Graft copolymers: 1. Synthesis and characterization of poly(styrene-g-2-vinylpyridine)*

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A method of synthesizing poly(styrene-g-2-vinylpyridine) graft copolymers has been perfected. Attempts involving carbanionic initiation from partly metallated poly(*p*-bromostyrene) have not given the expected results. On the other hand, carbanionic deactivation of monofunctional living poly(2-vinylpyridine) on partly chloromethylated polystyrene has allowed us to obtain the expected graft copolymers. Several features have been examined: the influence of the grafting reaction on the way in which mixing of parent homopolymers is achieved; the effects of the nature of the counterion and temperature and the influence of different parameters on the yield of grafting and the problem of the elimination of the ungrafted homopolymer. No side reaction is observed at the time of grafting. Careful characterization of the resulting products shows they present a narrow molecular weight distribution, they are homogeneous in chemical composition, their structure is well defined with respect to the length of the backbone, and the number and the length of grafts; in addition the architecture of the graft molecule can be predicted.

Poly(vinyl pyridines) (PVP) possess the remarkable property of being easily transformed into hydrosoluble polymers. This chemcical modification, consisting of a quarternization reaction on the nitrogen atom of the pyridine units, leads to polymers having a polyelectrolytic character.[1,2] If the macromolecular poly(vinyl pyridinium) chains thus obtained are a copolymer moiety, it can be seen that it is possible to prepare hydrophilic-hydrophobic copolymers. Such polymers are specially interesting, firstly because water can be considered as a particular solvent, and secondly because, being soluble both in water and organic solvents, these polymers can lead to systems similar to those obtained with classical amphiphiles like soaps, namely oil-water emulsions[3] or microemulsions.[4]

If polystyrene (PS) is chosen as the hydrophobic part, the synthesis of such amphiphilic polymers requires, as a first step, the preparation of polystyrene-poly(vinyl pyridine) copolymers (PS-PVP). Block or graft copolymers can be considered. The synthesis of PS-PVP block copolymers has already been studied by Sigwalt and Fontanille[5] and Grosius and Gallot.[6] We are interested in amphiphilic graft copolymers. More precisely, we have studied the grafting of poly(vinyl pyridine) side chains (PVP) onto a backbone of polystyrene (PS): the results of the investigations will be presented in this paper and the two following articles of this series.

In order to obtain copolymers with narrow molecular weight and composition distributions, we used methods derived from anionic polymerization.[9,10] *A priori* two methods can be utilized: grafting by carbanionic initiation and grafting by carbanionic deactivation.

This paper deals with the preparation of poly(styrene-g-2-vinyl pyridine) copolymers (PS-g-P2VP) by means of these two processes.

EXPERIMENTAL

The experimental concerns only the carbanionic deactivation process.

Materials

Chloromethylated polystyrene (PSCl). PSCl is obtained by partial chloromethylation of polystyrene. The latter is synthesized by a classical anionic process, in THF, with cumylpotassium as initiator.

The chloromethylation of PS has been studied by several authors[11-14] and notably by Candau and Rempp.[15] The latter have stated the conditions for obtaining partly chloromethylated polystyrene without a Friedell-Craft type side reaction, and leading to linkings between chains. We have followed the same experimental procedure: chloromethyl methyl ether* (Fluka, technical grade) reacts with polystyrene in carbon tetrachloride solution in the presence of stannic chloride as catalyst. Experiments were carried out at room temperature and the degree of chloromethylation was adjusted by the time of reaction and the concentration of $SnCl_4$. It must be noted that, due to the sensitivity of $SnCl_4$ to moisture it is difficult to obtain reproducible results. Results from several chloromethylation experiments are given in *Table 1*.

Characteristics of samples were checked by light scattering (M_{LS}), g.p.c. and elemental analysis (i.e. chlorine content).

Before the coupling reaction, the treatment of PSCl in order to eliminate any traces of occluded air (which would 'kill' the living ends), was as follows. (i) PSCl was dissolved in benzene and freeze-dried; (ii) it was redissolved in highly pure THF condensed under vacuum from a solution of sodium-benzophenone complex; (iii) the solution of PSCl

* This work forms part of J. Selb's Thesis, University of Strasbourg (1978).

* This material should be used with extreme caution because of its carcinogenic nature.

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Table 1 Chloromethylation of polystyrene

Ref	Polystyrene			CCl_4 (ml)	CME (ml)	$SnCl_4$ (ml)	Time (h)	Chloromethylated polystyrene					Ref
	Characteristics	Weight (g)	Conc. (%)					M_{LS}	M_W/M_n g.p.c.	%Cl	Degree of chloro-methylation	Number of CH_2Cl per chain	
T1A	M_{LS} = 52 000	20	2	1 000	40	2	7.5	51 000	1.12	0.56	1/60	8.3	T1A
T1B	M_W/M_n (g.p.c.) = 1.13	20	2.4	850	40	4	19	54 000	1.13	2.91	1/11.3	44	T1B
T1C		20	2.4	850	40	4	18.5	54 000		3.07	1/10.7	46.5	T1C
T2A		20	2	1 000	40	2	7.5			0.26	1/130	4.4	T2A
T2B	M_{LS} = 60 000	30	2.4	1 250	60	4.5	13.75	60 000	1.14	1.42	1/23.6	24	T2B
T2C	M_W/M_n = 1.08-1.11	10	2.5	400	20	3	14	70 000[b, c]	1.11	3.9	1/8.3	80	T2C
T2D		6.6	2.4	275	13.5	1.3	13			1.70	1/19.6	29	T2D
T3A	M_{LS} = 230 000	20	2.5	800	40	5.5	16	290 000[c]		3.46	1/9.4	283	T3A

