

# Graft copolymers: 3. synthesis and characterization of poly (styrene-g-4 vinylpyridine)

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Poly (styrene-g-4 vinylpyridine) graft copolymers have been synthesized by the carbanionic deactivation of monofunctional living poly (4-vinylpyridine) onto partially chloromethylated polystyrene. To perfect this method of synthesis, several features have been examined: the conditions under which monodisperse homopoly (4-vinylpyridine) is obtained, the effect on the grafting of the way the mixing of parent homopolymers is carried out, temperature effects, the effect of different parameters on grafting yield, and the stability of resulting copolymers. It has been shown that in some cases, unused chlorinated sites remaining on the backbone of copolymer may lead, after grafting, to a cross-linking process which strongly affects the molecular structure of samples. The conditions under which this unwanted phenomenon can be avoided, have been specified. Thus, a wide range of graft copolymers of various degree of branching have been prepared. Their careful characterization shows they are homogeneous in chemical composition, of narrow molecular weight distribution and of well defined structure, i.e. the length of the backbone, the number and the length of the grafts are known.

## INTRODUCTION

Copolymers containing poly (4-vinylpyridine) (P4VP) (as well as homopoly (4-vinylpyridine)) are less frequently synthesized and studied than those with poly (2-vinylpyridine) moiety probably because of the small number of good solvents for P4VP. For instance, tetrahydrofuran (THF), one of the most common solvents used in anionic polymerization is not a solvent for P4VP.

Yet, if polyvinylpyridines are used as base polymer for the synthesis of polyvinylpyridinium chains, the possibilities of obtaining different types of polymers are greater with P4VP than P2VP. Indeed this chemical modification, which consists of a quaternization of the nitrogen atom, P4VP is more reactive than P2VP – the nitrogen atom being situated in the para position in relation to the polymeric chain in P4VP, whereas it is in ortho position for P2VP. Therefore, the latter can only be quaternized 100% with a hydrogen halide, but even in the case of an alkyl halide with a short hydrocarbon chain length like ethyl bromide, the authors have obtained a maximum quaternization yield of only 50%. In contrast, for P4VP, quantitative quaternization has been reached with alkyl bromides having a much longer hydrocarbon chain (up to 18 carbon atoms).

Consequently if polymers possessing a hydrophilic character are desired, it is better to start from P4VP. As far as the preparation of hydrophilic-hydrophobic copolymers is concerned, if polystyrene (PS) is used as the hydrophobic part, PS-P4VP copolymers are of greater interest than PS-P2VP copolymers.

The synthesis of PS-P4VP block copolymers has already been studied.<sup>2</sup> The purpose of this work is the synthesis and the characterization of PS-P4VP graft copolymers, more precisely the grafting of P4VP onto PS (PS-g-P4VP copolymers) which have never been reported.

The same method as that employed to graft P2VP onto

PS(3), derived from the well known synthesis of comb-shaped PS<sup>4-10</sup> has been used. The principle of this method is the carbanionic deactivation of a living polymer onto partially chloromethylated polystyrene. Nevertheless, with P4VP, a problem arises due to its insolubility in THF. With PS-*b*-P4VP block copolymers, this problem is slight since the copolymers remain in solution in THF, owing to the polystyrene blocks synthesized first<sup>2\*</sup>, but this is not the case with PS-g-P4VP graft copolymers. Indeed, for the latter it is impossible to operate in pure THF, because the grafting by carbanionic deactivation requires the previous synthesis of the pyridine chains. This is possible, as we shall see later, only in the presence of DMF. Accordingly, despite the similarity of chemical structure between 2VP and 4VP, it was unclear that, for P4VP, a simple transposition of results obtained for PSVP<sup>3</sup> could be made, since the grafting conditions are necessarily different. This is emphasized by the fact that in preliminary attempts of grafting, some PS-g-P4VP copolymers exhibit molecular weights much higher than expected. For this reason, as for PS-g-P2VP copolymers,<sup>3</sup> a careful study of the grafting of living P4VP on PSCI has been carried out.

## EXPERIMENTAL

### Materials

*Chloromethylated polystyrene (PSCI)*. The data for the preparation of samples of partially chloromethylated polystyrene, and their characteristics have already been given.<sup>3</sup>

*Dimethylformamide (DMF)*. The process for purification of DMF is as follows: the greatest part of water present within DMF is removed by heteroazeotropic distillation with benzene (10% in volume) under atmospheric pressure;

\*Note: it is even possible to prepare in THF monodisperse copolymers PS-*b*-P4VP, whose 4VP content reaches 90%<sup>11</sup> without macroscopic precipitation of products in the reaction media

Table 1. Polymerization of 4-vinylpyridine

	DMF %	Polymer concentration	$M_{\text{theoretical}}$	$M_{\text{measured}}$ (LS)	Remarks
PNG14	15%	2.5%	22 000	24 000	
PNG19	15%	3%	13 000	53 000	a
PNG21	33%	2%	12 000	31 000	b
JP1	30%	1%	10 000	10 000	
JP2	15%	1%	10 000	11 000	

a — partial precipitation during the synthesis ( $M_{\text{LS}}$  of this precipitated fraction: 600 000)

b — slight gelatinous precipitate during the synthesis

then DMF is stored over  $\text{P}_2\text{O}_5$  for one day (elimination of water and dimethylamine) and afterwards over BaO for one day (elimination of water and formic acid). Just before use, DMF is distilled under reduced pressure of nitrogen (Bp = 54°C at 20 mm Hg) and recovered into an ampoule isolated from room atmosphere.

