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Quantitative Quaternization of Poly(4-Vinyl Pyridine)

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ABSTRACT

Quaternization of poly(4-vinyl pyridine), (P4-VP) by common alkyl halides can be performed with relatively low (up to 65–70%) conversion yields. Here we describe fully quaternization of P(4-VP) with activated halides such as chloro 2-propanone and 2-chloroacetamide in dimethylformamide (DMF) at room temperature.

Key Words: Poly(4-vinyl pyridine); Quaternization; Activated halides.

INTRODUCTION

Cationic polyelectrolytes, in general, have many potential applications in sludge dewatering[1] and in the design of new membranes[2] etc. Most outstanding examples of cationic polyelectrolytes are quaternary ammonium polymers. Polymerization of vinyl monomers with quaternary ammonium groups is of special importance to attain such polymers with high molecular weights. Many ammonium monomers appear in the literature which were prepared by the usual methods of organic chemistry. However, a relatively small number of hydrolytically stable ammonium monomers are commercially available. Among these, diallyl dimethyl ammonium chloride (DADMAC), methacryloyloxy ethyl trimethyl ammonium chloride (MOTAC) and vinyl benzyl trimethyl

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ammonium chloride (VIBTAC) have wider applications, presumably due to non-hydrolysability of their polymers.

Radical polymerization of DADMAC can be achieved only in concentrated aqueous solutions.[3] Similarly, diallyl morpholinium bromide has been demonstrated to give relatively low molecular weight cyclopolymers with pyrrolidinium moieties in the main chain.[4] MOTAC and VIBTAC monomers, on the other hand, yield high molecular weight polymers. The monomer VIBTAC is prepared by a reaction of vinylbenzyl chloride with trimethyl amine. Since commercial vinyl benzyl chloride is a mixture of meta, para isomers and ethyl vinyl benzene, the polymer of VIBTAC is a copolymer rather than homopolymer.[5] A number of quaternized dimethylamino alkyl acrylates have been described in the literature.[6] Of particular interest, are their methacrylate analogues due to reasonable hydrolytic stability of the methacrylate ester group. Perhaps MOTAC is the only commercial monomer yielding high molecular weight polymer consisting of quaternary ammonium groups in each repeating unit.

Quaternization of polyvinyl pyridines might be considered as an alternative choice to attain quaternary ammonium polymers. Preparation of vinyl pyridinium monomers is almost impossible due to their spontaneous polymerization yielding pyridinium moieties in the main chain.[7] Also, post quaternization of the P(4-VP) does not proceed with quantitative conversions. Typically, 65–70% of quaternization is most common with alkyl halides. This has been credited to the neighboring group effect.[8] Methyl iodide (iodomethane) is a most favorable reagent to attain high quaternization yields, up to 95%. As far as we know a quantitative queternization of P(4-VP) has not been reported so far. Here, we describe a simple procedure for fully quaternization of P(4-VP) with chloro 2-propanone, and 2-chloroacetamide.

EXPERIMENTAL

4-Vinyl pyridine (Fluka), chloro 2-propanone (chloroacetone) (Acros Chemicals) were distilled before use. All the other chemicals were analytical grade commercial products. 2-Chloroacetamide (Fluka), DMF (E. Merck), and were used as supplied.

^{1}H-NMR and ^{13}C-NMR spectra were recordered by a Bruker AC 250 NMR Spectrometer.

Poly(4-Vinyl Pyridine)

This was prepared from vinyl pyridine (4-VP) as follows: 55.0 ml distilled water was placed in three-necked flask equipped with a reflux condenser and a nitrogen inlet. 16.3 ml (0.15 mol) 4-VP was added to the flask under nitrogen flow. The solution of 0.4 g (1.5 mmol) $K_2S_2O_8$ in 5.0 ml distilled water and the stirred solution was heated to 70°C for 2 h. A white precipitate was filtered and washed with water. The crude product was dissolved in 100 mL DMF and reprecipitated in 500 mL of 1M NaOH solution. The product filtered was dried at 40°C for 3 h. Dry polymer was dissolved in another 100 ml of DMF and reprecipitated in 300 ml ethylacetate.

