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Synthesis and Characterization of Polyvinylpyridine Macromonomers

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SUMMARY

Macromonomers of polyvinylpyridine were obtained anionically, by reacting unsaturated electrophiles onto a "living" polyvinylpyridine solution. The end-standing unsaturation is either a methacrylic ester function or an α-methylstyrene group. Several experimental problems had to be solved to get polymers of adequate and predetermined molecular weight and of low polydispersity, and to have the molecules fitted quantitatively with unsaturation at chain end. A careful characterization procedure was used to check the ability of the method to yield well defined macromonomers.

INTRODUCTION

Ionic methods are known to be well suited for the synthesis of macromonomers, short polymer chains fitted quantitatively with a polymerizable unsaturation at chain end. This unsaturation can be introduced either upon initiation with an unsaturated initiator (MASSON, 1982), or upon deactivation of the"living" sites by means of an unsaturated compound (SIERRA-VARGAS, 1982).

The present note deals with the synthesis of polyvinylpyridine macromonomers, and with the characterization results on the samples obtained. The interest of polyvinylpyridine arises from the easy quaternization (HOOVER 1970) whereby the polymer becomes water soluble, and behaves as a polyelectrolyte. The final aim of the present work is to get access to various types of graft copolymers (SELB,1980) fitted with randomly distributed polyvinylpyridine grafts, to establish the effect of solvent and pH on the conformations and on the overall dimensions of macromolecules (MARIE, 1976) and to investigate the ability of such species to give yield to emulsions (MARIE,1976) or microemulsions.

EXPERIMENTAL

- Solvents and monomers were purified carefully and made free of protonic impurities, according to classical procedures.
- The polymerizations were carried out in tight reactors fitted with efficient stirring and temperature control, under a slight overpressure of dry oxygen-free argon.
- Initiators. Several metalorganic initiators were used: diphenylmethyl potassium was obtained from diphenylmethane and potassium naphtenide, according to a method previously described (NORMANT,1960).

1.1-diphenyl-3 methyl pentyllithium resulted from the addition of sec. butyllithium onto diphenylethylene, the reaction being carried out in THF, at -30°C. This initiator is stable in THF solution, for 3 or 4 days, at least.

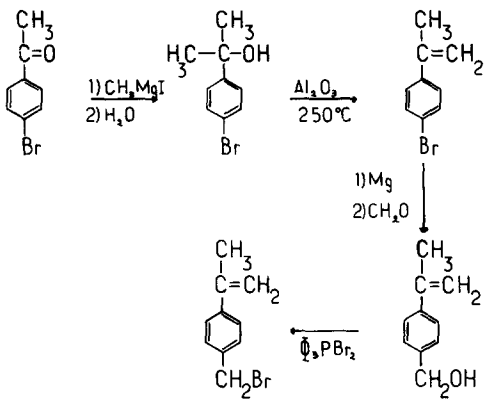
The initiator solution was titrated by means of acetanilide.

Deactivators and reagents

Ethylene oxide was kept for 4 hours over sodium wire, degassed and vacuum distilled.

Methacryloyl chloride was treated with calcium hydride, vacuum distilled and stored under argon, and in the dark.

p.bromomethyl α-methylstyrene was synthesized in the laboratory, starting from p.bromoacetophenone. This four-step synthesis is schematized below:



The overall yield with respect to p.bromoacetophenone is of the order of 40%. The pure p.bromomethyl- α-methylstyrene is a white crystalline solid melting at 41°C. It was never described before, to our knowledge.

Characterization data

.Elementary analysis:

Calc. C %	56.89	H %	5.25	Br %	37.85
Found C %	56.70	H %	5.26	Br %	38;08

.N M R ^{1}H : - CH_3 ... : 2.0 ppm
- CH_2 ... : 4.3 ppm
= CH_2 ... : 4.9 and 5.2 ppm
ArH ... : 7.1 ppm

RESULTS AND DISCUSSION

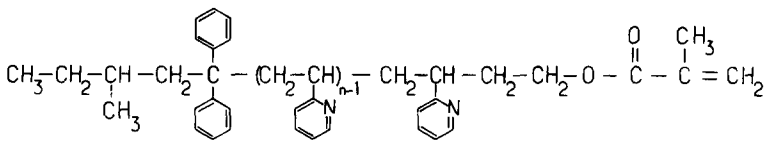
It has been known for a long time that vinylpyridines are susceptible to polymerize anionically, in aprotic solvents (THF), to yield "living" polymers (CHAMPETIER, 1962). The rate constants of growth are very high, and polymerization can be considered instantaneous. This is a disadvantage if polymers of low molecular weight and narrow molecular weight distribution (MWD) are wanted: in many cases a marked broadening of the MWD is observed, and the first problem that had to be solved was to find experimental conditions such as to get defined polymers. The best results were obtained with 1.1-diphenyl-3 methylpentyl lithium as the initiator, the reaction being carried out at very low temperature (-90°C) and the monomer (diluted with twice its volume of solvent) being introduced slowly into the reactor.

An additional difficulty arises with 4-vinylpyridine, as THF is a precipitant for the polymer; as soon as molecular weights of the order of 1000 are formed precipitation of the polymer occurs whereby no control of the chain growth can be exerted anymore. However, 15% of DMF added to the THF suffice to maintain the polymer in solution.

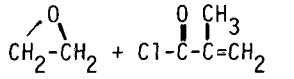
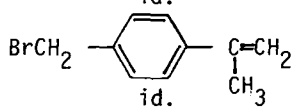
Once the polymer is formed some of it is sampled out for characterization purposes. The rest of the "living" polyvinylpyridine solution is used for the synthesis of the macromonomer, by means of deactivation with an unsaturated electrophile. Two pathways have been attempted:

. Methacryloyl chloride can be reacted onto the living sites of the polyvinylpyridine. However, a side reaction between the carbanionic sites and the methacrylic double bond can be expected, and also detected by size exclusion chromatography (GPC).