CME – chloromethylmethylether
M_{LS} – molecular weight measured by light scattering
[a] – degree of chloromethylation = average number of chlorinated sites/total number of styrene sites
[b] – $(dn/dc)_{THF}$ (measured) = 0.193
[c] – in the case of samples T2C and T3B, the high degree of chloromethylation led to some intermolecular linkings

was degassed several times under vacuum and finally, (iv) the ampoule of this reagent was placed in an argon atmosphere before fitting to the grafting flask.

Solvent (THF), monomer (2VP). These were purified following standard procedure, i.e. two distillations over calcium hydride and under vacuum for 2-vinyl pyridine (2VP) (Fluka reagent: b.p., 54°C at 14 mm Hg), and several distillations over sodium then sodium-benzophenone complex for tetrahydrofuran (THF).

Diphenylmethylsodium (or potassium). This initiator for 2VP polymerization was prepared according to the method of Normant and Angelo[16] by metallation of diphenylmethane by sodium- (or potassium-) naphthalene, in a THF medium under an inert atmosphere. We used an excess of diphenylmethane to naphthalene in order to avoid the presence of sodium-naphthalene complex in the solution of the initiator. The concentration of the initiator solution was determined by dosing with acetanilide.

Synthesis

Apparatus and experimental conditions. All grafting experiments were performed under an argon atmosphere. For experiments involving the transfer of living polymer solution from one flask to another, we used an apparatus described elsewhere.[17]

Graftings carried out according to the following recommended procedure, are simpler since no transfer of solution is required. The reactor is formed by a flask with a magnetic stirrer, to which are fitted different ampoules containing the reagents (2VP, PSCl solution). Samples can be taken by aspiration using a tube and a rubber cap ('suba-seal' type) permits the introduction of the initiator by means of a syringe. The apparatus is equipped with well-fitting Teflon taps ('Quickfit Rotaflo') which do not contaminate reagents. All parts of the apparatus are separately connected either to vacuum, or to the argon line. By repeating the vacuum-argon cycle any traces of atmospheric contamination are eliminated. The argon circuit is composed of stainless steel pipes and flexible tubes and is connected by glass-metal junctions to the reactor. The argon (Air Liquide, N55) is very pure and needs no supplementary purification. At the time of reaction, a slight over-pressure or argon, but with no permanent circulation, is maintained within the reactor.

This apparatus allows operation under conditions of purity near to those obtained under vacuum with a sealed-glass system, but with the advantage of being more practical. Moreover, it must be noted that in the range of molecular weight of the living polymer synthesized here ($7\,000 < M < 30\,000$) less drastic purity conditions are needed to obtain monodisperse samples than for very high molecular weights. The results of the present work are evidence of the effectiveness of the experimental technique described for obtaining monodisperse samples.

Polymerization of 2-vinyl pyridine. The last traces of impurities remaining in THS and on the reactor surfaces are removed by addition of diphenylmethylsodium until persistent colouration of the solution is obtained. The required quantity of initiator is then added. Polymerization of 2VP is achieved at – 70°C by slow dropwise addition of monomer. The completion of polymerization can be considered as being reached immediately.

Grafting. Following the various experiments reported in this paper, the best recommended procedure for the grafting reaction is as follows:

(i) when preparation of living P2VP is finished, sample is taken from the solution to allow characterization of the copolymer grafts;

(ii) the solution of P2VP is always kept at low temperature and the PSCl solution is added quickly, with vigorous stirring;

(iii) the mixture is then allowed to warm up gradually to room temperature, to activate the grafting;

(iv) after 1 h, if the decolouration is not complete, the ungrafted living chains are 'killed' with methanol;

(v) the crude copolymer is precipitated in heptane, and dried under vacuum.

Characterization of resulting products

Fractionation. The problem of fractionation of the products, which is one of the results of this work, is discussed in detail in the text. The fractional precipitation was performed in a standard way successive additions of precipitant (heptane) into the polymer solution (THF-methanol

mixture). The successive precipitated phases were recovered, concentrated to dryness, redissolved in benzene and freeze-dried.

Elemental analysis. Elemental analysis is used to determine the number of available chloromethylated functions on the starting backbone by dosing of the chlorine content, and the chemical composition of graft samples, i.e. P2VP content by dosing with nitrogen.

Osmometry. Number-average molecular weights were measured using a Mechrolab 502 high speed membrane osmometer, using toluene as solvent. The accuracy of the measurements is limited by the relatively high molecular weights of our samples.

Light scattering. Molecular weight measurements by light scattering (M_{LS}) have been made on a FICA photometer at λ = 5460 Å, in THF solution. Following the well-known compact structure of graft copolymers, the size of molecules is small in spite of relatively high molecular weights. Hence, all measurements have been carried out only at an angle of scattering of 90° since no angular dissymmetry appears in the scattered light at this angle.

