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Synthesis of poly(*N*-vinyl-2-pyrrolidone) and copolymers with methacrylic acid initiated by the photo-Fenton reaction

Gilmene Bianco, Marcelo H. Gehlen*

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13566-590 São Carlos, SP, Brazil

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Abstract

The photochemically enhanced Fenton reaction producing hydroxyl radicals is used as the initiation step of the free-radical polymerization of 1-vinyl-2-pyrrolidone (VP) and copolymerization with methacrylic acid (MAA) at room temperature. The poly(*N*-vinyl-2-pyrrolidone) (PVP) homopolymer obtained by photo-Fenton method has a low molecular weight ($M_\mathrm{w} = 54{,}000\,\mathrm{g\,mol^{-1}}$) and polydispersity of about 3.1. The copolymerization of VP with MAA results in statistical copolymers with molecular weight in the range of $(80–230) \times 10^3\,\mathrm{g\,mol^{-1}}$ and polydispersity in between 2.4 and 1.7, when using a feed composition of MAA from 10 to 40 wt.%. The copolymers have high percent of MAA relative to feed composition due to the higher reactivity ratio of MAA compared with VP. The photopolymerization rate is determined from dilatometry measurements, and its dependency with concentration of the Fenton reagent is established.

Keywords: Poly(*N*-vinyl-2-pyrrolidone); Photo-Fenton; Free-radical initiation

1. Introduction

Polymeric materials based on poly(*N*-vinyl-2-pyrrolidone) (PVP) and its copolymers have found intense applications as hydrogels and membranes used in drug-delivery systems, adhesives formulations, and in photographic and lithographic coatings [1]. The low chemical toxicity of PVP, its solubility properties in water and in organic solvents as well as its ability to complex with many kind of substrates like dyes, surfactants, and other polymers [2–4], have promoted its use as a protective colloid in pharmaceutical and cosmetics products.

The commercial production of PVP is carried out mainly by a free-radical polymerization of 1-vinyl-2-pyrrolidone solution in water with hydrogen peroxide as initiator and ammonia as activator [1]. The initiation step in that method is the thermal decomposition of the peroxide forming hydroxyl radical which attacks the vinyl double bond producing the macro-radical of the propagation step. The polymer formed has a molecular weight in the range of 10^3–10^6, depending on the temperature and chemical composition of the reaction system. The bulk polymerization in the presence of hydrogen peroxide is also possible by heating the system about 100 °C, but the final product usually has a low molecular weight and a high polydispersity. Azo-initiators have been also applied in polymerization and copolymerization with the convenience of working at a lower temperature [5–7]. The disadvantage of azo-initiators is the possible introduction of harmful and toxic chemical side products as compared to the hydrogen peroxide decomposition method. This is an important issue in view of the special applications of PVP polymers.

1-Vinyl-2-pyrrolidone (VP) may also be polymerized with H_2O_2 under UV radiation yielding high molecular weight polymers [8]. The need of far UV radiation, the low extinction coefficient of the peroxide and the light absorption by the monomer in the UV region, reduce the application of that procedure. Photoinitiators based on redox systems containing aromatic compounds and aliphatic amines have been also used in radical polymerization of VP [9,10].

In this work, we introduce an initiating step based on the peroxide photo-decomposition using a Fenton reagent. The polymerization of VP and its copolymerization with methacrylic acid (MAA) initiated by photo-Fenton reaction are investigated. Molecular weight, degree of polymerization, and polydispersity of the products are determined by size exclusion chromatography (SEC). Copolymer composition is determined from elemental microanalysis and conductometric titration with NaOH. The products are analyzed by ^{13}C RMN and FTIR spectroscopies, and the glass transition temperatures are determined by thermalgravimetric

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* Corresponding author. Tel.: +55-16-273-9951; fax: +55-16-273-9952.
E-mail address: marcelog@iqsc.sc.usp.br (M.H. Gehlen).

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analysis. The polymerization rates are determined from photodilatometry, following basic procedures described in the literature [11–15].

2. Experimental

N-Vinyl-2-pyrrolidone (VP) and MAA from Aldrich were used after removing their inhibitors by standard treatments. Hydrogen peroxide at 30%, and ferrous sulfate from Synth were used as received.