**Tetrahydrofuran (THF), 4-vinylpyridine (4VP).** Purification processes are well known, they are distilled several times: on calcium hydride and under vacuum for 4VP (Bp: 63°C at 14 mmHg), on sodium, then sodium-benzo-phenone complex for THF.

**Diphenylmethylsodium.** The preparation of this initiator for polymerization of 4VP has been mentioned earlier.<sup>3</sup>

### Synthesis procedure

**Apparatus and experimental conditions.** These have already been outlined elsewhere.<sup>3</sup>

**Polymerization of 4VP.** Possible in THF-DMF mixed media, at low temperature (–70°C), with diphenylmethylsodium as initiator. The best conditions (ie DMF and polymer concentrations) for monodisperse samples are discussed later.

In practice the recovery of homopoly(4-vinylpyridine) can be difficult. Indeed the smallest molecular weight samples, about 10 000, at low concentration, 1%, in the THF-DMF mixture, do not precipitate either in heptane or in water. If the polymeric solution is concentrated by solvent evaporation, it becomes richer in DMF and is then immiscible with heptane. In order to correctly recover the sample, it is necessary to operate as follows: the solution is concentrated by means of a rotary evaporator until nearly dry (the greatest part of DMF is removed under high vacuum) and after THF is added; from the solution obtained the precipitation of P4VP in heptane occurs satisfactorily.

**Grafting.** The recommended grafting procedure, considering the results of miscellaneous experiments mentioned in this paper is as follows: at first, mono-carbanionic poly(4-vinylpyridine) is prepared under the above prescribed conditions; a part of solution is sampled in order to characterize the grafts of the future copolymer; the solution of PSCl in THF is added rapidly to the living polymer solution kept at low temperature, and with vigorous stirring; the grafting reaction is accelerated by bringing the reactional mixture to room temperature. Under these conditions, the completion of the reaction is reached within 1 hour at the most. The end of the reaction is indicated by discoloration of the whole solution if there is an important deficiency of living P4VP<sup>⊖</sup> towards chloromethyl functions. In the opposite case, the unreacted carbanions are deactivated by methanol.

Table 2. Effect of the order of introduction of parent homopolymers on the grafting reaction

Order of introduction of reagents	Ref. NG9	Ref. NG10	Line
<b>Backbone</b>	chloromethylated polystyrene $M_w = 52\ 000$ degree of chloromethylation 1/60 ie 8.3 Cl/chain		
<b>Grafts</b>	poly(4-vinylpyridine) initiator of polymerization: diphenylmethylsodium polymerization temperature, –70°C $M_w = 15\ 000$		
<b>Grafting</b>	reaction temperature, $\approx 0^\circ\text{C}$		
	P4VP <sup>⊖</sup> into PSCl	PSCl into P4VP <sup>⊖</sup>	
	$M_{\text{measured}}$ (LS)		
	77 000	68 000	(1)
	2VP content	63%	69.7%
			(2)
<b>Crude copolymer</b>	$M_{\text{theoretical}}$ * (total grafting)		
	140 000	172 000	(3)
<b>Theoretical* composition of crude copolymer</b>	Homo-polymer P4VP	28% $M_w = 15\ 000$	40% $M_w = 15\ 000$
	Graft copolymer	72% $M_w = 101\ 000$	60% $M_w = 103\ 000$
			(4)
			(5)
<b><math>M_w</math> graft copolymer after elimination of homopolymer</b>	99 000	109 000	(6)

\*calculated as explained in the experimental part of reference 3

Operating with an excess or a shortage of living polymer is controlled by the degree of chloromethylation of the starting polystyrene: when the degree of chloromethylation is low (less than 1/60) not all of the chlorinated sites participate in the grafting reaction. Consequently it is necessary to use an excess of P4VP<sup>⊖</sup> in relation to the desired yield of grafting. If the degree of chloromethylation is higher (between 1/50 and 1/30), by starting from a number of living ends of the order of 70 to 80% higher than the number of chlorine functions, it is thus possible to obtain a copolymer nearly free of homopolymer. When the degree of chloromethylation is very high (higher than 1/20) it is imperative to operate with a strong excess of carbanions, if not the resulting product is unstable.

### Characterization of resulting products

**Fractionation.** The purification of copolymers by eliminating the ungrafted homopolymer can sometimes be achieved by extraction using methanol which is a solvent for P4VP. However, this method is only suitable for a few copolymers ie those whose 4VP content is less than about 50% (see for instance, samples NG9 and NG10 in Table 2). In most cases, this purification method is inapplicable because copolymers, which are rich in 4VP, are also soluble in the extraction solvent.

Fractionation by fractional precipitation is a more general method. Furthermore, it allows not only the graft copolymer itself to be isolated, but also copolymer fractions with narrower molecular weight distributions to be obtained and afterwards the characterization polydispersity of the sample. Fractional precipitation was performed in a standard way by successive additions of a precipitant into the polymer solution.