Refractive index increments of copolymers (dn/dc) have been calculated from the chemical composition and dn/dc values of parent homopolymers (at λ = 5460 Å; PS/THF, dn/dc = 0.196; P2VP/THF, dn/dc = 0.170). The latter value which we have measured is notably different from that reported in the literature[18] but it is nevertheless corroborated by several dn/dc measurements on our copolymers.

For copolymers, it is known[19] that M_{LS} is an apparent molecular weight (M_{app}) which can be very different from the weight-average molecular weight (M_w). However, here it is quite admissible to consider that $M_{app} = M_w$ because dn/dc of the copolymer is high, the difference between dn/dc of both types of blocks is small, and our copolymers are homogeneous in chemical composition.

Characterization procedure. The whole of the characterization operation achieved for each copolymer is as follows. From M_w of parent homopolymers and their initial proportion (% 2VP), and M_w of gross copolymer (G), it is possible to calculate the molecular weight of the graft copolymer itself ($M_{graft,\ co}$), and also the composition of the gross sample formed by the mixture of the graft copolymer and ungrafted P2VP:

$$M_{\text{graft co}} = \frac{m + \sqrt{m^2 + 4M_{th}(G - m)}}{2}$$

and

$$\%\ \text{Graft copolymerization} = M_{\text{graft co}}/M_{th}$$

with $m = M_{P2VP} = M_{grafts}$, $G = M_{gross\ copolymer}$, $M_{th} = M_{backbone}/(1 - \%\,2VP/100)$ = theoretical molecular weight of sample under the assumption of total grafting.

After fractionation, every fraction is characterized by its M_w determined by light scattering (M_{LS}) and its chemical composition from elemental analysis. The molecular weight of the backbone can be calculated from these data. Since the length of P2VP graft is known by sampling, we can also calculate the number of grafts and their spacing along the backbone.

The yield of grafting is the ratio of number of grafts thus determined to the initial number of chlorinated functions.

Of course, parameters such as number of chlorinated sites, number of grafts, spacing of grafts, are average values because chloromethylated functions, and consequently grafts, are distributed at random along the backbone.

From the characteristics of each fraction we can determine M_w of the graft copolymer itself, the content of the latter in the crude product, and M_w of the backbone. These results are compared respectively with M_{co} and the theoretical composition of the crude sample calculated as above, and M_w of the starting PSCl.

GRAFTING OF P2VP FROM PS BY CARBANIONIC INITIATION

Principle of the reaction

The principle of this grafting process developed in particular by Rempp *et al.*[20–23] is as follows. Reactive sites are created along a macromolecular chain destined to form the backbone of the graft copolymer. These sites are able to initiate anionic polymerization of the monomer constituting the grafts. The base polymer is then used as a multifunctional initiator.

The starting polymer is poly(*p*-bromostyrene) (PPBS) which has a chemical structure close to that of polystyrene and moreover it can easily give organometallic sites by metallation with the help of lithium naphthalene, for instance. It has been shown that these are able to initiate the polymerization of vinyl monomers.[20] Furthermore, if metallation is followed by deactivation with a protonolysis agent (like methanol), a *p*-bromostyrene unit is converted to a styrene unit. Unfortunately, during metallation, unwanted intermolecular or intramolecular linkings may be formed by a reaction of the Wurtz-Futtig type. Dondos and Rempp have reported the experimental conditions for avoiding such a reaction.[20] Instead of using a PS-PPBS random copolymer as recommended by other authors[22] in order to limit side couplings, we preferred to keep a PPBS which has been previously partly debrominated as the base polymer. This debromination is achieved progressively, just before grafting, by several successive metallations and deactivations.

When the first two steps of the reaction, debromination and formation of actives sites, are completed, the last phase is achieved by addition of 2VP. Then, the colour of the solution passes from red-violet to the characteristic red of poly(vinyl pyridyl) carbanions, effectively polymerization of 2VP.

Characterization of resulting products

The molecular weights of the products, measured by light scattering in THF, are much smaller than theoretical molecular weights calculated from the molecular weight of the backbone and the quantity of 2VP (*Table 2*).

The characterization of products by fractionation shows that the polymer is very polydisperse in weight and that most fractions consist of 2VP homopolymer. This result is similar to that obtained by Decker,[23] when trying to prepare comb-shaped polystyrene by the same method.

The presence of homopolymer can be explained if it is admitted that the initiation of the polymerization is carried out by electronic transfer instead of by nucleophilic attack as expected. This hypothesis, involving the presence

Table 2 Grafting by carbanionic initiation from poly(*p*-bromostyrene)

		Sample 1	Sample 2
M_W backbone (PPBS)	Before metallation	27 000	52 000
	After metalliation	25 000	51 000
Yield of metallation		25%	15%
2-vinyl pyridine (%)		95%	95%
M copolymer	Theoretical	500 000	1 000 000
	Measured	140 000	79 000

of radical ions, is corroborated by work of Halasa and co-workers.[24]

The exact mechanism of this reaction requires careful study which is outside of the scope of the current work.

As the grafting by carbanionic initiation from PPBS gave unexpected results, this method has been abandoned and carbanionic deactivation has been used.