To prevent this side reaction to occur, an intermediate addition of ethylene oxide (MARIE, 1982) was attempted. The nucleophilicity of the site would be thus drastically reduced, but the resulting alcoholate function should be still active enough to react quantitatively with the methacryloyl chloride. The reaction should be carried out under conditions such as to avoid the polymerization of ethylene oxide, one single such unit being introduced into the chain. It was found that the attack of polyvinylpyridine anion onto the ethylene oxide is rather slow even at 0°C. Once the color of the polyvinylpyridine anion has vanished the methacryloyl chloride is added and the macromonomer thus obtained can be represented as follows:



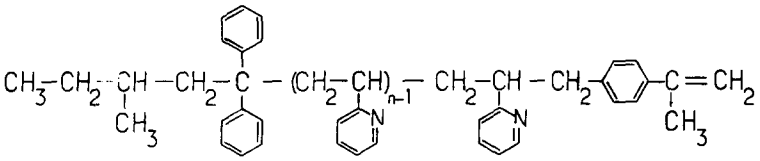
. p-bromomethyl-α-methylstyrene was reacted directly with the "living" polyvinylpyridine in THF solution, at low tempetature (-80°C). In this case it could be anticipated that no side reaction would take place as the sensitivity of α-methylstyrene type unsaturations to nucleophilic attack is far less than that of vinylpyridine. The deactivation reaction proceeds at once and the metal bromide precipitates out. No change in the GPC diagram can be detected upon deactivation; the macromonomer exhibits exactly the same MWD as the polyvinylpyridine precursor. This

References	$\bar{M}_{n,th}$	$\bar{M}n$	$\bar{M}_w$ LS	$\bar{M}_n$ GPC	$\bar{M}_w$ GPC	$\bar{M}_w/\bar{M}_n$ GPC	Deactivating Agent
2586	6 000	6 600	7 100	6 200	7 500	1.2	
2649	4 000	5 000	3 500	3 500	5 000	1.4	id.
2646	4 000	4 600	4 800	4 300	5 100	1.2	
2661	2 000	2 400	2 300	2 100	2 300	1.1	id.
2669	1 000	1 400	1 400	1 100	1 500	1.4	id.
2675 [1]	2 000	2 500	2 300	2 100	2 300	1.1	id.
2657 [2]	4 000	3 900	6 200	-	-	-	id.

1) Initiator is : 1.1-diphenyl-3 methyl pentyllithium
2) 4- vinylpyridine

Table 1 - Characterization data of polyvinylpyridine macromonomers

indicates that no side reaction involving the double bond of the electrophilic deactivator has taken place. Thus the ω (α-methylstyryl) polyvinylpyridine macromonomers can be represented as:



The macromonomers are carefully purified; the solution is first concentrated, and the salt is removed by filtration. Then the rest of the THF is removed. The polymer is redissolved in dry benzene, and freeze-dried after second filtration, or it is precipitated directly in cold heptane. Table 1 shows the results of the characterization measurements carried out on the various polyvinylpyridine macromonomers that have been prepared. The yields are always close to quantitative. The molecular weights measured are generally in good agreement with the values calculated from the monomer to initiator mole ratio. The double bond titration gives values of M_n (assuming one double bond per molecule) that are in fair agreement with the values of M_n originating from size exclusion chromatography with polystyrene calibration (Fig.1). A series of light scattering measurements confirmed the M_w data arising from GPC. Finally it should be pointed out that the NMR diagrams (Fig.2) show the two peaks of the double bonded methylene groups, but integration leading to M_n values is meaningsless owing to the accuracy of the measurements.

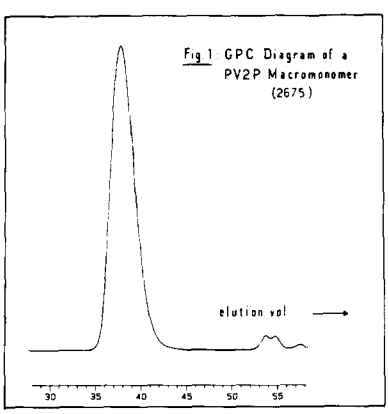


Fig 1: GPC Diagram of a PV2P Macromonomer (2675)

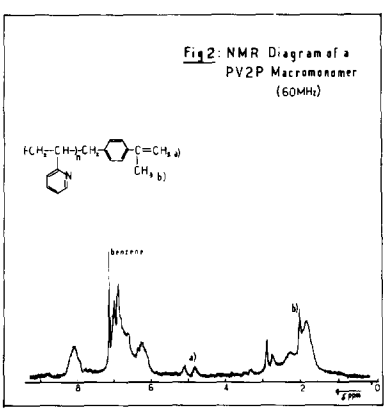


Fig 2: NMR Diagram of a PV2P Macromonomer (60MHz)

CONCLUSION

It can be concluded that well defined macromonomers of polyvinylpyridine can be obtained by deactivation of ω -carbanionic polyvinylpyridine by means of unsaturated electrophiles.

The most efficient procedure includes use of low temperature and of a lithium initiator, to get sharp molecular weight distribution and to ensure adequate control of M_n; direct reaction of the "living" species with p.bromomethyl-α-methylstyrene was found very satisfactory as no side reaction can be detected. The macromonomers thus obtained are fitted with an α-methylstyrene type unsaturation. The other method involving two steps (ethylene oxide and methacryloyl chloride) is equally satisfactory; in both cases functionalization can be considered quantitative.

The use of these macromonomers for the synthesis of amphiphilic graft copoymers will be described in a forthcoming paper.

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