The choice of a solvent-precipitant pair is delicate because solvents for PS-P4VP copolymers are rare, especially

Table 3. Effect of the residual chlorine functions on the stability of PS-g-P4VP copolymers

Ref	Chloromethylation degree of the base polystyrene	Yield of grafting	Chloromethylation degree after grafting	Behaviour of the copolymer
NG8	1/11	50%	1/22	insoluble
NG11	1/11	55%	1/24	a
NG22	1/11	70%	1/36	b
NG26	1/19.6	78%	1/89	stable
NG9	1/60	40%	1/100	stable
NG25	1/19.6	83%	1/115	stable
NG18	1/23.6	87%	1/180	stable
NG14	1/40	80%	1/200	stable
NG27	1/9.4	100%	0	stable

a—just after synthesis:  $M_{\text{measured}}/M_{\text{theoretical}} = 2.8$  product becoming insoluble after a few weeks

b— $M_w$  increases by 14% within three months

when the 4VP content is high, as is the case for our PS-g-P4VP copolymers. DMF and chloroform, which are solvents for both moieties of the copolymer cannot be used because the former is immiscible with heptane, the usual precipitant of PS-P4VP copolymers, and the latter, whose density is high, is not practical. Methanol is a solvent for copolymers at high 4VP content, but it is very difficult to reprecipitate P4VP from solution in methanol. THF or benzene, solvents used by Grosius for PS-b-P4VP block copolymers<sup>2</sup> do not work here, because our copolymers are richer in 4VP and are insoluble in these solvents.

For these reasons, we have chosen an initial mixed solvent (methanol-THF), the precipitant being heptane. Methanol permits not only the initial dissolution of products, but furthermore its presence is necessary to obtain a good separation graft copolymer-ungrafted homopolymer. The latter problem has already been treated for PS-g-P2VP graft copolymers.<sup>3</sup> The methanol content depends upon the respective molecular weights of the graft copolymer and the homopolyvinylpyridine and is adjusted before fractionation by comparison of the  $\gamma$  of precipitation of the homopolymer sample and that of the crude copolymer ( $\gamma = \text{volume of precipitant/whole volume of solution}$ ). A too low methanol content can lead to insufficient differentiation of the  $\gamma$  of precipitation of the homopolymer and the copolymer—this case is illustrated by sample NG14 in Table 13.

From a practical point of view, the final recovery of samples by the subsequent precipitation of the viscous phase obtained from fractional precipitation leads to hard and compact products, which is annoying for their future use. To obtain powdery samples the process is as follows: the precipitated phase is concentrated until dry, then the copolymer is redissolved in benzene with addition of the minimum of methanol necessary for its solubilization and recovered by freeze-drying.

*Elemental analysis.* The dosing of nitrogen allows us to determine the P4VP content within the samples.

*Light scattering.* Molecular weight measurements by the light scattering technique ( $M_{\text{LS}}$ ) have been made on a FICA photometer at  $\lambda = 5460 \text{ \AA}$ , in DMF solution. Most of the measurements have only been carried out at a scattering angle of  $90^\circ$ . Graft macromolecules despite their relatively high molecular weight, are too small to give rise to any angular dissymmetry in the scattered light (excepted for sample NG27 in Table 16).

Refractive index increments of copolymers ( $dn/dc$ ) have

been either measured (on a Brice-Phoenix differential refractometer) or calculated from chemical composition and  $dn/dc$  values of the parent homopolymers (at  $\lambda = 5460 \text{ \AA}$ , PS/DMF :  $dn/dc = 0.166$ , P4VP/DMF :  $dn/dc = 0.153$ ). The latter value which we have measured is notably different from that reported in literature<sup>2</sup> but it is nevertheless corroborated by  $dn/dc$  measurements performed on our copolymers.

$M_{\text{LS}}$  determined for the copolymers are apparent molecular weights,  $M_{\text{app}}$ , but it is assumed that  $M_{\text{app}} = M_w$  for the same reasons as those given for PS-g-P2VP graft copolymers.<sup>3</sup>

*Characterization procedure.* The whole of the characterization operation achieved for each copolymer is exactly the same as that described in the experimental part of the paper relative to PS-g-P2VP graft copolymers.<sup>3</sup>

## RESULTS AND DISCUSSION

The same features of the synthesis of PS-g-P2VP copolymers<sup>3,12</sup> have been studied here: the effect of the order of introduction of reagents (PSCl added into the living polymer solution or vice-versa); the stability of copolymers, ie the study of a specific instability phenomenon; the effect of the temperature; the yield of grafting; the careful characterization of copolymers; Before studying the grafting reaction, we shall deal with the problem of the P4VP synthesis.

### Synthesis of poly(4-vinylpyridine)

Dimethylformamide (DMF) is one of the rare solvents for P4VP usable in anionic polymerization. However, it is of little practical use: its purification is fastidious, it is difficult to remove during the recovery of products ( $B_p: 150^\circ\text{C}$ ) and furthermore it is immiscible with heptane a common precipitant for polyvinylpyridines. In order to limit the disadvantages resulting from the use of DMF, the authors have chosen to polymerize 4VP in THF-DMF mixed media. A small content of DMF is often sufficient to avoid the precipitation of P4VP during the polymerization. For example, when the required molecular weight is higher than 20 000 a mixture containing 5% of DMF is suitable if the polymer concentration is low, about 1%. For higher polymer concentrations, about 3%, it is better to use a greater percentage of DMF, 15%. However if the molecular weight is less than 20 000, there is sometimes a partial precipitation of polymer during the polymerization, even if the medium is richer in DMF, 30% (Table 1); the resulting product is then strongly polydisperse. It can be seen (Table 1) that, against expectations, samples whose theoretical average molecular weights are the smallest, appear to be the least soluble in the reactive medium, for a given polymer concentration.