GRAFTING OF P2VP ONTO PS BY CARBANIONIC DEACTIVATION

Principle of the reactions

The principle of the carbanionic deactivation process is that a polymer bearing electrophilic functions distributed along the chain and a monofunctional living polymer react together. By means of their extremities, which are deactivated on the electrophilic functions, the mono-carbanionic macromolecular chains fix themselves onto the main chain and form the grafts of the copolymer.

Hence the grafting of P2VP onto PS by means of the carbanionic deactivation method implicates the presence on the PS chain of functions with an electrophilic character. We have chosen a backbone with chloromethyl-styrene units for different reasons[25] and especially because the chloromethylated functions borne by an aromatic nucleus are particularly reactive (contrary to halogen atoms located on benzene nuclei,[15,25] or ester functions[26]) and their insertion in a macromolecular chain is easy employing chemical modification of the starting polystyrene.[11-15]

Stannett *et al.* have already shown that it is possible to graft P2VP onto chloromethylated polystyrene.[35] However, these authors have observed that the grafting reaction, carried out in benzene, is accompanied by side reactions.

In this work, a new and systematic study of the grafting of P2VP onto PSCl has been performed, in a THF medium for the following reasons:

Firstly, it has been established that the use of a polar solvent decreases the extent of side reactions.[11, 27, 29, 31] This may be ascribed to the stronger ionic character of the carbon-metal bond in a polar medium.[27]

Secondly, the synthesis of P2VP in THF, at low temperature and by means of diphenylmethylsodium as initiator, leads to monodisperse polymer,[38] which is not expected if the polymerization is carried out in a non-polar solvent by means of butyllithium.

It should also be noted that Stannett *et al.* have limited their study to the preparation of polymers bearing few grafts (at a maximum of one graft per 75 styrene units). In our study we have attempted to prepare a wider range of copolymers and especially samples with a greater degree of branching.

Study of the grafting reaction

In order to establish the best conditions for the grafting reaction we have examined several features of this synthesis. Firstly, the influence of different experimental factors on the characteristics of the copolymers have been investigated: the order of introduction of the reagents (chloromethylated polystyrene added to the solution of living polymer, or *vice versa*); the nature of the counterion; the temperature of the grafting.

Furthermore, the careful characterization of resulting products led us to examine problems relative to: the yield of the grafting reaction; the purification of the copolymer (elimination of the homopolymer); the stability of the copolymer (this last feature will be treated in a subsequent paper).[7]

Effect of the order of introduction of the reagents. In previous studies concerning the grafting of living polystyrene onto partly chloromethylated polystyrene, different authors[11, 30-32] have reported that side reactions occur and lead to polymers having a molecular weight much higher than expected. This has been explained by metal-halogen interchange on some chloromethylated sites (instead of the expected nucleophilic substitution), followed by a coupling between these metallated sites and other chloromethyl functions yielding intermolecular crosslinkings. Altares *et al.*,[11] and Candau and Franta[31] have shown that the extent of this crosslinking reaction depends particularly on the order of addition of the reagents (i.e. living polymer and chloromethylated polystyrene) in the reactional medium. This side reaction can be minimized if the PSCl solution is slowly added into the solution of living PS, and not with the reverse procedure.

In order to check whether a similar phenomenon occurs with poly(2-vinyl pyridine), we achieved two grafting reactions with the same chloromethylated polystyrene and the same living poly(2-vinyl pyridine), but by reversing their order of introduction. The results of both experiments are given in *Table 3*.

We can see that the order of introduction of the pre-polymers has no effect on the products formed since both copolymers exhibit identical molecular weights (column 1 of *Table 3*). Nevertheless, in both experiments, the measured molecular weight (line 1) and the theoretical molecular weight calculated in the case of a quantitative grafting (line 3) are quite different. This discrepancy in molecular weight can be explained by the presence of ungrafted poly(vinyl pyridine) within the crude copolymers. Knowing the proportion (line 2) and the molecular weights of the parent homopolymers, we can calculate using the hypothesis of a lack of side reaction, the quantity of ungrafted homopoly (vinyl pyridine) and the molecular weight of the graft copolymer (lines 4 and 5) (see calculation in the Experimental).

We have also experimentally determined the molecular weight of the copolymer after elimination of the homopoly (2-vinyl pyridine) (lines 6 and 7). This operation has been effected by extraction with the help of methanol (a good solvent for P2VP but a non-solvent for the copolymer).

The measured and calculated values of the molecular weight of the copolymers are in remarkable agreement. This result is proof that no side reactions appeared whatever the order of introduction of the base homopolymers in the reactor. This lack of secondary reaction can be explained

Table 3 Effect of the order of introduction of parent homopolymers on the grafting reaction

Backbone:	chloromethylated polystyrene M_w = 52 000; degree of chloromethylation 1/60 i.e. 8.3 Cl/chain
Grafts:	poly(2-vinylpyridine) initiator of polymerization: diphenylmethyl-potassium polymerization temperature: − 70°C M_w = 19 000
Grafting:	reaction temperature ≅ 0°C whole concentration of polymer: 2% [P2VP⁻]/[-CH_2Cl] = 0.70

