Graft copolymers: 2. Specific instability of some poly (styrene-g-2-vinyl pyridines) obtained from chloromethylated polystyrene

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Some poly(styrene-g-2-vinyl pyridine) graft copolymers synthesized by carbanionic deactivation of living poly(2-vinyl pyridine) onto partly chloromethylated polystyrene are not stable in their dry state. This instability appears by a progressive increase in the molecular weight. The exact mechanism of crosslinking has been investigated. The instability occurs for polymers whose residual chloromethylation of the backbone after grafting is the greatest. The different methods of avoiding this side reaction are discussed and compared.

INTRODUCTION

In the preceding paper of this series,[1,2] we have seen that it was possible to graft side chains of poly(2-vinyl pyridine) (P2VP) onto a backbone of polystyrene (PS) by carbanionic deactivation of living poly(2-vinyl pyridine) (P2VP^e) onto partly chloromethylated polystyrene (PSCl).[3,4] It was pointed out that, unlike the grafting of living polystyrene onto PSCl,[3,4] the reaction is not accompanied by side reactions like intermolecular couplings between molecules of graft copolymer. Consequently, poly(styrene-g-2-vinyl pyridine) copolymers have the predicted molecular weight and their molecular characteristics can be well defined.

However, if this feature is valid for products just after their synthesis, it is not always the case later on for all copolymers. Indeed, for some copolymers a more or less marked phenomenon of instability appears. This unusual behaviour is very annoying since, as we shall see, the structure of our copolymers may be rapidly and strongly affected. Of course, such copolymers are not available for a later study of their properties.

In this paper, we shall define under what conditions this instability occurs and how it can be avoided.

EXPERIMENTAL

Preparation of poly(styrene-g-2-vinyl pyridine) graft copolymers

The preparation is described in the first paper of this series.[2]

Dechlorination

Lithium-naphthalene, used as the metallation agent of chlorine functions, was prepared according to the method of Scott[5] and Szwarc[6] by the action of lithium on naphthalene in THF medium and under argon atmosphere. Instead of using equimolecular quantities of these reagents, we started from a slight excess of naphthalene in order to avoid the presence of a fine black powder of lithium in the solution.

Afterwards, the solution was titrated by means of acetanilide.

In all experiments, the metallation of polymer was achieved in THF media, under inert atmosphere, and at low temperature (about $-70°C$). The lithium-naphthalene was added via a syringe through a rubber cap, while the reaction medium was vigorously stirred. The dechlorination reaction was immediately completed by deactivation of the organometallic sites and of the excess of lithium-naphthalene with the help of methanol.

For a graft copolymer, these operations are effected just after its synthesis, in the grafting flask itself.

Sometimes, we observed a precipitation of lithium-naphthalene by addition into the copolymer solution. This phenomenon is a nuisance since the organometallic complex can then no longer bring about the dechlorination reaction. This behaviour is not only due to the poor solubility of Li-naphtalene in THF at low temperature, because under the same temperature conditions such a precipitate does not appear in the absence of the polymer, nor does it appear when the solution contains only polystyrene. On the other hand, in the presence of P2VP this precipitation shows itself even at higher temperatures (about $0°C$). No further study was carried out in order to explain this phenomenon. In any case, the precipitate formation can be avoided if one operates with Li-naphtalene at low concentrations (lower than 1.10^{-4} mole/cm^3). Under these conditions, the metallation reaction occurs correctly.

If, after treatment, the polymer is immediately recovered by precipitation into heptane, the resulting product is contaminated by a great deal of mineral impurities (LiCl, LiOH) which are very difficult to eliminate afterwards by filtration or centrifugation, and perturb the measurements of light scattering. The best method is to allow, at the end of reaction, the decantation of solvent-soaked impurities so as to separate them before recovery of the polymer.

Quaternization

The quaternization of nitrogen atoms of P2VP chains was here achieved with hydrogen chloride. This reaction was not performed with aqueous solutions of chlorhydric acid because, when using this method, water is very difficult to

remove during the recovery of product and the yield of quaternization never exceeds 90%. Therefore, it is better to use gaseous HCl which is bubbled through the solution. After a few minutes, the reactional medium becomes turbid, followed by a white gelatinous precipitate. The reaction is considered to be terminated when HCl escapes out of the solution. The precipitation of the product is completed in ethyl ether. After drying, the polyelectrolyte is stored under dry atmosphere, because of its hygroscopic nature.

