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

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ABSTRACT

Macromonomers of 2-oxopropylmethacrylate-terminated poly(N-vinyl-2-pyrrolidone) is produced by cationic polymerization using HClO_4 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 amphiphilic 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 M_n . However, a reverse behavior of the viscosity variation with regard to M_n 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, ^{13}C 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-pyrrolidone 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-pyrrolidone) 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) [Poly (4VP-*co*-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 over 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 LummoChemiluminescence 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 copolymers 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 azobisisobutyronitril (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.

Tab. 1. Experimental conditions and cationic polymerization yields of N- vinyl-2- pyrrolidone initiated by HClO₄

Macromonomer	[monomer]	[HClO ₄]	[2HPMA]	Yield
	mol L ⁻¹	mol L ⁻¹	mol L ⁻¹	%
PVP1	2.71	0.611	1.20	92
PVP2	2.65	0.31	0.5	91
PVP3	4.05	0.23	0.48	94
PVP4	3.10	0.17	0.32	89
PVP5	2.92	0.11	0.23	74

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

Sample	[P] ₀	[M] ₀	[AIBN]	M _n (g.mol ⁻¹)	M _w /M _n
P4VP-g-PVP1	0.321	2.50	0.02	67500	1.3
P4VP-g-PVP3	0.21	2.50	0.02	71000	1.32
P4VP-g-PVP5	0.18	2.50	0.02	75000	1.41

[P]₀: initial PVP macromonomer molar concentration as determined from UV analysis.

[M]₀: initial 4-Vinylpyridine comonomer molar concentration

[AIBN]: initial azobisisobutyronitrilinitiator 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

M_n number-average molecular weight, M_w weight-average molecular weight, and polydispersity (M_w/M_n) 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 (M_n) 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 ($\epsilon = 8463$ at $\lambda_{\max} = 220$ nm in acetonitrile).

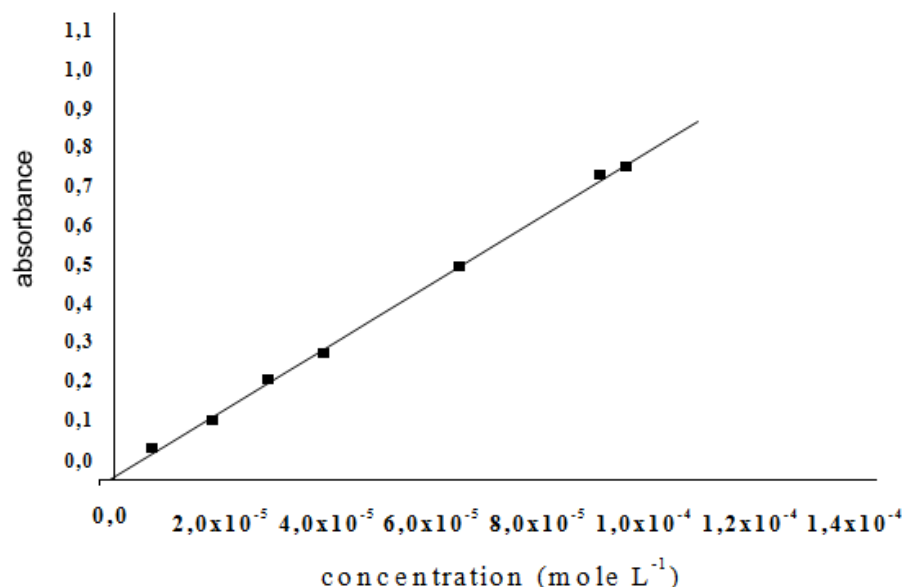


Fig. 1. 2HPMA Calibration curve taken as a model (solvent:acetonitrile, $\lambda_{\max} = 220$ nm) [15]

Figures 2, 3 and 4 show UV absorbance spectra of VP ($\lambda_{\max} = 235$ nm), 2HPMA ($\lambda_{\max} = 220$ nm) and PVP macromonomer ($\lambda_{\max} = 210$ nm), respectively.

