

Research Article

Synthesis of Poly(*N*-vinyl-2-pyrrolidone-co-methyl methacrylate) by Maghnite-H⁺ a Non-toxic Catalyst

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Abstract

In the present work poly (*N*-vinyl-2-pyrrolidone-co-methyl methacrylate) copolymers were prepared successfully and cleanly by a one step process via cationic copolymerization of *N*-vinyl-2-pyrrolidone (NVP) with methyl methacrylate (MMA), in heterogeneous phase using “Maghnite-H⁺” (Mag-H⁺) as catalyst in bulk, Maghnite is a montmorillonite sheet silicate clay exchanged with protons to produce Maghnite-H⁺. Temperature is varied between 20 and 80 °C. The effects of reaction temperature, amount of Mag-H⁺ on the yield and the intrinsic viscosity (η) were investigated. A typical reaction product of poly (NVP-co- MMA) was analyzed by infra red spectroscopy (FTIR) and ¹H-NMR, ¹³C-NMR spectroscopy as well as by viscosimetry. © 2014 BCREC UNDIP. All rights reserved

Keywords: Maghnite-H⁺; *N*-vinyl-2-pyrrolidone; methylmethacrylate; montmorillonite; copolymerization

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1. Introduction

Poly (MMA) (PMMA) is one of the best polymeric materials broadly used for insulation devices manufacture. Its electrical properties are highly influenced by many environmental parameters such as temperature, mechanical constraints, and humidity. Therefore, investigations on the effects of these constraints have been made by numerous researchers [1-3]. Recently, Ajithkumar *et al.* showed a redox copolymerization of *N*-vinyl-2-pyrrolidone (NVP) with methyl methacrylate (MMA) using titanium(III)-dimethylglyoxime [Ti(III)-DMG] as a redox initiator in aqueous sulfuric acid-alcohol media [4]. Poly (*N*-vinyl-2-pyrrolidone) (PNVP)

has received increasing attention as a material for numerous applications in medicine applications in medicine and pharmaceuticals because of its ability to bind reversibly to various molecules in solution while maintaining excellent biocompatibility with the human body [5-10]. Moreover, various types of copolymers such as vinyl chloride/methyl methacrylate [11], styrene/methyl methacrylate [12], vinyl pyrrolidone/ethylene dimethyl acrylate [13] were produced using suspension polymerization. In this respect, it is even more interesting to use “Maghnite-H⁺” as catalyst to prepare (NVP-MMA) copolymers by one step in bulk at room temperature. Mag-H⁺, a new non-toxic catalyst can be easily separated from the polymer product and regenerated by heating to a temperature above 100 °C [14]. Maghnite has both Brönsted and Lewis acid sites and when ex-

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changed with cations having a high charges density, as protons, produce highly active catalysts for acid-catalysed reactions. Intercalated organic molecules are mobile and can be highly polarized when situated in the space between the charge clay layers. These exchanged Montmorillonites have been successfully used as catalysts for the reactions polymerization [15-21]. The purpose of this paper is also to study the copolymerization of NVP with MMA. The novelty of this search for new initiators remains a subject of topical interest. There is still a great demand for heterogeneous catalysis under mild conditions and environmentally friendly processes. Montmorillonite, a class of inexpensive and noncorrosive solid acids have been used as efficient catalysts for variety of organics reactions. The reactions catalyzed by montmorillonites are usually carried out under mild conditions with high yields and high selectivities and workup of these reactions is very simple, only filtration to remove the catalyst and evaporation of the solvent are required. Montmorillonite catalysts are easily recovered and reused [22, 23].