The polymer filtered was dried at 40°C under vacuum for 24 h. Yield: 15.2 g (96.4%). Viscosity of the polymer $[\eta] = 0.25\,\text{dL}\cdot\text{g}^{-1}$ (at 30 ± 0.2°C in methyl ethyl ketone/isopropanol (86/14) mixture, 1 g/dL).

Mark-Houwing parameters given ($K = 3.8\cdot10^{-4}$, $\alpha = 0.57$) for this solvent mixture,[9] indicates a $M_v = 88.000$ Da's of molecular weight.

Quaternization of Poly(4-Vinyl Pyridine)

P4-VP (5.25 g, 0.05 mol repeating unit) was dissolved in 25 ml DMF and 75.0 mmol an active halide (chloro 2-propanone or 2-chloroacetamide). The solution was stirred at room temperature. The mixture became a light green and a white precipitate formed after 1 h stirring with chloro 2-propanone. At the end of reaction, the mixture was filtered and washed with acetone (50 ml) and ether (25 ml). Vacuum dried products were stored in tightly closed dark bottles. Relevant yields were collected in Table 1. The quaternized polymer with acetonyl function decomposes at 255°C. Decomposition of its acetamide analogue takes place at 249°C.

Determination of the Chlorine Contents

The chlorine contents of the quaternization products were determined as follows: 0.2 g of the quaternization product was mixed with 3.0 g powdered $NaOH{-}Na_2CO_3$ (1:1) mixture in a porcelain pot. The mixture was heated and fused by a naked flame of a Bunsen burner. After cooling to the room temperature, the mixture was digested in distilled water and filtered.The filtrate and washings were combined and neutralized with 2M HNO_3 solution. The solution was diluted to 1000 mL in a volumetric flask. Ten ml of the solution was used for analysis of chloride contents by a mercuric thiocyanate method as described in the literature.[10]

Table 1. Quaternization characteristics of P(4-VP).

Reagent	React. time	Practical yield (%)	Chlorine content ($\text{m.mol}\cdot\text{g}^{-1}$)		Quaternization yield[a] (%)	Viscosity $[\eta]$[b]($\text{dL}\cdot\text{g}^{-1}$)	PDT[c] (°C)
			Theor.	Found			
Chloro 2-propanone	24 h	99.7	5.06	5.1 ± 0.05	100.6	2.9	255
2-Chloro acetamide	72 h	98.9	5.03	5.0 ± 0.05	99.4	1.9	249

[a] Based on the chlorine analyses.

[b] Intrinsic viscosity determined by Fuoss-Strauss method (in water, at 30 ± 0.1°C, without salt).

RESULTS AND DISCUSSION

Quaternization of poly (4-vinyl pyridine) takes place quantitatively with chloro 2-propanone (chloroacetone) and 2-chloro acetamide as depicted in Sch. 1.

Unlike simple alkyl halides yielding low quaternization yields, chloromethyl functions activated by adjacent electron withdrawing groups react with the pyridine nitrogen to give fully quaternized poly (4-vinyl pyridines).

The rates of quaternizations can be compared visually by the appearance of first precipitations for each reagent. The reaction is faster with chloroaceton. Although we have not studied kinetics of the quaternizations, reactivity of the chloromethyl functions is proportional to the electron deficiency of the adjacent groups and chloroacetone is faster in the quaternization, as expected.

Based on these estimates, the reaction periods have been selected 24 and 72 h for chloro 2- propanone and 2-chloroacetamide, respectively. Extents of the quaternizations can be estimated by;

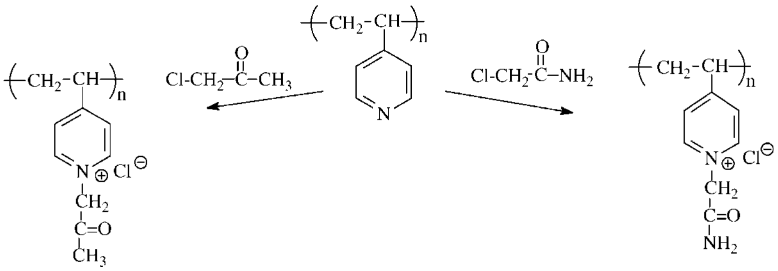
a) Conversion yields, b) chlorine contents and, c) NMR spectra. The results shown in Table 1 reveal quantitative quaternizations in each case.

