Copolystyrene derivatives: study of chemical modification of copoly(styrene acrylonitrile) (PSAN)

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Some possibilities of chemical modification of copoly(styrene acrylonitrile) (PSAN) have been investigated with the aim of preparing hydrophilic polymer derivatives bearing aromatic rings with amino and nitro substituents *ortho* to each other. Different reactivities of the aromatic and nitrile residues have been observed in relation to their microenvironments. Various copolystyrenes substituted by 4-acetyl, 4-acetamido and 3-nitro-4-amino groups were synthesized and characterized (^{13}C nuclear magnetic resonance and infra-red spectroscopy). The hydrolysis of nitrile residues in the copolymers was also studied under different experimental conditions and led to hydro-swellable polyacrylamides.

(Keywords: copoly(styrene acrylonitrile); chemical modification; 3-nitro-4-aminophenyl residues; nitrile hydrolysis; copolyacrylamides; ^{13}C nuclear magnetic resonance data)

INTRODUCTION

Study of the literature reveals that nowadays polymers capable of specific interactions are already widely used in many fields such as drug release systems[1], enzyme analogues[2] or organic supported reagents[3,4]. This type of polymer, bearing particular reactive groups on side-chains, can be prepared either by polymerization of appropriate monomers or by chemical modification of preformed polymers. The chemical properties of these polymers are mainly governed by their macromolecular design. Indeed, the final characteristics of functionalized polymers are closely related to their extent of functionalization, micropolarity and network structures, such as flexibility or steric hindrance[5,6].

The aim of this study is to difunctionalize in positions 3 and 4 the phenyl residues of copolymers of styrene and acrylonitrile, and subsequently to hydrolyse the nitrile groups. This paper reports the synthesis of acrylamide-type copolymers with substituted aromatic residues from linear copoly(styrene acrylonitrile) (PSAN); styrene molar fraction $F_{sty} \sim 0.55$ as determined by n.m.r., i.e. styrene capacity $C_{sty} = 0.0067\ eq\ g^{-1}$.

These modified polymers, bearing amino–nitro aromatic moieties, are precursors for more complex structures such as 3,4-diaminophenyl and benzimidazole units[7].

EXPERIMENTAL

The starting PSAN was purchased from Janssen Co. (styrene content $\simeq 70\%$ by weight); synthetic-grade reagents and pure solvents (Puran grade from SDS) were used without further purification for polymer modifications.

Chemical modification of the polymers

Monosubstitution of PSAN. The *p*-acylation of polystyrene residues was achieved with acetyl chloride and aluminium chloride as described previously[8]; the use of other acylating conditions[9] (*Table 1*) led to lower extents of functionalization. In a typical experiment (run 2), 10 g of PSAN gave 11 g of *p*-acetylated polymer (PI) with 3×10^{-3} eq g^{-1} of acetyl capacity for soluble acetylated polymers ($\nu(C{=}O) = 1680\ cm^{-1}$). For $F_{acyl} = 0.3$: calc. C 81.1, H 6.8, N 6.9, O 5.1%; found C 81.0, H 6.8, N 6.8, O 5.0%. The acetamide derivative (PII) ($\nu(C{=}O) = 1670\ cm^{-1}$) was prepared from PI with a mixture of $AcOH/H_2SO_4$ and NaN_3 (Schmidt rearrangement) by following known literature procedures[8,10]. For $F_{NHAc} = 0.3$: calc. C 77.6%, H 6.8, N 10.6%; found C 77.7, H 7.0, N 9.9%.

o-Disubstitution of PSAN. PII was nitrated (PIII) ($\nu(NO_2) = 1515, 1350\ cm^{-1}$) either in concentrated nitric acid ($t = -15°C$, 3.5 h; for $F_{NHAc} = 0.22$: calc. C 62.7, H 5.0, O 17.8%; found C 63.1, H 5.1, O 16.9%) or with ammonium nitrate–trifluoroacetic acid (TFA)[11] in nitrobenzene ($t = 20$–$70°C$) or in chloroform ($t = 20°C$; for $F_{NHAc} = 0.22$: calc C 62.7, H 5.0, O 17.8%; found C 69.8, H 5.96, O 12.5%).

Anilide and/or nitrile hydrolysis. Hydrolytic runs were carried out with PSAN, PII and PIII as reported in *Table 3* with various reagents (KOH, H_2SO_4, CF_3CO_2H, CH_3SO_3H), under heterogeneous conditions (method 1: water–alcohol medium) or homogeneous conditions (methods 2 and 3: organic medium). Deacetylation led to the formation of the amino copolymers PIV and PV, characterized by strong i.r. absorptions due to C_{ar}–NH_2 residues (3450, 1620 cm^{-1}) and total or partial disappearance of the C=O band (1670 cm^{-1}). Nitrile hydrolysis led to the copolyacrylamide derivatives PVI and PVII, characterized by the strong i.r. absorption of the $CONH_2$ group (1660 cm^{-1}) and the disappearance of CN (2230 cm^{-1}).

