcoal. Successive crops of crystals had m. p.s between 178° and 182°, which were not depressed on admixture with 2:4-dinitrobenzoic acid.

Filtrate (ii) was extracted with ether (150 ml.), 300 ml. of (ii) being used at a time, and the ether extract re-used. After evaporation, residue (vii) was obtained (7.7 g.). Residue (vii), crystallised from water (charcoal), gave crops of crystals with m. p.s between 177° and 181°, undepressed on admixture with 2:4-dinitrobenzoic acid.

Oxidation of Low-nitrogen Nitropolystyrene with Manganese Dioxide.—Nitropolystyrene (20 g.; N, 12.3%) was suspended in 75% (w/w) sulphuric acid (300 g.), and manganese dioxide (95 g.; MnO_2 content, 80%) was gradually added at 135° during 12 hours. The liquid was poured into water (350 ml.) and filtered when cold, giving a residue (i) and a filtrate (ii). Residue (i) was washed with water (50 ml.), the washings being added to (ii), and the residue suspended in water (120 ml.), made alkaline, and filtered hot, giving a filtrate (iii) and residue (iv). Residue (iv), washed with dilute sulphuric acid and water, dried, and analysed for nitrogen, was shown to contain nitropolystyrene (11.5 g.).

Ether-extraction of filtrate (ii) yielded 2:4-dinitrobenzoic acid (1.3 g.). Filtrate (iii) was made acid, left overnight in a cool place, and filtered to give a residue (v) and filtrate (vi). Residue (v) and the ethereal extract of filtrate (vi) gave crystals (total yield 1.5 g.) which on recrystallisation from water had m. p. 241° (undepressed by *p*-nitrobenzoic acid).

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IMPERIAL CHEMICAL INDUSTRIES LIMITED,
NOBEL DIVISION, STEVENSTON, AYRSHIRE.

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