Reaction yields and chlorine analyses results of both establish quantitative quaternizations. Minor differences are in experimental error limits. Resulting quaternization products are very hygroscopic and difficult to handle, as expected. However, the samples washed with ether can be manipulated for about 5 min. under open atmosphere without wetting, due to surrounding ether vapors.

More direct evidence for the quaternizations are obtained by NMR spectra (Fig. 1) of the products.

Thus, the quaternization induces a deshielding effect on P(4-VP) protons and about 1 ppm of down-field shifts are observed in each case. Methylene groups adjacent to the quaternary nitrogen give broad singlets at 5.7 and 5.6 ppm's for the cases of chloro 2-propanone and 2-chloro acetamide, respectively.

In the former case, additional methyl group exhibits a discernible singlet, which is broadening with the other aliphatic proton signals, around 2.4 ppm. Those down-field shifts allow us to predict the extent of the quaternizations. For instance, ^{1}H-NMR spectra of the product with acetamide groups, obtained in 24 h. reaction time, show additional peak at 6.7 ppm due to unreacted pyridine moieties (16.0%). In other words, absence of this peak in the spectra of the product obtained after a 72 h reaction period indicates



Scheme 1. Quaternization of P (4-VP) with chloro 2-propanone and 2-chloro acetamide.

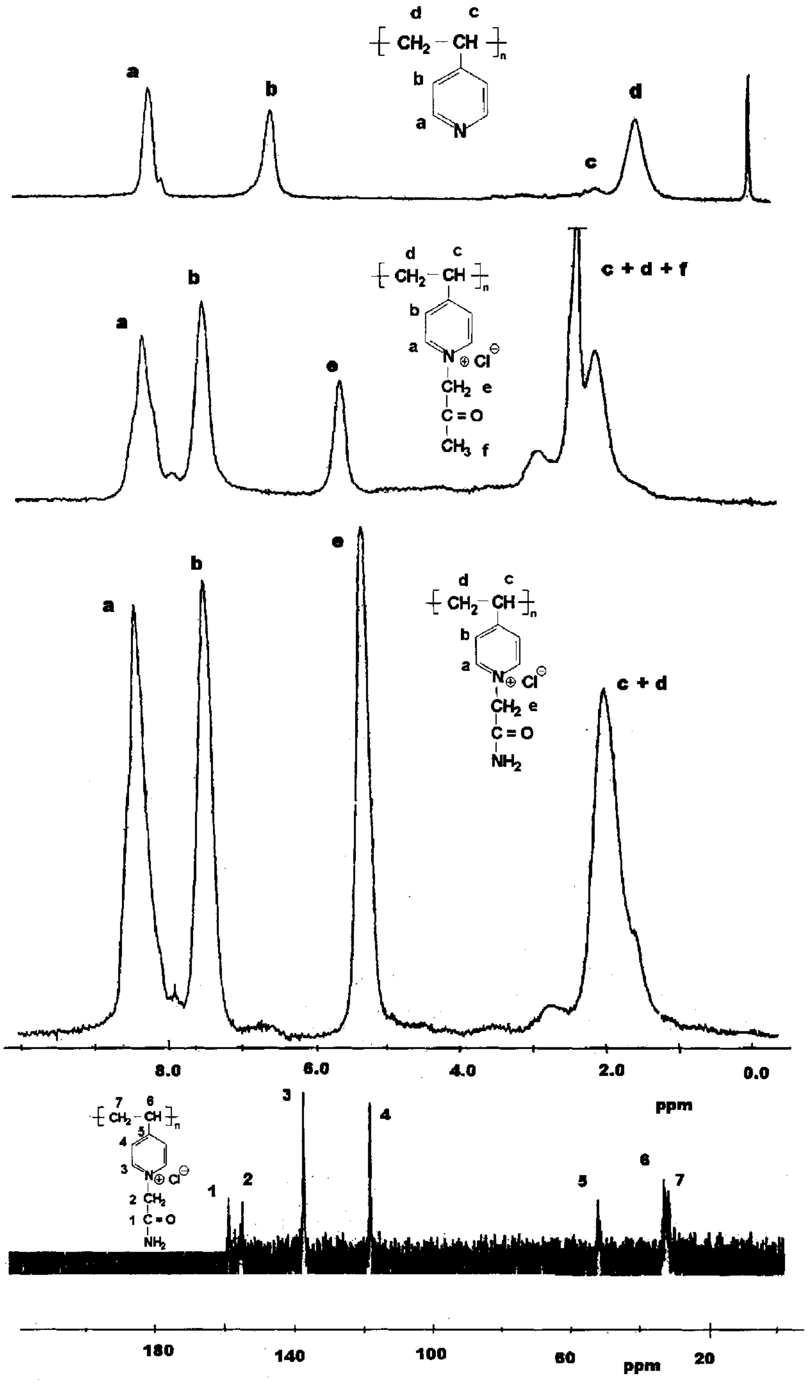


Figure 1. ^{1}H-NMR spectra of P (4-VP) in DMSO-d_6, and ^{1}H-NMR, C-NMR spectra of its quaternary derivatives in D_2O.

a quantitative quaternization. As expected, protons of the amide nitrogen do not give any resonance signal in D_2O solvent due to deuterium exchange. Also, ^{13}C-NMR spectra of this product reveals incorporation of the acetamide group, qualitatively, by the carbon signals of C=O and CH_2 groups at 159 and 152 ppm's, respectively. Both polymers undergo thermal decomposition around 200°C by foaming presumably due to evolution of the side groups involved. Melting temperature of the polymers with acetonyl and acetamide functions are 255°C and 24°C, respectively.