2. Material and Methods

2.1. Materials

Maghnite-H⁺ was prepared according to the process similar to that described by Belbachir *et al.* [14]. Raw-Maghnite (20 g) was crushed for 20 minutes using a prolabo ceramic balls grinder. It was then dried for 2 hours at 105 °C the Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until saturation was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried at 105 °C. N-Vinyl-2-pyrrolidone, was obtained from Aldrich, dried over CaH₂ and distilled under vacuum. Methyl methacrylate purchased from Aldrich were sequentially washed with NaHSO₃ aqueous solution and water and then dried

with anhydrous CaCl₂, followed by distillation in a nitrogen atmosphere under reduced pressure. The yield calculation formula is:

$$\text{Yield} = \frac{\text{mass of product obtained (copolymer)}}{\text{theoretical mass of products (mass of monomer (MMA) + mass of monomer (NVP)}}$$

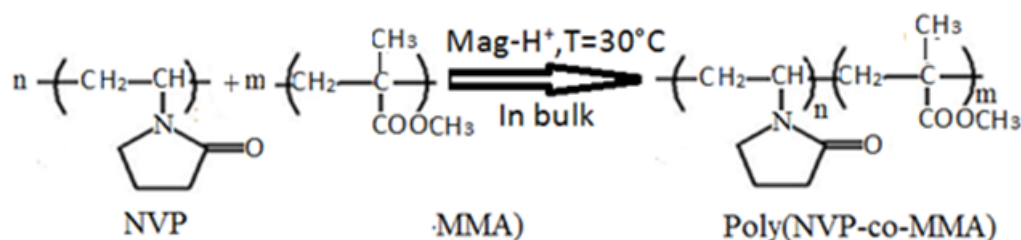
2.2. Procedure and Copolymer Characterization

Copolymerizations were carried out in stirred flasks at different temperatures between 20 and 80 °C. The catalyst was dried in a muffle at 120 °C over night and then transferred to a vacuum desiccator containing P₂O₅. After cooling to room temperature under vacuum, the mineral was added to the N-vinyl-2-pyrrolidone (1 g, 0.009 mol), Methyl methacrylate (5 g, 0.05 mol) mixture preliminary kept in stirred flask. At the required time, an aliquot of the reaction mixture was then taken in such manner as to exclude any clay mineral and slowly added to methanol with stirring. The precipitated copolymer was filtered off and dried under vacuum and weighed. Intrinsic viscosity (η) measurements were performed at 25 °C in acetone using a capillary viscometer SEMATECH (VISCOLOGIC TL1). The sample concentration was 1 mg/ml. ¹H-NMR and ¹³C-NMR spectra were recorded on an AM 300 FT Bruker instrument using deuterated chloroform as solvent, and tetramethylsilane (TMS) as internal standard. FT-IR measurements were performed using Alpha-FTIR-Spectrometer BRUKER optics Diamond ATR.

3. Results and Discussion

3.1. Characterization of Products

The FTIR spectrum of the copolymer (Figure 1), the reaction taking place is shown in Scheme 1. The characteristic absorption bands of PMMA are clearly visible, the C=O stretching vibration of ester group appears around 1723 cm⁻¹, the two doublet bands at (1143,



Scheme 1. Synthesis of Poly (NVP -co-MMA)

1189 cm^{-1}) and (1238 cm^{-1}) correspond to the C–O stretching vibrations of ester groups [24]. The absorptions around 1387 and 1428 cm^{-1} characterize the asymmetric bending vibrations of (C–CH₃) and (C–CH₂) bonds, respectively. PNVP represents a strong C=O absorption peak from the amide group of the copolymer at 1695 cm^{-1} . A medium strong absorption band of the C–N group appears at 1278 cm^{-1} , and C–H stretching vibration frequencies are observed near 2949 cm^{-1} .

The ¹³C NMR spectrum of NVP/MMA copolymer in CDCl₃, along with the signal assignments, is shown in Figure 2. The carbonyl car-

bon (C=O) signals for both PNVP and PMMA resonate around 173.81-174.27 and 176.89-177.93 ppm. The side chain ring methylene carbon signals are assigned around δ 41.77 (^cCH₂), δ 29.24-29.64 (^eCH₂) and δ 16.42-17.94 ppm [25]. The methine and methylene carbon signals resonates around δ 45.20-45.90 (^bCH) and δ 31.15-31.32 (^aCH₂), the side chain ppm of PNVP, and The chemical shifts of various carbons in PMMA units of the copolymer are summarized below: δ 44.52-44.58 (^kC), δ 51.75 (ⁱCH₃), δ 54.23 (^gCH₂) δ 16.42-17.94 (^hCH₃) [26].

