

*Full Length Research Paper*

# Synthesis, characterization and kinetics studies of block copolymer consisting of N-vinyl-2-pyrrolidone and propylene oxide catalysed by Maghnite-H<sup>+</sup> (Algerian MMT)

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**Poly (N-vinyl-2-pyrrolidone) (PVP) is widely used in medicine due to its high biocompatibility, but Poly (propylene oxide), due to its amorphous nature, retains its flexibility at low temperatures and is impermeable to air, though hydrocarbons is a useful material in a number of applications. In this study, propylene oxide copolymerized with N-vinyl-2-pyrrolidone was targeted, which would combine the advantages of propylene oxide and N-vinyl-2-pyrrolidone to broaden the field of application, and the purpose of this paper is to study the cationic copolymerization of N-vinyl-2-pyrrolidone with propylene oxide by a montmorillonite clay called Maghnite-H<sup>+</sup> (Algerian MMT). This new non-toxic cationic catalyst exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers. Maghnite-H<sup>+</sup> can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C. The effect of some factors such as the amount of the catalyst (Maghnite-H<sup>+</sup>), the temperature of reaction and the solvent were discussed.**

**Key words:** Maghnite, vinyl monomers, ring opening polymerization, block copolymers, N-Vinyl-2-pyrrolidone, propylene oxide, <sup>1</sup>H NMR, FTIR.

## INTRODUCTION

Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole percentage to 100% of the repeating units. Polyelectrolytes may be anionic, cationic or amphiphilic and may be synthetic or naturally occurring. The preparation of poly (N-vinyl-2-pyrrolidone-block-propylene oxide) has gained noticeable interest and series of papers have been published by Siegel and Firestone in the late eighties (Firestone and Siegel, 1988; Siegel and Firestone, 1988). They investigated the influence of the physical and chemical properties and the effect of comonomer (NVP) and propylene oxide (OP) on the structure and morphology of copolymer.

Poly (N-vinyl-2-pyrrolidone) (PVP) is a well-known water soluble, biocompatible, and relatively amphiphilic

polymer. The highly polar amide confers hydrophilic and polar attracting properties to the polymer while the apolar methylene group in the backbone and the methine group in the ring contribute to its hydrophobic properties (Benahmed et al., 2001). It has been largely used in the pharmaceutical field (Le Garrec et al., 2004; Kobayashi et al., 1983) and it includes additives, cosmetics, coatings and biomedicines (Zhang and Lam, 2005).

The interest of Poly (propylene oxide) polymers is water soluble, in organic solvents, and its low toxicity.

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**Table 1.** Chemical composition of Mag-H<sup>+</sup> (catalyst).

Sample	Chemical composition										
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>	A <sub>s</sub>	PAF
Maghnite raw	69.3	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11
Maghnite-H <sup>+</sup>	71.7	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11

Poly (propylene oxide), due to its amorphous nature, retains its flexibility at low temperatures and is impermeable to air, though hydrocarbons is a useful material in a number of applications (Liu et al., 2001).

Propylene oxide doped nanocrystals have great potential as biological devices, but their use has been limited because most of these nanocrystals are hydrophobic. Here, our nanocrystals were prepared by simple block copolymer with poly (N-vinyl-2-pyrrolidone (PVP). Their morphological structure and physicochemicals properties were explored in detail. The results indicate that these nanocrystals (bloc copolymer) can be readily dispersed in water, forming a stable and transparent colloidal solution. These results suggest that these nanocrystals have great potential as luminescent labeling materials for biological applications.

In this study, propylene oxide copolymerized with N-vinyl-2-pyrrolidone was targeted, which would combine the advantages of propylene oxide and N-vinyl-2-pyrrolidone to broaden the field of application. And the purpose of this paper is to study the cationic copolymerization of N-vinyl-2-pyrrolidone with propylene oxide by a montmorillonite clay called Maghnite-H<sup>+</sup> (Belbachir and Bensaoula, 2001); this new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers (Benadda et al., 2009; Harrane et al., 2002: 790). Maghnite-H<sup>+</sup> can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C (Affaf et al., 2003). The effect of some factors such as the weather, the amount of the Maghnite-H<sup>+</sup>, the temperature, and the solvent are discussed. Techniques such as <sup>1</sup>H NMR and IR were used to characterize the products of the reaction.