The quaternized polyvinyl pyridines are completely soluble in water. Viscosity of their aqueous solutions shows typical strong polyelectrolyte behavior. Viscosity-concentration relationships match well with the Fuoss-Strauss equation[11] and c/η vs. $\sqrt{c}$ plots give straight lines. From those plots, intrinsic viscosities were found 2.9 and 1.9 $\mathrm{dL\,g^{-1}}$ (with 0.998 and 0984 correlation factors) for the case of chloroacetone and 2-chloroacetamide, respectively. A great difference in the viscosities might be due to greater hydrophilicity of the acetamide function which makes water a better solvent. In the case for chloro 2-propanone, the quaternized P(4-VP) is not affected by acids. However, an immediate dark brown coloration takes place when a NaOH solution is added. Detailed investigations dealing with their chemistry and solution behaviors remain to be studied. Nevertheless, structurally, these are expected to be suitable for some transformation reactions. For instance, the polycation with acetamide might be of interest for preparing high molecular weight polycarbobetaines by hydrolysis of the acetamide groups involved.

CONCLUSION

P(4-VP) can be quaternized quantitatively by reacting with active chloromethyl groups, in DMF at room temperature. The quaternization presented is more likely to be common for all active halomethyl functions.

Quaternized polyvinylpyridines, in general, are expected to find applications in battery industry as ion conducting polyelectrolyte. One interesting report[12] indicates that a mixture of solid polyvinylpyridinium salt with solid $AlCl_3$ form molten salts having high ionic conductivities of about $10^{-2}\,\mathrm{S\cdot cm^{-1}}$ at room temperature.

The molten salts have been reported to be casted into thin films and their conductivities are influenced by the quaternization degree.[13]

Comparing with a 4 week reaction period, at 100°C, to attain high quaternization (about 90%) of the P(4-VP) with simple alkyl halides,[14] the method presented offers a simple solution for full quaternization of P(4-VP).

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