Amphiphilic graft copolymers with hydrophobic poly(4-vinylpyridine) backbone and hydrophilic poly(n-vinylpyrrolidone) side chains synthesis and characterization

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ABSTRACT

Macromonommers of 2-oxopropylmethacrylate-terminated poly(N-vinyl-2-pyrrolidone) is produced by cationic polymerization using HClO₄ as an initiator. Termination (end capping) step is accomplished using 2-hydroxypropylmethacrylate (2HPMA) and the polymer product has different chain lengths of molecular weight averages ranging from 500 to 3000 g/mol. The study also synthesised amphipathic graft copolymers having hydrophobic poly(4-Vinylpyridine) as a backbone chain and hydrophilic poly(N-vinyl-2-pyrrolidone) (PVP) as side chains of various lengths. The copolymer synthesis was accomplished by free radical copolymerization of ω-oxopropylmethacrylate PVP in the presence of 4-Vinylpyridine using 2,2-azobisisobutyronitrile (AIBN) as an initiator. Measurements of the dynamic viscosity of the polymer solution (20% weight of macromonomers in ethanol) show that the viscosity is proportional to the average molecular weights Mₙ. However, a reverse behavior of the viscosity variation with regard to Mₙ is observed for graft copolymer samples. The viscosity variation with respect to the graft copolymer mass must be due to steric effects, which are strongly pronounced in grafted copolymer chains. Appearance of the number of side chains attached to poly(4-Vinylpyridine) backbone reveals that the grafting reaction has occurred with good efficiency. The structure and composition of amphiphilic graft copolymers were characterized by, UV–visible, FTIR, ¹H NMR, ¹³C NMR and spectroscopy.

Keywords: Cationic polymerization, macromonomer, radical free copolymerization, amphiphilic graft copolymers, dynamic viscosity.

INTRODUCTION

Graft copolymers have important application in the polymer industry [1,2] and have recently received a lot of attention [3,4] In fact, these grafted copolymers are widely utilized as surface modifiers for coatings, adhesives, dispersants and compatibilizing agents in polymer blends and also for biomedical use. In particular, the amphiphilic graft copolymers have been extensively investigated for their particular physico-chemical properties and self-assembly morphologies [5].4-Vinyl pyridine (4VP) is a functional monomer and the N atom on pyridine ring is a strong donor of electrons. Thus, Polyvinylpyridine and its derivatives have been widely studied, with particular interest in inhibition of corrosion Fe, Cu, Al, Zn, and their alloys in acidic media [6,7]. Especially, homo and copolymers of N-vinyl-2-pyrolidone are of great interest in a number of industrial applications and have been utilized, for instance, in the preparation of membranes for ultrafiltration, as light sensitive coating material for lithographic printing plates and for the preparation of carbon fibers. Poly(N-vinyl-2-pyrolidone) or PVP has good properties including high solubility in water and organic solvents, very low toxicity, good biocompatibility, high complexation ability and good film forming and adhesive characteristics [8,9]. It is frequently used as a comonomer [10] mainly because of its amphiphilic character.
N-vinyl-2-pyrrolidone is very sensitive to most known free radical initiators and can lead to polymers of very high mass [11], which may hinder the copolymer formation. Alternatively, cationic polymerization can be used to limit the growth of polymer mass to few thousands. Besides, the use of water, alcohols, acids or anhydrides can inhibit the growth of the polymeric chain by the fixation of OH-, OR-, RCOO- anions on the propagated carbocation [12,13].

This kind of copolymer was synthesized by another way such as Copolymer beads of 4-vinyl pyridine (4VP) and n-vinyl pyrrolidone (NVP) were synthesized by suspension polymerization with various compositions of 4VP: NVP (10:0, 9:1, 8:2, 7:3, 6:4, and 5:5). The spherical shape and the macroporous nature similar to the 4VP homopolymer were noticed in copolymers of 6:4 and 5:5, while others were nonporous. The copolymer beads were characterized by FTIR, NMR, SEM, TGA, and dilute solution viscosity. Equilibrium sorption percentages in water were proportional to the content of NVP in the copolymer. The copolymers displayed higher Cu2+ metal uptake capacity because of their amphiphilic nature. Such copolymer beads with higher ion chelating capacity and improved hydrophilicity may be more suitable for protein immobilization, catalysis, drug delivery etc. [14].

