

# NITRATION OF POLYSTYRENE PART—1

## EFFECT OF MOLECULAR WEIGHT OF POLYMER ON NITRATION

(MISS) I. BAJAJ AND S.R. CHATTERJEE

Defence Science Laboratory, Delhi

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Polystyrene in the molecular weight range,  $3.67 \times 10^4$  to  $47.86 \times 10^4$  has been nitrated in fuming nitric acid at  $50^\circ\text{C}$  and degree of substitution of nitro group per monomeric unit in the polymer chains varying from 1.03 to 1.11 has been obtained. Molecular weight of the initial polymers have been found to have no appreciable effect on the degree of substitution. Degradation of the polymer chain is, however, found to be more pronounced in high molecular weight polymers.

Nitration of polystyrene results in a mono-or di—substituted product depending on the conditions of the nitration experiment. Nitro polystyrene can be used as a binder for explosives<sup>1</sup>. Various methods of nitration of polystyrene have been reported in the literature<sup>2-4</sup>. But no systematic study appears to have been made so far to find the effect of molecular weight of the initial polymer on nitration. The work reported in the present communication was undertaken with a view to studying the effect of molecular weight of polystyrene on nitration and on degradation associated with nitration.

### EXPERIMENTAL PROCEDURE

#### *Polymer used*

Polymers used in the nitration experiments were obtained by fractionating<sup>5</sup> of a polystyrene sample prepared in the laboratory by bulk polymerisation of styrene, using benzoyl peroxide as catalyst. Six fractions of polymer differing in molecular weight were prepared from 1.5% solution of polystyrene in benzene using methyl alcohol as precipitant.

#### *Determination of molecular weight*

Molecular weight of the fractionated polystyrene samples was determined by measuring the viscosity of the polymer solutions in benzene at  $35^\circ\text{C}$  ( $\pm 0.02^\circ\text{C}$ ) using an Ostwald capillary viscometer. Average molecular weight of the polymers was calculated from the intrinsic viscosity,  $[\eta]$ , using the following equations<sup>6</sup>.

$$[\eta] = 1.72 \times 10^{-4} [M]^{0.73}$$

#### *Nitration*

Powdered polystyrene (1 gm.) was added with stirring to fuming nitric acid having specific gravity 1.52 (15 ml.) in a conical flask. Polystyrene dissolved immediately with evolution of heat. Temperature was kept below  $20^\circ\text{C}$  during addition of the polymer. The mixture was then heated in a thermostat at  $50^\circ\text{C}$  for one hour. The deep yellow solution after cooling was poured in ice-cold water resulting in yellow flakes as precipitate. The precipitate was thoroughly washed with water until free from acid. The sample thus prepared was dried in a vacuum oven at  $60^\circ\text{C}$  for 12 hours.

*Nitrogen estimation*

Zinc-iron reduction method<sup>7</sup> for the estimation of nitrogen in a nitro compound was followed using a Pregl semi-micro distillation apparatus<sup>8</sup>. The accuracy of the method was tested by estimating the nitrogen content of a standard nitro compound, and *p*-nitrophenol. Average of three nitrogen estimations was recorded.

*Degree of substitution (n)*

The degree of substitution, (*n*) was calculated from the following equation on the basis of the expected empirical formula of nitropolystyrene,  $C_8H_{8-n}(NO_2)_n$  :

$$n = \frac{104 \times N}{(1400 - 45 N)}$$

where *N* is percentage of nitrogen.

## RESULTS AND DISCUSSION

Results of nitration experiments conducted under identical conditions in fuming nitric acid are summarised in Table 1.

TABLE 1

EFFECT OF MOLECULAR WEIGHT OF POLYSTYRENE ON NITRATION IN FUMING NITRIC ACID (SP. GR. 1.52) AT 50°C.

Sample No.	Molecular Weight	Nitrogen %	Degree of Substitution <i>n</i>
Fr-1	478,600	9.63	1.036
Fr-2	417,800	9.84	1.068
Fr-3	312,600	9.83	1.068
Fr-4	167,500	9.91	1.080
Fr-5	71,450	9.92	1.081
Fr-6	36,730	10.10	1.111

(Time of nitration in all samples is 1 hour)

TABLE 2

DEGRADATION OF POLYSTYRENE ON NITRATION

Sample No.	$(\eta)$ of polystyrene in benzene (dl/gm)	$(\eta)$ of nitropolystyrene in nitrobenzene (dl/gm)
Fr-1	1.65	1.74
Fr-2	1.48	1.70
Fr-3	1.21	1.73
Fr-4	0.78	1.74
Fr-5	0.43	1.72
Fr-6	0.27	1.71

For the wide range of molecular weight of the polystyrene used for nitration, the nitrogen content of the product varies from 9.63% for the highest molecular weight fraction to 10.1% for the lowest molecular weight fraction corresponding to the variation in the degree of substitution, ( $n$ ), from 1.03 to 1.11. Since introduction of one nitro group per styrene unit in the polymeric chain is equivalent to 9.4% nitrogen in the product, it can be concluded that nitration of polystyrene in fuming nitric acid under identical conditions at 50°C results in a mono-substituted product. Thus, for more than twelve-fold difference in molecular weight of polystyrene used in the nitration experiments, difference in the nitrogen content of the product is only 0.5% which clearly indicates that molecular weight of the initial polymer has practically no effect on the degree of substitution in the nitrated product.

Nitration of polystyrene always results in some degradation of the polymer chain<sup>3</sup>. A knowledge of the molecular weight of the polymer before and after nitration could give a quantitative picture of the extent of degradation. In the absence of a relationship connecting the intrinsic viscosity with molecular weight of nitropolystyrene, a comparison was made between the intrinsic viscosity of the initial polymers and the products (Table 2). Intrinsic viscosity,  $[\eta]$ , being proportional to the molecular weight, this comparison will, at any rate, give a qualitative idea on degradation occurring during nitration.

It was, however, not possible to measure the viscosity of polystyrene and mono-nitropolystyrene in the same solvent the latter being soluble only in a limited number of solvents like nitrobenzene, fuming nitric acid and concentrated sulphuric acid. Higher value of the intrinsic viscosity of nitropolystyrene as compared to polystyrene, is probably due to the extended configuration of the nitropolymers in nitrobenzene. It will be evident from Table—2 that the intrinsic viscosity of the nitrated products is more or less closer despite the wide difference in intrinsic viscosity of the initial polystyrene used in nitration. This suggests that irrespective of the molecular weight of the initial polymers used in this study, the molecular weight of the products almost reaches a limiting value and the higher molecular weight polymers are more degraded during nitration than the lower molecular weight polymers. A similar observation was made by Zenftman<sup>3</sup> in the nitration of polystyrene by a mixture of nitric acid and sulphuric acid.

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