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N-alkyl-3-vinylpyridinium salts: homopolymerization of the hexadecyl derivative and behaviour study of the polymer in aqueous media

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SUMMARY

We report on the preparation and the characterization of R-alkylated quaternary salts (with R = CH_3, $C_{12}H_{25}$, $C_{16}H_{33}$, X = Br^-) derived from 3-vinylpyridine (3-VP). Our first attempts on free radical polymerization of 1-hexadecyl-3-vinylpyridinium bromide in benzene solution were described. The viscosimetric behaviour and binding of dye (Methyl Orange) to this homopolymer in aqueous media were interpreted as the formation of compact coils resulting in the presence of hydrophobic microdomains.

INTRODUCTION

For the two last decades there has been an increasing interest in the synthesis and the study of the behaviour in aqueous media of amphiphilic cationic polymers whose field of applications can widen from tensioactive systems to enzymes analogues. These polymers can be prepared either by polymerization of a quaternized vinylic heterocyclic monomer (e.g. alkylvinylimidazolium or pyridinium salts) or by quaternization of a preformed polymer (e.g. a polybase). Refeering to the peculiar case of the pyridine derivatives (the poly(2 or 4 vinylpyridinium salts (1,2), the most frequent in the literature), the first pathway was not always applicable because the N-alkyl-2- or 4-vinylpyridinium salts are known for their instability and the inherent difficulties for their isolation (except for 1-methyl-4-vinylpyridinium salts and 1-alkyl-4-vinylpyridinium triflates (3). As for the second possibility, the quaternization of the poly(2 or 4-vinylpyridines) is never complete and leads in the most cases to the formation of copolymers. Therefore we have choosen the particular case of the 3-vinylpyridine (a derivative which has received only a few attention in the literature). It is less reactive than 2- or 4-vinylpyridines and able to give alkylpyridinium salts we suppose to be more easily isolable. This paper reports on the conditions of quaternization of 3-vinylpyridine and the results of preliminary experiments concerning the homopolymerization. Further physicochemical characterization including viscosity measurements and dye binding have revealed the formation of hydrophobic microdomains in aqueous solutions.

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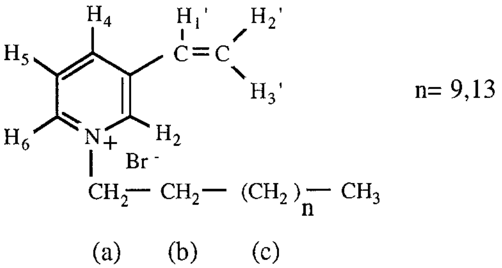
EXPERIMENTAL

Quaternary salts of 3-vinylpyridine

All the quaternization reactions were carried out in the presence of hydroquinone that prevents from homopolymerization.

(C_{12} and C_{16} derivatives). To a solution of 1.47 g (14 mmol) of 3-vinylpyridine in a suitable polar medium (mixture acetonitrile/chloroform 50/50 v/v), the corresponding 1-bromoalkane (28 mmol) was added dropwise under an Argon atmosphere. Then the reaction mixture was maintained under stirring for 2 days at 60°C (T = 50°C for C_{12} derivative). 1-hexadecyl and 1-dodecyl-3-vinylpyridines were purified by two recrystallisations from ethylacetate. In the case of the methyl derivative, the quaternization reaction with methylbromide was carried out in ethylacetate at 0°C overnight. After cooling the quaternary salt was precipitated by addition of ether, filtered and dried under vacuum (T = 25°C, 1 hour). Then the crude material was recrystallized from a mixture ethylacetate/acetonitrile 50/50 v/v).



- 1-hexadecyl-3-vinylpyridinium bromide. m.p. 75°C

I.R. (KBr) ν (C=C) 1630 cm^{-1} ν (aliphatic CH) = 2870-2950 cm^{-1}.

^1H NMR ($CDCl_3$, TMS)

δ (ppm) 0.87 (3 H, t, CH_3) ; 1.29 (26H, m, H_c) ; 2.04 (2H, m, H_b) ; 5.04 (2H, t, Ha) ; 5.8 ($H_{2'}$, d, $J_{H_{2'}H_{1'}}$ = 11 Hz) ; 6.37 ($H_{3'}$, d, $J_{H_{3'}H_{1'}}$ = 17.6 Hz) ; 6.89 ($H_{1'}$, dd, $J_{H_{1'}H_{3'}}$ = 17.6 Hz, $J_{H_{1'}H_{2'}}$ = 11 Hz) ; 8.00 (H_5, dd, $J_{H_5H_4}$ = 8.2 Hz, $J_{H_5H_6}$ = 6.1 Hz) ; 8.38 (H_4, m, $J_{H_4H_5}$ = 8.17 Hz, $J_{H_4H_2}$ = 1.6 Hz) ; 9.2 (H_6, m, $J_{H_6H_5}$ = 6 Hz) ; 9.7 (H_2, m, $J_{H_2H_4}$ = 1.64 Hz).