## EXPERIMENTAL

### Reagents

The monomers (PVP, PO) (Aldrich 99%) were purified by fractional distillation under reduced pressure, and were used as received. Raw-maghnite, Algerian Montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite).

### Activation of Maghnite-Na<sup>+</sup>

Maghnite-H<sup>+</sup> was prepared according to the process reported in our previous study (Harrane et al., 2005).

Raw-Maghnite- Na<sup>+</sup> (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h 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 neutralization 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. Table 1 shows the elementary compositions of Protons exchanged samples.

### Characterization of catalyst (Maghnite-H<sup>+</sup>)

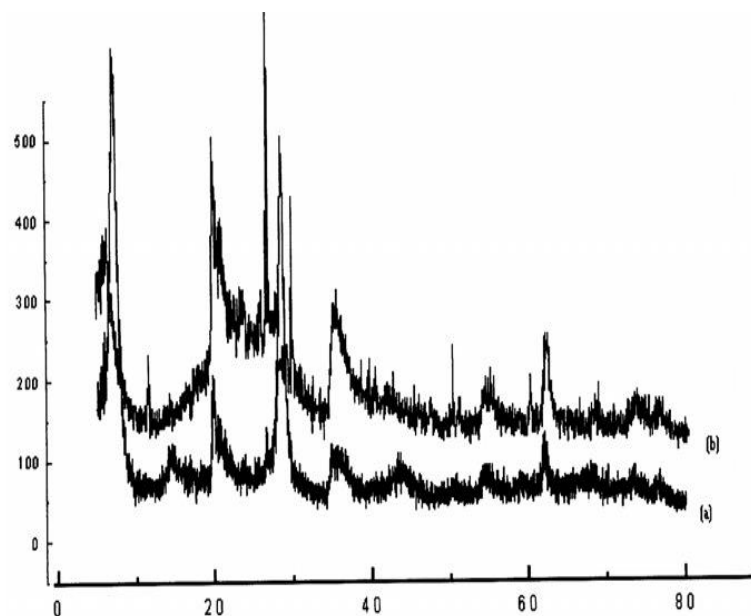
The x-ray powder diffraction profiles shown in Figure 1 exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in raw-Maghnite. Under acid treatment, all trace of calcite was removed in "Maghnite-H<sup>+</sup>". The increase in basal spacing from 12.5 Å in "raw-Maghnite", characteristic of a single water layer between the sheets, to a 15.02 Å value in "Maghnite" for two interlamellar water layers reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment.

The thermal characterizations of the composites include thermogravimetric analysis (TGA). Figure 2 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-Na<sup>+</sup>. The TGA of pure Maghnite-Na<sup>+</sup> shows two stages of weight loss. The first weight loss in Na<sup>+</sup>-Mag which is below 100°C is as a result of the release of free water. The second weight loss which is around 600°C is associated with the dehydroxylation of silicate structure (Percec and Wang, 1992). The total weight loss is only 13.94% up to 800°C. As can be expected, Maghnite-Na<sup>+</sup> shows a high thermal stability.