In fact, we have observed that the part of polymer which precipitates during the synthesis is formed by very high molecular weight P4VP (eg  $M_w = 600\ 000$  for the precipitated moiety of sample PNG19 with expected molecular weight  $M_w = 13\ 000$ ). Therefore, the higher molecular weight is due to the presence of a small amount of P4VP having a very high molecular weight. This can be explained by insufficient dispersion of the monomer which, because of the very fast polymerization rate, polymerizes locally before being dispersed in a homogeneous way in the reactional medium. As a proof of this, it can be seen that the

Table 4. Behaviour of a mixture of chloromethylated polystyrene and poly(4-vinylpyridine)

Mixture	33.4% chloromethylated polystyrene $M_w = 52\ 000$ 66.6% poly(4-vinylpyridine) $M_w = 64\ 000$
$t = 0$	mixing: $M_{\text{theoretical}} = 60\ 000$
$t = 2$	$M_{\text{LS}} = 59\ 000$
$t = 9$	$M_{\text{LS}} = 79\ 000$
$t = 50$	partly insoluble product

importance of the precipitation phenomenon decreases as the reactor is more vigorously stirred.

In order to avoid the formation of a polymer with too high a molecular weight, it is necessary to effect the polymerization at a higher dilution, 1% (samples JP1, JP2 in Table 1).

#### Effect of the order of introduction of reagents

It has been shown that at the time of the reaction between a living polymer and the chloromethyl functions (in particular for the synthesis of comb-shaped polystyrene), the order of introduction of these two reagents into the reactor can effect the structure of the products obtained.<sup>4,7</sup> Therefore, as for the study of grafting of P2VP<sup>o</sup> onto PSCl<sup>3</sup> the authors have examined whether copolymers had identical characteristics whatever the order of introduction of parent homopolymers in the reactional medium.

To answer this question, two copolymers have been synthesized from identical PSCl and identical P4VP<sup>o</sup>, one by addition of P4VP<sup>o</sup> into the PSCl solution and the other by the reverse procedure (Table 2). In order to avoid any possibility of side-reactions analogous to those occurring for PS-g-P2VP copolymers,<sup>12</sup> copolymers have been prepared bearing few residual chlorine functions.

First it must be noted, that one would not expect to obtain two exactly similar products, since the quantity of 4-vinylpyridine is not the same for the two experiments (line 2 of Table 2). Even in the case of a total grafting, the theoretical molecular weights would be different (line 3). Furthermore, the grafting is far from complete as is indicated by the molecular weights measurements (line 1) which are lower than those theoretically expected (line 3). From these two features, it can be seen that the crude copolymers hold different contents of homopolymer, and their molecular weights cannot be directly compared to check the effect of the order of introduction of the reagents.

However, knowing the proportion and the molecular weight of the parent homopolymers, we can calculate, as for PS-g-P2VP copolymers,<sup>3</sup> the quantity of the ungrafted homopolymer (line 4) and the molecular weight of the graft copolymer itself (line 5). Also the latter can be isolated by extraction of homopoly(4-vinylpyridine) using methanol. Thus, for each experiment, one can compare on one hand the molecular weight calculated under the assumption of the absence of side reactions (line 5) and on the other hand, the  $M_w$  measured after elimination of the ungrafted homopolymer (line 6). A good agreement between these two values was noted for each sample, which indicates that grafting occurs without side reactions.

So it appears that the difference between samples NG9 and NG10 is due to slightly different experimental conditions (the grafting has been favoured for the sample NG10, because of the presence of a greater number of living ends) and not to side reactions analogous to those encountered during the grafting of living PS onto PSCl.<sup>4,6-8</sup> If this had

been the case, the unwanted reaction would have been observed for the copolymer NG9 which then would have the greatest molecular weight.<sup>4,7</sup>

The too high molecular weight obtained for some PS-g-P4VP copolymers as mentioned in the introduction, is the consequence of another type of side reaction, which has already been met for PS-g-P2VP graft copolymers.<sup>12</sup> This feature is treated in the next section.

#### Stability of copolymers

As for PS-g-P2VP copolymers,<sup>12</sup> we have observed that the grafting of P4VP onto PSCl sometimes leads to products which are not stable. However the phenomenon of the progressive increase in molecular weight is here much stronger. Whereas with 2VP it shows itself only after several days, with 4VP, some copolymers exhibit very high molecular weight only a few hours after their synthesis (eg: sample NG11 in Table 3). The whole reticulation of products and consequently even their insolubility in solvents can be reached. The observation of the behaviour of different copolymers shows, as for PS-g-P2VP copolymers, the effect of the residual chlorine functions on the stability of products (Table 3).

These results lead us to believe that the side reaction is analogous to that appearing for PS-g-P2VP copolymers. Therefore, we think that this reaction is also an intermolecular quaternization reaction between nitrogen atoms of pyridine units, and chloromethyl functions.<sup>12</sup> In the case of PS-g-P4VP copolymers the reaction is faster and its extent is more important than for PS-g-P2VP copolymers because of the more accessible nitrogen atom for 4VP than for 2VP, which thus favours intermolecular couplings.

As for PS-g-P2VP copolymers,<sup>12</sup> the existence of pyridinium groupings has not been observed by u.v. or i.r. spectroscopy, because of a weak percentage of quaternized vinylpyridine units. Nevertheless, we have detected by argentimetry the presence of chlorine ions within the upper solution of a whole reticulated PS-g-P4VP polymer.