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Characterization of the polymers

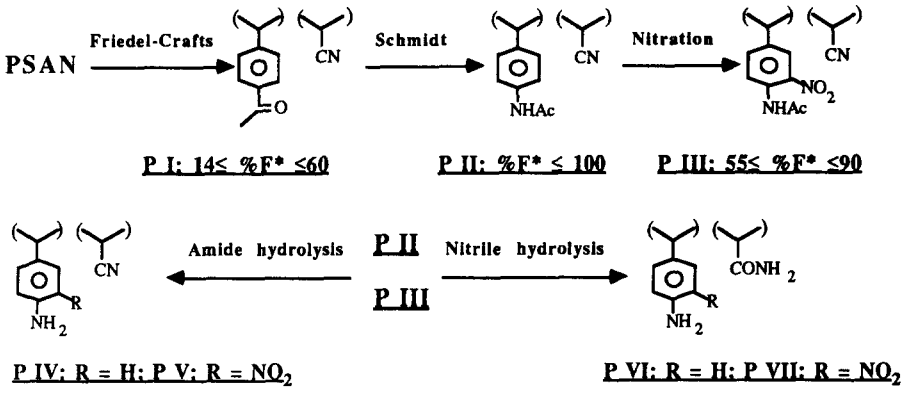
Elementary analyses were carried out by the CNRS Central Department of Microanalysis; i.r. spectra were recorded in KBr pellets with a Perkin–Elmer 580 spectrophotometer and n.m.r. spectra were recorded in DMSO-d_6 or $CDCl_3$ with a Jeol FX 100 spectrometer. The assignments of the chemical shifts reported in Scheme 2 were made with the help of cumene and polystyrene derivatives as references.

RESULTS AND DISCUSSION

The chemical modifications applied to the preparation of copolystyrene derivatives were as shown in *Scheme 1*.

Little information regarding the reactivity of the aromatic ring of PSAN and the structure of the resulting modified copolymers is available in the literature (acylations[12,13] and sulphonations[14–16]). However, Kopic and coworkers have recently published an interesting report[17] on the alkaline hydrolysis of PSAN: they have established that a strong relationship exists between the distribution of triads of the repeating units in the copolymer and the hydrolysis rate constants, which demonstrates the dominant influence of the structure of the copolymer on the hydrolysis rate.

It seems that in our investigation the results obtained for the acylation of the aromatic ring of PSAN also demonstrate the strong influence of the copolymer structures on the extent of functionalization. Indeed, in spite of the use of varied acylating conditions (*Table 1*) we found the existence of a limited rate of functionalization (~50%) for the preparation of *p*-acetylated PSAN, soluble in $HCCl_3$ or in dimethylformamide (DMF), compared with the quantitative acylation of polystyrene under the same conditions[8,10]; this result indicates the influence of the nitrile group. A higher rate of functionalization can be attained by repetitive acylation (yield > 50%, estimated from i.r. spectra and elementary analysis in *Table 1*, run 6), but the resulting modified polymers are only swellable in solvents such as DMF. In the light of published ^{13}C n.m.r. data[18,19], the examination of the spectra of the starting PSAN gives the following estimation of triad distribution: SSS, 144.5 ppm, 8%; ASS or SSA, 142.5 ppm, 47%; ASA, 140.2 ppm, 45%, calculated from peak areas of the C_1 carbon of the phenyl ring; SAS, 121.7 ppm, 71%; AAA and AAS, 120.2 ppm, 29%, calculated from peak areas of the carbon of the nitrile group. The low value of the SSS triad and the high value of the SAS triad indicate a marked tendency to an alternating polymer structure, rather than to a block structure for the starting PSAN. From this observation it is quite obvious that the extent of acylation of PSAN (~50%) that we found can be