The polymerization of VP was carried out using an aqueous 5 M solution of the monomer. In the copolymerization experiments, the amount of MAA relative to VP was varied up to 40% in weight, but the total concentration of vinyl monomers was kept constant at 5 M. The Fenton reagent was an aqueous solution in the monomer medium of 2.5×10^{-4} M of $FeSO_4$ and 0.01 M of H_2O_2 with a pH of about 4.5. The solutions containing the Fenton reagent were irradiated at 365 ± 10 nm using a monocromator and 200 W high pressure Xenon lamp, with samples placed into quartz tubes at room temperature (300 K). The extinction coefficient at 365 nm of the Fenton reagent is $7\,\mathrm{mol\,l^{-1}\,cm^{-1}}$.

PVP was precipitated in acetone and washed several times with this solvent to remove unreacted monomer. The copolymers were precipitated in water given a white solid which was filtered and washed with water to remove unreacted water soluble monomers. All samples were dried under vacuum in a dessecator before analysis.

The molecular weight distributions of polymers were determined by SEC using a Schimadzu chromatograph (RID-6A detector) with an ASAHIPAK GS-520+320 column. The solvent was a $NaNO_3$ 0.1 M aqueous solution/ methanol in a 80/20 (v/v) mixture (flow rate of $1\,\mathrm{ml\,min^{-1}}$). The molecular weight standard was poly(acrylic acid)-sodium salt from Polymer Laboratories (calibration kit 2140-0100 PAA/01). The ^{13}C RMN spectra were recorded on a Bruker DRX 400 spectrometer with polymer samples in D_2O. The IR spectra were measured in a Bomem MB 100 FTIR spectrophotometer. Thermal analysis was performed in a Schimadzu equipment with a DSC-50 module. The DSC scans were recorded in N_2 atmosphere with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ and using 8 ± 1 mg of powdered samples. All samples were submitted to a previous heating scan to eliminate residual traces of solvent and water. The recorded data was then obtained in a second scan of the sample previously treated.

The fractions of MAA in the copolymers were determined from conductometric titration with standard NaOH base, and the results were compared with the data obtained from CHN microanalysis (Perkin-Elmer, Model 2400).

The light induced polymerization was monitored by dilatometric measurements using a home made equipment consisting of an irradiation system and a capillar dilatometer containing two capillaries attached to a cylindrical reaction vessel. The irradiation system is based on a 200 W Hg (Xe) lamp and Oriel power supply, water filter for IR blocking, and a monocromator for wavelength selection, all aligned in an optical rail.The reaction vessel, 12 ml volume and an internal diameter of 2.5 cm, was placed in a constant temperature bath ($30\pm0.02\,^{\circ}$C) in front of the light beam. The light intensity at 365 nm, determined by using a $K_3[Fe(C_2O_4)_3]$ chemical actinometer, had a value of $4.3\times10^{-10}\,\mathrm{einstein\,s^{-1}}$. The polymerization rates (R_p) were calculated using the following equation [11,12]:

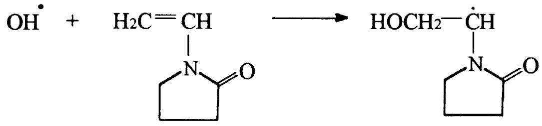
$$R_\mathrm{p} = \frac{\Delta h}{Ff\Delta t}[m] \tag{1}$$

where h is the contraction per volume ($\Delta V/V$, where V is the initial volume) in the capillary (measured with a cathetometer) at time t, f the volume fraction of the monomer in solution, $[m]$ the molar concentration of monomer, $F = (d_\mathrm{p} - d_\mathrm{m})/d_\mathrm{p}$ is the contraction factor related with the densities of the polymer and the monomer. In the situation of a copolymerization, it is assumed that the volumetric change is additive, and the overall rate observed is related to the sum of contraction effects of the two monomers each one related to its proper F and f factors.

3. Results and discussion

The initiation step of the polymerization kinetics of VP by thermal decomposition of hydrogen peroxide is described by the following mechanism [1]:

$$H_2O_2 \overset{\Delta}{\rightarrow} 2OH^{\bullet} \tag{2}$$



(3)

The initiation step forming hydroxyl radicals by thermal decomposition of peroxide (Eq. (2)) may be replaced by a photochemically enhanced Fenton reaction [16,17]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \tag{4}$$

$$Fe^{3+} + H_2O \overset{h\nu}{\rightarrow} Fe^{2+} + H^+ + OH^{\bullet} \tag{5}$$

with irradiation of the samples in the 365 nm region. The advantage of this procedure is that the photopolymerization reaction at room temperature can be controled by changing the light intensity and the concentration of the Fenton reagent.

