Preparation of crosslinked polymers using acenaphthylene and the chemical modification of these polymers

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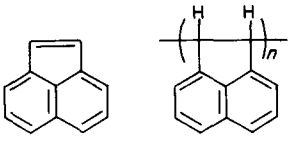
Acenaphthylene was homopolymerized, was copolymerized with divinylbenzene, and was copolymerized with both styrene and divinylbenzene using free radical initiated suspension polymerizations. The acenaphthyl residues in these polymers were more reactive to electrophiles than the phenyl residues in polystyrenes. Thus, bromo, chloro, and iodo groups were introduced using reaction conditions under which polystyrenes did not react. Other groups introduced were sulphonic acid, nitro, 2-chlorobenzoyl, carboxylic acid *via* cleavage of 2-chlorobenzoyl or *via* direct metalation then reaction with carbon dioxide, chloromethyl, and formyl.

(Keywords: acenaphthenes; polyacenaphthenes; acenaphthylene-styrene copolymers; suspension polymerization; chemical modification of polymers)

INTRODUCTION

There has recently been considerable interest in polymer-supported catalysts, reagents, and protecting groups[1-3]. Generally they have been prepared by the chemical modification of *crosslinked* polystyrenes. As part of a programme to investigate other types of polymers as supports we have prepared a range of polymers using acenaphthylene (**1**) and investigated their chemical modification. Such polymers are of interest because (i) acenaphthylene (**1**) is readily available, (ii) the acenaphthyl residues (**2**) in these polymers, being derivatives of naphthalene, should be more easily modified by electrophilic substitution than the phenyl residues of polystyrene, and (iii) polymers containing a high proportion of residues (**2**) may well have relatively slow chain motions thereby reducing the rate of intrachain reactions and hence assisting 'site-isolation'[4].



(1) (2)

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus. Infra-red spectra were measured for KBr discs using a Nicolet MX-1 FT-IR instrument. ^{13}C n.m.r. were measured on a Varian CFT-20 instrument.

Polymers were filtered-off using No. 4 grade sintered-glass filters and were dried in a vacuum oven (0.2 mm Hg) at 50°C to constant weight. Elemental analyses were carried out by Butterworths Microanalytical Laboratories, Teddington, Middlesex. The degree of substitution (DOS) is the fraction of aromatic residues in the polymer which bear the substituent in question.

All the starting materials were commercial samples and unless indicated otherwise were not purified further. Acenaphthylene (**1**) was recrystallized from methanol. Styrene and divinylbenzene (55% isomers of divinylbenzene: 45% isomers of ethylstyrene) were washed with aqueous sodium hydroxide (2N) then water to remove inhibitors. Azobisisobutyronitrile (AZBN) was recrystallized from warm ethanol. Poly(vinylpyrrolidone) had $\bar{M}_n = 44\,000$. The linear polystyrene had $\bar{M}_n = 174\,000$ (by g.p.c.). *N,N*-Dimethylformamide (DMF), tetrahydrofuran (THF), and methylene chloride were dried by distillation from calcium hydride.

Polymerizations

The polymerizations were carried out using a baffled reactor (600 ml) similar to that described by Ledwith *et al.*[5]. The general procedure was as follows. An aqueous solution of poly(vinylpyrrolidone) (3.0 g in 450 ml) was placed in the reactor and stirred (650 r.p.m.) at 80°C under nitrogen. A mixture of the feedstock (see *Table 1* for quantities) and AZBN (0.5 g) was added dropwise and stirring was continued for 16 h with a second portion of AZBN (0.5 g) being added after 6 h. At the end of the reaction period the contents of the reactor were poured into water (1 h) and allowed to settle. The aqueous solution was decanted off and the solid product washed several times with water using decantation to effect separation. The solid was then collected on a sintered glass filter and successively washed with hot water (500 ml), 50% aqueous ethanol (3 × 200 ml), then ethanol (3 × 200 ml). The crosslinked polymers were transferred to a soxhlet apparatus and extracted overnight with tetrahydrofuran, then dried in a vacuum oven for 2 days. The linear polymer was dissolved in chloroform (1% w/v) and reprecipitated into ethanol (10 fold excess), then collected and dried as above. The yields were as recorded in *Table 1*.