Order of introduction of reagents		P2VP⁻ into PSCl	PSCl into P2VP⁻	Line
Crude copolymer	$M_{measured}$(LS)	103 000	101 000	(1)
	2VP content	66.6%	65.7%	(2)
	$M_{theoretical}$* (total grafting)	156 000	152 000	(3)
Theoretical* composition of crude copolymer	Homopolymer (P2VP)	20.5% M_w = 19 000	20% M_w = 19 000	(4)
	Graft copolymer	79.5% M_w = 124 000	80% M_w = 121 000	(5)
Fractionation of crude copolymer	Soluble fraction in methanol	M_w = 18 000		(6)
	Insoluble fraction in methanol	M_w = 123 000	M_w = 121 000 M_n = 123 000	(7)

*Calculated as explained in the experimental part (see 'characterization procedure')

by a stronger polarization of the carbon-metal bond for poly(vinyl pyridyl) than for polystyryl carbanions. Indeed, work by Sigwalt's group[39] and Zwarc's group[40] have shown that in the case of living P2VP the metallic cation is preferentially solvated by the last two monomeric units of the polymeric chain, because of the existence of a long pair of electrons on the nitrogen atom. This 'intramolecular solvation' hinders the dissociation into free ions (the dissociation constant of the active centres is much lower for the living P2VP than for PS)[39, 40] but increases the charge separation in the ion pairs $PV2P^-, M^+$.[40]

This explanation is consistent with the findings of Yen[27] who claimed that the grafting reaction is favoured with respect to the metallation reaction the stronger the ionic character of the carbon-metal bond. This hypothesis is also in agreement with Price's results concerning the grafting of polyisoprene onto chloromethylated polystyrene.[36] This author describes a decrease in the side reactions by addition of tetramethylethylene diamine (TMEDA) which preferentially solvates the ion pairs.

In addition, more recently, Japanese authors[35] have demonstrated that, in THF, living polystyrene gives fewer side-reactions if Li^+ is used as counterion rather than K^+, and it is well-known that PS^-Li^+ are the more dissociated ion pairs in THF.

The order of addition of starting polymers being unimportant, one can add either the solution of PSCl into the P2VP solution, or P2VP⁻ into the PSCl solution. Each method has advantages and disadvantages: (a) concerning the experimental device, the first method is easier because both reactions, polymerization of vinyl pyridine and grafting, are carried out in the same reactor without transfer of the solution; (b) if the grafting reaction is very fast (this is so at room temperature), by adding PSCl to P2VP⁻ an excess of living polymer must be used, or else the grafting may be inhomogeneous. Indeed, with a deficiency of P2VP⁻, the extent of grafting will be more important for the first chains of chloromethylated polystyrene coming into the reaction medium. However, with an excess of living ends, it may later prove difficult to eliminate ungrafted homopolymer. On the other hand, if P2VP⁻ is added to PSCl solution, no excess of carbanions is required.

We shall see further that careful study of the reaction leads us to choose one of these two procedures.

Nature of the counterion

In our first experiments, we used poly(vinyl pyridyl) carbanions with potassium as counterions, in order to be under the best conditions of reactivity. However, the use of diphenylmethylpotassium as initiator for polymerization of 2VP presents a disadvantage: it does not allow small weight-average molecular weight (M_w < 15 000) P2VP to be obtained due probably to the unfavourable (initiation rate/propagation rate) ratio.

However, with diphenylmethylsodium, we prepared polymers with lower molecular weights without difficulty i.e. M_w about 5000. Nevertheless, it was necessary to check whether $P2VP^- Na^+$ was sufficiently reactive. For this purpose we carried out a grafting reaction, for which the experimental conditions and results are summarized in *Table 4*. These results show that $P2VP^- Na^+$ has a sufficient reactivity to react on chloromethyl functions, with a yield equivalent to that obtained when potassium is used as an associated metal with carbanions.

Effect of the temperature of grafting

Influence on the structure of the copolymers. The grafting experiments whose results have just been given were carried out either at − 70°C (sample NG2 in *Table 3*) or at 0°C (samples NG3 and NG4 in *Table 2*). In both cases, we have noted that no side-reaction appears. Therefore, the temperature of grafting has no influence on the structure of

Table 4 Reaction between poly(2-vinyl pyridyl)-sodium and chloromethylated polystyrene

Sample:	NG2
Backbone:	Chloromethylated polystyrene, M_w = 52 000 degree of chloromethylation, 1/60 i.e. 8.3 Cl/chain
Grafts:	Poly(2-vinyl pyridine) initiator of polymerization, diphenymethyl-sodium polymerization temperature, − 70°C M_w = 12 500
Grafting:	Reaction temperature, − 70°C whole concentration of polymer: 2% [P2VP⁻]/[-CH_2Cl] ≅ 1.05 PSCl solution added into living poly(vinyl pyridine) solution

Crude copolymer	$M_{measured}$(LS)	88 000
	% P2VP	66.6%
	$M_{theoretical}$* (total grafting)	156 000
Theoretical* composition of crude	Homopolymer P2VP	26% M_w = 12 500
	Graft copolymer	74% M_w = 115 000
Fractionation of crude copolymer	Soluble fraction in methanol	M_w = 13 000
	Insoluble fraction in methanol	M_w = 113 000 M_w = 114 000