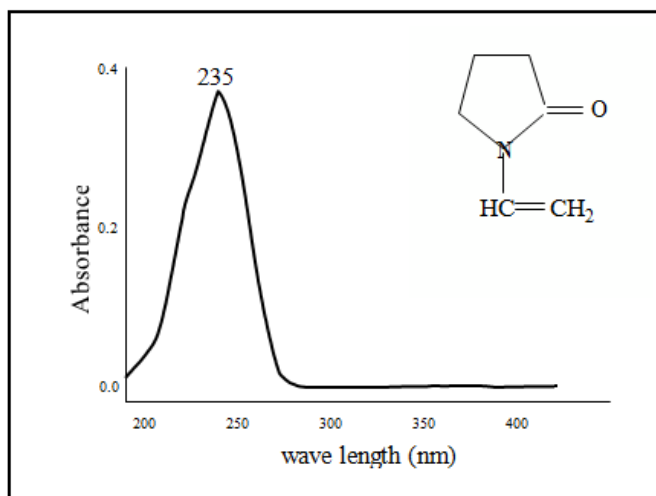


Fig. 2. UV absorbance spectra of VP in acetonitrile[15]

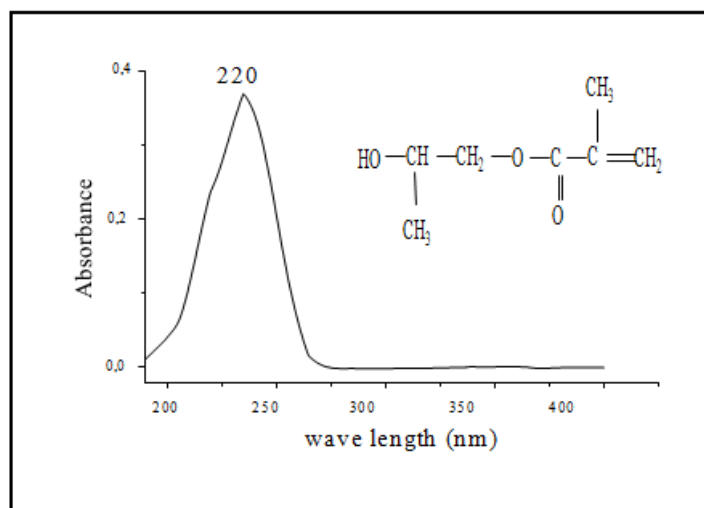


Fig. 3. UV absorbance spectra of 2HPMA in acetonitrile[15]

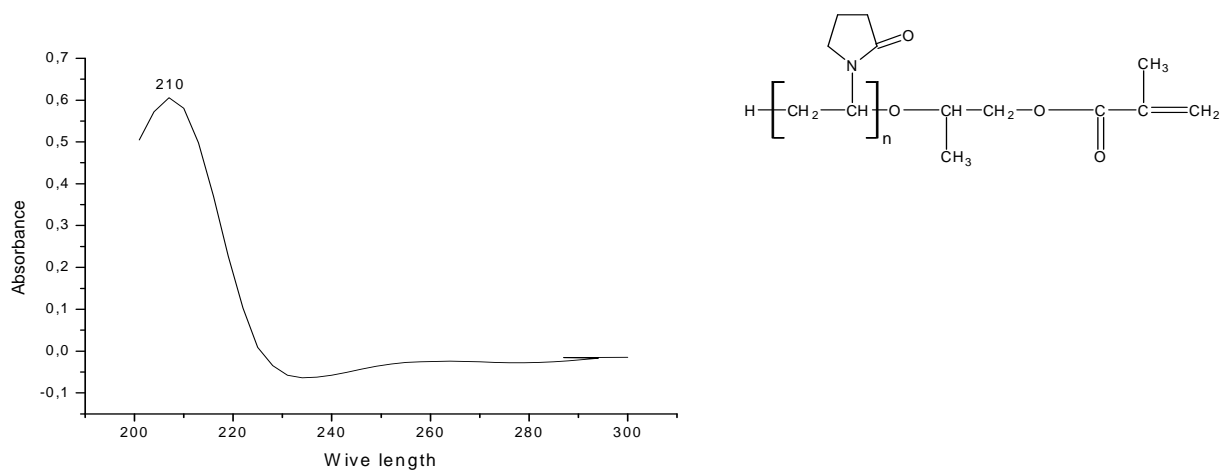


Fig. 4. UV absorbance spectra of ω -Oxopropylmethacrylate PVP macromonomer in acetonitrile

The UV absorbance spectra in Figure 4 shows the disappearance of the monomer double bond ($\lambda_{\max} = 235$), and the appearance of a new maximum of absorbance at $\lambda_{\max}=210\text{nm}$ 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], $[\eta] = k.M^a$. Table 1 provides the values of the average-number of molecular weights determined in three different ways: theoretically, by UV analysis and viscosity measurements.

Tab. 3. Number-average molecular weights of PVP polymers

Macromonomer	Mn (Theory)	Mn (UV)	Mn(Viscosity)
PVP1	500	750	8940
PVP2	1000	1290	1220
PVP3	2000	2100	1995
PVP4	2000	2100	2320
PVP5	3000	3150	3380

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.