The structure of the Poly (NVP -co- MMA) was determined by ¹H-NMR. Figure 3 shows

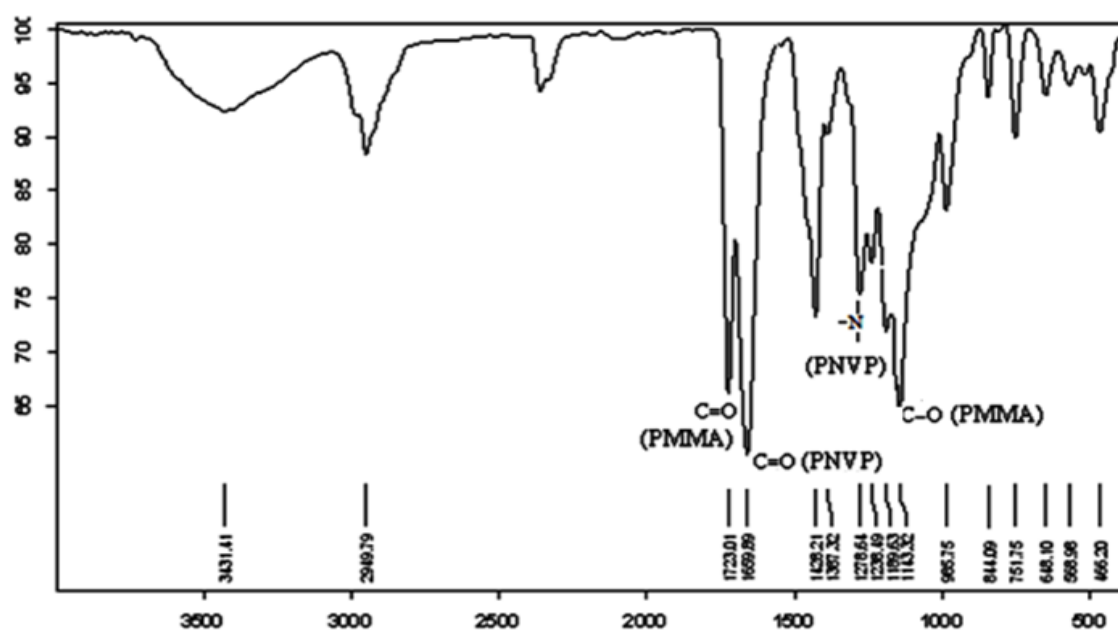


Figure 1. FTIR spectrum of Poly (NVP-co-MMA)