Recently Fatima Zohra Sebaa et al have been synthetic amphiphilic graft Copolymers with hydrophobic poly (α-methylstyrene) backbone and hydrophilic poly (N-vinylpyrrolidone) side chains [15]. we are aspirated from their procedure to product ower copolymer, this is a new method to synthesize this kind copolymer, different from that used by Hajime Karatani et all (Polymer Effect of 4-vinyl pyridine-N-vinylpyrrolidone copolymer is LummolChemiluminescence and Its Application to Determinations of Trace Copper (II)) [16].

This study has been conducted in order to produce amphiphilic graft copolymers with hydrophilic side chains of defined sizes. We have chosen a method using a precursory polymer [17, 18] using a macromonomer, which was prepared according to the indirect method using an unsaturated deactivating agent.

In the near future we will study the efficiency of our copolymer to Determinations of Trace Copper (II).

Our objective, in the very near future, is to investigate the application of the copolymer in prevention of corrosion and Application to Determinations of Trace Copper (II) then we will make a comparison of its performance with the copolymères synthesizes by Hajime Karatani et all[14].

MATERIALS AND METHODS

The monomers, N-vinyl-2-pyrrolidone (Sigma-Aldrich), and 4-Vinylpyridine (4VP) was distilled under reduced pressure and stored below 6°C. Perchloric acid (HClO4, Prolabo) is used as received. AIBN azobisisobutyronitrile (Fluka) was employed as the free radical initiator for the polymerization was used after recrystallization from ethanol. N,Ndimethylformamide (DMF) was purified by vacuum distillation before use. All solvents, ether and methanol were purified by standard procedures.

Synthesis of poly (N-vinyl-2-pyrrolidone) macromonomers PVP

N-Vinyl-2-pyrrolidone (PV) was dissolved in 10 mL of freshly distilled chloroform and then placed under nitrogen atmosphere in a three-necked flask equipped with a condenser and magnetic stirring. The flask was thermostated at 30 °C and then perchloric acid was introduced into the mixture.

<table>
<thead>
<tr>
<th>Tab. 1. Experimental conditions and cationic polymerization yields of N- vinyl-2- pyrrolidone initiated by HClO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macromonomer[monomer][HClO4][2HPMA]Yield mol L-1 mol L-1 mol L-1 %</td>
</tr>
<tr>
<td>PVP1</td>
</tr>
<tr>
<td>PVP2</td>
</tr>
<tr>
<td>PVP3</td>
</tr>
<tr>
<td>PVP4</td>
</tr>
<tr>
<td>PVP5</td>
</tr>
</tbody>
</table>

After 24h, 2-hydroxypropylmethacrylate was added to the reaction mixture. The polymerization was terminated upon introducing dimethylamine. The precipitate was filtered, washed off with ether and dried in vacuum.

Table 1 shows the experimental conditions and the experimental yields.

Synthesis of amphiphilic graft copolymer poly(4-Vinylpyridine)-graft-poly(N- vinylpyrrolidone)

10mL of freshly distilled DMF were placed in a three-necked flask provided with a condenser, nitrogen and magnetic bar and thermostated at 60 °C. The PVP macromonomer and 4-Vinylpyridine were dissolved in DMF. The
polymerization was initiated by AIBN (see Table 2). After 24 hours, the product was dissolved with methanol and the copolymer precipitated into an excess of ether. The copolymer was purified three times by such precipitation.

