The nitration of polystyrene

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Four methods for the nitration of polystyrene are compared: (i) direct nitration with a nitric acid/sulfuric acid mixture; (ii) nitration in carbon tetrachloride with acetyl nitrate; (iii) nitration in *N,N'*-dimethylformamide with a nitric acid/sulfuric acid mixture; and (iv) nitration in 3-nitrotoluene with a nitric acid/sulfuric acid mixture. It is demonstrated that the first three methods give products with low degrees of substitution and lead to a broadening of the molecular weight distribution, but that method (iv) gives poly(4-nitrostyrene) with minimal effect on the breadth of the molecular weight distribution. The glass transition temperature for poly(4-nitrostyrene) is found to approach 194.6°C at high molecular weights.

(Keywords: polystyrene; poly(4-nitrostyrene); nitration; glass transition temperature)

INTRODUCTION

The first attempts to nitrate polystyrene involved boiling the polymer in fuming nitric acid[1,2]. Subsequently, a mixture of nitric and sulfuric acids was utilized, but severe degradation of the polymer occurred[3–5]. Attempts to minimize the degradation by nitration with acetyl nitrate using carbon tetrachloride as a solvent gave products with very low nitrogen contents[6,7]. The nitration of polystyrene solubilized in *N,N'*-dimethylformamide with a mixture of nitric and sulfuric acids gave a monosubstituted product which was degraded[8].

In this contribution, four methods for the nitration of polystyrene are compared: (i) direct nitration with a nitric acid/sulfuric acid mixture; (ii) nitration in carbon tetrachloride with acetyl nitrate; (iii) nitration in *N,N'*-dimethylformamide with a nitric acid/sulfuric acid mixture; and (iv) nitration in 3-nitrotoluene with a nitric acid/sulfuric acid mixture. It is shown that the last method gives poly(4-nitrostyrene) with minimal effect on the breadth of the molecular weight distribution, and glass transition temperatures are given for samples of this polymer.

EXPERIMENTAL

Reagents

Polystyrene samples having narrow size distributions were synthesized by anionic polymerization. Molecular weight data, obtained by gel permeation chromatography, are given in *Table 1.*

N,N'-dimethylformamide (May & Baker) was distilled under reduced pressure (54–56°C/16 mmHg) prior to use. 3-Nitrotoluene (Aldrich) was stirred for up to 48 h with phosphorus pentoxide under a dry nitrogen atmosphere and distilled under reduced pressure (120–121°C/4 mmHg) prior to use. Propan-2-ol (Fisons) was refluxed over calcium oxide for 8 h then distilled (82–82.5°C/760 mmHg) prior to use.

Nitric acid, s.p. 1.42 (Aldrich), sulfuric acid (Aldrich), acetic acid (BDH), acetic anhydride (BDH), carbon tetrachloride (Fisons) and ethanol (Burroughs, AR) were used as received.

Nitration of polystyrene

(i) Nitration with nitric acid/sulfuric acid mixture. Polystyrene (5.0 g) was added to a round-bottomed flask equipped with a mechanical stirrer, a thermometer and an addition funnel. Nitric acid (80.0 cm^3) was added to the polymer with vigorous stirring under a dry nitrogen atmosphere. This was followed by the slow addition of sulfuric acid (20.0 cm^3) at 0°C. The reaction mixture was subsequently left stirring at either 30°C or 50°C for up to 24 h.

The reaction mixture was poured slowly into an excess

Table 1 Average molar masses for polystyrene samples

Sample	$\bar{M}_n$ (10^3 g mol^{-1})	$\bar{M}_w$ (10^3 g mol^{-1})	$\bar{M}_w/\bar{M}_n$
PS1	4.51	5.10	1.12
PS2	5.02	5.45	1.09
PS3	5.74	6.31	1.10
PS4	7.42	8.38	1.13
PS5	9.41	10.45	1.11
PS6	20.53	24.23	1.18
PS7	23.42	27.17	1.16
PS8	41.44	45.58	1.10
PS9	59.26	65.19	1.10
PS10	186.3	210.5	1.13

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of aqueous sodium hydroxide (25.0 g in 60.0 cm^3). The precipitate was filtered and washed with water until a neutral pH was achieved. The product was subsequently dissolved in *N,N'*-dimethylformamide, reprecipitated in water and left stirring for 4 h at 40°C. The polymer was recovered by filtration, washed with water then methanol, and dried to constant weight at 50°C under vacuum.