The molecular weight of the linear polymer was measured using a Knauer membrane osmometer with toluene as the solvent; found $\bar{M}_n = 333\,000$. The molecular weight distribution was determined by g.p.c. with THF as the solvent; found $\bar{M}_w/\bar{M}_n = 4$.

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Table 1 Polymerizations using acenaphthylene (1)[a]

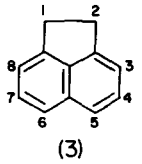
Polymerization No.	Designation of polymer[b]	Feedstock: Acenaphthylene (g)	Styrene (g)	Divinylbenzene[c] (g)	Toluene (ml)	Yield: (g)	(%)[d]
1	AL	25.0	–	–	5	23.0	92
2	AX3	50.0	–	2.6	10	34.1	68
3	AX6	25.0	–	2.6	5	19.0	76
4	AX20	25.0	–	16.7	60	29.8	71
5	ASX3 (20:80)	13.4	36.6	3.0	–	35.0	66
6	ASX3 (40:60)	25.0	25.0	3.0	–	40.0	75
7	ASX3 (70:30)	38.7	11.3	3.0	5	41.4	78

[a] See experimental section for details of polymerization procedures
[b] A = acenaphthylene, S = styrene, L = linear, X = crosslinked. The final figure is the nominal percentage of crosslinking
[c] Commercial material containing 55% of isomers of divinylbenzene
[d] Weight of product as a percentage of the total weight of monomers

The linear polymer had λ_{max} (2% THF in ethanol) 290, 300, 307, 314, and 325 nm (log ε 3.88, 3.91, 3.88, 3.87, and 3.71). Acenaphthene (**3**) had λ_{max} (2% THF in ethanol) 277, 286, 299, 308, 317, and 322 nm (log ε 3.97, 3.96, 3.81, 3.65, 3.20, and 3.38).

The ^{13}C n.m.r. spectra of acenaphthene (**3**) and a typical 3% crosslinked poly(acenaphthylene) are shown in *Figure 1* and summarized in *Table 2*.

Bromination of acenaphthene (**3**)



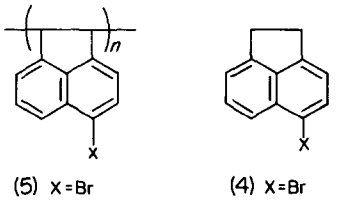
(3)

The following procedure is based on that of Ross, Finkelstein and Petersen[6].

(a) *N*-Bromosuccinimide (9.0 g, 50 mmol) in DMF (25 ml) was added to a suspension of acenaphthene (**3**) (7.7 g, 0.05 mol) in DMF (25 ml) and the mixture stirred at 20°C for 2 h. The solution was then added to water and the product filtered off and dried under vacuum at 20°C: yield = 11.6 g, corresponding to a 98% yield. Recrystallization from ethanol gave 5-bromoacenaphthene (**4**), m.p. 52°C–53°C (ref. 6, 52°C). See *Figure 2* and *Table 2* for ^{13}C n.m.r. spectrum.

(b) An attempt to brominate acenaphthene (**3**) by treatment with a solution of bromine in chloroform at reflux temperature for 6 h was unsuccessful. The starting material was quantitatively recovered.

Bromination of linear polyacenaphthylene



(5) X = Br (8) X = Cl (9) X = I

(4) X = Br (6) X = Cl (7) X = I

(a) *N*-Bromosuccinimide (4.50 g, 25 mmol) in DMF (25 ml) was added to a vigorously stirred mixture of the linear polymer (3.85 g, 25 mmol) and DMF (12.5 ml) at 20°C. Seventeen hours later the reaction mixture was added to water (375 ml). The solid was collected on a sintered glass filter, washed with water (3 × 200 ml), and dried. The product (5.19 g) had ν_{max} 1075, 1390, and 1425 cm^{-1} and Br = 29.8% corresponding to a DOS of 0.80. See *Figure 2* and *Table 2* for the ^{13}C n.m.r. spectrum.

