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Copolymerization of Polyvinylpyridine Macromonomers with Styrene

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Summary

Free radical copolymerization of ω(α-methylstyryl)poly (2-vinylpyridine) macromonomers with styrene was performed. After separation of residual macromonomer the graft copolymers were submitted to a careful characterization.

The copolymers were generally of rather low molecular weight and the average number of grafts per backbone chain was found close to unity. Nevertheless, these polymeric species tend to give aggregates and/or emulsions in selective solvents of the grafts, a typical behaviour of graft copolymers.

Introduction

In a previous publication (1) we have described the synthesis of poly(vinylpyridine) macromonomers, using anionic polymerization techniques, the unsaturation being introduced upon deactivation. Macromonomers with an end-standing methacrylic ester function - or with an α-methylstyrene end-group - have been made and characterized. The same method has been extended to synthesize ω-styryl polyvinylpyridine macromonomers, using p.bromomethylstyrene as the unsaturated deactivation agent.

The aim of the present article is to discuss the ability of the end-standing unsaturation to undergo copolymerization with styrene or with α-methylstyrene. The resulting graft copolymers, involving polyvinylpyridine grafts of known length and distributed at random, should be of interest as amphiphilic polymer species. In organic solvent media the behaviour of a graft copolymer depends upon the relative affinity of the backbone and of the grafts for the solvent chosen (2).

It is well-known that upon addition of a few drops of hydrochloric acid to a suspension of PVP in water, dissolution ensues quaternization of the pyridine functions thus renders the grafts hydrophilic (3). Conversely, addition of a base, such as KOH, to a solution of a polyvinylpyridinium salt induces the precipitation of the polymer from its solution.

It can thus be anticipated that the solubility properties of a graft copolymer consisting of PVP grafts attached to a hydrophobic backbone should be strongly pH dependent. In acidic media some protection of the hydrophobic part by the polyelectrolytic grafts is expected to occur, whereby stable emul-

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sions or even molecular dispersions could be obtained, depending upon the number and length of the grafts, and upon their ionization degree. In aqueous alkaline solution no protection can be exerted by the grafts.

Let us first comment on some attempts to homopolymerize polyvinylpyridine macromonomers by means of anionic polymerization techniques. When efficient initiators (such as butyllithium) were used, even at low temperatures, side reactions of the living sites on the pyridine rings (4,5) prevented the formation of the expected polymacromonomers. The more stabilized metal organic compounds (such as 1,1-diphenylmethyl pentyllithium) (1) proved unable to initiate the polymerization of the styrene or α-methylstyrene type unsaturations of the macromonomers under the conditions chosen.

The same difficulties were encountered in attempts to copolymerize α-methylstyrene with ω(α-methylstyryl) polyvinylpyridine using various anionic initiators, such as butyllithium or phenylethyl potassium, at low temperature: side reactions involving the pyridine rings cannot be avoided.

These experiments are to be repeated with polyvinylpyridine macromonomers fitted with a methacrylic ester function at chain end. However the synthesis of such macronomers is not straight forward.

Free radical copolymerization experiments

Well-defined macromonomers of polyvinylpyridine were made anionically according to the method previously described (1); p.bromomethyl- α-methylstyrene was used as the unsaturated deactivator of the living sites. Characterizations data, shown on Table 1, include weight average molecular weights obtained by light scattering; number average molecular weights resulting from the chemical titration of the end-standing unsaturation (under the assumption that each molecule carries one double bond). Furthermore size exclusion chromatography (SEC) was meant to check the breadth of the molecular weight distribution in the macromonomer samples. Polystyrene calibration was used, which does not introduce large errors with THF as the elution solvent.

Table 1 - Characterization data of ω(α-methylstyryl) poly(2-vinylpyridine) macromonomers

Sample	M_n	M_n^* SEC	M_w^* SEC	M_w^*/M_n^* SEC	M_w,LS
2646 (I)	5 700	4 300	5 100	1,2	4 800
2675 (II)	3 400	2 100	2 300	1,1	2 300
2835 (III)	2 300	2 100	2 300	1,1	2 300
2836 (IV)	4 400	3 600	4 000	1,1	4,400

M_n by chemical end-group determination

The free radical copolymerization of these ω(α-methylstyryl) polyvinylpyridine macromonomers with styrene were carried out in benzene solution, at 60°C, with freshly recrystallized azobis(isobutyronitrile) as the free radical initiator. The macromonomer had been made water free by freeze-drying. The solvent and comonomer had been dried in the usual way, by repeated distillation over sodium wire. The reaction mixtures (listed in Table 2) were introduced into tubes and degassed several times, the tubes were then sealed and kept in a thermostat at 60°C for 6 hours. This duration was chosen to get overall yields in the range of 40-50%. The tubes were then cooled, opened and the polymers recovered by precipitation in cold isooctane.