(*ii*) *Nitration in carbon tetrachloride with acetyl nitrate.* Polystyrene (5.0 g) was dissolved in carbon tetrachloride (100 cm^3) in a round-bottomed flask equipped with a mechanical stirrer, a thermometer and an addition funnel. Nitric acid (35.0 cm^3) was added with vigorous stirring under a dry nitrogen atmosphere. This was followed by the slow addition of acetic anhydride (40.0 cm^3) at 10°C. The reaction mixture was subsequently left at either 30°C or 50°C for 2 h. Reactions conducted at 50°C resulted in the precipitation of a pale yellow polymer.

The reaction mixture was added to an excess of ethanol. The precipitate was filtered and washed with water then methanol. The product was redissolved in *N,N'*-dimethylformamide, reprecipitated in water and left stirring for 4 h at 40°C. The polymer was recovered by filtration, washed with water then methanol, and dried to constant weight at 50°C under vacuum.

(*iii*) *Nitration in* N,N'*-dimethylformamide with a nitric acid/sulfuric acid mixture.* Polystyrene (5.0 g) was dissolved in *N,N'*-dimethylformamide (100 cm^3) in a round-bottomed flask equipped with a mechanical stirrer, a thermometer and an addition funnel. Nitric acid (80.0 cm^3) was added with vigorous stirring under a dry nitrogen atmosphere. This was followed by the slow addition of sulfuric acid (20.0 cm^3) at 0°C. The reaction mixture was left stirring at 30°C for up to 12 h and samples removed at regular intervals.

The isolated samples were added to an excess of water. The precipitate was filtered and washed with water until a neutral pH was achieved. The product was redissolved in *N,N'*-dimethylformamide, reprecipitated in water and left stirring for 4 h at 40°C. The polymer was recovered by filtration, washed with water then methanol, and dried to constant weight at 50°C under vacuum.

(*iv*) *Nitration in 3-nitrotoluene with a nitric acid/sulfuric acid mixture.* Polystyrene (5.0 g) was dissolved in 3-nitrotoluene (100 cm^3) in a round-bottomed flask equipped with a mechanical stirrer, a thermometer and an addition funnel. Nitric acid (80.0 cm^3) was added with vigorous stirring under a dry nitrogen atmosphere. This was followed by the slow addition of sulfuric acid (20.0 cm^3) at 10°C. The reaction mixture was left stirring at 30°C for up to 12 h and samples removed at regular intervals.

Samples of the product in the form of a microemulsion were added to an excess of propan-2-ol and left stirring. The precipitate was filtered and washed with propan-2-ol, then redissolved in *N,N'*-dimethylformamide, reprecipitated in water and left stirring for 4 h at 40°C. The polymer was recovered by filtration, washed with water then propan-2-ol, and dried to constant weight at 50°C under vacuum.

Characterization of the nitrated products

Degree of substitution. The degrees of substitution, *n*, of the products were evaluated in three different ways: (a) from the yield; (b) from elemental analysis; and (c) from nuclear magnetic resonance spectroscopy. The latter technique also enabled the substitution position to be determined.

(*a*) *Yield.* The degree of substitution was estimated from the yield of product, assuming that there was no material loss in the recovery process and no side reactions, using

$$n=\frac{\text{mass of recovered polymer}}{1.433\times\text{mass of polystyrene}}$$

(*b*) *Elemental analysis.* Taking the product to be $C_8H_{8-n}(NO_2)_n$, the degree of substitution was determined from the percentage nitrogen by mass (N%) using

$$n=104\text{N}\%/(1400-45\text{N}\%)$$

or from the percentage carbon by mass (C%) using

$$n=(9600-104\text{C}\%)/45\text{C}\%$$

(*c*) *Nuclear magnetic resonance spectroscopy.* ^{1}H n.m.r. spectra of samples dissolved in deuterated dimethylsulfoxide (0.01 g cm^{-3}) were obtained using a 300 MHz Bruker AC300 nuclear magnetic resonance spectrometer.

Taking there to be three aliphatic hydrogens and, on average, $(5-n)$ aromatic hydrogens per repeat unit, the degree of substitution was determined using

$$n=5-\frac{3\Sigma I_{\text{aromatic}}}{\Sigma I_{\text{aliphatic}}}$$

where $\Sigma I_{\text{aromatic}}$ and $\Sigma I_{\text{aliphatic}}$ are the sums of the integrals for the peaks corresponding to aromatic and aliphatic hydrogens, respectively.