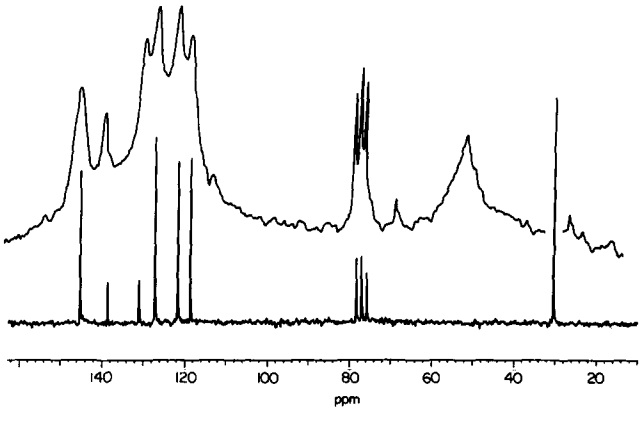


Figure 1 ^{13}C n.m.r. spectra of acenaphthene (**3**) (lower trace) and 3% crosslinked polyacenaphthene (**2**) (upper trace) for samples in $CDCl_3$

(b) An attempt to brominate the linear polymer by treatment with a solution of bromine in chloroform at reflux temperature for 6 h was unsuccessful. The recovered polymer had essentially the same infra-red spectrum as the starting material.

Bromination of crosslinked polymers

These reactions are summarized in *Table 3*. The following procedure (entry 2) is typical.

N-Bromosuccinimide (4.67 g, 26 mmol) in DMF (10 ml) was added to a suspension of polymer AX3 (4.00 g, 26 mmol) in DMF (40 ml) and the mixture stirred for 17 h. The product was then filtered off and washed successively with DMF (50 ml), THF (3 × 100 ml), and ethanol (3 × 100 ml). The dried product (4.93 g) had Br = 20.4%, corresponding to a DOS of 0.48.

It should be noted that bromination of polyacenaphthylene introduces new infra-red bands at 1075, 1390, and 1425 cm^{-1}, whereas bromination of polystyrene introduces new bands at 1075 and 1410 cm^{-1}. The infra-red spectra of the bromination products of all the ASX3 polymers had only the former set of bands.

Chlorination of acenaphthene (**3**)

This was carried out with *N*-chlorosuccinimide in DMF using the same procedures as for the bromination of

this compound[6]. The yield of 5-chloroacenaphthene (**6**) was 55% and it had m.p. 68°C–69°C (from methanol) (ref. 7, 70°C–71°C).

Chlorination of a crosslinked acenaphthylene–styrene copolymer

N-Chlorosuccinimide (2.16 g, 16 mmol) and polymer ASX3 (40:60) (2.00 g, 16 mmol of aromatic residues) were reacted together in DMF using the same general procedure as for the bromination of the polymers. The dried product (2.12 g) had Cl = 14.1% corresponding to a DOS of 0.57.

Iodination of a crosslinked acenaphthylene–styrene copolymer

Peroxyacetic acid (1.6 ml, 38% w/w) in methylene chloride (10 ml) was added dropwise to a vigorously stirred mixture of iodine (2.54 g) and polymer ASX3 (40:60) (2.00 g, 16 mmol of aromatic residues) in methylene chloride (25 ml) at 40°C. When the addition was complete the mixture was heated under reflux for 18 h. The polymer was then collected and washed as in the other halogenations. The dried product (2.37 g) had I = 18.3%, corresponding to a DOS of 0.22.

Sulphonation of crosslinked polyacenaphthylene

Chlorosulphonic acid (10.5 g, 90 mmol) was added dropwise to a vigorously stirred suspension of polymer AX3 (7.60 g, 50 mmol) in methylene chloride (80 ml) at 0°C. After 4 h the mixture was added to water (200 ml) and the beads filtered off and washed successively with water (2 × 40 ml) and ethanol (2 × 40 ml) then dried. The product (9.66 g) had ν_{max} 1030, 1050, and 1100 cm^{-1} and S = 11.84% corresponding to a DOS of 0.80. The ion exchange capacity, as determined by treatment with an excess of standard aqueous sodium hydroxide and back titration with standard hydrochloric acid, was 1.46 milli-equiv per g corresponding to a DOS of 0.28.

Nitration of crosslinked polymers

The method is based on that used by Crivello to nitrate linear polystyrene[8].