Calculated for $C_{23}H_{40}NBr$: C, 67.32 % ; H, 9.76 % ; N, 3.41 % ; Br, 19.51 %. Found : C, 67.14 % ; H, 9.53 % ; N, 3.36 % ; Br, 19.34 %.

- 1-dodecyl-3-vinylpyridinium bromide. m.p. 36-38°C

I.R. (KBr) ν (C=C) 1630 cm^{-1} ν (aliphatic CH) = 2870-2950 cm^{-1}.

^1H NMR ($CDCl_3$, TMS)

δ (ppm) 0.86 (3H, t, CH_3) ; 1.28 (18H, m, H_c) ; 2.00 (2H, m, H_b) ; 5.01 (2H, t, Ha) ; 5.75 ($H_{2'}$, d, $J_{H_{2'}H_{1'}}$ = 11 Hz) ; 6.36 ($H_{3'}$, d, $J_{H_{3'}H_{1'}}$ = 17.6 Hz) ; 6.89 ($H_{1'}$, dd, $J_{H_{1'}H_{3'}}$ = 17.6 Hz, $J_{H_{1'}H_{2'}}$ = 11 Hz) ; 8.04 (H_5, dd, $J_{H_5H_4}$ = 8.2 Hz, $J_{H_5H_6}$ = 6.1 Hz) ; 8.41 (H_4, m, $J_{H_4H_5}$ = 8.14 Hz, $J_{H_4H_2}$ = 1.6 Hz) ; 9.20 (H_6, m, $J_{H_6H_5}$ = 6Hz) ; 9.70 (H_2, m, $J_{H_2H_4}$ = 1.68 Hz).

Calculated for $C_{19}H_{32}NBr$. C, 64.40 % ; H, 9.04 % ; N, 3.95 % Br, 22.60 % ; Found : C, 64.02 % ; H, 8.97 % ; N, 3.91 % ; Br, 22.31 %.

- 1-methyl-3-vinylpyridinium bromide.
  m.p. 141-144°C
  I.R. (KBr) ν (C=C) 1630 cm^{-1} ν (aliphatic CH) = 2870 cm^{-1}.

^1H NMR ($CDCl_3$, TMS)

δ (ppm) 4.77 (3H, s, CH_3) ; 5.77 ($H_{2'}$, d, $J_{H_{2'}H_{1'}}$ = 11 Hz) ; 6.36 ($H_{3'}$, d, $J_{H_{3'}H_{1'}}$ = 17.6 Hz) ; 6.86 ($H_{1'}$, dd, $J_{H_{1'}H_{3'}}$ = 17.6 Hz, $J_{H_{1'}H_{2'}}$ = 11 Hz) ; 8.00 (H_5, dd, $J_{H_5H_4}$ = 8.1 Hz, $J_{H_5H_6}$ = 6.1 Hz) ; 8.39 (H_4, m, $J_{H_4H_5}$ = 8.07 Hz) ; 9.25 (H_6, m, $J_{H_6H_5}$ = 6.1 Hz) ; 9.70 (H_2, m, $J_{H_2H_4}$ = 1.6 Hz).

Calculated for $C_8H_{10}NBr$: C, 48.00 %, H, 5.00 % ; N, 7.00 % ; Br, 40.00 % ; Found : C, 47.56 % ; H, 5.50 % ; N, 7.10 % ; Br, 39.69 %.

Polymerization

General procedure

A solution of 2.44 x 10^{-4} mol of monomer dissolved in 5 ml of distilled benzene was introduced in a reactor and degassed under vacuum by application of the freeze-thaw technique. Then 0.6 % of initiator (molar percent/monomer) was added under Ar and the waterproof reactor was then immersed under magnetic stirring in a thermostated bath at 60°C for 24 hours. The mixture takes the appearance of a gel and solidifies after 10 mn reaction. After cooling, a solution was obtained by addition of a small amount of chloroform. Then the polymer was precipitated into acetone. After drying, the polymer was purified by dissolution in chloroform and reprecipitation in acetone. Finally, the polymer was filtered off and dried under vacuum at 50°C for 2 days.

Elemental analysis

Poly(1-hexadecyl-3-vinylpyridinium bromide) (PC_{16}-3-VP).