Molecular weight distribution. Changes in molecular weight distribution on nitration were monitored by gel permeation chromatography. Three columns were used, packed with PL gel (Polymer Laboratories) of nominal pore sizes 500, 10^4 and 10^5 Å. The eluent was *N,N*-dimethylacetamide at 70°C and the flow rate was 1.0 cm^3 min^{-1}. The detector was a differential refractometer (Waters, model 501).

For some samples, absolute number-average ($\bar{M}_n$) or weight-average ($\bar{M}_w$) molecular weights were determined. Values of $\bar{M}_n$ were determined with a vapour pressure osmometer (Knauer). Measurements were made on solutions of the polymer in *N,N'*-dimethylformamide at 90°C. Benzil and poly(ethylene oxide) ($\bar{M}_n=2\times10^4$ g mol^{-1}) were used as standards. Values of $\bar{M}_w$ were determined with a light scattering photometer (Sofica, model PGD40B).

Glass transition temperature. Glass transition temperatures, T_g, for the products of nitration by method (iv) were determined by differential scanning calorimetry using a Perkin–Elmer DSC model 4. Samples were first annealed by heating at 100 K min^{-1} to 210°C and maintaining at that temperature for 10 min before cooling to 0°C at 320 K min^{-1}. Thermograms were recorded between 0 and 210°C, the sample cooled at 320 K min^{-1} and the procedure repeated twice. Thermograms were recorded at five heating rates (5, 10, 20, 30 and 40 K min^{-1}), a different sample of polymer being used for each heating rate. Apparent values of T_g, taken as the mid-point of the inflection, increased with increasing heating rate, and were extrapolated to zero heating rate.

RESULTS AND DISCUSSION

The methods used for the nitration of polystyrene differ in various respects. Method (i), direct nitration with a nitric acid/sulfuric acid mixture, is essentially a reaction with a solid suspension. Method (ii), nitration in carbon tetrachloride with acetyl nitrate, utilizes a solvent for the substrate, but there is a tendency for the product to precipitate out. Method (iii), nitration in *N*,*N*'-dimethylformamide with a nitric acid/sulfuric acid mixture, utilizes a solvent for both substrate and product which is miscible with the acid mixture Method (iv), nitration in 3-nitrotoluene with a nitric acid/sulfuric acid mixture, utilizes a solvent for both substrate and product which is immiscible with the acid mixture.

Table 2 lists values of degree of substitution, *n*, obtained for some of the products of nitration of polystyrene PS4. Values of *n* determined from elemental analysis and from ^{1}H n.m.r. are in good agreement. Values of *n* determined from the yield of product are generally a little low, because of inevitable small losses during the recovery process. *Table 3* shows values of *n* from elemental analysis for representative samples of polystyrene nitrated by various methods. Errors on these values are ± 0.02.

It can be seen from *Tables 2* and *3* that only by method (iv) is complete monosubstitution ($n = 1$) achieved. *Figure 1* compares the ^{1}H n.m.r. spectrum of polystyrene with the spectrum of the monosubstituted product. For products prepared by method (iv) the ^{1}H n.m.r. spectrum exhibits two peaks in the aromatic region (at $\delta = 7.0$ and 8.0 ppm) of equal area, indicating *para*-substitution.

Changes in molecular weight distribution on nitration are illustrated by *Figure 2*, which shows gel permeation chromatography curves for polystyrene PS4 and for the products of nitration by various methods. Similar behaviour was observed on nitration of the other polystyrene samples.

Method (i) gives product with a bimodal distribution (*Figure 2b*). There is a peak at high elution volume corresponding to the original polystyrene, and a broad peak at lower elution volume. Clearly, direct nitration leaves unreacted polymer, suggesting that nitration has occurred only at the surface of polymer particles.

Methods (ii) and (iii) each give a single, broad peak at lower elution volume (larger hydrodynamic volume) than the original polystyrene (*Figures 2c* and *d*). The overall area of the peak is larger than that for the original