***%F: extent of functionalization , characterized from NMR and i.r. data.**

Scheme 1 Chemical modifications of PSAN

Table 1 Acylation of polystyrene derivatives

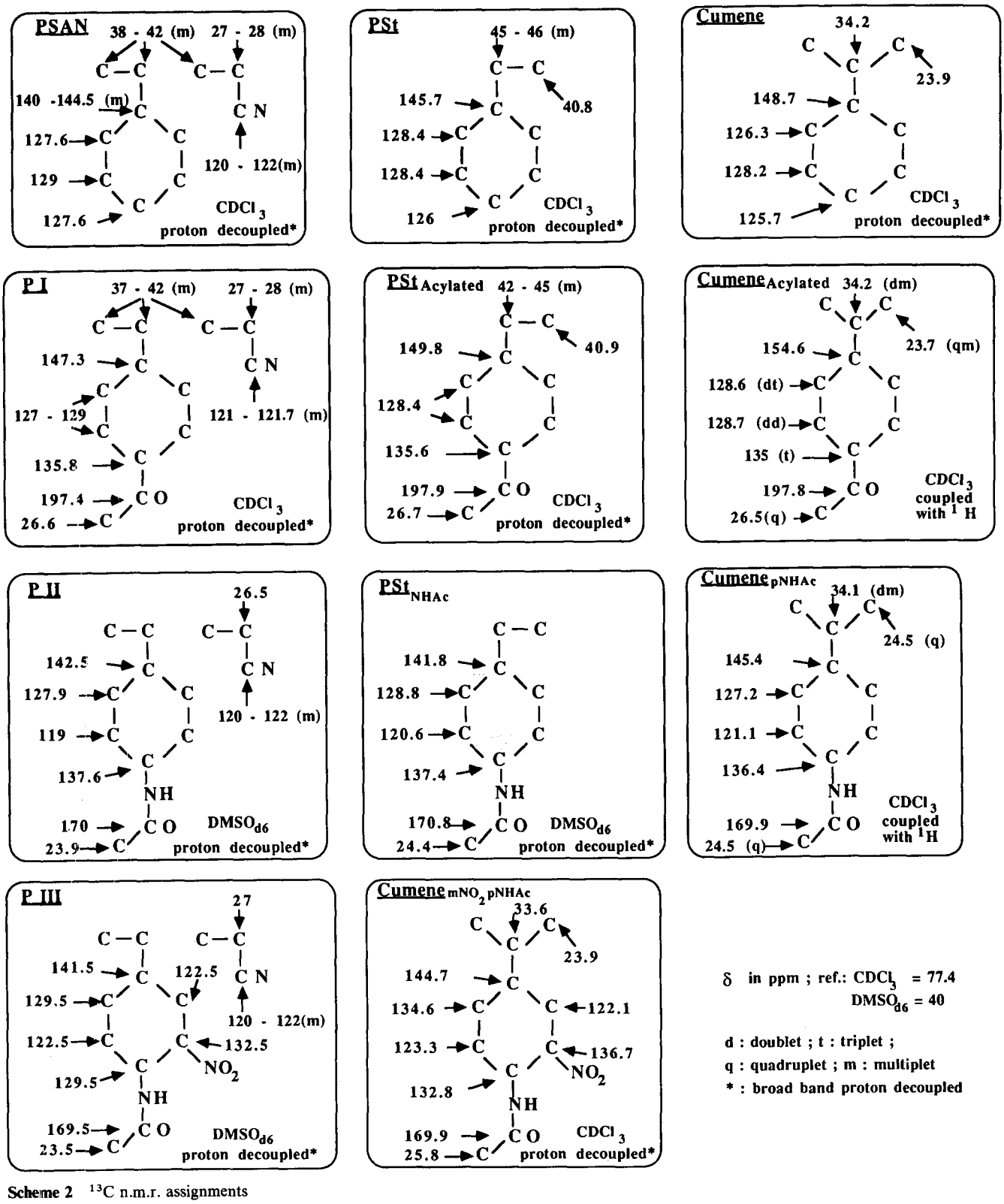
Runs: polymers	Experimental conditions[a]				Results and characteristics		
	AcCl (eq.)	$AlCl_3$ (eq.)	Solvent	t(h)	Yield (%)	F_{acyl}[c]	C_{acyl}[c] (10^3eq g^{-1})
1: PSt	1.5	2	CS_2	1.5	99	1	6.8
2: PSAN	1.5	2	CS_2	17	50	0.3	3.2
3: PSAN	1.5	1.5[d]	CH_2Cl_2	5	14	0.08	1
4: PSAN	2	2	CH_2Cl_2	20	32	0.16	2
5: PSAN	2	2	$PhNO_2$	20	23	0.12	1.5
6: PI[e]	3	4	CH_2Cl_2	20	50	>0.3	>3.2

[a] Used for 1 eq of aromatic units, at $T = 25°C$ except for run 6 at $T = 60°C$
[b] Yield of acylation determined from ^{13}C n.m.r. spectra and/or elementary analysis
[c] Molar fraction of acetylated styrene units in the modified PSAN; initial capacities of PSAN, $C_{arom} = 6.7 \times 10^{-3}$ eq g^{-1}, $C_{acryl} = 5.5 \times 10^{-3}$ eq g^{-1}
[d] With 2 eq of CF_3COOH
[e] Repetitive acylation

interpreted in terms of a microenvironmental effect. We can therefore conclude that, during acylation, the styrene units present in SSS and SSA triads behave like the styrene units of polystyrene itself, whereas this is not the case for the styrene unit of the ASA triad.