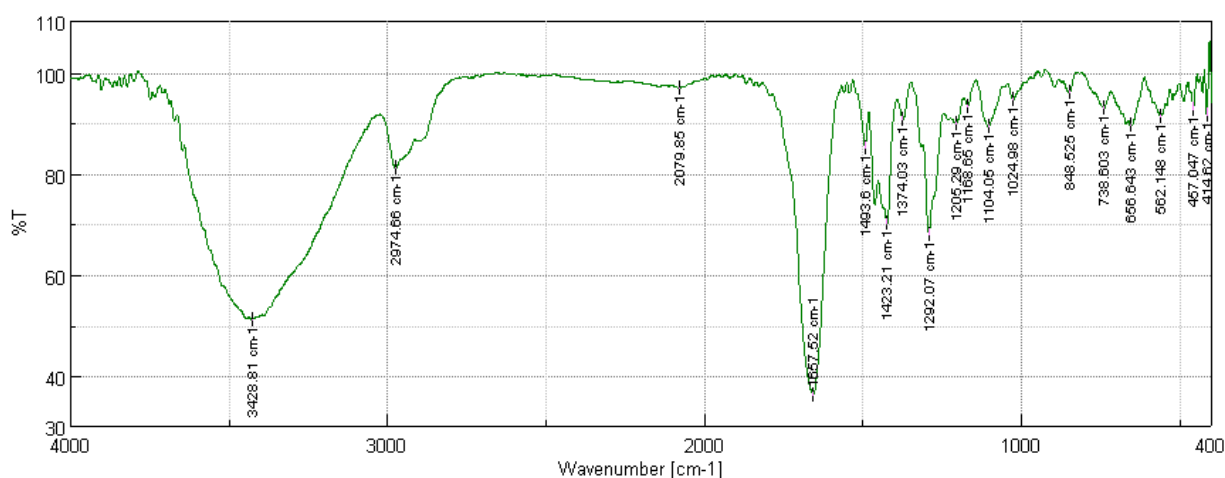


Fig. 5. FT – IR spectrum of the ω -oxopropylmethacrylate PVP in CHCl_3

The bands lying in the range wavelength of $1205 - 1024\text{ cm}^{-1}$ are assigned to the stretching C-O-C ester. However, peaks at lower wavelength of 738 cm^{-1} and 656 cm^{-1} correspond to the bending vibration of C-H and C-C, respectively. Upon observing the FT-IR spectra, one can notice the disappearance of the characteristic bands at 1630 and 981 cm^{-1} is related to the monomer double bond and the presence of a new characteristic peak at 1374 cm^{-1} which is due to the oxopropylmethacrylate double bond.

¹H-NMR Analysis

The macromonomer ¹H-NMR spectrum plotted in Figure 6 shows the characteristic peaks of the ω -oxopropylmethacrylate PVP.