Table 5 Extent of grafting as a function of the reaction time

Sample:	ref NG15	
Backbone:	Chloromethylated polystyrene	M_W = 52 000 47 Cl per chain
Grafts:	Poly(2-vinyl pyridine)	M_W = 8 000
Expected graft copolymer:	80% 2VP $M_{theoretical}$ = 260 000	
Grafting reaction at − 70°C		
t = 0	mixing of parent homopolymers	
t = 5 mn	1st sampling	M_{LS} = 153 000
t = 25 mn	2nd sampling	M_{LS} = 242 000

the polymer, contrary to observations made during the synthesis of comb-shaped polystyrene using the same method.[3]

Influence on the rate of the reaction. At room temperature, when the solution of living P2VP is added to the PSCl solution, we note, at the beginning of the reaction, an immediate decolouration of the carbanions, which indicates that the grafting reaction is nearly instantaneous. Afterwards, when the extent of grafting has increased, the decolouration is slower for two reasons: (i) the accessibility of chlorinated sites is reduced by the steric hindrance of side chains already fixed, and (ii) the concentration of available chlorinated functions has decreased – this factor is dominant.

At low temperature (− 70°C) the reaction is much slower (it is only completed after 1/2 to 1 h). When there is a serious shortage of carbanions with respect to chloromethyl functions, the end of the reaction is indicated by the complete decolouration of the solution; if there is an excess of carbanions the decolouration is, of course, never complete. Successive samplings of the solution denote the advance of the reaction as indicated by the example in *Table 5*.

From a practical point of view, an interesting consequence of the temperature effect on grafting is that the mixing of parent homopolymers can always be achieved by the most simple procedure i.e. by addition of PSCl solution to $P2VP^-$. This remains valid even if there is a deficiency of living ends on the condition to operate at low temperature. Under conditions, the mixture is homogeneous before grafting reaction occurs, since at this temperature, the grafting rate is slow. As previously mentioned, such a procedure would not be usable at room temperature, since grafting is then nearly instantaneous.

Yield of grafting

The yield of grafting is defined as the ratio of the number of grafts to the number of available chloromethylated sites. The number of chlorine atoms borne by the starting polystyrene is determined from elemental analysis. It must be noted that as the chlorine content within the chloromethylated PS is never high (3.5% at maximum), the accuracy of the determination is low, notably in the case of slightly chloromethylated PS used to obtain weakly grafted copolymers. As a consequence (and especially in the latter case) the determination of the yield of grafting is rather imprecise. However the yield of grafting is not a major consideration in the characterization of copolymers, since the number of grafts, an important characteristic of the product, can be determined independently and accurately.

Table 6 Example of polydispersity of a sample of poly(2-vinyl pyridine)

Light scattering	M_W = 15 000
Membrane osmometry	M_n = 14 000 M_W/M_n = 1.07

Indeed, if the number of grafts cannot be evaluated from the determination of residual chlorine (its content in the copolymer is very small), it can be calculated from the molecular weight of the copolymer and the parent homopolymers. This is justified since the grafting is not accompanied by side-reactions. It must be noted, however, that the number of grafts determined from the weight-average molecular weight can be slightly underestimated if the side chains have a certain polydispersity. We know that the grafts are monodisperse because of their mode of preparation. This has been checked for samples of P2VP (*Table 6*). Accordingly, the error in the evaluation of the number of grafts is negligible.

The miscellaneous grafting experiments we have carried out, lead us to the following remarks:

(i) when the backbone polymer bears few chloromethyl functions (degree of chloromethylation 1/60 i.e. 1 chlorinated site for 60 styrene units), the yield of grafting is limited (about 60%), even if there is an excess of carbanions. This limitation cannot be ascribed to steric hindrance (access of chlorinated sites becoming difficult because of the presence of the grafts already fixed), since we have been able to prepare copolymers bearing a much greater number of grafts. In fact, the yield of grafting depends essentially on the kinetics of the reaction (the grafting rate tends to cancel out when the concentration of chloromethyl functions becomes very small).

(ii) When the content of chloromethyl groups within the base polymer is higher (degree of chloromethylation > 1/40), more important yields of grafting are obtained. It is even possible to reach a grafting near to 100% if a large excess of $P2VP^-$ is present; afterwards, this surplus of homopolymer must be removed by fractionation.

(iii) If one wishes to obtain a crude copolymer free of homopolymer, it is necessary to operate with a deficiency of $P2VP^-$. In this case, the utilization of chlorinated functions must be limited to 80%. However, this method involves using only a part of chloromethyl groups in order to avoid the presence of ungrafted P2VP within the gross polymer, and cannot be applied to polystyrene for which degree of chloromethylation is high (greater than 1/25). Indeed, under these conditions we shall see, in a subsequent paper,[7] that copolymers bearing many chlorines on the backbone are not stable.