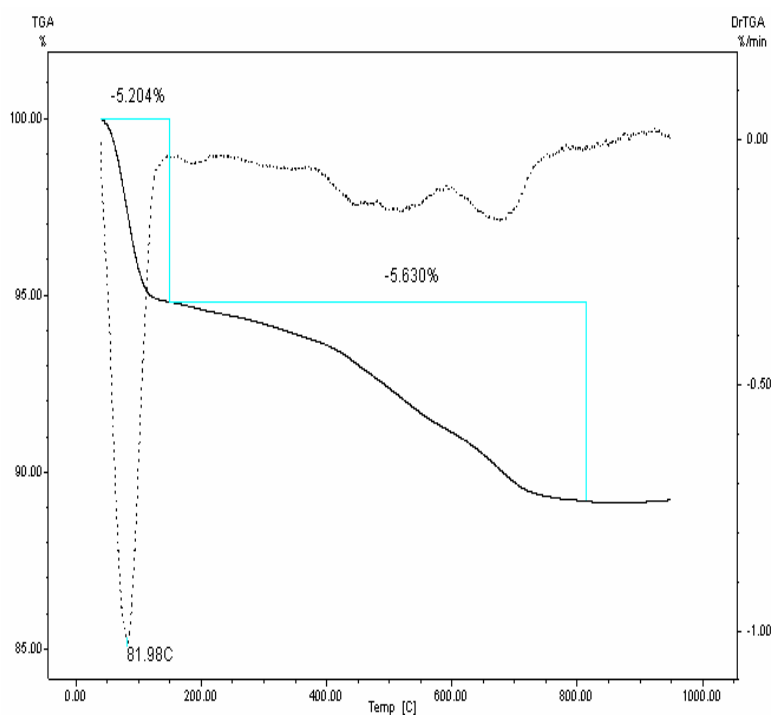
Figure 3 shows the characteristic FT-IR spectra of Na<sup>+</sup>-Mag and H<sup>+</sup>-Mag. The characteristic absorption peaks of MMT are assigned to the Si-O-Si skeleton vibration at 1037-1098 cm<sup>-1</sup>, the strong absorption bands of Si-O and Al-O bending vibration at 600-640 cm<sup>-1</sup> and the OH stretching vibration at 3445 cm<sup>-1</sup>.

### Polymerization procedures

The product was prepared by bulk polymerization in an Erlenmeyer flask of 100 ml by mixture of 4.5 g of (N-vinyl-2-pyrrolidone), 2.32 g of (propylene oxide) and 5% of Maghnite-H<sup>+</sup>. The mixture was stirred with a magnetic



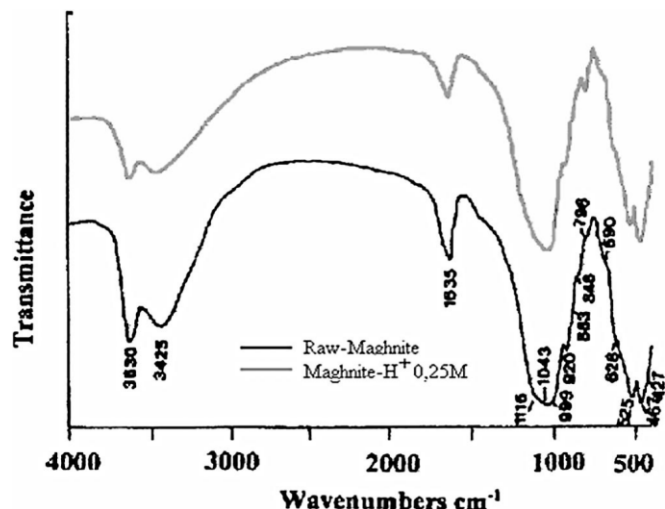
**Figure 1.** X-ray powder diffraction of (a) Maghnite-Na+; (b) Maghnite-H+ 0.25 M.



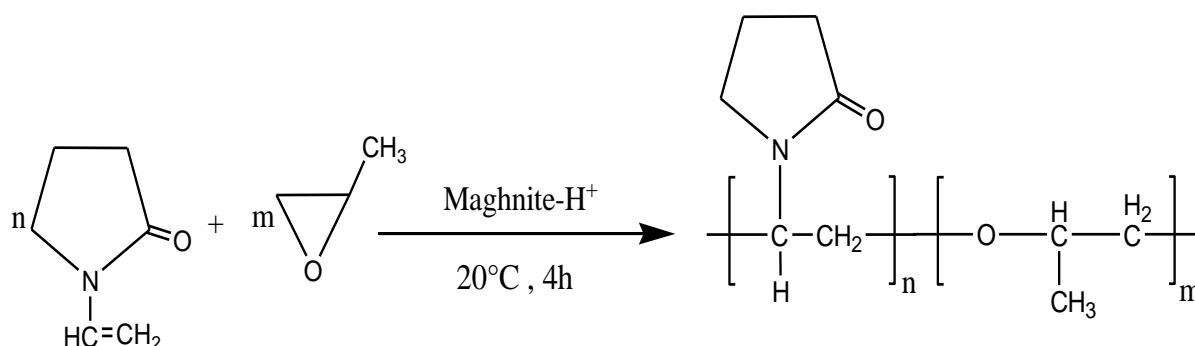
**Figure 2.** TGA curves of Maghnite-Na+ obtained in nitrogen atmosphere at a heating rate of 10°C/min.