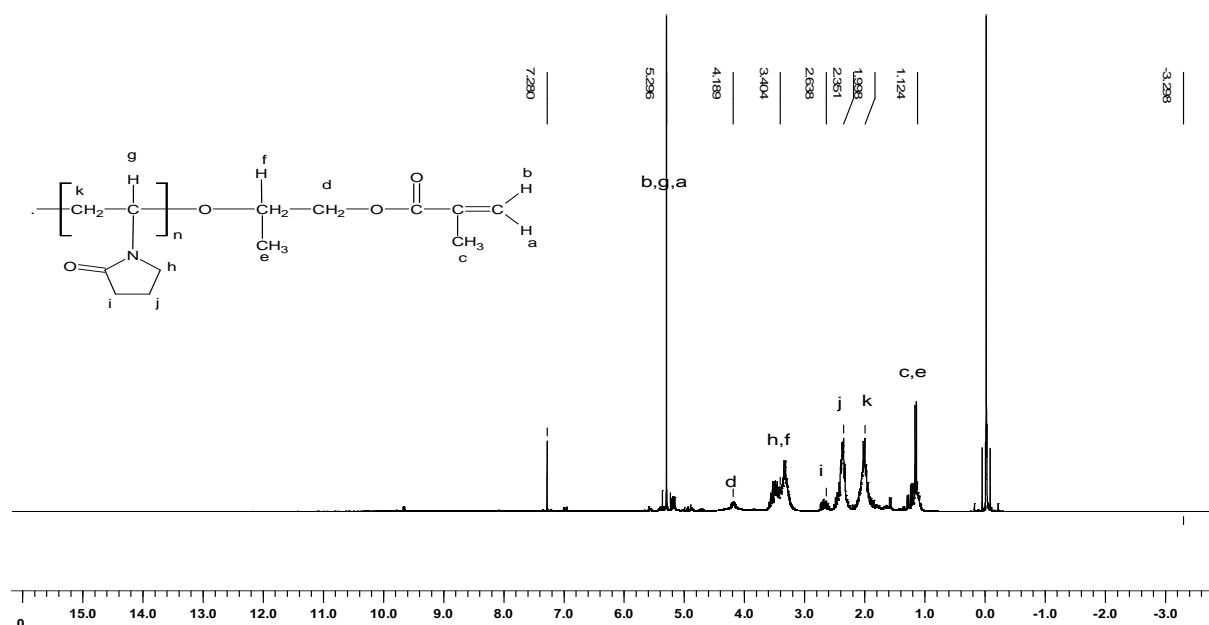


Fig.6. ¹H-NMR spectrum of ω-oxopropylmethacrylate PVP in CDCl₃

The resonance signals between 5.25-5.66ppm correspond to protons “a” and “b”, respectively. The methine backbone protons “g” of the VP units appears as a broad peak at 5.41ppm. Further, the methylene protons “d” show resonance signals at 4.18ppm whereas protons “h, f”, “j”, “i” and “k” resonate at 3.40ppm, 2.351ppm, 2.638, and 1.998ppm, respectively. Finally, the methane protons “e” and “c” show resonance signals at 1.12ppm.

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

¹H-NMR and ¹³C-NMR analysis of copolymers (P4VP-g-PVP)

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

¹H-NMR analysis of the PVP side chains confirms that the chains are capped with poly(4-vinylpyridine) backbone (Figure 10). The peak at δ=7.28ppm is attributed to the 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 and 1.958 ppm are attributed to the -CH-N- protons and -CH₂- groups of the PVP side chains, respectively.

The ¹³C-NMR spectrum of the copolymer shows peaks 174.110-176.416 ascribed to carbon C=O of VP and C=O HPMA respectively. The peaks observed at 41.790-47.605 ppm, and 31.415 ppm correspond to the CN and CH₂ carbon atoms respectively.

