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Series of Poly(4-vinylpyridine) Containing Quaternary Alkyl bromides: Synthesis and Determination Percentage of Quaternization

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Summary: In this study, we focus on the synthesis series of poly(4-vinylpyridine) (P4VP) containing quaternary alkyl bromides. The poly(4-vinylpyridine) (P4VP) was synthesized by conventional radical copolymerization and then the P4VP was quaternized by alkyl bromides containing chains consisting of 5 and 10 carbon atoms. Two copolymers series with three degrees of polymerization have been synthesized, the first poly[*N*-isopentyl(4-vinylpyridinium)] bromide P4VPIPBr (I); (II); (III) and the second poly[*N*-decyl(4-vinylpyridinium)] bromide P4VPBrD (I); (II); (III). The following techniques have been used to characterize the structure and composition of the cationic copolymers (P4VPIPBr) and (P4VPBrD), HNMR, conductimetry and viscometry.

Keywords: alkylbromides chains; characterization; poly(4-vinylpyridine) derivates; solubility; synthesis

Introduction

Considering such novel chemical properties as acidity, basicity and hydrophilic-hydrophobic balance, 4-VP is of great importance. The poly- or copolymers of 4-VP shown that the positively charged form of poly(4-VP) can be readily prepared via the quaternization reaction.[1] However, polymer scientists have a great interest to prepare polymer materials with precisely controlled molecular weight, which are synthesized by anionic, cationic, or step-growth polymerization traditionally.[2] More recently, Dizman et al.,[3] an interesting example, these are polyacrylamides with lateral pyridine rings which are then quaternized by different alkylbromides (C12, C14, and C16). Operating in a highly polar mixture acetonitrile-methanol at 60 °C, the degree of quaternization exceeds 90%. Damas et al.[4,5] have developed a series of copolymers poly(*N*-alkylacrylamide bromide-co-1-methyl-4-vinylpyridinium), obtained by quaternization of the copolymer precursor poly (*N*-alkylacrylamide-co-4- vinylpyridine).Also K. Medjahed et al.[6] have synthesized a series of copolymers poly(acrylamide-co-4-vinylpyridine) containing quaternary alkyl bromide (C8), the octane bromide cation of poly(acrylamide-co-4-vinypyridine) CPAVC8Br2 (I); (II); (III), three degree of quaternization (30% after 4h, 65% after 12h and 87% after 24h in the reaction times) of average molecular weight: 3.59×10^5; 8.22×10^5 and 24.45×10^5 g/mole respectively. The latter is synthesized by radical copolymerization in the presence of Azobisisobutyronitrile (AIBN). Then, the quaternization by methyl bromide, conducted in chloroform, methanol or chloroform/DMF. According to their hydrophobicity (number of carbon atoms in the chain *N*-alkylacrylamide), these polymers formed in aqueous micro-domain structure with a more or less compact. A typical example is the quaternization of poly(vinylpyridine). The first tests conducted by Strauss et al.[7,8] on the quaternization of poly(2-vinylpyridine) with 1- bromododecane in

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nitro ethane for 15 days at 80°C),with poly(4-vinylpyridine). Recently, the encouraging result obtained by addition of poly(4-vinylpyridine) (P4VP) derivatives, the poly(4-vinylpyridine poly-3-oxide ethylene) (P4VPPOE) obtained good results on the corrosion of pure iron in 1M H_2SO_4.[9,10] In our work the copolymer poly(4-vinylpyridine) was synthesized by radical copolymerization in solution and the cationic pyridine quaternary alkylbromide was prepared by quaternization of P4VP by different alkyl bromides chains (C5 and C10), many techniques have been used to characterize structure and composition of the cationic copolymers.

Experimental Part

Monomers and Alkylbromides

4VP (Aldrich, 98%) was washed with 0.1 N NaOH to remove inhibitor and was dried over CaCl2. The 4VP was distilled under reduced pressure (68 to 69 °C at 15 mmHg), just before use. Azobisisobutyronitrile (Aldrich, 98%) (AIBN) was used as initiator.

This is a very powerful initiating agent, was used to catalyze the polymerization of 4VP. Alkylbromides (Aldrich) with 5 and 10 carbon atoms in the chains as quaternising reagent was used. Methanol/Petrol ether as solvent was used to precipitate the copolymer bromide. The absolute ethanol was used as solvent for copolymers 4-VP and P4VP. A flask was equipped with a magnetic stirrer, a flow of inert gas (nitrogen) and a thermometer to check temperature.