stirrer at room temperature for 4 h. At the end of the reaction, a quantity of ethanol was then added to eliminate Maghnite-H<sup>+</sup> and oligomers. The resulting mixture

was filtered to remove the clay in an Erlenmeyer flask containing diethyl ether to precipitate the polymer. The resultant product was dried under vacuum at 40°C for 5 h.



**Figure 3.** FTIR spectra of raw-Maghnite and H-Maghnite-H+ 0.25 M.



**Figure 4.** Schematic representation of the synthesis of (NVP-OP) copolymer block catalysed by Maghnite-H+.

## Measurements

IR absorption spectrum was recorded on an FTIR/ATR spectrometer using the KBr pressed disc technique. FTIR was used to study the chemical structure of the polymer.

Measurement of  $^1\text{H}$  NMR spectra was conducted in  $\text{CDCl}_3$  solution under ambient temperature on a Bruker Vance 300 MHz instrument, operating at 300 MHz ( $^1\text{H}$ ). The TMS was used as the internal zero reference. The  $^1\text{H}$ NMR spectra were recorded.

The intrinsic viscosity  $[\eta]$  was measured in chloroform at  $25^\circ\text{C}$  using an Ubbelohde viscometer. Copolymer was dissolved in chloroform that had been exhaustively dried over molecular sieves. For each copolymer, the viscosity of five concentrations was measured.

## Purification of the products

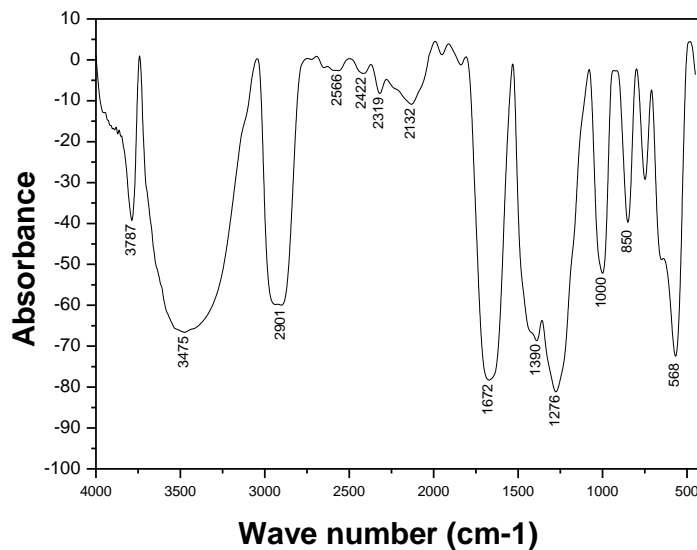
Purification and removal of unreacted monomer and low molecular weight polymers were carried out by dissolving the product in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and filtering to

eliminate the Mag-H+. Then, dichloromethane was removed by evaporation, the poly(NVP-block-OP) solution was precipitated in cold methanol. The precipitated copolymer was filtered and dried under vacuum. It was finally kept in refrigerator until use.