Determination of molecular weights

Weight-average molecular weights were determined by light scattering (M_{LS}) using a FICA photometer in THF solutions (except for quaternized polymers for which methanol-LiBr mixtures were used). As previously explained,[1] M_{LS} for copolymer can be equated to M_w.

RESULTS AND DISCUSSION

Instability phenomenon

We have observed that copolymers bearing a limited number of grafts (intergraft distance: ~ 100 styrene units of the backbone) and obtained from slightly chloromethylated polystyrene, are quite stable; even after several months, their molecular weights do not change. That is not always the case for copolymers bearing a greater number of grafts (distance between two grafts: 20–50 styrene units). Indeed, some products exhibit an 'anomalous' behaviour: in the dry state, their molecular weight increases progressively with time, as is illustrated by the example in *Table 1*.

This phenomenon is not due to any sort of oxidization reaction leading to a reticulation of products, because a copolymer kept under nitrogen and in presence of an antioxidizer also exhibits an increase in molecular weight.

Moreover, it should be noted that this phenomenon does not occur in dilute solution or at low temperature (see *Table 10*).

By comparing different copolymers, we ascertain that the lack of stability is related to the quantity of residual chlorine (*Table 2*).

Therefore, it appears that chlorine atoms take a part in the side reaction. This is confirmed by the fact that the molecular weight of sample NG7 (*Table 1*) does not increase further when the last chlorinated sites in the copolymer have been removed by an adequate chemical treatment (with the help of lithium-naphthalene).

However, the benzylic chlorine functions alone cannot be responsible, since chloromethylated polystyrene is quite stable. The poly(vinyl pyridine) chains must also intervene in

Table 1 Instability of a PS-g-P2VP copolymer, shown by an increase of the molecular weight

Time (days)[b]	Molecular weight[c]
0	236 000[d]
15	289 000
36	417 000
59	590 000
120	1 450 000
155	3 200 000

[a] Sample NG7. Backbone: chloromethylated polystyrene, M_w = 52 000, 46 Cl/chain; grafts: poly(2-vinyl pyridine), M_w = 8 000; foreseen yield of grafting, 50%; the product was kept without particular caution, at room temperature.
[b] Time/run synthesis.
[c] Molecular weight measured by light scattering.
[d] Theoretical.

Table 2 Effect of the residual degree of chloromethylation after grafting upon the stability of copolymers

Reference	Degree of chloromethylation		Yield of grafting	Stability of copolymer[a]
	Base polystyrene	After grafting		
NG2	1/60	1/150	60%	stable
AR11	1/45	1/150	70%	stable
NG16	1/23.6	1/67	65%	M increases ~10% within 14 days
NG15	1/11.3	1/22	50%	M increases ~ 20% within 11 days

[a] M ≡ molecular weight.

the increase in the molecular weight. Indeed, by comparing three graft polymers derived from an identical backbone of PSCl, but being distinguished by the nature of grafts (PS, P2VP, P4VP), we have observed that the comb-shaped PS is stable but there is an increase in molecular weight for both PS-g-PVP copolymers (*Table 3*).

This result clearly indicates that nitrogen atoms participate at the side reaction. This is further emphasized by the fact that the reticulation phenomenon is more strongly marked for PS-g-P4VP than for PS-g-P2VP. Indeed, it is well known that the reactivity of the nitrogen atom in the 2VP unit is reduced by the steric hindrance brought about by the polymeric chain in the *ortho* position in relation to nitrogen, whereas, for P4VP, the nitrogen function is more reactive because, being in the *para* position, it presents a better accessibility.