Furthermore, the hypothesis of an intermolecular quaternization reaction is confirmed by the behaviour of a mixture of parent homopolymers for which we have also observed an increase of the molecular weight (Table 4). However, this phenomenon is less strong for the mixture of homopolymers than for copolymers. This is undoubtedly due to a more marked segregation of polymeric chains of a different chemical nature in the case of the mixture, whereas for a copolymer the contacts between backbone and grafts are necessarily more important.

It should be noted that this reaction between homopolymers did not appear with the mixture polystyrene-poly(2-vinylpyridine).<sup>12</sup> This may be ascribed to the greater

Table 5. Effect of the temperature of storage on the stability of a copolymer

Sample ref. NG22 F1		
Unused chlorine functions 1 for 36 styrene units		
	1st measure of $M_w$ by LS	2nd measure of $M_w$ by LS (3 months later)
Product kept at room temperature		475 000
Product kept at -30°C	440 000	435 000

**Table 6.** Effect of the drying temperature on the rate of the side-reaction

Reference	NG8	NG11
Degree of chloromethylation of base polystyrene	1/11	1/11
Yield of grafting	50%	55%
Drying temperature (under vacuum)	45°C	20°C
Observations	Insoluble product 4 days after synthesis	Insoluble product after some weeks

reactivity already mentioned of 4VP units towards chloromethylated groupings.

The careful study of the stability of copolymers leads to the following observations: the reticulation phenomenon affects the copolymers in their dry state, at room temperature, if the residual chloromethylation degree is greater than about 1/100 (ie number of residual benzylic chlorine groups higher than 1 per 100 styrene units of the backbone); more precisely, when the residual chloromethylation content is between 1/50 and 1/100, the cross-linking reaction is relatively slow – it is possible to obtain products having the expected molecular weight provided that they are kept at low temperature (*Table 5*); on the other hand, if the residual chloromethylation content is higher than 1/30, the side reaction is very fast and the copolymers exhibit an anomalously high molecular weight just after their synthesis, such polymers are of course unsuitable for further studies; the cross-linkings do not occur during the synthesis itself (this feature will be treated in detail in the next section concerning the effect of the temperature), but only during and after the recovery of products; it is likely that the side-reaction occurs particularly after precipitation when the copolymer is still solvent-soaked, such an extremely concentrated medium having to favour this type of intermolecular reaction. This means that the manner in which the polymer is recovered and, in particular, the drying temperature can influence the evolution of the molecular weight. This is illustrated by the example of two samples (NG8 and NG11) of very similar characteristics, but which have been recovered under different conditions (*Table 6*); the crosslinking reactions do not appear in dilute solution (1 to 2%) and particularly during the fractionation by precipitation.

To obtain quite stable copolymers a yield of grafting of 100%, or at any rate such that the residual degree of chloromethylation is about 1/100 of styrene units of the backbone is desirable. This necessitates the use of a great excess of living polymer (a feature that will be treated in the section relating to the yield of grafting).

If the synthesis of PS-g-P4VP copolymers is only a step in the preparation of polystyrene-polyvinylpyridinium copolymers, the 'stabilization' can be obtained by immediate achievement of the quaternization reaction on pyridinic units. However, this procedure is only valid for copolymers with moderate residual chlorine content for which the reticulation is not very fast (ie degree of chloromethylation after grafting lower than 1/50).

In an earlier paper<sup>12</sup> it has been shown that the stabilization of PS-g-P2VP copolymers by a dischlorination process using lithium-naphthalene is possible – carried out directly after grafting within the reaction medium. This procedure cannot be used for PS-g-P4VP copolymers

**Table 7.** Effect of the temperature of the grafting

Chloromethylated polystyrene  $M_w = 60\ 000$ ; degree of chloromethylation: 1/23.6 ie 24 Cl/chain  
 Poly(4-vinylpyridine) temperature of polymerization,  $-70^\circ\text{C}$ ;  $M_w = 8\ 000$   
 Grafting  $[\text{P4VP}^{\ominus}] / [-\text{CH}_2\text{Cl}] = 1.2$ ; rapid addition of the PSCI solution in THF into  $\text{P4VP}^{\ominus}\text{Na}^{\oplus}$  solution

Ref. NG17		Ref. NG18	
Grafting at low temperature ( $-70^\circ\text{C}$ )		Grafting at room temperature	
$t = 0$	end of the PSCI addition	$t = 0$	end of the PSCI addition
$t = 5\ \text{mm}$	difficult precipitation of the polymer L.S. impossible (insoluble product)	$t = 1\ \text{mm}$	$M = 193\ 000$
$t = 15\ \text{mm}$		$t = 15\ \text{mm}$	$M = 196\ 000$
$t = 40\ \text{mm}$		$t = 65\ \text{mm}$	$M = 195\ 000$
$t = 100\ \text{mm}$	$M_{\text{LS}} = 160\ 000$		

because lithium-naphthalene reacts with DMF, a solvent whose presence is necessary for the synthesis of the copolymers.

#### Effect of the temperature

In order to study the role of the temperature on the grafting reaction, two syntheses have been effected from the same PSCI and the same P4VP<sup>⊖</sup> (*Table 7*). The first experiment was carried out at low temperature ( $-70^\circ\text{C}$ ) and the second at room temperature. For each experiment, the degree of advancement of the reaction has been followed by sampling at various times and by characterization of the resulting products.