Synthesis Copolymers Series of P4VPIPBr and P4VPBrD

Poly(4-vinypyridine) (P4VP) was prepared by radical polymerization of 4vinylpyridine in methanol, under vacuum, with azo-bis-isobutyronitrile (AIBN) as initiator, as described elsewhere.[11] The poly [N-isopentyl(4-vinylpyridinium)] bromide (P4VPIPBr) is fractionated by partial precipitation from methanol solution with ethyl petrol. The copolymer has been obtained by mixing 10g P4VP with 15.10 g of isopentylbromide (IPBr) in 100 ml chloroform (CH_3Cl) in a thermostatic bath (70 °C). After that, they were precipitated in petrol ether, washed in ethanol, then precipitated again in petrol ether and dried. The polymerization was fractionated by partial precipitation from methanol solution with petroleum ether. Poly[*N*-decyl(4-vinylpyridinium)] bromide (P4VPBrD) is obtained by mixing 2.92 g P4VP with 2.84 g of Bromodecane (BrD) in 30ml chloroform in a thermostatic bath (70 °C). P4VPBrD was obtained then precipitated in petrol ether, washed in ethanol, precipitated again in petrol ether and dried.

The molecular structure of the new synthesized Poly[*N*-decyl(4-vinylpyridinium)] bromide (P4VPBrD) and Poly[N-isopentyl(4-vinylpyridinium)] bromide is shown in Figure 1 and Figure 2.

Apparatus and Measurements

The polymers obtained were analyzed and characterized by (^{1}HNMR) DMX-500

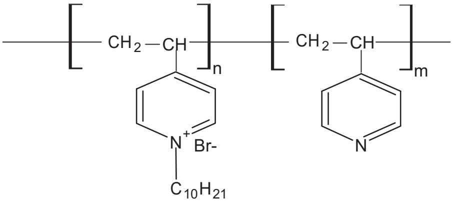


Figure 1.
Structure of P4VPBrD.

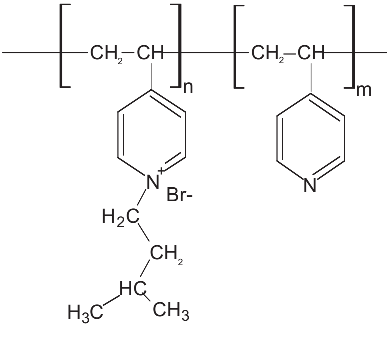


Figure 2.
Structure of P4VPIPBr.

Table 1.
Determination of quaternization percentage

Copolymer serie	P4VPIPBr (I)	P4VPIPBr (II)	P4VPIPBr (III)	P4VPBrD (I)	P4VPBrD (II)	P4VPBrD (III)
Quaternisation %	6	18	79	25	45	60
After times (h)	3	24	72	24	120	240
Molecular weights (10^{-5} g·mol^{-1})	4.2	4.7	7.16	5.9	7.22	9.45

(Bruker Company, Germany) and D_2O/DCl as the solvent.

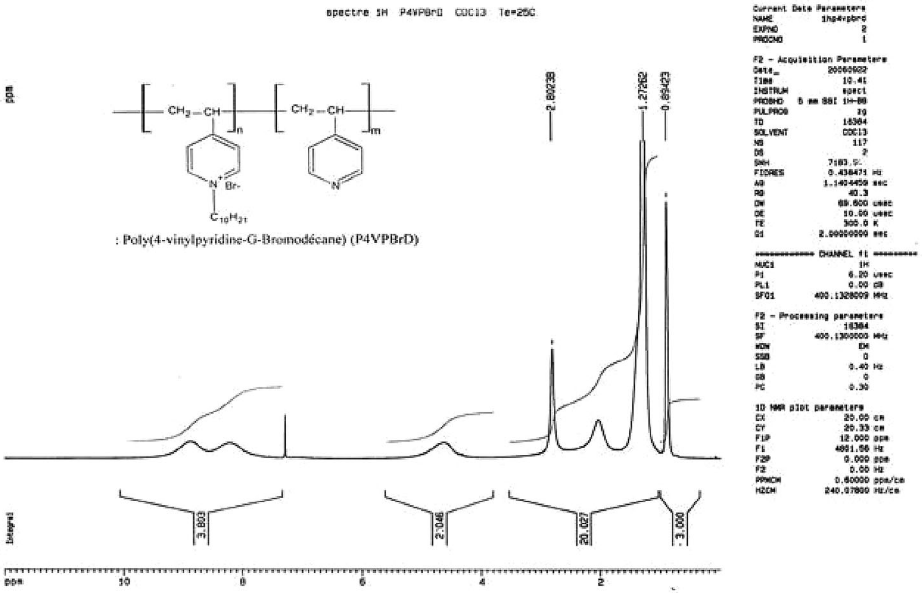
The viscosity technique was using (Ubbelohde viscometer) to determined molecular weight, with a thermostatic bath at 25 ± 0.1 °C.