(a) 2% Crosslinked polystyrene (2.08 g, 20 mmol) was stirred with chloroform (70 ml) for 1 h. Ammonium nitrate (1.6 g, 20 mmol) and trifluoroacetic anhydride (10 ml) were added and the mixture stirred at 20°C for 16 h. The product was filtered off and washed successively

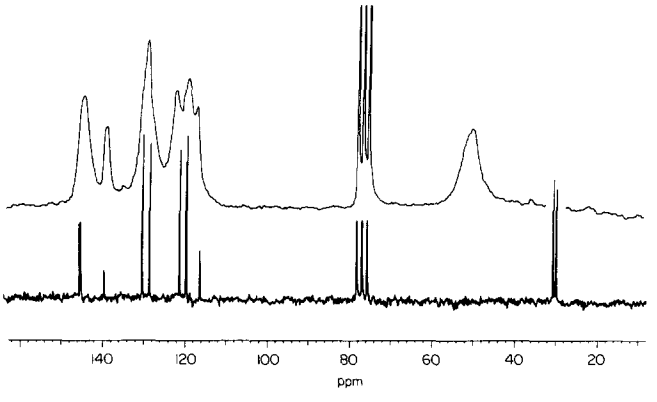
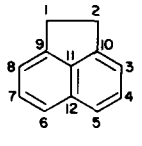
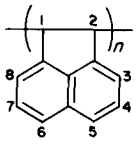
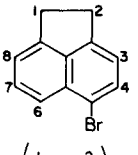
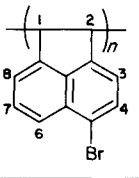


Figure 2 ^{13}C n.m.r. spectra of 5-bromoacenaphthene (**4**) (lower trace) and brominated linear polyacenaphthene (upper trace) for solutions in $CDCl_3$

Table 2 ^{13}C n.m.r. shifts for acenaphthene, 3% crosslinked polyacenaphthylene[a], 5-bromoacenaphthene, and brominated linear poly(acenaphthylene)[b]

		Chemical shifts[c]											
		C–1	C–2	C–3	C–4	C–5	C–6	C–7	C–8	C–9	C–10	C–11	C–12
	[d]	30.2	30.2	118.9	127.5	121.9	121.9	127.5	118.9	145.6	145.6	139.0	131.3
	[a]	51.0	51.0	119.3	127.5	122.5	122.5	127.5	119.3	145.6	145.6	139.3	130.0
		30.5*	29.5*	119.9*	130.5*	116.5	121.4	128.7	119.7*	145.8*	145.5*	139.9	130.6*
	[b]	50.8	50.8	119.7	130.6*	117.4	122.6	129.6	119.7	145.1	145.1	139.5	129.6*

[a] Polymer AX3, see *Table 1*
[b] Prepared by bromination of polymer AL, see *Table 1*
[c] For samples in $CDCl_3$. Shifts in p.p.m. downfield from Me_4Si
[d] Assignments made on the basis of the results of Jones, Grant and Kuhlmann[11]
* Assignments tentative

Table 3 Bromination of polymers prepared using acenaphthylene (1)[a]

Entry	Polymer[b]	Weight of polymer (g)	Weight of NBS (g)	Weight of product (g)	% of bromine by elemental analysis	DOS
1	AL	4.00	4.50	5.19	29.7	0.80
2	AX3	4.00	4.67	4.93	20.4	0.48
3	AX6	4.00	4.67	4.67	24.0	0.60
4	AX20	4.00	4.67	4.68	24.6	0.62
5	ASX3 (20:80)	2.00	3.13	2.07	0.6	0.10
6	ASX3 (40:60)	4.00	4.67	4.85	19.7	0.38
7	ASX3 (70:30)	2.00	2.59	2.40	19.5	0.41
8	SL	1.04	1.78	1.04	1.2	0.02
9	SX2	1.04	1.78	1.04	0.8	0.01

[a] See experimental section for typical reaction procedures
[b] See *Table 1* for details of polymers

with portions (50 ml) of chloroform, methanol, water, and finally with methanol. The dried product (2.91 g) had ν_{max} 1516 and 1343 cm^{-1} and N = 7.35%, corresponding to a DOS of 0.71.

(b) A similar reaction was carried out using polymer ASX3 (40:60) (2.47 g, 20 mmol of aromatic residues). The dried product (3.19 g) had ν_{max} 1519 and 1345 cm^{-1} and N = 7.12%, corresponding to a DOS of 0.81.

2-Chlorobenzoylation of linear and crosslinked polymers

(a) A mixture of 2-chlorobenzoyl chloride (7.00 g, 40 mmol) and stannic chloride (10.42 g, 40 mmol) was added dropwise to a vigorously stirred mixture of polymer AX3 (7.60 g, 50 mmol) at 20°C. The reaction was allowed to proceed for 21 h, then the polymer was filtered off and washed successively with portions (50 ml) of methylene chloride, THF, THF–water (1 vol:1 vol), THF–conc. hydrochloric acid (3 vols:1 vol), conc. hydrochloric acid, water, THF, methanol, and methylene chloride. The dried product (10.79 g) had ν_{max} 1660 cm^{-1} and Cl = 8.15% corresponding to a DOS of 0.51.