Table 2 - Characterization data of polyvinyl-2 pyridine macromonomers copolymerized with styrene: experimental conditions

(1)	Styrene		Macromonomer		Amount of reaction product		Overall yield
	g	mole.l^{-1}	g	mole.l^{-1}.10^2	Insoluble g	Soluble g	%
2799 (I)	7,1	2,43	4	2,51	2,7	0,3	27
2800 (II)	7,1	2,43	2,4	2,52	2,2	1,7	41
2809 (I)	7,1	2,13	4	2,19	4,6	1,2	52
2810 (II)	7,1	2,27	2,4	2,35	5	0,21	54
2846 (III)	10,4	2,22	2,3	2,22	2,9	2,2	40
2847 (IV)	10,4	2,22	4,4	2,22	3,2	3,3	43

(1) : Macromonomer used in copolymerization (see Table 1)

The raw reaction product contains both the graft copolymer and the unconverted macromonomer (Fig. 1a). The separation of these two constituants involves great difficulties. Selective precipitation of the reaction mixture into methanol - a solvent of the PVP chains - is not satisfactory as the solubility properties of a graft copolymer largely depends upon those of the grafts. Nevertheless precipitation into cold methanol was used in some instances: only part of the unconverted P2VP macromonomers was removed, as revealed by the SEC diagram obtained on the precipitate (Fig.1 b,c). It was found more satisfactory to precipitate out the whole polymer content of the reaction mixture into isooctane , a non-solvent of both polymeric constituents, and to remove the excess macromonomer in a separate operation. Two different methods were used:

. Dialysis in water, buffered at pH 4, was attempted first. This process is extremely slow and after a week the amount of P2VP macromonomer extracted is still quite small, in spite of its relatively low molecular weight. It should be noted that the difference in size between the graft copolymer and the macromonomer is not very large, due to the branched structure of the former, and to the fact that in water solution the polystyrene part must have collapsed.

GPC DIAGRAMS

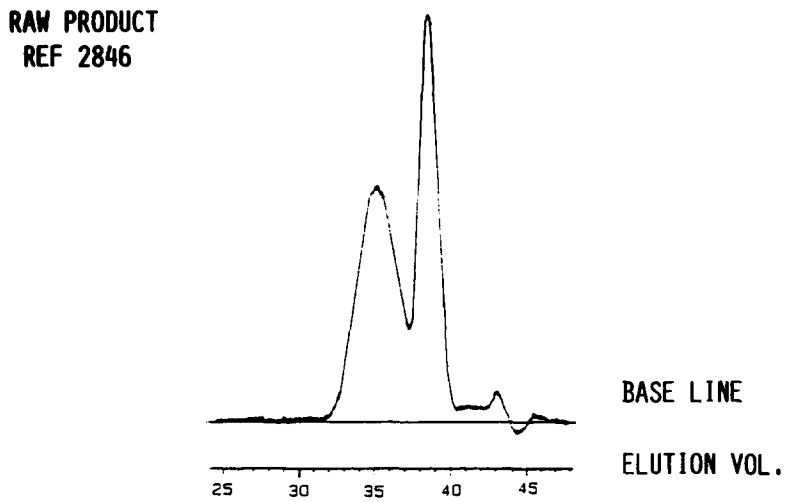

FIG. 1A

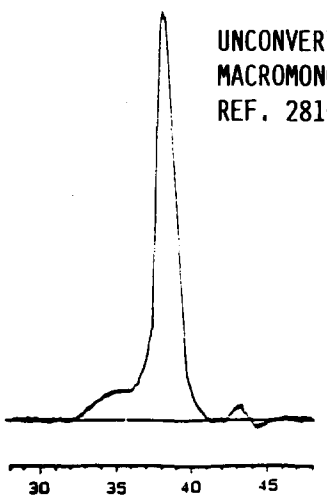

FIG. 1B

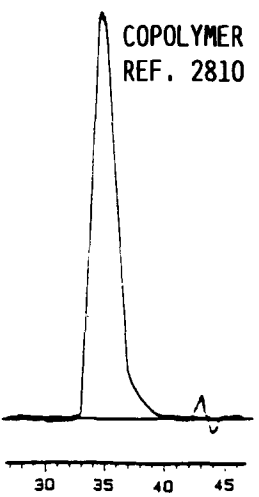

FIG. 1C

. Fractionate precipitation of raw mixture of graft copolymer and P2VP macromonomer remains the most efficient method of separation, provided the solvent-precipitant mixture is selective enough. The system that was chosen: benzene-isooctane, proved satisfactory, in some cases at least, as it can be seen from the SEC traces of the four fractions obtained from one of our samples (Fig.2):the first fraction, which is the largest, contains almost no residual macromonomer, and the last one is almost free of graft copolymer. There are however cases in which the separation between graft copolymer and unconverted macromonomer is not as easy.

Characterization of the graft copolymers

Owing to the difficulties encountered to quantitatively separate the unconverted macromonomer, account has to be taken of the residual macromonomers in the fractions. This amount was evaluated from the SEC diagrams.