The results obtained with sample NG17 (*Table 7*) are explained by the fact that at low temperature, the grafting occurs slowly as also observed for P2VP.<sup>3</sup> So, the initial samples are formed by only slightly grafted copolymer and a great deal of homopolymer. Precipitation of the crude product is difficult as the homopolymer has a low molecular weight. Furthermore, as the backbone still bears numerous chlorinated sites, cross-linking reactions occur and after one day the product becomes insoluble in DMF. For the following samples, the extent of the grafting is greater, the crude copolymer has a high molecular weight and thus the precipitation of the product is easy. In addition the amount of residual benzylic chlorine is low, therefore the possibility of cross-linking no longer occurs and thus the products are stable and soluble in DMF. This result is very important: it shows that side reactions observed for the first removed samples do not occur during the grafting itself but after the recovery of the polymers. In the other experiment (sample NG18), at room temperature, the reaction is on the contrary very fast and is finished within a few minutes.

These data have the result that even if there is a shortage of living polymer in relation to chloromethyl functions, an homogeneous grafting can still be obtained. This is even the case for addition of the PSCI solution into the P4VP<sup>⊖</sup> solution but it is necessary to achieve the mixing of parent homopolymers at a low temperature. Under these conditions, the reaction occurs slowly and the grafting is not favoured for the first PSCI chains present within the solution as would be the case at room temperature.

In addition, it has been shown previously<sup>5</sup> that side

**Table 8.** Yield of grafting: effect of the initial degree of chloromethylation

Polymer concentration, 3% [P4VP <sup>⊖</sup> ]/[−CH <sub>2</sub> Cl] ≈ 1.2		
Ref.	Chloromethylation degree of PSCI	Yield of grafting obtained
NG10	1/60	53%
NG14	1/40	80%
NG18	1/23.6	87%

couplings appearing during the grafting of living polystyrene onto chloromethylated polystyrene, occur chiefly at low temperature. We have already seen that this type of secondary reaction did not appear during the grafting of P4VP<sup>⊖</sup> at room temperature. The experiment concerning sample NG17 shows that this is also the case at low temperature.

The fact that only the desired nucleophilic substitution occurs at the expense of an unwanted metal-halogen interchange that would lead to side couplings, is explained by a greater polarization of the carbene-metal bond for P4VP<sup>⊖</sup>, M<sup>⊕</sup> than for PS<sup>⊖</sup>, M<sup>⊕</sup> as already mentioned for grafting of P2VP onto PSCI.<sup>3</sup> Indeed for P4VP<sup>⊖</sup>, M<sup>⊕</sup>, the electro-attractive effect of pyridine nucleus at first favours the dissociation of the ion-pair. Furthermore, it has been postulated<sup>13</sup> that counter-ions are probably solvated by poly(4-vinylpyridine) chains, by means of the lone pair of electrons of nitrogen atoms. In addition, the ionic character of the carbene metal bond must be increased by the presence of DMF (for which the dielectric constant is higher than for THF).

#### Yield of grafting

The remarks concerning the yield of grafting stated for PS-g-P2VP copolymers<sup>3</sup> remain true for PS-g-P4VP copolymers. In particular the maximum yield of grafting is above all a function of the concentration of reactive groupings (chloromethyl functions on the one hand, carbanions on the other hand). Thus for a given concentration in polymer within the reactional medium, the yield of grafting increases with the initial degree of chloromethylation of the polystyrene (Table 8). For a given degree of chloromethylation, the yield of grafting increases with the copolymer concentration, which is logical since it is an intermolecular reaction. As expected, the grafting is favoured by the presence of an excess of living polymer (Table 9). To ensure that all chlorine functions are used, it is necessary to operate with a large excess of carbanions (Table 10). An increase in temperature seems to slightly favour the yield of grafting (Table 11). In any case, after mixing of reagents, permitting the reaction to take place at low temperature is of no interest since the grafting rate is activated by an increase of the temperature, and also P4VP carbanions are stable at room temperature during the reaction-time.<sup>13</sup> If the experimental conditions (ie reagents concentration) are such that the grafting is not complete, the maximum yield of grafting is generally reached after less than one hour. Though unreacted functional groups remain, it is useful to allow the reaction to continue for a longer time as illustrated in Table 12.

#### Characterization of copolymers

Fractionation results for four copolymers (ref.: NG14, NG25, NG22, NG27) differing mainly by their degree of branching (the distance between two grafts is respectively

**Table 9.** Yield of grafting: effect of the concentration of living ends in relation to the concentration of chloromethyl functions

Ref.	[P4VP <sup>⊖</sup> ]/[−CH <sub>2</sub> Cl]	Yield of grafting
NG9	0.75	43%
NG10	1.10	53%

**Table 10.** Yield of grafting: achievement of a quantitative grafting

Ref.	Chloromethylation degree of PSCI	[P4VP <sup>⊖</sup> ]/[−CH <sub>2</sub> Cl]	Yield of grafting
NG22	1/11	1.10	70%
NG27	1/9.4	1.80	100%

**Table 11.** Yield of grafting: effect of the temperature

Reference*	NG17	NG18
Grafting temperature	−70°C	20°C
Crude copolymer: $M_{LS}$	160 000	194 000
Graft copolymer: $M_{calculated}^{\dagger}$	215 000	240 000
Number of grafts	18.75	22
Yield of grafting	74%	87%

\* see Table 7

† mode of calculation explained in reference 3

**Table 12.** Effect of the time of reaction on the completion of grafting

Chloromethylated polystyrene $M = 60\ 000$ chloromethylation degree: 1/19.6		
Poly(4-vinylpyridine) $M = 10\ 000$ [P4VP <sup>⊖</sup> ]/[−CH <sub>2</sub> Cl] = 0.9		
Mixing of parent homopolymers achieved at low temperature (−70°C) and after the reactional medium has been brought slowly to room temperature (the discoloration of the solution is not complete)		
$t = 0$	Mixing of parent homopolymers	$M$ theoretical of the graft copolymer: = 335 000
$t = 60$ mn	1st sample	$M_{LS} = 247\ 000$
$t = 190$ mn	2nd sample	$M_{LS} = 245\ 000$

50, 24, 17 and 9 styrene units) are summarized in Tables 13–16.