Table 7 Effect of the number of grafts, at the same chemical composition, upon the solubility of copolymers in selective solvent for grafts

Ref of sample	NG3	NG5
$M_{copolymer}$	123 000	125 000
$M_{backbone}$	52 000	52 000
M_{graft}	19 000	7 500
Number of grafts/chain	3.7	9.7
% P2VP	57.7%	58.4%
Solubility in methanol	Nil	Partial

Table 8 Simultaneous elimination of ungrafted homopolymer and polydispersity characterization of a graft copolymer in a single fractionation by fractional precipitation

Sample:	NG23
Backbone:	Chloromethylated polystyrene, M_W = 54 000 degree of chloromethylation, 1/10.7 i.e. 47 Cl/chain
Grafts:	Poly(2-vinyl pyridine), M_W = 7 000
Grafting:	Whole concentration of polymer: 2% $[P2VP^-]/[-CH_2Cl] \cong 1.10$
Crude copolymer:	% P2VP = 87% $M_{'theoretical'}$ = 415 000 (if whole P2VP would be able to graft) $M_{measured}$(LS) = 250 000 theoretical composition* 77.3% copolymer M = 321 000 22.7% homocopolymer M = 7 000
Fractionation:	initial solution at 1.75% of polymer in the 20% methanol–80% THF mixture precipitant: heptane

Fraction	$\gamma^\dagger$	Weight (%)	2VP content (%)	M light scattering	Backbone $M_{calculated}$	Number of grafts per chain	Intergraft distance‡
1	0.375	26.9	83.6	388 000	63 500	46.3	13.1
2	0.379	19.2	83.0	357 000	60 500	42.3	13.6
3	0.383	3.8	81.5	320 000	59 000	37.2	15.1
4	0.390	14.1	83.0	300 000	51 000	35.6	13.6
5	0.401	7.7	81.8	270 000	49 000	31.6	14.8
6	0.412	1.9	82.8	237 000	41 000	28.0	13.9
7	0.444	9.6	94.8	53 000	(2 800)	(7.2)	(3.7)
8	–	16.7	98.5	10 000	–	–	–

Findings and comments:

Fractions F1 to F6 (73.7% in weight): graft copolymer
M_W (calculated) = 343 000
$M_{backbone}$ (calc) = 58 000

The weight-average molecular weight of the copolymer calculated from the molecular weights of the fractions is slightly larger than expected (M = 321 000), because of the smaller molecular weight graft molecules in the fraction No 7

Fraction F7: its characteristics show it is essentially composed of homopolymer with a weak percentage of graft copolymer

Fraction F8: homopolymer

Yield of grafting' 81%

†See mode of calculation in the experimental part ('characterization procedure')
γ = volume of precipitant/whole volume of solution
‡the spacing of grafts is expressed in number of styrene units

PURIFICATION OF SAMPLES BY ELIMINATION OF THE HOMOPOLYMER. POLYDISPERSITY CHARACTERIZATION OF COPOLYMERS

When the copolymer possesses few grafts (maximum 1 for 100 styrene units) and if these are rather short (M < 20 000), then the copolymer, whose VP content is less than 60%, is insoluble in methanol. Thus the homopoly(vinyl pyridine) can be removed by extraction with this solvent. This has been achieved for example with the copolymers NG2, NG3, NG4 studied above (*Tables 3* and *4*).

However, the use of this method is very limited. If the copolymers possess a higher number of grafts, they can be partly soluble in methanol (*Table 7*).

In any case, beyond a 2VP content of 75%, copolymers are always completely soluble in methanol. It is then necessary to employ fractionation by precipitation. By this technique, not only the purification of the crude copolymer by elimination of the homopolymer is expected, but also information on the polydispersity of the graft copolymer itself.

The solvent-precipitant pair (THF-heptane) usually employed for the fractionation of PS-P2VP block copolymers[6] is not suitable, because we have observed that all fractions contained homopoly (2-vinyl pyridine).[25] In order to obtain a selective fractionation we used the solvent/non-solvent system THF-methanol/heptane. Indeed, methanol being both non-solvent for polystyrene and solvent for P2VP, the precipitation of the copolymer was favoured over that of the homopolymer (*Table 8*). It must be noted that the methanol content depended upon the composition and molecular weight of the copolymer.

If a very high methanol content was necessary to eliminate P2VP, the fractionation of the graft copolymer itself was not satisfactory since it is not the highest molecular weights which are recovered at first (*Table 9*, part a).

Consequently, if not only elimination of the homopolymer but also the characterization of the polydispersity of the copolymer is required, it is necessary to operate two successive fractionations. After a first fractionation carried out from a solution rich in methanol in order to remove P2VP, the fractions of copolymer are put together and a new fractionation is performed again by means of the THF-heptane pair which can be used since there is no more homopolymer remaining (*Table 9*, part b).

In addition, we shall mention an example of a copolymer synthesized with a deficiency of living polymer and which, in principle, would not contain homopolymer (*Table 10*); however, the last fraction, of low molecular weight, certain-

Table 9 Elimination of the ungrafted homopolymer, and polydispersity characterization of a graft copolymer by two successive fractionations

Sample: NG13

Backbone: Chloromethylated polystyrene, M_W = 52 000
degree of chlormethylation, 1/60 i.e. 8.3 Cl/chain

Grafts: Poly(2-vinyl pyridine), M_W = 21 000

Crude copolymer: % P2VP = 78.7%
$M_{theoretical}$* (total grafting) = 244 000
$M_{measured}$(LS) = 94 000
Theoretical composition* 59% copolymer M = 144 000
41% homocopolymer M = 21 000