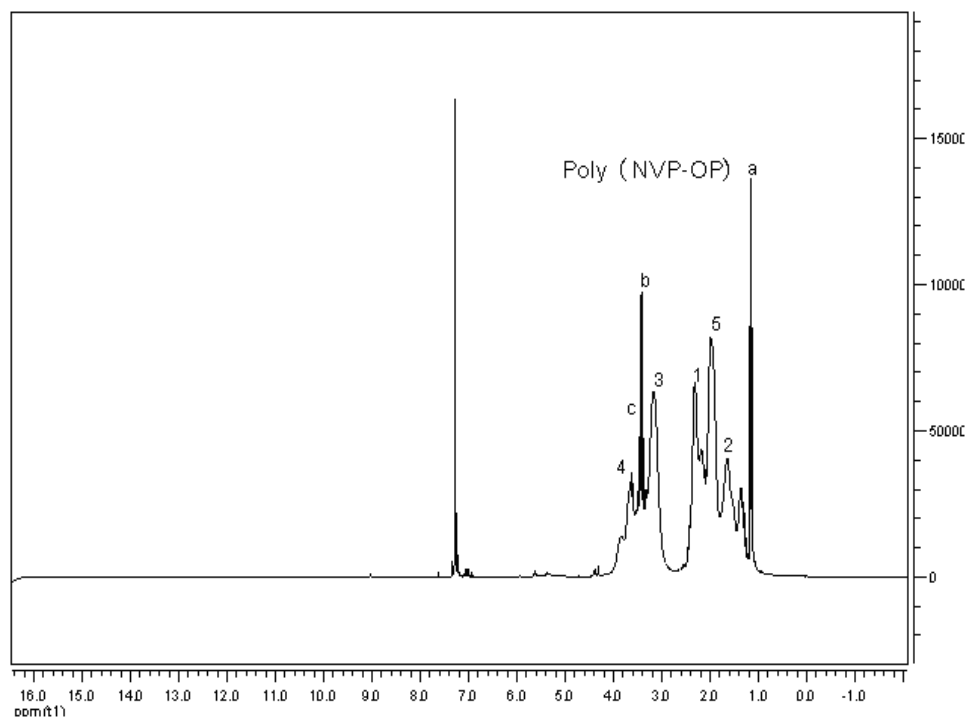
## RESULTS AND DISCUSSION

### Characterization spectroscopic and thermal of product

The present study is concerned with polymerization and examination of the catalytic activity of Algerian proton exchanged montmorillonite clay. These exchanged montmorillonites were successfully used as catalysts for the reactions of polymerization (Yahiaoui et al., 2003; Njopwouo et al., 2006). The cationic copolymerization of N-vinyl-2-pyrrolidone with propylene oxide was examined in the presence of Maghnite-H $^+$  powder in bulk at room temperature (Figure 4).



**Figure 5.** IR spectrum of poly (NVP-OP) polymerized with Maghnite- $H^+$  at room temperature.



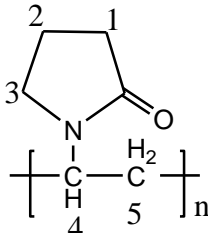
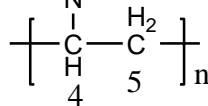
**Figure 6.**  $^1H$  NMR spectrum of poly (NVP-OP) polymerized with Maghnite- $H^+$  at room temperature.

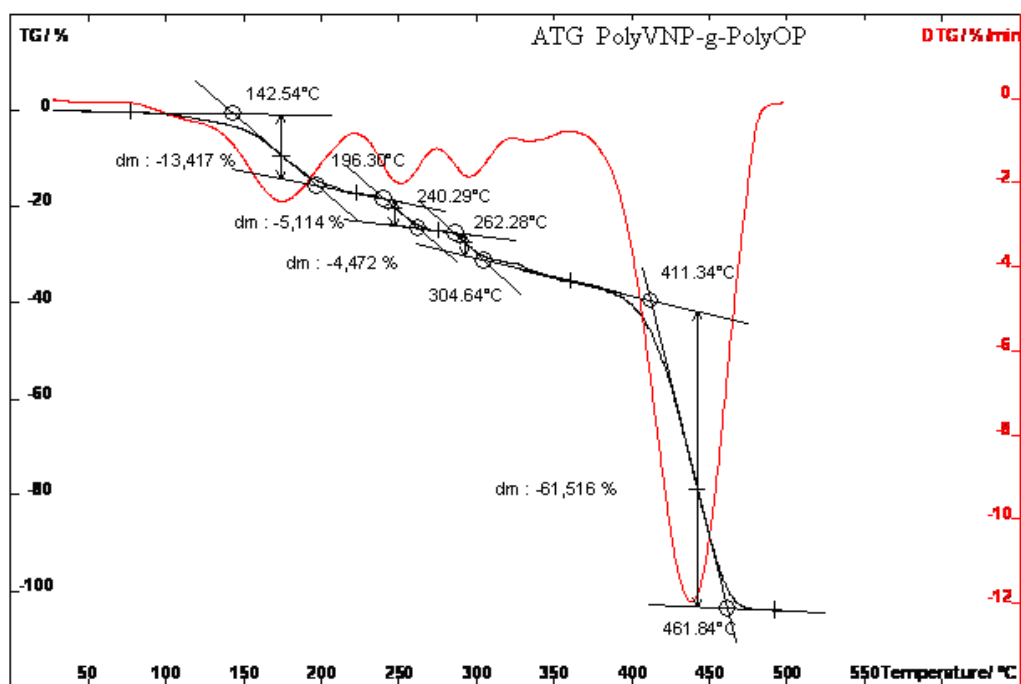
Figure 5 shows the spectra for copolymer. The N-vinyl-2-pyrrolidone carbonyl vibration  $C=O$  occurs at around  $1672\text{ cm}^{-1}$ . The characteristic vibration of  $C-O-C$  band is observed respectively at  $1000\text{ cm}^{-1}$ . A weak absorbance around  $3475\text{ cm}^{-1}$  assigned to the hydroxyl group was observed. This indicated that polypropylene oxide possessed hydroxyl groups as the end groups. The