Knowing the fractionation yield and the weights of the individual fractions it is possible to evaluate the overall composition of the graft copolymers. It was expected to check the values obtained by comparison with data obtained from refractive index measurements. However this system proved quite unfavorable, as the refractive index increments of both homopolymers in dioxane are not far apart (0.161 and 0.169).

Light scattering measurements were carried out on dioxane solutions of the fractions. Fluctuations in composition within the samples - if any importance - should not harm the values of the molecular weight, because of the small difference between the dn/dc of the polymeric constituents.

The results are gathered on Table 3.

Table 3 - Characterization data of copolymers

	$M_{n,(1)}$	$M_{w,LS(2)}$	
2800	3 400	18 100	(1) M_n macromonomers (chemical titration)
2846	2 300	17 600	(2) $M_{w,LS}$ measured in dioxane
2847	4 400	18 400	

A few comments should be made:

. Light scattering Zimm plot exhibit an unexpected angular variation of the scattered intensity (Fig.3). This reveals association phenomena of several molecules to aggregates. The molecular weights shown generally result of intensities measured at high angles on solutions of low concentration. They can be considered as the true values of M_w, and the

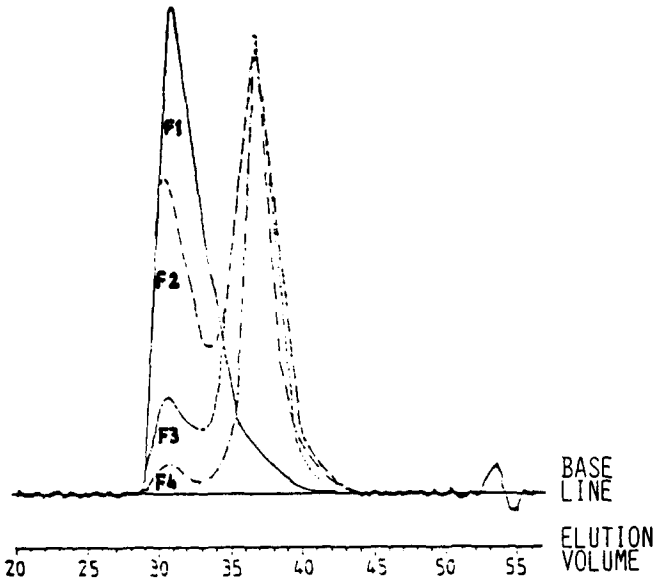

FIG.2 - FRACTIONATION SEC DIAGRAM OF SAMPLE REF.2846

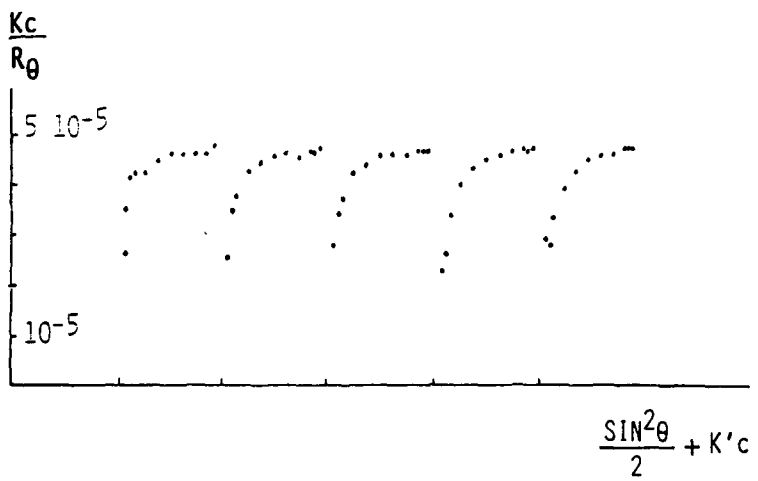

FIG. 3 - ZIMM-PLOT OF 2846 F1 (ETHYLACETATE)

reproducibility is rather good. If ethylacetate or THF are chosen as solvents instead of dioxane, the aggregate formation is enhanced, and the M_w measurements are less reliable.

- The molecular weights obtained for the graft copolymers are lower than expected. However if styrene had been homopolymerized under the same conditions, with the same amount of initiator, the molecular weight of the polymer would have been only slightly higher: there is no need to cale for extensive chain transfer during the copolymerization process.
- In most cases the number of grafts per copolymer molecule should be close to one. This value is compatible with the mole content of the macromonomer - in the reaction mixture account being taken of the molecular weight of the copolymer.

The α-methylstyrene site at chain end of the macromonomer was chosen on purpose, because of its relatively low reactivity ratio, in order to decrease the probability of formation of macromonomer diads in the copolymer. A consequence is that the fluctuations in composition within a sample should remain rather low. However this cannot be checked experimentally with the desirable accuracy.

It was worthless to investigate in great detail the morphology and the solution behaviour of graft copolymers containing one single graft per molecule. New experiments will aim at getting higher molecular weights, and several grafts per molecule. A possible starting point would be P2VP macromonomers with a more reactive unsaturation at chain end.

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