(b) A similar experiment also carried out on polymer AX3 (3.80 g) but at 0°C for 4 h gave a product (5.02 g) which had ν_{max} 1660 cm^{-1} and Cl = 6.60% corresponding to a DOS of 0.38.

(c) A similar experiment to (a) was carried out using polymer AL (2.55 g). At the end of the reaction period the reaction mixture was added to a mixture of methanol (400 ml) and dilute hydrochloric acid (50 ml). The precipitate was collected, dissolved in methylene chloride (50 ml) and re-precipitated into methanol (500 ml). The product was collected and dried. The dried product (5.24 g) had ν_{max} 1660 cm^{-1} and Cl = 8.50% corresponding to a DOS of 0.54.

Cleavage reactions

The procedure is based on that used with polystyrene derivatives[9].

(a) A mixture of 2-chlorobenzoylated polymer AX3 (3.04 g, 7 mmol, prepared in (a) above), water (0.26 g, 14 mmol), and dry THF (30 ml) was vigorously stirred at 20°C under nitrogen for 30 min. Potassium t-butoxide (5.44 g, 48 mmol) was added and the mixture stirred at 20°C for 16 h then heated under reflux for 48 h. The polymer was filtered off and washed successively with portions (2 × 50 ml) of dilute hydrochloric acid, water, ethanol, THF, and ether. The dried product (2.22 g) had ν_{max} 1688 cm^{-1} (broad) (carboxyl group). In order to isolate any 2-chlorobenzoic acid formed in the cleavage the above washings were evaporated to near dryness then treated with aqueous sodium hydroxide (10 ml, 2 N). The aqueous solution was washed with ether (3 × 50 ml), then acidified with dilute hydrochloric acid and extracted into ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated to dryness. The residue (10 mg), which would contain any 2-chlorobenzoic acid, was negligible. Assuming the cleavage was quantitative the fraction of residues carrying a carboxyl group was 0.54.

A portion of the dried polymer was esterified into diazomethane using the previously described procedure[9]. The product had ν_{max} 1715 cm^{-1}; there was no band apparent near 1660 cm^{-1}.

(b) A mixture of 2-chlorobenzoylated polymer AL (3.00 g, 7.2 mmol, prepared in (c) above), water (0.26 g), and dry THF (40 ml) was stirred at 20°C under nitrogen. Potassium t-butoxide (5.44 g) was added then the mixture was heated at 45°C for 1½ h. Addition to a stirred mixture of concentrated hydrochloric acid (10 ml) and water (600 ml) afforded a brown precipitate which was collected, washed with water (100 ml) and dried. The product (2.60 g) had ν_{max} 1690 cm^{-1} (broad). No 2-chlorobenzoic acid was found in the washings. Assuming the cleavage was complete the fraction of residues bearing a carboxyl group was 0.54.

A portion of the dried polymer was esterified with diazomethane[9]. The product had ν_{max} 1715 cm^{-1}; there was no band apparent near 1660 cm^{-1}.

Reaction of linear poly(acenaphthylene) with n-butyl lithium then carbon dioxide

To a stirred solution of polymer AL (0.50 g, 3.3 mmol) in THF (10 ml) was added dropwise a solution of n-butyl lithium in hexane (5.1 ml, 1.6 M, 8.3 mmol). The mixture was stirred under a nitrogen atmosphere for 2 h at 20°C then the resultant black mixture was poured onto a stirred slurry of solid carbon dioxide in THF (20 ml). A yellow precipitate formed and after stirring for 1½ h the reaction mixture was poured into methanol and the precipitated polymer filtered off, washed and dried. The product (0.48 g) had ν_{max} 1682 cm^{-1}.

A sample of the above product was esterified with diazomethane[9]. The product had ν_{max} 1719 cm^{-1}.

Chloromethylation of 3% crosslinked polyacenaphthylene

These reactions were carried out using a procedure previously used with polystyrene[9].