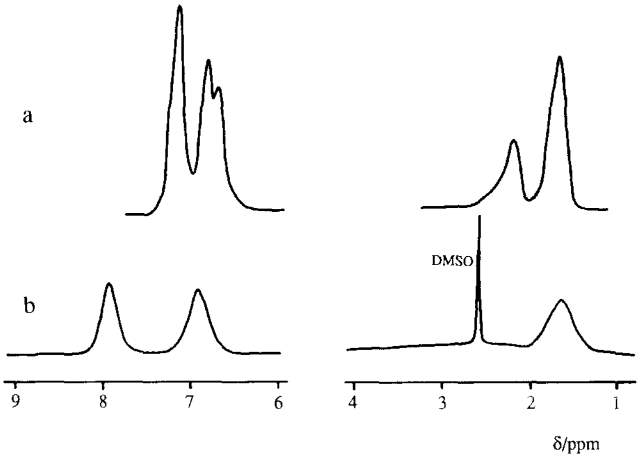

Figure 1 ^{1}H n.m.r. spectra of (a) polystyrene PS4 and (b) poly(4-nitrostyrene) prepared from PS4 by method (iv)

Table 2 Degree of substitution determined from (a) yield, (b) elemental analysis and (c) ^{1}H n.m.r. for polystyrene PS4 nitrated by various methods at 30°C

Reaction time (h)	Analytical method	Degree of substitution, *n*			
		Synthetic method (i)	Synthetic method (ii)	Synthetic method (iii)	Synthetic method (iv)
1	(a)	0.04±0.01	–	–	–
	(b)	0.07±0.02	–	–	–
	(c)	0.07±0.01	–	–	–
2	(a)	0.10±0.02	0.27±0.05	0.13±0.03	0.71±0.14
	(b)	0.09±0.02	0.36±0.02	0.16±0.02	0.87±0.02
	(c)	0.10±0.01	0.32±0.03	0.16±0.02	0.98±0.09
6	(a)	0.40±0.12	–	0.19±0.04	0.79±0.16
	(b)	0.51±0.02	–	0.27±0.02	0.88±0.02
	(c)	0.51±0.05	–	0.26±0.03	0.89±0.09
9	(a)	–	–	0.29±0.06	0.87±0.17
	(b)	–	–	0.38±0.02	0.94±0.02
	(c)	–	–	0.39±0.04	0.92±0.09
12	(a)	0.60±0.18	–	0.33±0.07	0.86±0.17
	(b)	0.64±0.02	–	0.41±0.02	1.02±0.02
	(c)	0.66±0.07	–	0.42±0.04	0.96±0.10

Table 3 Degree of substitution for polystyrene nitrated by various methods

		Degree of substitution, *n*, from elemental analysis					
Substrate	Reaction time (h)	Method (i) at 30°C	Method (i) at 50°C	Method (ii) at 30°C	Method (ii) at 50°C	Method (iii) at 30°C	Method (iv) at 30°C
PS4	2	0.09	0.09	0.36	0.47	0.16	0.87
	6	0.51	0.58	–	–	0.27	0.88
	12	0.64	0.81	–	–	0.41	1.02
PS5	2	0.10	0.11	0.31	0.48	0.19	0.85
	6	0.44	0.54	–	–	0.24	0.88
	12	0.63	0.70	–	–	0.36	1.00
PS6	2	0.09	0.09	0.20	0.31	0.17	0.88
	6	0.41	0.51	–	–	0.28	0.92
	12	0.55	0.68	–	–	0.38	1.00
PS8	2	0.10	0.19	0.19	0.17	0.19	0.94
	6	0.28	0.34	–	–	0.30	0.94
	12	0.31	0.51	–	–	0.42	0.99
PS9	2	0.10	0.08	0.09	0.15	0.21	0.93
	6	0.26	0.29	–	–	0.29	0.93
	12	0.28	0.39	–	–	0.46	1.01

Table 4 Theoretical and experimental average molar masses and glass transition temperatures for poly(4-nitrostyrene) prepared by method (iv)

	Average molar mass (10^3 g mol^{-1})				T_g (°C)	
	Theoretical		Experimental			
Substrate	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$	Heating rate 5 K min^{-1}	Extrapolated
PS1	6.46	7.31	5.91	–	191.0	191.0
PS2	7.19	7.81	–	–	191.1	191.0
PS3	8.22	9.04	7.96	–	191.3	191.3
PS4	10.63	12.01	–	–	191.8	191.9
PS5	13.48	14.97	13.13	15.87	192.4	192.4
PS6	29.41	34.71	–	–	193.5	193.5
PS7	33.55	38.93	34.31	–	193.6	193.5
PS8	59.37	65.30	–	61.37	194.4	194.1
PS9	84.90	93.40	–	89.42	194.3	194.3
PS10	266.9	301.6	–	–	194.4	194.3

Table 5 Glass transition temperatures[a] for polystyrene and polystyrene derivatives

Polymer	T_g (°C)
Polystyrene	100
Poly(4-chlorostyrene)	110
Poly(4-carboxystyrene)	113
Poly(4-bromostyrene)	118
Poly(4-hydroxymethylstyrene)	140
Poly(4-iodostyrene)	156
Poly(4-phenylstyrene)	161
Poly(2,6-dichlorostyrene)	167
Poly(2-dimethylaminocarbonylstyrene)	190
Poly(4-nitrostyrene)	195
Poly(4-propoxysulfonylstyrene), isotactic	217

[a] From reference 9 except for poly(4-nitrostyrene), this work

polystyrene because nitration increases the refractive index. It appears that more uniform substitution was obtained than for method (i), but that considerable degradation and/or crosslinking has occurred.