Careful examination of these data, leads to observations similar to those drawn from the characterization of PS-g-P2VP.<sup>3</sup> In particular, for each copolymer, the expected and the measured molecular weights agree perfectly and the sample has a narrow molecular weight distribution.

Only for sample NG14 (Table 13) were the expected results relative to the composition of the crude copolymer and the molecular weight of the graft copolymer not obtained exactly. This is explained by the fact that the solvent-precipitant pair used for this fractionation was not completely efficient in separating the homopolymer from the copolymer as was seen for PS-g-P2VP copolymers.<sup>3</sup> Effectively, by ultracentrifugation measurements it has been observed that copolymer fractions contain a little homopolymer (especially for fraction n° 4 which exhibits a higher 4VP percentage and a smaller inter-grafts distance).

It can also be observed from sample NG27 that a large number of P4VP grafts can be fixed on a polystyrene backbone with a quantitative use of benzylic chlorine groups if a strong excess of living polymer is used.

Table 13. Fractionation of a copolymer with a 'small' degree of branching (1 graft for 50 styrene units)

Sample	NG14						
Backbone	chloromethylated polystyrene $M_w = 60\,000$ degree of chloromethylation: 1/40 ie 14.4 Cl/chain						
Grafts	poly(4-vinylpyridine) $M_w = 24\,000$						
Grafting	solvent: 15% DMF – 85% THF whole concentration of polymer: 3% [PV4P <sup>1</sup> ]/[-CH <sub>2</sub> Cl] = 1						
Crude copolymer	%4VP = 85.2% $M_{theoretical}^a$ (total grafting) = 405 000 $M_{measured}$ (LS) = 270 000 theoretical composition <sup>a</sup> { 81% copolymer $M = 328\,000$ 19% homopolymer $M = 24\,000$						
Fractionation	initial solution at 2.5% of polymer in a 20% methanol – 80% THF mixture precipitant: heptane						
Fraction $\gamma^b$	Weight %	4VP content %	$M_{LS}$ (DMF) <sup>c</sup>	Backbone $M_{calcul.}$	Number of grafts per chain	Intergrafts distance <sup>d</sup>	
1	0.140	57.2	82.5	374 000	65 500	12.8	49
2	0.158	19.5	82	231 000	41 600	7.9	51.5
3	0.171	8.2	83	170 000	28 900	5.9	47
4	0.186	6.1	87.1	81 000	10 400	2.9	35
5	–	9.0	98.5	37 000	–	–	–

<sup>a</sup> see mode of calculation in reference 3  
<sup>b</sup>  $\gamma$  = volume of precipitant/total volume of solution  
<sup>c</sup>  $M_{LS}$  = molecular weight measured by light scattering  
<sup>d</sup> the spacing of grafts is expressed in number of styrene units of the backbone  
 Average molecular weights calculated from the molecular weights of the fractions: whole of fractions – crude copolymer,  $M_w = 281\,000$ ; fractions F1 to F4 (91% in weight) – graft copolymer  $M_w = 305\,000$ ; fraction F5 (9% in weight) – homopolymer  $M_w = 37\,000$ .  
 Yield of grafting  $\approx 80\%$

Table 14. Fractionation of a copolymer with a 'middle' degree of branching (1 graft for 24 styrene units)

Sample	NG25						
Backbone	chloromethylated polystyrene: $M_w = 62\,000$ degree of chloromethylation: 1/19.6 ie 30 Cl/chain						
Grafts	poly(4-vinylpyridine) $M_w = 9\,800$						
Grafting	solvent: 18% DMF – 82% THF whole concentration of polymer: 1.3% [P4VP <sup>1</sup> ]/[-CH <sub>2</sub> Cl] = 0.9						
Crude copolymer	%4VP = 81.5% $M_{theoretical}^*$ (total grafting) = 335 000 $M_{measured}$ (LS) = 250 000 theoretical composition <sup>a</sup> { 86.5% copolymer $M = 290\,000$ 13.5% homopolymer $M = 9\,800$						
Fractionation	initial solution at 1.4% of polymer in a 50% methanol – 50% THF mixture precipitant: heptane						
Fraction $\gamma$	Weight %	4VP content %	$M_{LS}$ (DMF) <sup>*</sup>	Backbone $M_{calcul.}$	Number of grafts per chain	Intergrafts distance	
1	0.340	42.7	79.9	350 000	70 000	28.5	23.7
2	0.355	25.1	80.3	276 000	54 000	22.6	23.1
3	0.375	11.1	78.5	233 000	50 000	18.7	25.7
4	0.414	4.2	77.5	162 000	36 500	12.8	27.4
5	–	16.9	98	11 000	–	–	–

Average molecular weight calculated from the molecular weight of the fractions: whole of fractions – crude copolymer,  $M_w = 253\,000$ ; fractions F1 to F4 (83% in weight) – graft copolymer  $M_w = 302\,000$ ; fractions F5 (16.9% in weight) – homopolymer,  $M_w = 11\,000$ ; backbone:  $M_w = 61\,000$ .  
 Yield of grafting: 83%

\* significance of these values as in Table 13

## CONCLUSION

It has been shown that living poly(4-vinylpyridine) reacts easily with partly chloromethylated polystyrene and leads to graft copolymer. No side reaction accompanying the grafting reaction itself has been ordered.