Calculated for $C_{23}H_{40}NBr$: C, 67.32 % ; H, 9.76 % ; N, 3.41 % ; Br, 19.51 %. Found : C, 67.29 % ; H, 9.68 % ; N, 3.47 % ; Br, 18.95 %.

Viscosity

The measurements were performed at 30°C (for 1-propanol and mixtures 1-propanol-water) and 25°C (for $CHCl_3$) using a SCHOTT-GERÄTE AVS 310 viscosimeter. Intrinsic viscosities [η] (in chloroform) were obtained from extrapolation of the linear plots η_{sp}/c vs polymer concentrations.

UV-vis spectroscopy

UV-vis absorption spectra of Methyl Orange (2.5x10^{-5} M) in the presence of the polysoap (8x10^{-7}- 1.7x10^{-4} unit M) were recorded on a SHIMADZU UV-2101 PC spectrophotometer at 30°C in aqueous solutions (1-propanol 3%+ ethanol 1%) buffered at pH=7.1 with HEPES (0.015 M) I=6x10^{-3} M ($NaNO_3$).

RESULTS AND DISCUSSION

3-vinylpyridine has been prepared from 3-pyridinecarboxaldehyde via a Wittig reaction (4) but using sodium hydride as the base.

Quaternization

An homologous series of 1-alkyl-3-vinylpyridinium salts, (table 1) in which the hydrophile-hydrophobe balance is a function of the chain-length, has been prepared in order to obtain cationic polyamphiphiles (for R = C_{12} and C_{16}) or polyelectrolytes (for R = CH_3). The preliminary quaternization reactions were performed in ethylacetate as suggested by Salamone (13) for the preparation of vinylimidazolium iodides. However good results were obtained only in the case of 1-methyl-3-vinylpyridinium bromide (90 % yield in raw material). For the longer chain substituted compounds (C_{16} and C_{12}) the yields do not exceed 30-40 % and in this case the better results were obtained by carrying out the quaternization in a more polar medium such as a mixture acetonitrile/chloroform. The addition of chloroform was necessary to increase the solubility of the reactants, especially the alkylbromides. Nevertheless it was noted that for the long-chain substituted monomers, the quaternization reactions remain slower (2 days) than for the methyl derivative (overnight). An interesting property of these cationic monomers was their water solubility and despite the presence of the increasing hydrophobic part (e.g. C_{16}), all the compounds remain largely soluble.

Product	Operating conditions		Yield
CH_3-3-VP	Solvent Ethylacetate (1.5 ml) 3-VP (2.38 mmol) CH_3Br (4.76 mmol)	T = 0°C t = overnight	90 %
C_{12}-3-VP	$CH_3CN/CHCl_3$ 1/1 (4 ml) 3-VP (8.38 mmol) $C_{12}Br$ (16.76 mmol	T = 50°C t = 2 days	60 %
C_{16}-3-VP	Ethylacetate (3ml) 3-VP (2.24 mmol) $C_{16}Br$ (2.46 mmol)	T = 40°C t = 1 week	30 %
C_{16}-3-VP	$CHCl_3$ (10 ml) 3-VP (8.79 mmol) $C_{16}Br$ (17.6 mmol)	T = 60°C t = 2 days	39 %
C_{16}-3-VP	$CH_3CN/CHCl_3$ (1/1) (10 ml) 3-VP (14 mmol) $C_{16}Br$ (28 mmol)	T = 60°C t = 2 days	85 %

Table 1 : quaternization of 3-vinylpyridine

- CH_3-3-VP	1-methyl-3-vinylpyridinium bromide
- C_{12}-3-VP	1-dodecyl-3-vinylpyridinium bromide
- C_{16}-3-VP	1-hexadecyl-3-vinylpyridinium bromide.

Polymerization

We report on a few comparative attempts concerning the homopolymerization of the 1-hexadecyl-3-vinylpyridinium bromide (table 2).

Initiator (molar percent/monomer)	Monomer concentration	Temperature °C	Polymer yield	Time (hrs)	[η] (a) ml.g^{-1}
A.I.B.N. 2 %	1	70	96	20	27
1 %	1	70	88	16	76
A.D.V.N. 1 %	0.5	60	87	24	73
	0.5	60	77	24	31
1 %	0.5	60	73	24	85
0.6 %					

Table 2 : homopolymerization of 1-hexadecyl-3-vinylpyridium bromide (solvent benzene).
(a) Intrinsic viscosity in $CHCl_3$ at 25°C
A.I.B.N. = a, a'-Azoisobutyronitrile
A.D.V.N. = 2,2-Azo-bis(2,4-dimethylvaleronitrile).