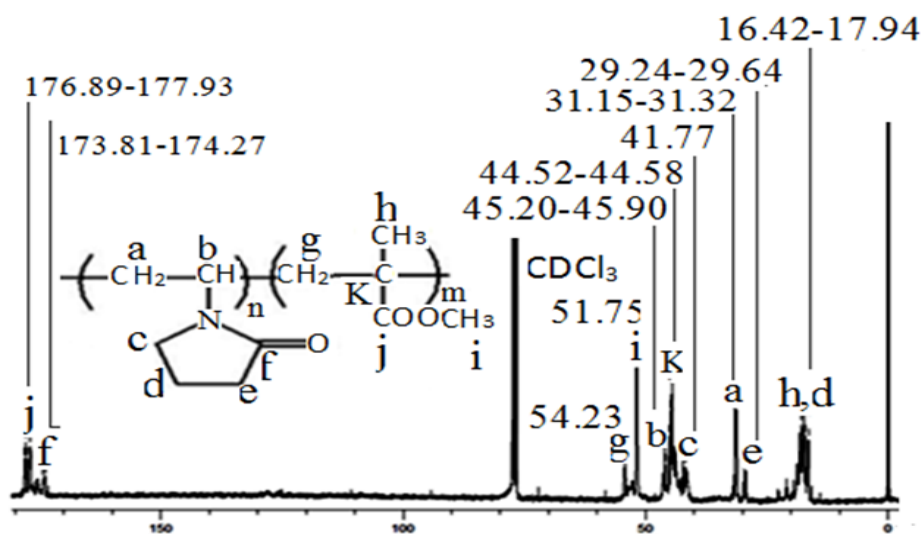


Figure 2. ¹³C-NMR spectrum of Poly (NVP-co-MMA)

the chemical shifts of PNVP, the methine and methylene proton signals resonates around δ 4.26-4.34 and 1.87 ppm. The side chain methylene proton signals can be assigned around δ 3.16-3.25 ($^c\text{CH}_2$), δ 2.38 ppm ($^e\text{CH}_2$) and δ 2.16 ppm ($^d\text{CH}_2$) [25]. Respectively, and others attributed to PMMA, the methoxy protons appear at 3.58 ppm ($^h\text{CH}_3$), methyl protons at 0.82-1 ppm ($^g\text{CH}_3$) and methylene protons between 1.82 ppm ($^f\text{CH}_2$) [27].

3.2. Effect of Temperature on Copolymerization.

Table 1 shows the experimental results for the copolymerization of VP (0.009 mol) with MMA (0.05 mol) induced by "Maghnite- H⁺ 0.25 M" proceed in bulk at different temperatures. It was found that Maghnite-H⁺ by itself possesses good activity as catalyst for the copolymerization. The yield of copolymerization and the intrinsic viscosity reach maximum values around 60-80 °C. On the other hand, with the increase in the reaction temperature above 90 °C the intrinsic viscosity and the yield of the obtained copolymers decrease progressively suggesting the possible occurrence of thermal degradation.

3.3. Effect of Amount of Mag-H⁺ on Copolymerization

The effect of the amount of Maghnite-H⁺ on the copolymerization was examined (Table 2). It can be noted that the yield increases with increasing "Maghnite"- H⁺ 0.25 M proportion. Indeed, using various amounts of Mag-H⁺, 4, 6,

8, 10 and 12 % by weight, the polymerization was carried in bulk at 60 °C. The polymerization rate increases with the amount of Mag-H⁺. In contrast, the intrinsic viscosity (η) is inversely proportional to the amount of Mag-H⁺, in which the effect of Mag-H⁺ as a catalyst is clearly shown. These results show the effect of Maghnite-H⁺ as a cationic catalyst. Similar results were obtained by Belbachir *et al.* [16-21].

3.4. Effect of Reaction Time on Copolymerization

Polymerization using 10 % of Maghnite- H⁺ 0.25 M was carried in bulk at 60 °C and the reaction was monitored at various times. The re-

Table 1. Effect of reaction temperature on the polymerization

| T (°C) | Yields (%) | $[\eta]$ (dl/g) ^a |
|--------|------------|------------------------------|
| 20 | 43.25 | 0.65 |
| 30 | 45.22 | 0.72 |
| 40 | 47.36 | 0.94 |
| 50 | 53.22 | 1.27 |
| 60 | 55.20 | 1.43 |
| 70 | 52.14 | 1.30 |
| 80 | 45.00 | 1.11 |

^a [NVP] = 0.009 mol, [MMA] = 0.05 mol, 10 % of Maghnite-H⁺ 0.25 M, Reaction time =6 h
^a Determined in CH₂CH₂ at 25 °C