Tab. 2. Experimental conditions of the poly(4-Vinylpyridine)-graft-poly(N-vinylpyrrolidone) copolymers synthesis and molecular weight data

<table>
<thead>
<tr>
<th>Sample</th>
<th>[P]₀</th>
<th>[M]₀</th>
<th>[AIBN]</th>
<th>Mn (g mol⁻¹)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4VP-g-PVP1</td>
<td>0.321</td>
<td>2.50</td>
<td>0.02</td>
<td>67500</td>
<td>1.3</td>
</tr>
<tr>
<td>P4VP-g-PVP3</td>
<td>0.31</td>
<td>2.50</td>
<td>0.02</td>
<td>71000</td>
<td>1.32</td>
</tr>
<tr>
<td>P4VP-g-PVP5</td>
<td>0.18</td>
<td>2.50</td>
<td>0.02</td>
<td>75000</td>
<td>1.41</td>
</tr>
</tbody>
</table>

[P]₀: initial PVP macromonomer molar concentration as determined from UV analysis.
[M]₀: initial 4-Vinylpyridine comonomer molar concentration
[AIBN]: initial azobisisobutyronitril initiator molar concentration
P4VP-g-PVP1: poly (4-Vinylpyridine) – graft – PVP1
P4VP-g-PVP3: poly (4-Vinylpyridine) – graft – PVP3
P4VP-g-PVP5: poly (4-Vinylpyridine) – graft – PVP5
Mn: number-average molecular weight, Mw: weight-average molecular weight, and polydispersity (Mw/Mn) were all determined by GPC using poly(4-Vinylpyridine) standard and DMF as eluent.

RESULTS AND DISCUSSION

Characterization of PVP macromonomer
- UV analysis of methacryloyl chain end

UV analysis was employed to observe the fixation of the chromophoric oxopropylmethacrylate group on the PVP chain end and also to determine the number-average molecular weight (Mn) of the polymer. Assuming only one chromophoric group was attached to the polymeric chain end and using molecular extinction coefficient of a molecular model, in this case the 2HPMA, the molecular weights of the samples were calculated. Thus, with the aid of a calibration curve representing the variations of the optical density according to the 2HPMA concentration in acetonitrile, a curve closely following the Beer Lambert’s law (Figure 1) was obtained and it allowed to determine the 2HPMA molecular extinction coefficient taken as a model (ε = 8463 at λmax= 220 nm in acetonitrile).

Fig. 1. 2HPMA Calibration curve taken as a model (solvent: acetonitrile, λmax=220 nm) [15]
Figures 2, 3 and 4 show UV absorbance spectra of VP (λ_max = 235 nm), 2HPMA (λ_max = 220 nm) and PVP macromonomer (λ_max = 210 nm), respectively.

Fig. 2. UV absorbance spectra of VP in acetonitrile[15]

Fig. 3. UV absorbance spectra of 2HPMA in acetonitrile[15]

Fig. 4. UV absorbance spectra of ω-Oxopropylmethacrylate PVP macromonomer in acetonitrile
The UV absorbance spectra in Figure 4 shows the disappearance of the monomer double bond ($\lambda_{\text{max}} = 235$), and the appearance of a new maximum of absorbance at $\lambda_{\text{max}} = 210$ nm which characterizes the oxopropylmethacrylate double bond. The values of the number-average molecular weights of the polymer, which were obtained from UV analysis, are listed in Table 1.

**Determination of the number-average molecular weights by viscosimetry**

Viscosity measurements were used to determine average molecular weights of the synthesized polymer samples. The Mark-Houwink equation was employed to calculate the viscosity average molecular weights $[23, 24]$, $[\eta] = k \cdot M^a$. Table 1 provides the values of the average-number of molecular weights determined in three different ways: theoretically, by UV analysis and viscosity measurements.