For all the reactions, we have chosen our laboratory improved conditions in the case of the polymerization of alkylvinylimidazolium bromides, the best results being obtained with benzene as the solvent and azobisbutyronitrile as the free radical initiator. When the initiator and the monomer concentrations are respectively 2 % (molar percent/monomer) and 1M, the conversion is quasi-quantitative but the intrinsic viscosity of the polymer does not exceed 27 ml/g ($CHCl_3$; 25°C). When taking half of the initiator amount we observe a high increase of the viscosity ([η] = 76 ml/g) with a slight decrease of the polymer yield. Initiator concentrations below 1 % have not allowed better polymer viscosity. The use of an other initiator such as A.D.V.N. (2,2'-Azo-bis(2,4-dimethylvaleronitrile) which allows a lower temperature reaction (T = 60°C) affords under the same conditions (initiator = 1 % [monomer] = 1M), identical results as those with AIBN: [η] = 73 ml/g).

However the best result was obtained [η] = 85 ml/g when the homopolymerization is driven at lower concentrations both in initiator (0.6 %) and monomer (0.5M).

Behaviour in aqueous solutions

These first results concerning the homopolymerization of a quaternary salt of the 3-vinylpyridine highlight the ability to obtain polymers with very interesting molecular weights. Moreover it has to be noticed the good solubility of this polymer in aqueous media (water + 4 .% 1-propanol v/v) and that the resulting polymeric solutions are able to solubilize hydrophobic compounds (e.g. 5,(6)-alkylbenzimidazole). An other interesting property of these polymers is their ability to give hydrophobic microdomains in aqueous media. A normal hydrodynamic behaviour was observed in chloroformic solution and linear plots of η_{red} vs polymer concentration were obtained. In dipolar protic solvents (e.g. 1-propanol or aqueous 1-propanol solutions), a polyelectrolyte-like behaviour was found. A more detailed study was undertaken with 1- propanol and increasing water contents. As shown in fig (1), a sharp decrease in η_{red} was observed as the percentage of water was increased up to 10%. For higher water contents no change was observed in η_{red}. These viscosity variations evidence a change in the conformation of the polysoap. For the solvent composition, neat 1-propanol or a mixture 1-propanol with water < 10%, there is a particular state where interactions between the polymer and the solvent molecules generate a highly characteristic extended form adopted by the polymer whereas , as the percentage of water is increased another state appears where hydrophobic groups interact by forming either intra or inter molecular association.

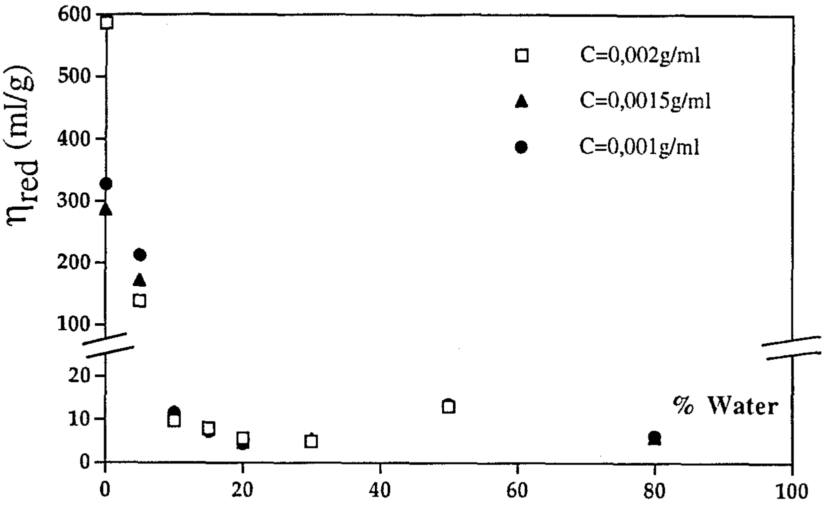


Figure 1: Reduced viscosity as function of the percentage of water in the mixture 1-propanol- water; T= 25°C

The formation of these microdomains has been also considered by studying the interactions of a solvatochromic dye and the cationic homopolymer (PC_{16}-3-VP). For this purpose the uv-visible spectra of methyl orange are often used so as to detect qualitatively a hydrophobic environment in an aqueous medium. A currently used technique such as the fluorescence spectroscopy with pyrene as the probe cannot be applied in our case because of the well-known quenching phenomenon of the long-chain quaternized pyridinic units.