following results may present the preliminary information on such mechanistic aspects of the copolymerization.

The polymerization reaction was performed as indicated in This study's experimental. Sample was withdrawn, purified and analysed by  $^1H$  NMR spectroscopy. In Figure 6, the corresponding spectra of the prepared block copolymer (NVP-OP) is shown. With the appearance

**Table 2.** Different peaks of the  $^1\text{H NMR}$  spectrum of copoly (NVPD-OP).

Nature of protons	Displacement (ppm)
$-\text{CH}_3$	1.1
$-\text{CH}_2-\text{O}$	3.5
$-\text{CH}-\text{O}$	3.4
	1 : 2.4 2 : 1.65 3 : 3.14
	4 : 3.7 5 : 2

**Figure 7.** TGA and TDA curves of a pure poly (NVPblock-OP) obtained in nitrogen atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$ .

of the necessary proton peaks and to confirm the structure of product (Fechine et al., 2004; Birte et al., 2002), the different peaks of the product were regrouped in Table 2.

Figure 7 shows the thermogravimetric analysis of our product in optimization condition. Thermogravimetric analysis (TGA) measures the weight change of a material depending on the temperature (and time) in a controlled atmosphere. Its main uses include measuring thermal stability and composition of a material. A rate of decomposition at about  $142^\circ\text{C}$  with a weight loss of 13.41% of

the sample corresponds to the NVP monomer, which is due to the presence of a small amount of the monomer; this temperature is in agreement with the temperature boiling the NVP monomer given in theory, then there is another degree of decomposition to  $240.29^\circ\text{C}$  with a weight loss of 5.114% which is the poly (PO) linear. Then decomposition at  $304.64^\circ\text{C}$  has the weight loss of 4.472%, which is due to the presence of poly (OP) cyclic. The main decomposition step is about  $461^\circ\text{C}$  with 61.516% mass loss of the sample corresponding to the formed block copolymer poly (NVP-block-OP).

**Table 3.** Copolymerization of NVP with OP initiated by Maghnite-H<sup>+</sup>.

Time (min)	Yield (%)	Intrinsic viscosity ( $\eta$ )
60	29.6	5.82
120	35.40	6.90
210	46.09	7.85
300	60.70	10.86
390	63.87	12.88
1080	68.92	8.32
1440	71.32	6.93