<table>
<thead>
<tr>
<th>Macromonomer</th>
<th>$M_n$ (Theory)</th>
<th>$M_n$ (UV)</th>
<th>$M_n$ (Viscosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP1</td>
<td>500</td>
<td>750</td>
<td>8940</td>
</tr>
<tr>
<td>PVP2</td>
<td>1000</td>
<td>1290</td>
<td>1220</td>
</tr>
<tr>
<td>PVP3</td>
<td>2000</td>
<td>2100</td>
<td>1995</td>
</tr>
<tr>
<td>PVP4</td>
<td>2000</td>
<td>2100</td>
<td>2320</td>
</tr>
<tr>
<td>PVP5</td>
<td>3000</td>
<td>3150</td>
<td>3380</td>
</tr>
</tbody>
</table>

Values of the number-average of molecular weights determined by UV analysis and viscosity measurements are quite close to theoretical ones. These results suggest that the contribution of transfer reactions may be of little importance and therefore the reaction can be assimilated to a “living system”.

**FT-IR analysis**

The FT-IR spectra of the PVP macromonomer in Figure 5 shows a band absorption occurring at 1657 cm$^{-1}$ which corresponds to the carbonyl group (C=O) and a peak at 2980 cm$^{-1}$ due to C-H stretching in CH$_2$ and CH$_3$ groups. The bands appearing between 1423 and 1493 cm$^{-1}$ correspond to the CH$_2$ scissor vibration of a VP unit. The peak at 1292 cm$^{-1}$ is attributed to N-C stretching vibration.

**1H-NMR Analysis**

The macromonomer 1H-NMR spectrum plotted in Figure 6 shows the characteristic peaks of the $\omega$-oxopropylmethacrylate PVP.
Fig. 6. $^1$H-NMR spectrum of $\omega$-oxopropylmethacrylate PVP in CDCl₃

The resonance signals between 5.25-5.66 ppm correspond to protons “a” and “b”, respectively. The methine backbone protons “g” of the VP units appears as a broad peak at 5.41 ppm. Further, the methylene protons “d” show resonance signals at 4.18 ppm whereas protons “h, f”, “j”, “i” and “k” resonate at 3.40 ppm, 2.35 ppm, 2.63 ppm, and 1.998 ppm, respectively. Finally, the methane protons “e” and “c” show resonance signals at 1.12 ppm.

Characterization of poly(4-Vinylpyridine) – graft – PVP copolymers

$^1$H-NMR and $^{13}$C-NMR analysis of copolymers (P4VP-g-PVP)

The poly(4-vinylpyridine) – graft – PVP copolymers (P4VP-g-PVP) were characterized by $^1$H-NMR and $^{13}$C-NMR which generated the spectra shown in Figures 7 and 8, respectively.

$^1$H-NMR analysis of the PVP side chains confirms that the chains are capped with poly(4-vinylpyridine) backbone. Figure 10. The peak at δ=7.28 ppm is attributed to pyridine ring and the signal that resonates at 1.092 ppm is assigned to the -CH₃ of poly(4-vinylpyridine) backbone. The signals observed at 5.077 ppm and 1.958 ppm are attributed to the -CH–N– protons and –CH₂ – groups of the PVP side chains, respectively.

The $^{13}$C-NMR spectrum of the copolymer shows peaks 174.110-176.416 ascribed to carbon C=O of VP and C=O of HPMA respectively. The peaks observed at 41.790-47.605 ppm, and 31.415 ppm corresponds to the CN and CH₃ carbon atoms respectively.
Fig. 7. $^1$H-NMR spectrum of poly(4-vinylpyridine) – graft – PVP copolymer (P4VP-g-PVP) in DMSO

Fig. 11. $^{13}$C-NMR spectrum of poly(4-vinylpyridine) – graft – PVP copolymer (P4VP-g-PVP) in DMSO
CONCLUSION

In this study, oxopropylmethacrylate-terminated poly(N-vinyl-2-pyrrolidone) was produced by cationic polymerization using perchloric acid as an initiator. Termination (end capping) step was accomplished using 2-hydroxypropylmethacrylate and the polymer chains produced have molecular weight averages ranging from 500 to 3000 g/mol. Also, a series of amphiphilic graft copolymers were synthesized by free radical copolymerization, using azobisisobutyronitrile (AIBN) as an initiator. The graft copolymers consist of hydrophobic poly(4-Vinylpyridine) backbone and hydrophilic poly(N-vinyl-2-pyrrolidone) side chains.

REFERENCES

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