The present results show that PVP obtained by the photo-Fenton initiation method has a molecular weight of $54{,}000\,\mathrm{g\,mol^{-1}}$ and a polydispersity of about 3.1 (see Table 1). The termination step occurs presumably by hydroxyl radical recombination with the macro-radical. The characteristic ^{13}C RMN signals of the initiating chain group –CH_2–OH and of the terminal group –RCH–OH were observed at 71.6 and 74.5 ppm, respectively supporting the

Table 1
Molecular weight (M_w), polydispersity (σ), monomer composition and glass transition temperature (T_g) of PVP and poly(VP-co-MAA) obtained by photo-Fenton reaction[a,b]

Feed (wt.%)	M_w (g mol^{-1})	σ	MAA (wt.%)	T_g (K)
0	54000	3.1	0	446
10	82000	2.4	36 (42)	432
20	133000	2.1	50 (48)	438
30	155000	2.1	46 (41)	438
40	191000	1.7	53 (50)	437

[a] $[H_2O_2] = 0.01$ M; $T = 300$ K.

[b] Value within brackets is the weight percent of MAA in the copolymers determined from CHN elemental microanalysis.

assumption of initiation and termination by the hydroxyl radical. The ^{13}C NMR spectrum of PVP in D_2O in the complementary region of 15–50 ppm obtained here was similar to the reported data in literature [18–20].

It should be mentioned that without light, there is practically no polymerization. The photochemically enhanced Fenton reaction, due to the feedback characteristic of the Fe^{2+}/Fe^{3+} coupled equilibrium, should give a higher concentration of hydroxyl radical in the photostationary state, and therefore to a higher stationary concentration of initiation centers for polymerization.

Copolymerization of VP with MAA was readily achieved by the photo-Fenton method of initiation. The properties of the copolymers obtained are summarized also in Table 1. The copolymers have higher molecular weight than that of homopolymer PVP. A comparison of size distribution from SEC analysis of PVP and poly(VP-co-MAA) is illustrated in Fig. 1. The polydispersity of the copolymers are smaller than that obtained for PVP.

The amount of MAA monomer in the copolymers was determined from CHN analysis as well as from conductometric titration with NaOH. In all the samples, the weight percent compositions of monomers determined by the two methods were similar. The final percent of MAA in the copolymer is larger than the percent used in the initial reaction feed. The higher reactivity of MAA and its self and cross association-addition rate to VP by hydrogen bonding and further interaction with the macro-radical may enhance its incorporation into the polymer chain even when used in a low mass percent relative to MAA in the reaction bath. The participation of H-complexes in copolymerization of acrylic acid with VP has been discussed in the literature [21]. Previous results have shown that the mole fraction of VP incorporated into the copolymer with acrylic acid has a small change from about 0.43 to 0.53 with a change from 0.6 to 0.9 molar fraction of VP in the monomer feed composition. This same trend appears in the data of Table 1 where copolymer composition is given as a function of the weight percent in the feed.

The reactivity ratios of MAA + VP determined according to the Fineman–Ross method [22], are: $r_{\mathrm{MAA}} = 0.56$ and $r_{\mathrm{VP}} = 0.04$ at 300 K as measured by the photo-Fenton initiation method. The product of the reactivity ratios is less than 1, indicating that the copolymer has a tendency toward alternation, but the larger r_{MAA} results in a copolymer richer in MAA monomer.

The glass transition temperature (T_g) of the PVP and copolymers were determined and their values are listed on Table 1. The value of T_g for PVP is in agreement with data reported in literature of 448 K [23]. The change on the T_g value of the poly(VP-co-MAA) can be ascribed to an interplay of two effects. The incorporation of MAA decreases the T_g of the copolymer when compared with PVP, reflecting the effect of a lower T_g for MAA when compared with the homopolymer of PVP. On the other hand, the increase of molecular size favors an increase of T_g.