(a) Treatment of polymer AX3 (7.60 g, 50 mmol) with chloromethyl methyl ether (3.20 g, 40 mmol) and stannic

chloride (10.50 g, 40 mmol) in dry methylene chloride (80 ml) at 0°C for 4 h gave a dried product (9.00 g) which had ν_{max} 1250 and 1270 cm^{-1} and Cl = 11.1% corresponding to a DOS of 0.56.

(b) A similar experiment with the same polymer (7.60 g) but a reaction time of 21 h at 20°C gave a dried product (8.80 g) which had Cl = 7.2% corresponding to a DOS of 0.34.

Oxidation of chloromethyl resins

The chloromethylated polymer AX3 (4.00 g, prepared in (b) above) was oxidized using DMSO and sodium bicarbonate following the literature procedure for chloromethylated polystyrene[9]. The product (4.89 g) had ν_{max} 1680 cm^{-1}, no bands at 1250 and 1270 cm^{-1}. Assuming the oxidation was quantitative, the fraction of residues bearing a formyl group was 0.34.

Oxidation of formyl resin

The above product (0.25 g) was oxidized with peroxyacetic acid (38% w/w) and methanesulphonic acid using the literature procedure for formyl polystyrene[9]. The black product (0.29 g) had ν_{max} 1711 cm^{-1}. Esterification of a portion with diazomethane using the usual procedure[9] gave a product with ν_{max} 1720 cm^{-1}.

RESULTS AND DISCUSSION

(1) Preparation of polymers

Acenaphthylene (**1**) has previously been homopolymerized and copolymerized with other monomers, including styrene, using various types of initiator[10]. In the present work acenaphthylene (**1**) was homopolymerized, was copolymerized with divinylbenzene (DVB), and was copolymerized with both styrene and DVB (see *Table 1*). Since most of the products were crosslinked, they were prepared by suspension polymerization with free radical initiation. High yields of product were obtained by carrying out the polymerization at 80°C for 16 h, and by using two portions of AZBN, the second being added after 6 h. In several cases it was necessary to add small amounts of toluene to the feedstock to ensure that all the acenaphthylene (**1**) dissolved. In one case a relatively large amount of toluene was added in order to produce a macroporous product.

The ^{13}C n.m.r. spectra of the linear and the 3% crosslinked homopolymers were essentially the same as that of acenaphthene (**3**)[11], the saturated monomer, except that the signals were broader (see *Figure 1* and *Table 2*). The u.v. spectra of the linear homopolymer and acenaphthene (**3**) were of similar shape and intensity. The spectra confirm, therefore, that the homopolymers consisted very largely, if not entirely, of repeat units (**2**).

(2) Reactions of polymers

Bromination reactions. Bromination of the various polymers was studied in some detail, mainly with a view to showing that the acenaphthyl residues (**2**) were more reactive than the phenyl residues in the copolymers or in polystyrene.

Polystyrenes are generally brominated by treatment with bromine and thallium(III) triacetate or some other Lewis acid[12]. Since acenaphthene (**3**) is reported[13] to react with bromine in boiling chloroform in the absence of any catalysts, it was anticipated that the polymers prepared using acenaphthylene (**1**) would behave similarly. However, all our attempts to brominate the linear and 3% crosslinked homopolymers under these conditions failed. Even acenaphthene (**3**) failed to react. The reasons for this are not clear, but our observations cast some doubt on the early reports[13].

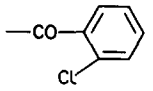
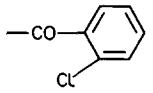
An alternative brominating agent which reacts with acenaphthene (**3**) without the need for a catalyst is *N*-bromosuccinimide (NBS) in *N,N*-dimethylformamide (DMF)[6]. As expected, this reagent reacted smoothly with all the polymers containing residues (**2**), but not with linear or 2% crosslinked polystyrene (see *Table 3*). The bromination yields were determined by elemental analysis. The DOSs obtained were always less than the percentage of acenaphthyl residues (**2**) in the polymer and this strongly suggests that only the latter were brominated. Comparison of the infrared and ^{13}C n.m.r. spectra of the brominated copolymers with those of brominated polyacenaphthylene and brominated polystyrene were consistent with this conclusion.

Acenaphthene (**3**) reacts with NBS in DMF to give the 5-bromo derivative (**4**)[6]. The ^{13}C n.m.r. spectra of this and the bromination products from the linear and 3% crosslinked homopolymers were very similar (see *Figure 2* and *Table 2*), except that the signals of the polymers were broader. This strongly suggests that bromination of the polymers afforded products containing residues (**5**), but without the spectra of 3-bromo- and 4-bromoacenaphthene this cannot be certain.