From these data we can estimate that this instability is the result of the quaternization of some nitrogen atoms by chloromethyl groupings, which would lead to linkings according to the following scheme:
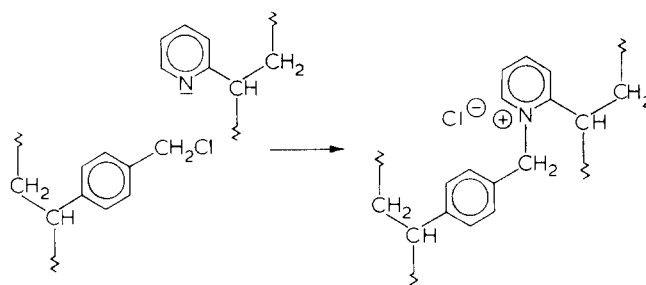
A priori, such a reaction in the dry state is surprising. We have attempted to detect, by ultra violet or infra red spectroscopy, the presence of characteristic absorption bands of pyridinium groupings. Our attempts have been

Table 3 Effect of the nature of grafts on the stability of branched polymers obtained from PSCl

Nature of polymer		Yield of grafting	Theoretical molecular weight	Molecular weight	
				Just after synthesis	2 months after synthesis
NG24	comb-like PS	65%	400 000	370 000	370 000
NG7	PS-g-P2VP	50%	236 000	289 000	590 000
NG11	PS-g-P4VP	60%	260 000	700 000	insoluble polymer

[a] Base chloromethylated polystyrene: M_w = 52 000, 46 Cl/chain.
[b] Measured by light scattering.

negative, but this does not necessarily prove that the presumed intermolecular reaction does not occur. Indeed, it must be remembered that a very small percentage of pyridinic units participating in the crosslinking reaction are sufficient to bring about a great increase in molecular weight. This being so, it is possible that the absorption bands of vinyl pyridine groups are much more important than eventual absorption bands relative to pyridinium groupings. The latter absorption bands, situated at wavelengths near to those of VP units, are then masked.

If it is admitted that linkings are generated between chloromethyl functions and pyridine nuclei, the same reaction must also appear for a mixture of two homopolymers PSCl and P2VP. Contrary to prediction, the mixture is stable even when the number of chloromethyl functions is high (*Table 4*).

This lack of reaction can be explained by the incompatibility between homopolymers and in consequence the segregation of chains with different chemical natures. In this case, the contacts between reactive groups would be reduced to a minimum. On the other hand, for a copolymer the reaction possibilities are greater, because the segregation is necessarily limited by numerous contacts between backbone and grafts.

In conclusion, we have not obtained formal verification that the involved side reaction is effectively an intermolecular quaternization reaction. Nevertheless, the study of stabilization of PS-g-P2VP copolymers treated further in this paper and the study of the stability of PS-g-P4VP copolymers given in another article[7] give some indirect confirmation of our hypothesis concerning the instability of some of our products.

Production of stable copolymers

To obtain stable products we can either:
prepare copolymers which, but their chemical nature, do not present any possibility of side reactions (i.e. with no more reactive groups responsible for the side reaction), or, for copolymers having unstable characteristics (i.e. presenting possibilities of side reactions), operate in such a way that these side reactions cannot occur. This 'stabilization' can be sought directly during or after the grafting.

'Stabilization' obtained during the grafting. So as to prevent this side reaction, the consumption of chloromethyl groups must be maximized. Many experiments we have performed show that to obtain stable products, the number

Table 4 Behaviour of mixtures of chloromethylated polystyrene and poly(2-vinyl pyridine)

Mixture		Time (days)	Molecular weight[b]
Poly (2-vinyl pyridine): Chloromethylated	62% M_w= 8 600	0[a]	25 800[c]
polystyrene -44 Cl/chain:	38% M_w=54 000	2	27 100
		12	28 200
		78	29 300
		280	28 900
Poly (2-vinylpyridine): Chloromethylated	74.6% M_w=70 000	0[a]	66 000[c]
polystyrene -63 Cl/chain:	25.4% M_w=55 000	2	67 000
		59	67 000

[a] Mixing achieved by dissolution in benzene, and freeze drying.
[b] Measured by light scattering.
[c] Theoretical molecular weight.

of residual chlorinated sites must not be greater than 1 per 100-150 styrene units. This implies, when the base polystyrene has a high chloromethylation (about 1/10 of styrene units), that the yield of grafting is at least 90%. In order that this is the case it is necessary, as we have seen,[2] to operate with a strong excess of living polymer and in sufficiently concentrated media (2-3% in polymer). Then, the ungrafted homopolymer must be eliminated and this is not always easy.[2]