A typical plot of the monomer conversion as a function of time is illustrated in Fig. 2. The rates of polymerization and copolymerization were determined from the linear plots of

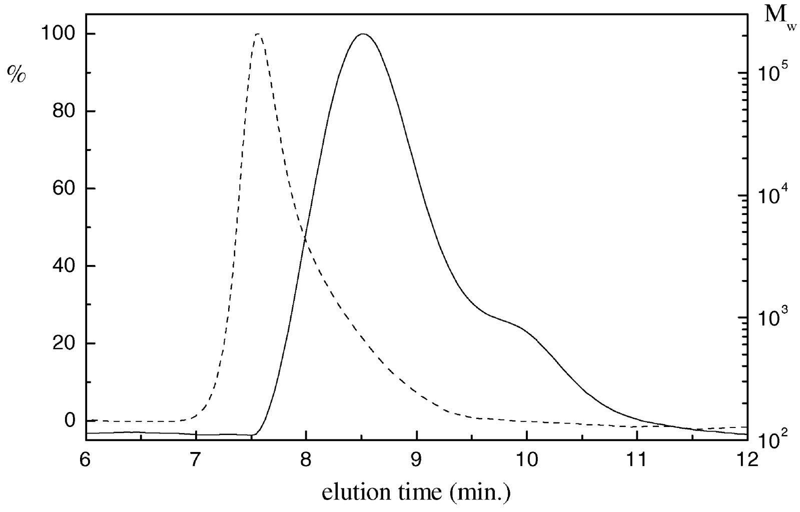


Fig. 1. SEC profiles of PVP (solid line) and poly(VP-co-MAA) (dashed line) obtained from radical polymerization and copolymerization (feed was 40% of methacrylic acid) initiated by photo-Fenton reaction.

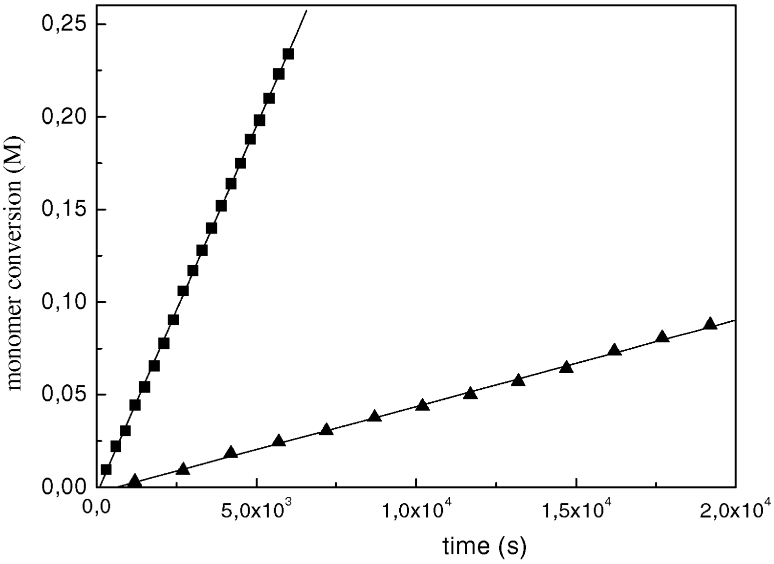


Fig. 2. Monomer conversion as a function of irradiation time obtained from photodilatometry. (▲): Polymerization of VP; (■): copolymerization of VP with MAA (90 wt.% of VP); $T = 300$ K.

the dilatometric measurements as a function of time, following Eq. (1). In the case of copolymerization, the density of the copolymer was practically independent of composition, and therefore an average density $d_p = 1.15$ was assumed. The values of R_p are reported in Table 2, together with the respective polymerization yields. The R_p in copolymerization increases by 10-fold in the first addition of MAA as a result of the higher reactivity in cross-propagation. However the value of R_p quickly saturates, and for concentrations of MAA larger than 20 wt.%, there is a small lost of efficiency.

The polymerization rate of VP depends on the concentration of added Fe^{2+}, as seem from the data in Fig. 3. Considering that most of the hydroxyl radicals formed react with the vinyl monomer due to its high concentration in solution, the photostationary condition gives

$$\frac{1}{2}k_{in}[m][OH^{\bullet}] = k[Fe^{2+}][H_2O_2] = \Phi I_a, \qquad (6)$$

where k and k_{in} are the rate constant of hydroxyl radical production (Eq. (4)) and of addition reaction of hydroxyl radical to VP, respectively, Φ and I_a are the photochemical quantum yield and absorbed light intensity of the reaction step given in Eq. (5), respectively.