Chlorination and iodination reactions. Acenaphthene (**3**) reacts with *N*-chlorosuccinimide in glacial acetic acid[7], or, we find, DMF, to give 5-chloroacenaphthene (**6**), and with iodine and peracetic acid in methylene chloride[14] to give 5-iodoacenaphthene (**7**). 2% Crosslinked polystyrene did not react significantly with either of these reagents, but a 3% crosslinked copolymer prepared using acenaphthylene and styrene (mole ratio, 40:60) reacted smoothly with both reagents to give chlorinated and iodinated products (see *Table 4*) which almost certainly contained residues (**8**) and (**9**) respectively. The DOS obtained in the chlorination reaction was greater than that expected for monochlorination of the acenaphthyl residues (**2**). Since polystyrene did not react, presumably some of the residues (**2**) were dichlorinated. These reactions again demonstrate that polymers containing acenaphthene residues (**2**) are more easily modified by electrophilic substitution than polystyrene.

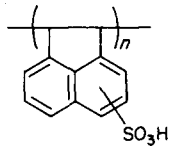
Sulphonation. Sulphonation of polystyrene is used to produce strongly acid catio exchange resins[15]. We found that 3% crosslinked poly(acenaphthylene) reacted smoothly with chlorosulphonic acid in methylene chloride at 0°C and at 20°C to give polymer-supported sulphonic acids (**10**), but the degree of substitution as estimated by titration (0.28) was much less than that estimated by sulphur analysis (0.80). This strongly suggests that substantial 'sulphone bridging' occurred to afford residues (**11**)[15]. This may well occur more readily

Table 4 Some functional groups introduced into polymers containing acenaphthyl residues (**2**)

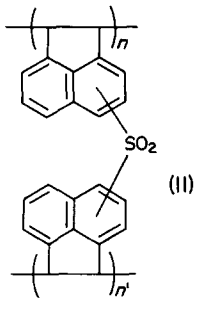
Polymer[a]	Group introduced	DOS[b]	Polymer	Group introduced	DOS
AL	—Br	0.80[c]	AL		0.57
AX3	—Br	0.51[c]			
ASX3 (40/60)	—Cl	0.57	AX3		0.54
ASX3 (40/60)	—I	0.22	AL	$-CO_2H$	0.57[e]
			AL	$-CO_2H$	*ca.* 0.12[f]
AX3	$-SO_3H$	0.28[d]	AX3	$-CO_2H$	0.54[e]
			AX3	$-CH_2Cl$	0.56
ASX3 (40/60)	$-NO_2$	0.81	AX3	—CHO	0.34

[a] See *Table 1* for details of polymers
[b] Based on all aromatic residues
[c] See *Table 3* for other examples
[d] By titration
[e] By cleavage
[f] *Via* direct metallation

than with polystyrene because the acenaphthene residues (**2**) are more reactive.

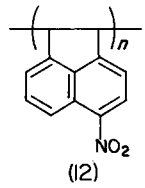


(10)

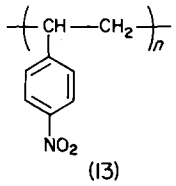


(11)

Nitration. Linear poly(acenaphthylene) has previously been nitrated using concentrated nitric acid in various solvents[16]. We sought a milder reagent and used ammonium nitrate and trifluoroacetic anhydride in chloroform[8]. Excellent results were obtained both with a 3% cross-linked styrene–acenaphthylene copolymer and with 2% crosslinked polystyrene. The degree of substitution obtained with the copolymer was higher than the fraction of acenaphthyl residues (**2**) present, probably because both the latter and the phenyl residues reacted giving residues (**12**) and (**13**) respectively. Residues (**2**) may also have been dinitrated.

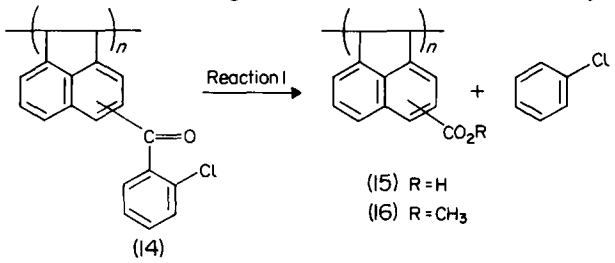


(12)



(13)

Friedel–Crafts acylation: introduction of carboxyl groups. The linear and the 3% crosslinked polyacenaphthylenes reacted smoothly with 2-chlorobenzoyl chloride and stannic chloride to give products containing residues (**14**), the yields being estimated from chlorine analyses.