As shown in fig (2 and 3), at very low polymer concentrations ($8.5x10^{-7}$ - $1.2x10^{-5}$ M) the absorption curves are similar in shape to that of dye in molecular dispersion. The absorption maximum value (λ_{max}) of methyl orange was found to be equal to that of the free dye in aqueous solutions λ_{max} = 465 nm. In the range of polymer concentrations near the equivalence point (dye concentration = $2.5x10^{-5}$ M) the absorption at 465 nm decreases and the corresponding peak becomes more asymetric with a shoulder on the left-hand side at around 390 nm. This band centered in the case of CTAB near 370 nm was attributed to interactions of the dye with amorphous mixed micelles (14). At higher polymer concentrations (near the cmc for classical surfactants) the absorption at 465 nm completely disappears whereas a third absorption band appears with a maximum near 420 nm accompanied by a slight bathochromic effect. This band is characteristic of the absorption of methyl orange in a non-aqueous microenvironment.

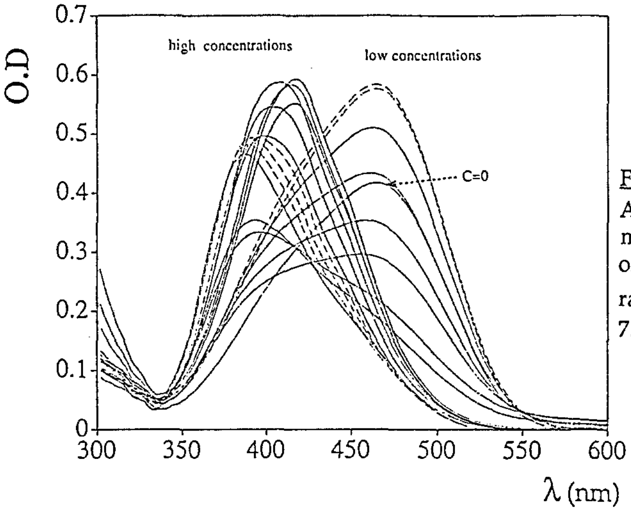


Figure 2:
Absorption curves of 2.5×10^{-5} M methyl orange in the presence of PC_{16}-3-VP; concentrations ranging from 8.5×10^{-7} M to 7.7×10^{-4} M

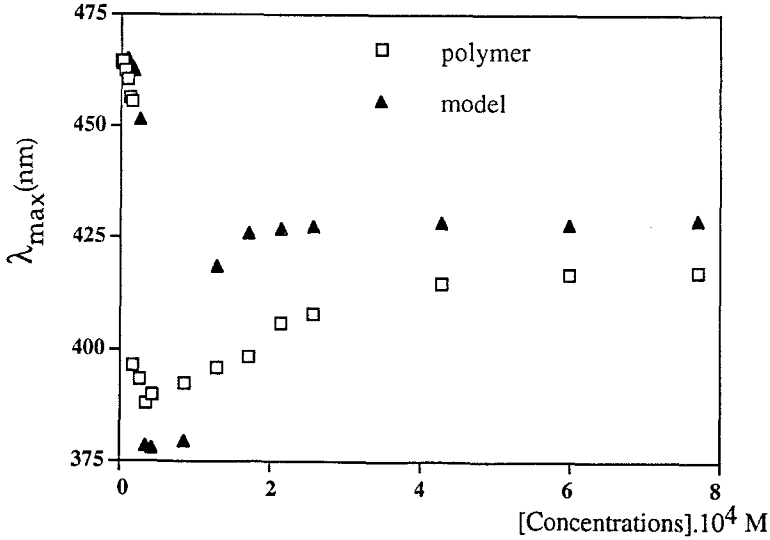


Figure 3: Variation of the absorption maximum of methyl orange as function of polymer and model concentration; T=30°C; [methyl orange]= 2.5×10^{-5} M

Taken as a whole, the absorption bands λ_{max}, shifted hypsochromically as the polymer concentration increases by going from 465 nm (in neat water) to 420 nm (comparable to the absorption in an organic solvent e.g. ethanol), is typical of the formation of a hydrophobic microenvironment surrounding the dye. This behaviour of the polymer in an aqueous solution may be compared to that of a classical surfactant such as CTAB or better, the polymer model (e.g. 1-hexadecyl-3-ethylpyridinium bromide) (fig (2). For the model, a lower overall hypsochromic effect is observed with a final λ_{max} = 429 nm.

Studies are now in progress in our laboratory for evaluating the influence of these microdomains on bimolecular reactions (e.g. hydrophobic activated esters hydrolysis in the presence of long-chain catalysts).

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