Table 2
Rate constants and yields of the polymerization and copolymerization of VP with MAA initiated by photo-Fenton method[a]

Feed (wt.%)	R_p ($\times 10^{-5}$ M s^{-1})	$\Phi_p (\times 10^{-3})$
0	0.5	1.3
10	4.0	11.2
20	4.8	13.5
30	3.9	10.8
40	3.6	10.0

[a] $[H_2O_2]$: 0.01 M; T: 300 K; and $I_0 = 4.3 \times 10^{-10}$ einstein s.

The saturation behavior observed in the plot of polymerization rate as a function of the initial $[Fe^{2+}]$ concentration is ascribed in part to an inter-conversion of Fe^{2+}/Fe^{3+}, and the correction of this effect would approach the rate to the half-power of the initiator concentration. However, the inhibition of monomer radicals by Fe^{3+} in a redox process is not ruled out, and could be an important factor at a high iron concentration. The correlation of the polymerization rate with the absorbed light intensity by Fe^{3+} is difficult to obtain due to the overlap of the absorption spectra of several species present in solution.

Finally, copolymers were synthesized at a higher concentration of hydrogen peroxide. The properties of the copoly-

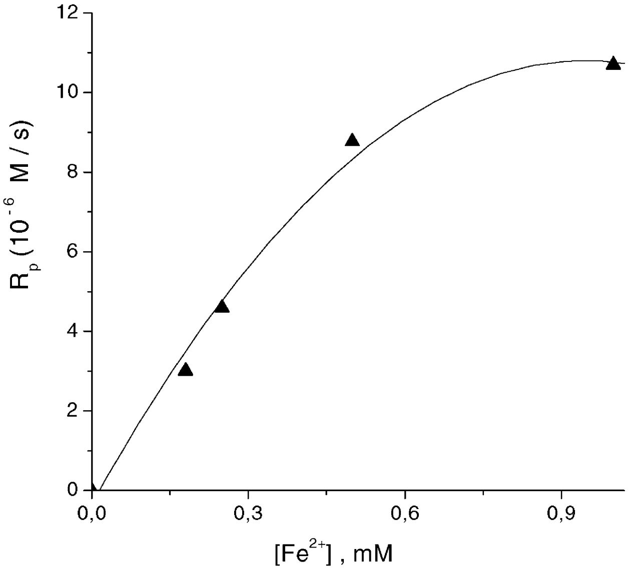


Fig. 3. Rate constant of VP polymerization as a function of the initial concentration of iron(II). $T = 300$ K.

Table 3
Poly(VP-co-MAA) prepared at high concentration of $[H_2O_2] = 0.1\,M$ by photo-Fenton reaction[a]

Feed (wt.%)	M_w ($g\,mol^{-1}$)	σ	MAA (wt.%)
10	52000	3.9	47 (46)
20	102000	2.3	40 (37)
30	134000	2.2	49 (53)
40	114000	2.1	57 (55)

[a] Value within brackets is the weight percent of MAA in the copolymer determined from CHN elemental microanalysis.

mers obtained by the photo-Fenton reaction are reported in Table 3. A decrease of M_w and an increase of polydispersity are observed in agreement with what is expected from radical polymerization mechanism as the initiator concentration is increased.

4. Conclusions

The photo-Fenton reaction has been largely applied in oxidative degradation of organic pollutants for water treatment [16,17], and in some special cases in depolymerization technique [24,25]. This is the first case where the method is used to produce polymer and copolymers of VP widely employed in the industry. The advantage of the proposed method is the convenience of working at room temperature, as well as allowing a control of the initiating step by changing the reaction conditions. Formally, the method of initiation is a dual process, containing a thermal (Eq. (4)) plus a light assisted step (Eq. (5)) for hydroxyl radical generation. Using low light intensity and low concentration of the Fenton reagent, most of the hydroxyl radicals formed will react with the vinyl monomers producing propagating radicals. The properties of polymers obtained resemble those obtained by traditional thermal peroxide decomposition.

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