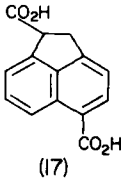
(14)

(15) R = H
(16) R = CH_3

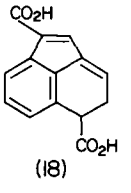
Most of the 2-chlorobenzoyl groups were probably in the 5-position.

Analogy with the reactions of 2-chlorobenzoylated polystyrenes[9] suggested that residues (**14**) would be cleaved regiospecifically, as shown in reaction (**1**), by the potassium t-butoxide–water reagent to give polymers with residues (**15**). This proved to be the case with both the linear and the crosslinked polymers. No 2-chlorobenzoic acid, which would have been formed from the alternative cleavage mode, was isolated from either cleavage reaction. The infra-red spectra of the products showed strong broad carbonyl bands at 1690 cm^{-1}. Since it was possible that these broad bands masked smaller bands at 1660 cm^{-1} due to unreacted residues (**14**), both acids were esterified with diazomethane to give residues (**16**). The infra-red spectra of the esters showed strong sharp bands at 1715 cm^{-1}, but none at 1660 cm^{-1}. This is clearly a useful method for introducing carboxyl groups into polyacenaphthylenes.

An alternative method for introducing carboxyl groups was investigated briefly. The linear polyacenaphthylene was treated successively with n-butyl lithium then carbon dioxide. A portion of the product was esterified with diazomethane. The infra-red spectra of both the acid and ester were very similar to those of the polymers discussed above, except that the intensity of the carbonyl bands was only *ca.* 20% that of the previous products. Since there were no bands attributable to unconjugated carbonyl groups, it is clear that the poly(acenaphthylene) did not behave in an analogous manner to acenaphthylene itself with these reagents[17]. The latter affords a mixture of acids (**17**) and (**18**) in modest total yield[17]. The reason for the difference in behaviour is not clear, but may arise either because a carbanionic site on the polymer backbone would be tertiary as compared with secondary with acenaphthene, or because if such a carbanion did form it may well be less reactive than that from acenaphthene for steric reasons.

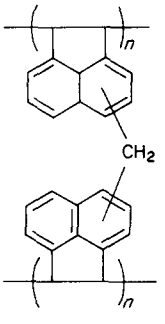


(17)



(18)

Chloromethylation: introduction of formyl groups. The introduction of chloromethyl groups into polystyrene is one of the most versatile methods for chemically modifying this polymer since the group reacts readily with a wide range of nucleophiles[1-3,18]. The 3% crosslinked polyacenaphthylene reacted smoothly with chloromethyl methyl ether at 0°C and after 4 h contained 3.12 mmol of chloromethyl residues per g. Carrying out the reaction at 20°C for 21 h produced a lower degree of chloromethylation. It may be that substantial 'methylene bridging' to give residues (**19**) occurred under the latter reaction conditions and that due to the reactivity of residues (**2**) it was more extensive than with polystyrene under similar conditions[19].



(19)

Treatment of the chloromethylated product with potassium bicarbonate in dimethyl sulphoxide at 155°C converted the chloromethyl groups into formyl groups[9]. However, treatment of this product with peroxyacetic acid and methanesulphonic acid in glacial acetic acid[9] in an attempt to oxidize the formyl groups into carboxyl groups gave a dark brown product with an infra-red substantially different from that of the previously described acid (**15**).

CONCLUSION

It is clear that polymers prepared using acenaphthylene (**1**) are readily modified to give polymers containing the functional groups shown in *Table 4*. In many cases the electrophilic aromatic substitution can be carried out under milder conditions than those required with polystyrenes. However, a possible complication in reactions such as sulphonation and chloromethylation is that crosslinking may be more substantial than with polystyrene due to the greater reactivity of the acenaphthyl (**2**) residues. The acenaphthyl residues (**2**) are readily metallated on the aromatic ring without the need of additives such as tetramethylethylenediamine[12,20].

ACKNOWLEDGEMENT

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