(a) 1st fractionation: initial solution at 1.6% of polymer in the 80% methanol-20% THF mixture
precipitant, heptane

	Fraction	γ*	Weight (%)	2VP content (%)	M_{LS}	$M_{calculated}$
	1	0.470	22.5	65.5	134 000	
	2	0.481	18.8	65.1	145 000	52%
	3	0.495	7.2	73.2	180 000	M = 148 000
	4	0.516	3.5	80.9	195 000	
	5	0.578	24.9	100	33 000	
	6	0.608	12.9	98.6	21 000	48%
	7	–	10.2	–	19 000	M = 26 000

(b) 2nd fractionation: regrouping of the fractions F1 to F4 of the 1st fractionation
initial solution at 1.45% of polymer in THF
precipitant, heptane

Fraction	γ*	Weight (%)	2VP content (%)	M_{LS}	M_{osm}	M_W/M_n	Backbone $M_{calculated}$	Number of grafts per chain	Intergraft distance*
1	0.286	4.5	75	210 000			52 500	7.5	67
2	0.314	1.5	–	160 000			–	–	–
3	0.421	28.5	66.5	143 000	132 000	1.08	48 000	4.5	102
4	–	65.5	63	133 000	128 000	1.04	49 000	4	118

*Significance of γ, intergraft distance, and theoretical values as in *Table 8*

ly contains P2VP homopolymer, but this fraction is only a small percentage of the copolymer (2%).

The full examination of these different results of fractionation leads to the following findings:

(1) when the copolymer contains P2VP homopolymer, it is possible to remove the latter, by means of the solvent-precipitant pair (THF-methanol/heptane) used, the methanol content within the solvent mixture being a function of characteristics of the copolymer;

(2) the different fractions have nearly the same chemical composition, which indicates that the composition heterogeneity is small;

(3) the molecular weight of the graft copolymer determined from molecular weight of different fractions is in very good agreement with the theoretical molecular weight calculated from the proportions and molecular weights of the parent homopolymers;

(4) the molecular weight polydispersity of every fraction is very small since the values of the weight-average and number-average molecular weights are very close (the ratio M_w/M_n is always less than 1.1);

(5) the molecular weight polydispersity of the graft copolymer after elimination of the homopolymer is also small, as indicated by the polydispersity index relative to the whole of the fractions;

(6) the molecular weight distribution of the backbone after grafting is the same as that of the starting polystyrene.

All these results confirm the lack of degradation or side-reactions during the grafting.

CONCLUSION

The purpose of this work, was to perfect the synthesis of poly(styrene-g-2-vinyl pyridine) copolymers. We have noted that the method of carbanionic initiation, from poly (*p*-bromostyrene), does not give the expected polymers. The method of carbanionic deactivation gives excellent results. Indeed, despite their known weak reactivity, poly (2-vinyl pyridyl) carbanions react easily onto partly chloromethylated polystyrene until a high degree of branching has been obtained. Furthermore, side reactions which occur during reaction between carbonions and chlorinated functions (e.g. for grafting on living polystyrene onto chloromethylated polystyrene) do not appear here. The PS-g-P2VP graft copolymers thus obtained exhibit a low polydispersity in weight and in chemical composition, samples are well defined by the length of backbone, the length and the number of grafts; moreover, these characteristics can be precisely adjusted at the start of the reaction.

During the study of the stability of our products, however, we have observed that another type of side reaction can affect the structure of copolymers. This side reaction does not appear at the time of grafting itself, but after the synthesis. This important problem will be treated in detail in the next paper.[7]

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Table 10 Fractionation of a copolymer free of homopolymer

Sample:	AR11
Backbone:	Chloromethylated polystyrene, M_W = 60 000 degree of chloromethylation, 1/44.3 i.e. 12.6 Cl/chain
Grafts:	Poly(2-vinyl pyridine), M_W = 28 000
Grafting:	whole concentration of polymer: 3% $[P2VP^-]/[-CH_2Cl]$ = 0.6
Crude copolymer:	% 2VP = 81% $M_{theoretical}$* (total grafting) = 316 000 $M_{measured}(LS)$ = 304 000
Fractionation:	initial solution at 3% of polymer in the 20% methanol–80% THF mixture precipitant, heptane

Fraction	γ*	Weight (%)	2VP content (%)	M_{LS} (THF)	M_{osm}	Backbone $M_{calculated}$	Number of grafts per chain	Intergraft distance*
1	0.350	14.6	82.3	380 000	–	67 000	11.1	58
2	0.357	21.4	80.9	343 000	–	65 000	9.9	63
3	0.365	15.6	81.7	329 000	–	60 000	9.6	60
4	0.375	18.0	80.2	282 000	–	56 000	8.1	67
5	0.387	14.6	79	261 000	256 000	55 000	7.4	72
6	0.400	9.5	76.5	222 000	180 000	52 000	6.1	82
7	0.420	4.4	78	149 000	–	33 000	4.1	76
8	0.645	2	84.7	56 500	–	8 500	1.7	47

Calculated average molecular weights from molecular weight of fractions

M_W = 298 000, M_n = 266 000 } M_W/M_n = 1.12

$M_{backbone}$ = 58 000

*Significance of γ, intergraft distance, theoretical values as in *Table 8*

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