'Stabilization' after grafting. In some cases, it is possible that one wishes to use the copolymer directly, without further purification by fractionation. Then, after synthesis, the copolymer must not contain homopolymer, which implies that the grafting is effected with a marked shortage of living polymer towards chloromethyl groupings. Unfortunately, under these conditions, as we have already reported, not all products are stable, the residual chlorinated sites leading to crosslinkings. To avoid the increase in molecular weight of copolymers, we have examined whether or not it was possible to use another method other than that of operation with an excess of carbanionic ends.

Since the side reaction involves the chloromethyl groups and the nitrogen atoms, two processes are theoretically possible to overcome this problem; we may 'block up' the nitrogen sites or eliminate residual chlorine groups.

'Blockage' of nitrogen sites. If the synthesis of PS-g-P2VP copolymers is only a step in the preparation of polystyrene-poly(vinyl pyridinium) copolymers, it suffices, to obtain stable products, to effect the quaternization reaction of nitrogen atoms just after grafting, and before the phenomenon of increasing molecular weight appears. Thus, the quaternized nitrogen atoms cannot react with chloromethyl functions (see *Table 10*).

The fact that the 'stabilization' can be so obtained confirms the hypothesis, mentioned previously, on the origin of the side reaction.

Elimination of residual benzylic chlorine. In order to suppress chloromethyl functions remaining on the backbone of the copolymer, one must use a reagent that readily reduces the 'reactive' chloromethyl functions to 'stable' hydrogened sites.

A treatment by lithium naphthalene allows this dechlorination: the organo-metallic complex can convert chlorine functions to organo-metallic sites and the latter are 'deactivated' later by protonolysis with the help of methanol for example.

Check for secondary effects. However, it was necessary to check that this reaction was not accompanied by secondary effects that could modify the polymer structure. To this end, we have studied successively the action of lithium-naphthalene on chloromethylated polystyrene, on poly (2-vinyl pyridine) and on PS-g-P2VP copolymers.

Action of lithium-naphthalene on PSCl. We have observed that the action of Li-naphthalene on chloromethylated polystyrene in THF media leads, as expected, to coupling reactions of Wurtz–Fittig type between metallated sites and the as yet unmetallated chloromethyl groupings.

For a given initial chloromethylation the importance of these couplings is a function of the way the metallation is effected (*Table 5*).
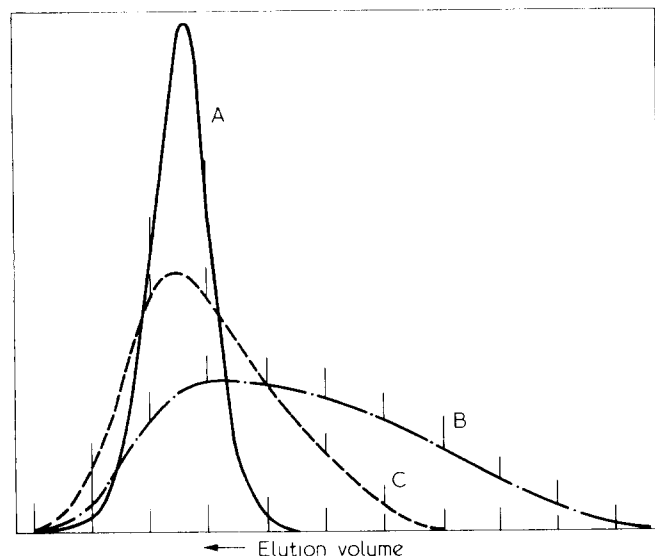
Figure 1 Gel permeation chromatograms of a chloromethylated polystyrene sample before (———) and after dischlorination reaction (experiments Z2, —·—·—; and Zl, — — — —). See experimental conditions in *Table 5*.