## Kinetics studies

### Effect of reaction time

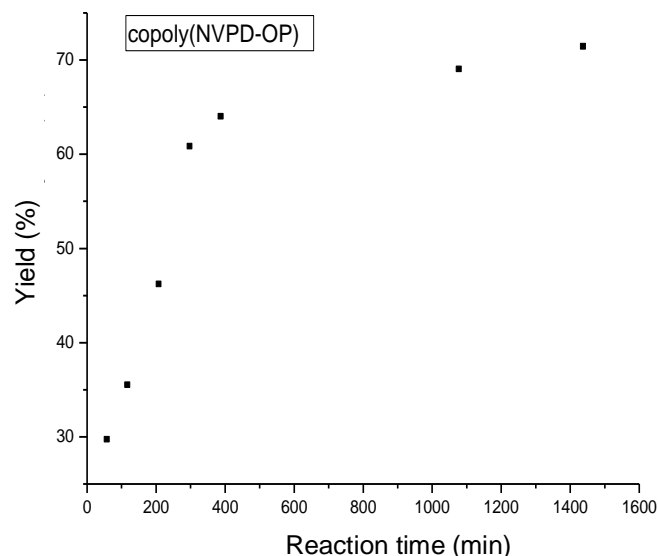
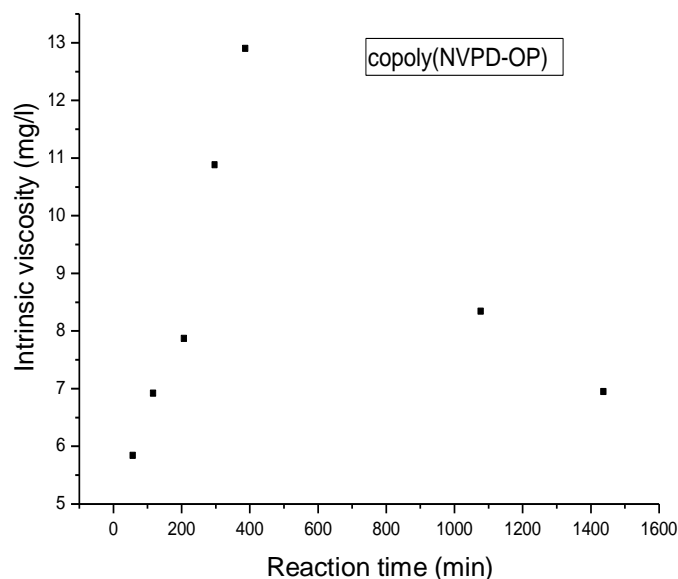
The copolymer was prepared by bulk copolymerization in sealed tubes. Each tube contains a mixture of 4.5 g of (N-vinyl-2-pyrrolidone), 2.32 g of (propylene oxide) and 5% of Maghnite-H<sup>+</sup>. The mixture was stirred with a magnetic stirrer at room temperature.

The reaction was monitored at various times to study the yield and intrinsic viscosity of the copolymer with reaction time. The results are given in Table 3. The yield (conversion of the total monomers) was calculated with the mass ratio of the copolymer to the total monomers in the feed. The process of the effect of reaction time is shown in Figures 8 and 9. The intrinsic viscosity [ $\eta$ ] was measured in chloroform at 25°C using an Ubbelohde viscometer. Copolymer was dissolved in chloroform that had been exhaustively dried over molecular sieves. For each copolymer, the viscosity of five concentrations was measured. It was found that the yield rate increased with copolymerization time of reaction, and at the end of the reaction, the polymerization proceeds very slowly.

The intrinsic viscosity [ $\eta$ ] of the copolymer increases with polymerization time and reaches a maximum after 390 min. The results show that after this period, the intrinsic viscosity [ $\eta$ ] of the copolymer decreases. This result suggests that chain transfer causes degradation of the copolymers. Similar results were obtained by Odian (2007) and Yahiaoui et al. (2003) in the polymerization of epichlorohydrin and propylene oxide by Maghnite-H<sup>+</sup> and Njopwouo et al. (1987) in the polymerization of styrene by montmorillonite-H<sup>+</sup>. However, the polymerization of N-vinyl-2-pyrrolidone was obtained by Harrane et al. (2002: 790-800).

### Effect of the amount of Maghnite-H<sup>+</sup> on polymerization

The polymerization of N-vinyl-2-pyrrolidone with (OP) indeed, using various amounts of Maghnite-H<sup>+</sup>, 2, 4, 5, 7, and 10% by weight, was carried out in bulk at room temperature for 2 h.