The molecular weights of copolymers series (P4VPBrD and P4VPIPBr) were estimated by the viscosimetry technique using ethanol as solvent.[12]

During the quaternization reaction, the percentage of alkylated groups was determinated by conductimetric titration of bromide ions with $AgNO_3$ in methanol. An aliquot 1 ml was taken with a pipette and diluted with 20 ml of ethanol. So, the alkylation was stopped and the bromide ions were titrated (Table 1) using a (RadioMeter Lab CDM).

Results and Discussion

The poly[*N*-isopentyl(4-vinylpyridinium)] bromide (P4VPIPBr) was fractionated by partial precipitation from methanol solution with ethylpetrol. The copolymer has been obtained by mixing 10 g P4VP with 15.10 g of isopentyl bromide (IPBr) in 100 ml chloroform (CH_3Cl) in a thermostatic bath (70 °C). Poly[*N*-isopentyl(4-vinylpyridinium)] bromide was obtained in three degrees of quaternisation (6%,18% and 79%). The first polymer (6%) P4VPIPBr (I) was obtained after 3 hours, the second (18%) P4VPIPBr (II) after 24 hours and the tertiary (79%) P4VPIPBr (III) after 72 hours. P4VPBrD was obtained in three degrees of quaternization P4VPBrD (I) at (25%), P4VPBrD



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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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PULPROG              zg
TD                16384
SOLVENT           CDCl3
NS                  117
DS                    2
SWH              7183.9
FIDRES         0.438471 Hz
AQ            1.1404459 sec
RG                 40.3
DW               69.600 usec
DE                10.00 usec
TE                300.0 K
D1           2.00000000 sec

============ CHANNEL f1 =========
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P1                 6.20 usec
PL1                0.00 dB
SFO1        400.1328009 MHz

F2 - Processing parameters
SI                16384
SF          400.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.40 Hz
GB                    0
PC                 0.30

1D NMR plot parameters
CX                20.00 cm
CY                20.33 cm
F1P              12.000 ppm
F1              4801.56 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           0.60000 ppm/cm
HZCM          240.07800 Hz/cm
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Figure 3.
^{1}H NMR spectrum of P4VPBrD copolymer in D_2O/DCl.

(II) at (45%) and P4VPBrD (III) at (60%) were obtained after 24, 120 and 240 hours respectively. The average molecular weight of P4VPBrD and P4VPIPBr are presented in (Table 1). Our results of quaternization rates are consistent with those cited by Damas et al.[4,5]

Characterization ^{1}H NMR Spectra

The Figure 3 shows the characterization ^{1}HNMR spectra of (P4VPBrD). The peaks ($\delta =$ ppm) at $\delta = 8.92$, $\delta = 8.\ 32$ and $\delta = 7.67$ are ascribed to the protons at 2.6 sites and 3.5 sites of the pyridine ring respectively. Comparing the ^{1}HNMR spectra of (P4VPBrD) with that of the polymer P4VP;[13] a new peak at $\delta = 2.\ 80$ is assigned to the alkyl protons group and $\delta = 0.\ 89$ to the $-CH_2-CH-$ were bonded with N atom in the pyridine ring. The signals at 1.56–1.24 are attributed to the protons of the carbon skeleton of the remainder of the quaternizing agent, and the proton-radical $-CH_2-$ $CH-$ of the copolymer, of non-related cycles quaternized pyridines. The very narrow peak obtained for a chemical shift of 0.93 corresponds to the proton of the methylene group $-CH_2-$ agent quaternising.

Conclusion

The copolymer Poly[*N*-decyl(4-vinylpyridinium)] bromide and Poly[*N*-isopentyl(4-vinylpyridinium)] bromide was synthesized by radical copolymerization, and then it was quaternized by different alkyl bromides (C5 and C10) to produce the cationic P4VPIPBr and P4VPBrD. Theirs structure and composition were characterized by the ^{1}HNMR spectra. We can measure the composition of the copolymer by determining the content of pyridine unit in the copolymers chains using the 4VP homopolymer as standard. As the quaternary reagent, was in excess alkyl bromides chains by a number of carbon atoms varying (C5 and C10), as quaternising reagent.

Following the results obtained, we deduced that the length of alkyl chains from C5 and C10 does not affect the degrees of the maximum rate of quaternization of P4VP in ethanol as solvent or the average molecular weights.

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