However two limiting conditions arise. The first is in the synthesis of low molecular weight poly(4-vinylpyridine), for which we have specified some requirements. The second is in avoiding the presence, on the backbone after grafting, of too large a number of residual benzylic chlorine functions because they are responsible for a specific cross-

Table 15. Fractionation of a copolymer with a 'high' degree of branching (1 graft for 17 styrene units)

Sample	NG22						
Backbone	chloromethylated polystyrene: $M_w = 54\,000$ degree of chloromethylation: 1/10.7 ie 47 Cl/chain						
Grafts	poly(4-vinylpyridine) $M_{LS} = 11\,000$						
Grafting	solvent: 20% DMF – 80% THF whole concentration of polymer: 1% [P4VP <sup>1</sup> ]/[-CH <sub>2</sub> Cl] = 1.10						
Crude copolymer	%4VP = 90.8% $M_{theoretical}^*$ = 590 000 (if whole P4VP would be able to graft) $M_{measured}$ (LS) = 280 000 theoretical composition <sup>*</sup> { 68.5% copolymer $M = 404\,000$ 31.5% homopolymer $M = 11\,000$						
Fractionation	initial solution at 1.5% of polymer in a 25% methanol – 75% THF mixture precipitant: heptane						
Fraction $\gamma$	Weight %	4VP content %	$M_{LS}$ (DMF) <sup>*</sup>	Backbone $M_{calcul.}$	Number of grafts per chain	Intergrafts distance	
1	0.172	56.2	86.5	440 000	59 000	34.6	16.5
2	0.185	8.6	84.1	318 000	50 500	24.3	20
3	0.237	3.7	84.5	198 000	31 000	15.2	19.4
4	0.279	7.4	100	22 000	–	–	–
5	0.307	6.2	98.5	11 000	–	–	–
6	–	17.9	–	6 000	–	–	–

Average molecular weight calculated from the molecular weight of the fractions: whole of fractions – crude copolymer,  $M_w = 285\,000$ ; fractions F1 to F3 (68.5% in weight) – graft copolymer  $M_w = 411\,000$ ; fractions F4 to F6 (31.5% in weight) – homopolymer,  $M_w = 10\,800$ ; backbone –  $M_w = 56\,000$ .  
 Yield of grafting: 69%

\* significance of these values as in Table 13

Table 16. Fractionation of a copolymer with a 'very high' degree of branching (1 graft for 9 styrene units) and complete use of chloromethyl functions

Sample	NG27						
Backbone	chloromethylated polystyrene: $M_w = 290\,000$ degree of chloromethylation: 1/9.4 ie 283 Cl/chain						
Grafts	poly(4-vinylpyridine) $M_w = 7\,500$						
Grafting	solvent: 19% DMF – 81% THF whole concentration of polymer: 1.1% [P4VP <sup>1</sup> ]/[-CH <sub>2</sub> Cl] = 1.8						
Crude copolymer	%4VP = 92.8% $M_{theoretical}^*$ = 4 000 000 (if whole P4VP would be able to graft) $M_{measured}$ (LS) = 1 500 000 theoretical composition <sup>*</sup> { 61% copolymer $M = 2\,450\,000$ 39% homopolymer $M = 7\,500$						
Fractionation	initial solution at 1.5% of polymer in a 25% methanol – 75% THF mixture precipitant: heptane						
Fraction $\gamma$	Weight %	4VP content %	$M_{LS}$ (DMF) <sup>*</sup>	Backbone $M_{calcul.}$	Number of grafts per chain	Intergrafts distance	
1	0.200	56.7	88.7	2 600 000	294 000	307	9.2
2	0.226	2.1	87.8	1 000 000	122 000	117	10
3	0.286	3.1	–	75 000	–	–	–
4	0.305	4.2	99	12 000	–	–	–
5	–	33.9	100	6 500	–	–	–

Average molecular weight calculated from the molecular weight of the fractions: whole of fractions – crude copolymer,  $M_w = 1\,500\,000$ ; fractions F1 and F2 (58.8% in weight) – graft copolymer,  $M_w = 2\,550\,000$ ; fractions F3 to F5 (41.2% in weight) – homopolymer,  $M_w = 12\,000$ ; backbone –  $M_w = 287\,000$ .  
 Yield of grafting: 100%

\* significance of these values as in Table 13

linking process that strongly affects the molecular structure of the samples.

Nevertheless, these difficulties have been overcome and the method of synthesis (of which the best recommended procedure is given in the experimental part) has allowed us to obtain a wide range of poly(styrene-g-4 vinylpyridine) graft copolymers even with a very high degree of branching. As the preformed parent homopolymers can be independently characterized, the structure of the resulting graft copolymer can be chosen *a priori* and well defined with respect to the length of the backbone and the number and the length of the grafts.

Such copolymers can be easily transformed into hydrophilic-hydrophobic copolymers by quaternization of nitrogen atoms of the pyridine units. The behaviour in solution of this amphiphilic copolymers will be the subject of future papers.

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