Method (iv) gives a single peak at lower elution volume than, but similar in breadth to, that of the original polystyrene (*Figure 2e*). It appears that this method, which was shown to give complete monosubstitution at the *para*-position, does not lead to significant degradation or crosslinking of the polymer. This is confirmed by a comparison of average molecular weights of the products, determined by vapour pressure osmometry or light scattering, with theoretical values based on those of the original polystyrene (*Table 4*).

Table 4 also shows values of T_g for the samples of poly(4-nitrostyrene) prepared by method (iv). The value

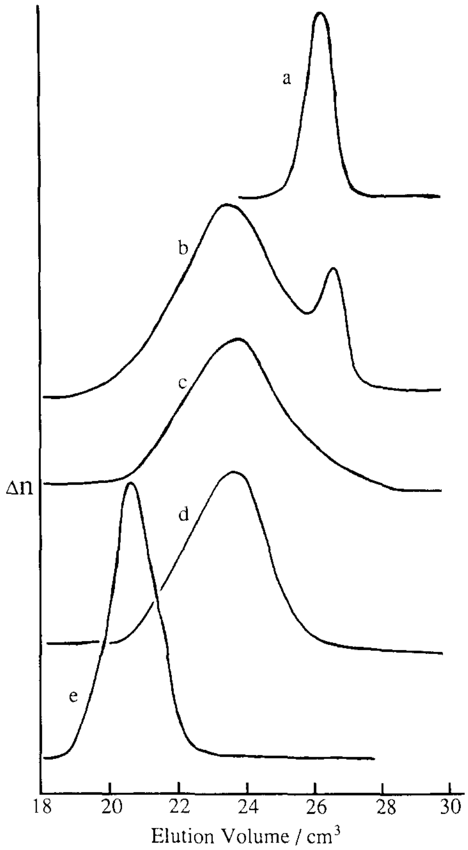

Figure 2 Gel permeation chromatography curves for (a) polystyrene PS4, and for the products of nitration of PS4 by (b) method (i), (c) method (ii), (d) method (iii) and (e) method (iv)

measured at a heating rate of 5 K min^{-1}, and the value obtained by extrapolation to zero heating rate, is given for each sample. A slight increase in T_g with increase in molecular weight is seen, as expected for polymers of moderate molecular weight. The value at high molecular weight approaches $T_g^{\infty} = 194.6$°C, as determined from a plot of T_g against $1/\bar{M}_n$. As far as the authors are aware, T_g for poly(4-nitrostyrene) has not been reported previously. For comparison, values quoted[9] for polystyrene and for a selection of polystyrene derivatives are listed in *Table 5*. The T_g for poly(4-nitrostyrene) is found to be considerably higher than that for polystyrene and significantly higher than for most other polystyrene derivatives, reflecting the greater chain stiffness and cohesive density of the polymer.

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REFERENCES

1 Blyth, P. and Hoffman, F. *Annalen* 1845, **53**, 316
2 Bachman, G. B., Hellman, H., Robinson, K. R., Finholt, R. W., Kahler, E. J., Filar, L. J., Heisey, L. V., Lewis, L. L. and Micucci, D. D. *J. Org. Chem.* 1947, **12**, 108
3 Zenftman, H. *J. Chem. Soc.* 1950, 982
4 Zenftman, H. and McLean, A., British Patent 616453, 1949; US Patent 2 572 420, 1950
5 Tsou, K. C., Lyem, A. and Halpern, B. D. US Patent 3 154 448, 1952
6 Blanchette, J. A. and Cotman, J. D. Jr *J. Org. Chem.* 1958, **23**, 1117
7 Walsh, D. J. PhD Thesis, University of Manchester, 1972
8 Bajaj, I., Kapoor, S. K. and Chatterjee, S. R. *Def. Sci. J.* 1968, **18**, 89
9 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975