Table 5 Effect of the mode of dechlorination of a chloromethylated polystyrene on its molecular weight[a]

	'Direct' metallation		'Reverse' metallation[d]	
	Progressive[b]	Rapid[c]	Excess of Li-naphthalene (X2)	Excess of Li-naphthalene (X4)
Reference molecular weight after treatment[e]	Z2	Z1	Z4	Z8
	1 100 000		71 000	67 000
GPC diagram number[f]	2	3		

[a] M_w = 52 000. Chloromethylation degree: 1/10.7 i.e. 47 Cl/chain. G.p.c.: diagram (see *Figure*). Experimental conditions: temperature, — 70°C. PSCl in solution at 0,5% in THF.
[b] Progressive addition of lithium-naphthalene into PSCl solution. After each addition of Li-naphthalene, the solution takes a red colour due to metallated sites, but coloration disappears almost instantaneously before even deactivation by methanol is possible. This indicates that couplings occur rapidly.
[c] Addition of Li-naphthalene all at once.
[d] Addition of the PSCl solution into Li-naphthalene solution.
[e] Measured by light scattering.
[f] See *Figure*.

Examination by l.s. and g.p.c. of the characteristics of polystyrene after treatment indicates that the linkings are minimized when PSC1 is added to Li-naphthalene, rather than with the reverse procedure. This result is not surprising because, in this case, the metallation reagent is always in excess within the reactional medium and the chloromethyl functions react preferentially with Li-naphthalene. On the other hand, by the direct metallation method, there is the simultaneous presence on the polymeric chains of chloromethyl functions and metallated sites. This leads to crosslinking and to a very strong increase in molecular weight. This phenomenon is the more marked as the deficiency of Li-naphtalene during the reaction is stronger i.e. the Li-naphtalene addition is slower (sample Z2 in *Table 5*).

Furthermore, if the density of chlorinated sites upon the polymer is weak (which is the case for the polymer back-

Table 6 Effect of the initial degree of chloromethylation of PSCl on side couplings during the dischlorination reaction

Reference	Degree of chloromethylation	Effect of treatment[b]
Z1	1/10.7	Strong increase of polydispersity[c]
Z12	1/23.6	Slight increase of polydispersity: before; M_w/M_n =1.14 after; M_w/M_n =1.22
Z5	1/60	Molecular weight not modified, equals 52 000

[a] Experimental conditions. 'Direct' metallation by rapid addition of Li-naphtalene into the PSCl solution at 0,5%. Excess of Li-naphtalene (4 x stoichiometric quantity). Reaction at low temperature, — 70°C. PSCl, M_w = 52 000
[b] Characterisation of products by g.p.c.
[c] See *Figure*.
[d] Measured by light scattering.

bone after grafting), the probability of formation of linkings is reduced and can even vanish (*Table 6*).

In addition, it can be assumed that, for a graft copolymer, the steric hindrance due to side chains minimizes these coupling reactions. We have observed such an effect for a comb-like polystyrene which presents an analogous molecular architecture to that of our copolymers (*Table 7*).

Action of lithium-naphtalene on P2VP. It is known[8] that action of Li-naphtalene on P2VP brings on a metallation of pyridine nuclei, which is accompanied by linking reaction especially where the extent of metallation is high. We have verified that effectively there is an increase in the molecular weight of P2VP even at low temperature (— 70°C) and for an extent of metallation limited at about 10% of the pyridine units (*Table 8*).

Action of metallated P2VP on PSC1. In our PS-g-P2VP graft copolymers, the number of vinyl pyridine units is plainly greater than the number of chloromethylated units (chloromethyl functions/2VP units < 1/100). During the treatment by Li-naphtalene, the side-metallation of P2VP may be favoured to the detriment of the required metallation of PSC1. In fact this is unimportant, since we have noted that metallated P2VP is itself able to bring about the dechlorination of PSC1.

Action of lithium-naphthalene on PS-g-P2VP copolymers. The results just reported, concerning the action of Li-naphtalene on two parent homopolymers, lead to two contradictory conclusions for a copolymer. Indeed, we have seen that, in order to limit crosslinking reaction between PS chains, it is preferable to add the polymer to the Li-naphtalene solution. However, if this experimental procedure is used for PS-P2VP copolymers, the first pyridinic chains

Table 7 Dechlorination reaction on a comb-like polystyrene with chloromethyl functions upon backbone

Comb-like polystyrene: 1/30 styrene units of backbone is still chloromethylated.