Acetamide groups were easily generated from PI by Schmidt rearrangement of the *p*-acetyl units. The quantitative extent of functionalization was determined from their ^{13}C n.m.r. spectra, which show the total disappearance of the acetyl peak ($\delta C = 197.4$ ppm). The ^{13}C n.m.r. data of the *p*-acetamide polymers are reported in *Scheme 2*.

The disubstitution of the styrene units was achieved by nitration, which is favoured in position 3. We used two nitrating agents (HNO_3 or TFA–NH_4NO_3), which give different results (*Table 2*). In the first case the functionalization is almost quantitative and leads to a polymer PIII, nitrated both on the anilide rings and on



Scheme 2 ^{13}C n.m.r. assignments

Table 2 Nitration of PII

Starting polymer	Experimental conditions	Results		
		O (%)	F (%)[a]	C^b (10^3 eq g^{-1})
PII: $F^c_{NHAc}=0.22$	HNO_3 65%	exp. 16.9	90	exp. 4.44
$F_{St}=0.33$	−10°C, 1 h	calc. 17.8		calc. 4.62
PII: $F_{NHAc}=0.22$	TFA–NH_4NO_3	exp. 12.5	44	exp. 2.05
$F_{St}=0.33$	$PhNO_2$, 25°C, 48 h	calc. 17.8		calc. 4.62
PSAN: $F_{St}=0.55$	TFA–NH_4NO_3	exp. –	59	exp. 3.1
	$CHCl_3$, 25°C, 72 h	calc. 16.6		calc. 5.2
PSt: $F_{St}=1$	TFA–NH_4NO_3	exp. 17.6	80	exp. 5.4
	$CHCl_3$, 25°C, 24 h	calc. 16.6		calc. 6.7

[a] Extent of functionalization determined from ^{13}C n.m.r. or elementary analysis
[b] Sum of capacity of nitrated aromatic rings
[c] Molar fraction of respective type of aromatic rings

Table 3 Anilide and nitrile hydrolysis of PSAN, PII and PIII

Polymer	Experimental conditions[a]			Results and i.r. characterizations
	Method	t (h)	T (°C)	
PII	1	15	80	PII: same as starting polymer
PII	2	24	70	PIV: ν(Ph–NH_2), ν(CN) (unchanged)
PII	3	5	70	PV: ν(Ph–NH_2), ν($CONH_2$)
PIII	1 or 2	16	80	PVI: ν(Ph–NH_2), ν(NO_2), ν(CN) (incomplete deacetylation)
PIII	3	9	110	PVII: ν(Ph–NH_2), ν(NO_2), ν($CONH_2$)
PSAN	1	15	80	PSAN: same as starting polymer
PSAN	2	15	70	PSAN: same as starting polymer
PSAN	3	4	70	PVIII: ν($CONH_2$)

[a] Method 1: water–alcohol suspensions of polymer with KOH 10% or H_2SO_4 20%
Method 2: solutions of polymers in $CF_3COOH \sim 80\%$
Method 3: solutions of polymers in $CH_3SO_3H \sim 98\%$

the unsubstituted aromatic rings. In the second case, the TFA–NH_4NO_3 reagent leads to a much lower extent of nitration. The difference in the reactivity of this latter reagent towards PSAN and PSt indicates that the unsubstituted aromatic rings are more difficult to nitrate in PSAN than in PSt. From these observations, it appears that TFA–NH_4NO_3 must be a more selective nitrating agent of the anilide rings of PII than HNO_3.

Finally, new hydrophilic copolystyrenes were obtained by hydrolysis of PII and PIII polymers (*Table 3*). We found that the nitrile groups of the product polymers are more readily hydrolysed than the nitrile group of PSAN. These results indicate that the substituted aromatic rings of PII and PIII markedly enhance the ability of the CN groups to be hydrolysed[17]. Under the gentle heterogeneous reaction conditions used, the nitrile and anilide residues are quite stable, whereas in homogeneous conditions, the use of CF_3CO_2H or CH_3SO_3H leads to the easy formation of free amino groups either in PSAN derivatives or in copoly(styrene acrylamide) derivatives. More drastic reaction conditions induce the formation of COOH residues and then the formation of gummy products.

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