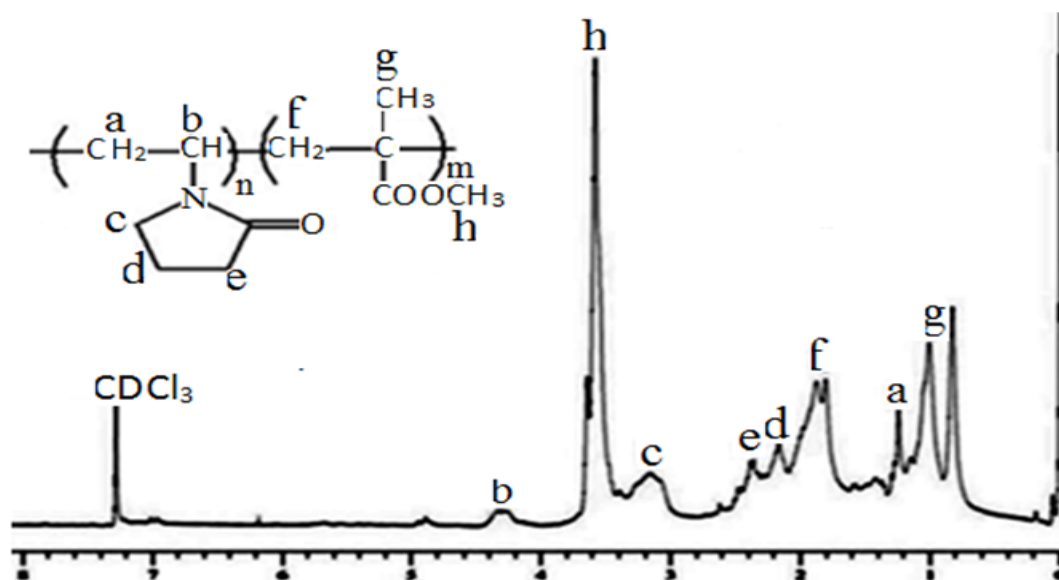


Figure 3. ¹H-NMR spectrum of Poly (NVP -co-MMA)

Table 2. Copolymerization using different amount of Maghnite-H⁺

| Mag-H ⁺ 0.25 M (%) | Yields (%) | [η] (dl/g) ^a |
|-------------------------------|------------|--------------------------------|
| 4 | 35.22 | 2.27 |
| 6 | 46.00 | 1.80 |
| 8 | 48.00 | 1.60 |
| 10 | 55.20 | 1.43 |
| 12 | 55.55 | 1.30 |

[MMA] = 0.05 mol; [NVP] = 0.009 mol, Reaction time = 6 h, T = 60 °C,

^a Determined in CH₂CH₂ at 25 °C

Table 3. Copolymerization using different amount of Maghnite-H⁺

| Time (h) | Yields (%) | [η] (dl/g) ^a |
|----------|------------|--------------------------------|
| 2 | 15.45 | 0.41 |
| 3 | 20.16 | 0.63 |
| 4 | 27.91 | 1.06 |
| 5 | 54.95 | 1.20 |
| 6 | 55.20 | 1.43 |

[MMA] = 0.05 mol, [NVP] = 0.009 mol, 10 % of Maghnite-H⁺ 0.25 M, T = 60 °C

^a Determined in CH₂CH₂ at 25 °C

sults are given in Table 3 shows the evolution of the yield and the intrinsic viscosity of the copolymer with reaction time. The intrinsic viscosity increases with polymerization time. On the other hand, the yield increases with the time and it can be noted that initially the polymerization proceeds very slowly; this can be considered as an induction period (4 h). At the end of this period the polymerization process becomes faster.

4. Conclusions

Bulk copolymerization of NVP with MMA was performed using maghnite-H⁺, a montmorillonite based catalyst of copolymer with the rise in the temperature and the increase in the quantity of catalyst. The results showed that Maghnite-H⁺ show higher catalytic activity for copolymerization reaction owing to its strong Brönsted acidity. The balance of copolymerization moves towards the formation. The copolymerization proceeds smoothly, and a simple filtration is sufficient to recover the catalyst. Moreover this acidic clay is inexpensive, stable and non corrosive. The structure of copolymers was confirmed by ¹H-NMR, ¹³C-NMR, and FTIR.

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