Direct metallation by Li-naphtalene.

Effect of treatment
 before metallation, M_w = 374 000
 after metallation, M_w = 398 000

Table 8 Action of lithium naphthalene on P2VP

Reference	P2VP molecular weight	
	Before metallation	After metallation
Z3	7 000	12 800
Z9	22 000	29 000
Z14	9 100	13 000

entering the reactional medium will be in the presence of a great excess of metallation reagent. This may increase the linkings between poly(vinyl pyridine) grafts. On the contrary, by addition of Li-naphtalene into the copolymer solution (which is the worst method for the PSCl moiety), the metallation extent on P2VP is very small (about 3-6%) and side reactions must thus be limited.

Test of procedures. It was necessary to test the two experimental procedures before choosing between them: the best results were obtained by addition of metallation agent into the polymer solution (*Table 9*).

Moreover, the 'direct' metallation method presents an experimental advantage that no transfer of solution is needed. Consequently the procedure is simple since the three successive reactions: polymerization, grafting and dechlorination are carried out in the same reaction flask.

So, it can be seen (*Table 9*) that treatment by lithium-naphthalene allows us to 'freeze-in' the structure of copolymers. However, if the 'stabilization' is obtained in this manner, the structure of the polymer may be affected. This pheno-menon which was not observed for sample NG12 (*Table 9*), is illustrated by the example of sample NG28 (see *Table 10*): the 'stabilization' is accompanied by a preliminary increase in molecular weight, which must be mainly due to linkings between pyridine chains.

Consequently, the usefulness of this 'stabilization' method is limited, especially as, during dechlorination reaction, there is always the possibility of intramolecular couplings, which are not observed by molecular weight measurements.

CONCLUSION

Our study clearly shows that, for some poly(styrene-g-2-vinyl pyridine) copolymers obtained from chloromethylated polystyrene, unused chlorine functions are responsible for an instability phenomenon appearing in the dry state by an increase in molecular weight.

In order to avoid this crosslinking, the best procedure is to use, at the time of grafting, nearly the whole of the chlorinated sites of the starting backbone. Under these conditions, the resulting copolymers are well defined[2] and quite stable.

In the opposite case, i.e. if the copolymers are instable, it is nevertheless possible to overcome this problem using different processes.

Thus, in *Table 10*, we summarize and compare the efficiency of the different 'stabilization' methods applied to the same copolymer.

Table 9 Effect of mode of treatment by lithium-naphthalene of a PS-g-P2VP copolymer (sample NG12)

Measurements taken	Molecular weight[a]		
	Untreated copolymer	Copolymer solution added into Li-naphtalene	Li-naphthalene added into copolymer solution
Just after synthesis	200 000	235 000	210 000
3 months after synthesis	320 000	240 000	210 000
1 year later	810 000		205 000

[a] Measured by light scattering.

Table 10 Comparison of different methods of 'stabilization' for a PS-g-P2VP copolymer

Product	Molecular weight[b]	
	Just after synthesis	50 days later
Copolymer kept at room temperature	505 000	655 000
Copolymer kept at low temperature	505 000	510 000
Copolymer kept in solution in THF (c = 1.8%)	505 000	510 000
Copolymer treated by Li-naphthalene	560 000	555 000
Copolymer quaternized by HCl	630 000	630 000

[a] Sample NG28. Backbone: chloromethylated polystyrene, M_w = 70 000; degree of chloromethylation: 1/8.3 i.e. 80 Cl/chain. Grafts: poly (2-vinyl pyridine), M_w = 8 000. Grafting: $[P2VP^e]/[-CH_2Cl]$ = 0.7. Residual degree of chloromethylation: 1/28. P2VP % = 86%. $M_{theoretical}$ = 500 000.
[b] Measured by light scattering.

We see that the copolymer which partially crosslinks in its dry state and at room temperature (first line) remains stable if it is kept at low temperature (second line) or in solution at room temperature (third line). The stability of the copolymer can also be obtained by chemical treat-ment i.e. 'blocking' the nitrogen functions (fifth line) or eliminating the residual chlorine functions (fourth line). (However, in the latter case, the dischlorination brings about an increase in the molecular weight of nearly 10%.)

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