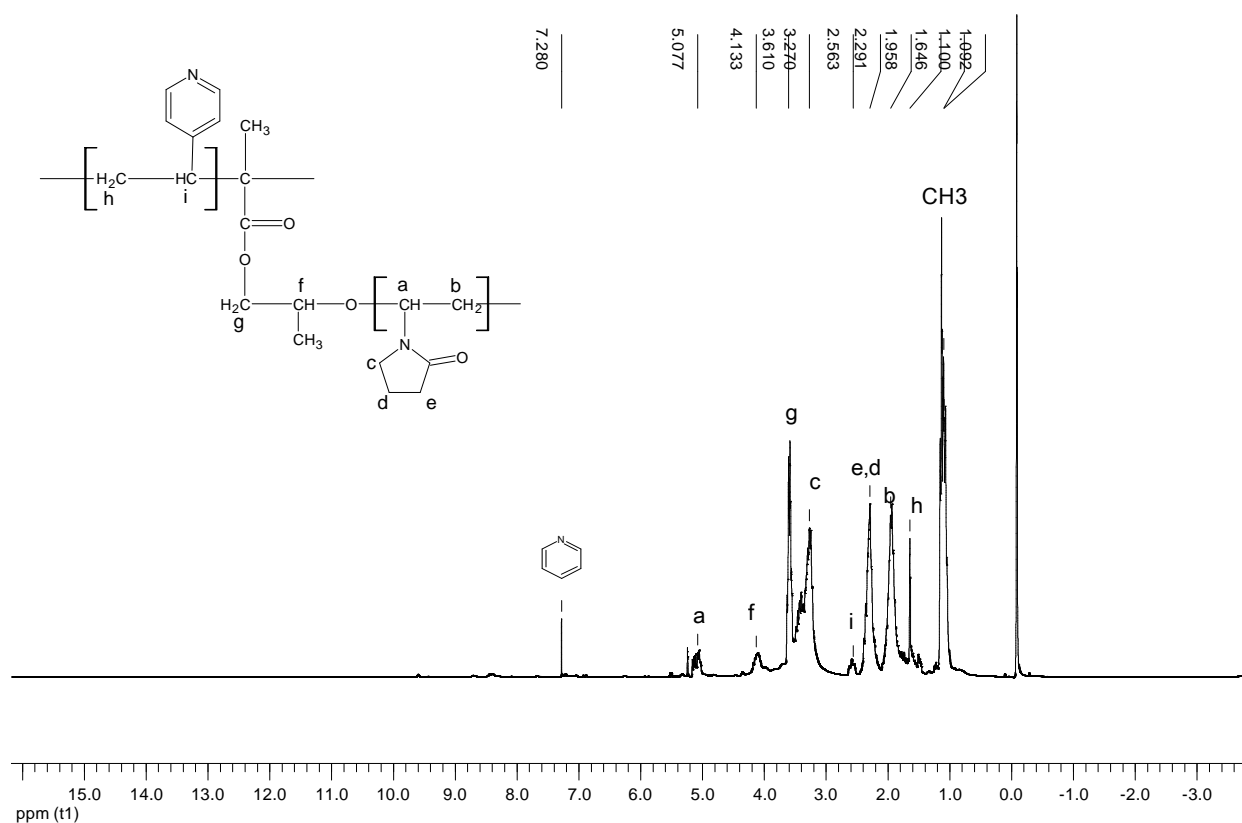


Fig. 7. ¹H-NMR spectrum of poly(4-vinylpyridine) – graft – PVP copolymer (P4VP-g-PVP) in DMSO

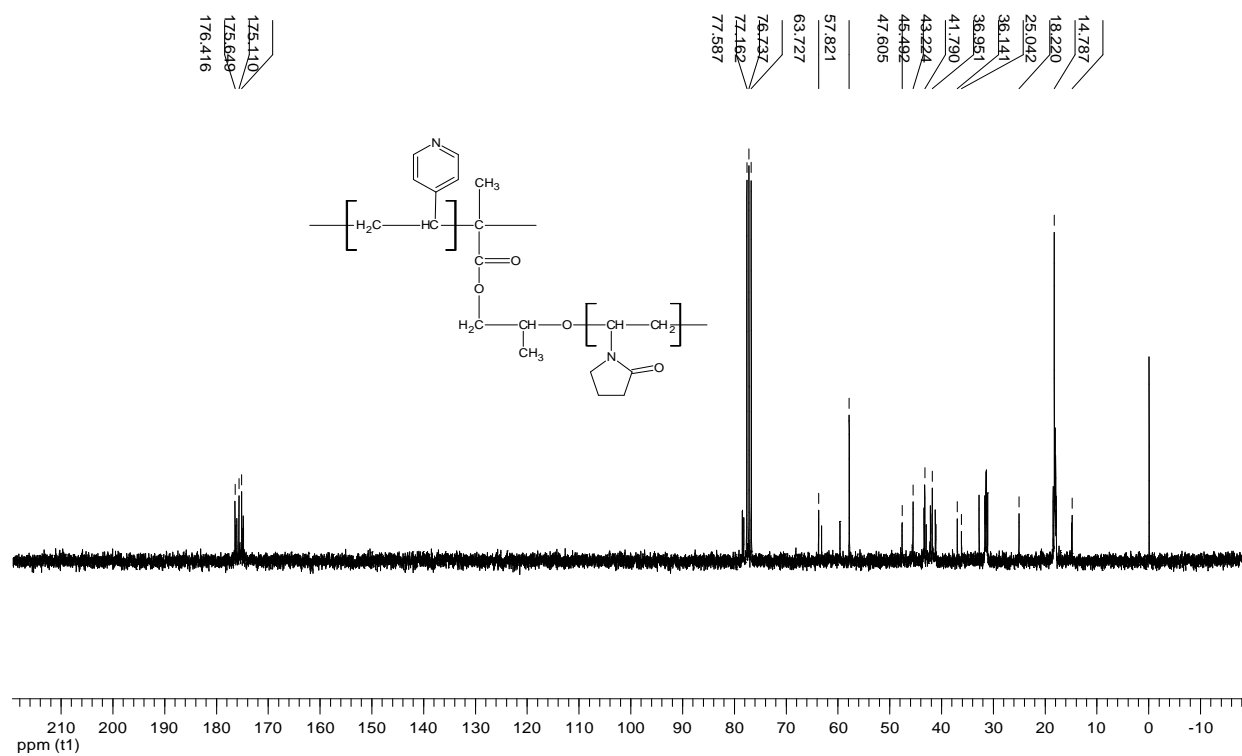


Fig. 11. ¹³C-NMR spectrum of poly(4-vinylpyridine) – graft – PVP copolymer (P4VP-g-PVP) in DMSO

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.

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