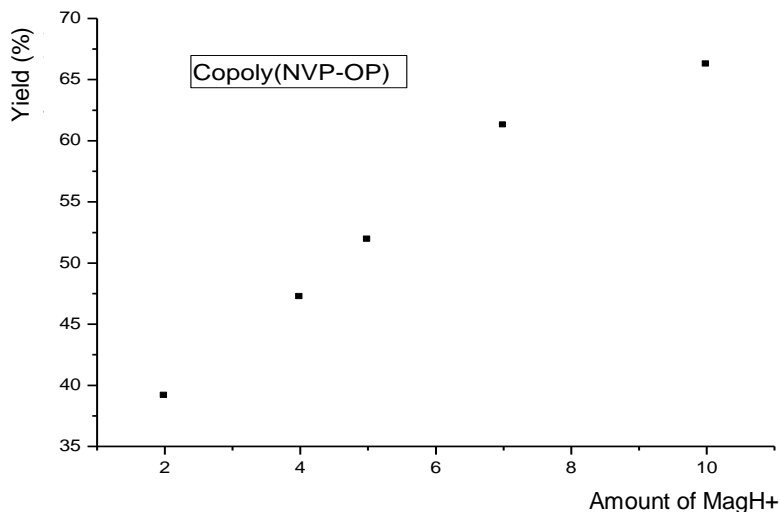
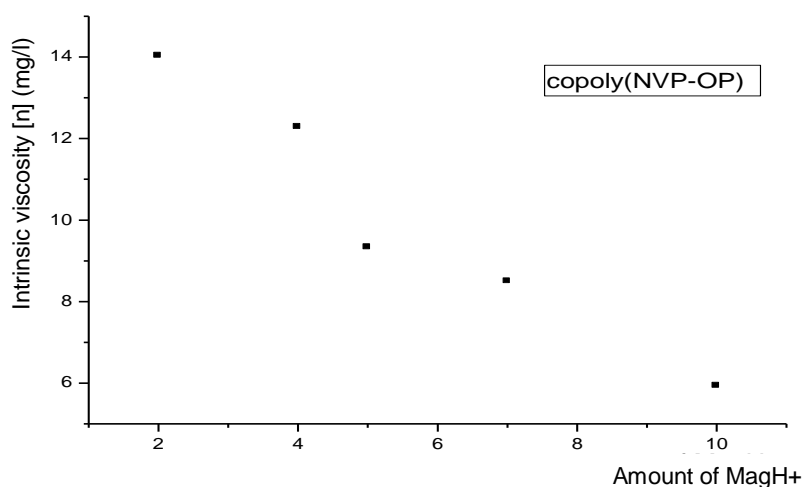
**Figure 8.** Yield of reaction time of poly (NVP-OP) catalyzed by Maghnite-H<sup>+</sup> (4.5 g), NVP (3.32 g) and OP (5% of Maghnite-H<sup>+</sup>).**Figure 9.** Intrinsic viscosity (mg/l) of poly (NVP-OP) catalyzed by Maghnite-H<sup>+</sup> (4.5 g), NVP (3.32 g) and 5% of Maghnite-H<sup>+</sup>.

Here, it can be observed from Table 4 and Figures 10 and 11 that the yield of polymerisation increases with increasing Maghnite-H<sup>+</sup> proportion, and decreases the intrinsic viscosity of the resulting copolymer. This result shows the effect of Maghnite-H<sup>+</sup> as a cationic catalyst.

This phenomenon is probably the result of the number of initiating active sites responsible for inducing polymerization; this number is dependent on the catalyst

**Table 4.** Copolymerization of NVP with OP initiated by Maghnite-H<sup>+</sup>.

Experiment	Catalyst (%)	Yield (%)	Intrinsic viscosity ( $\eta$ )
1	2	39.12	14.03
2	4	47.21	12.28
3	5	51.90	9.33
4	7	61.23	8.49
5	10	66.23	5.93

**Figure 10.** Effect of yield on the Maghnite-H<sup>+</sup> amount.**Figure 11.** Effect of intrinsic viscosity (mg/l) on Maghnite-H<sup>+</sup> amount.

amount used in the reaction. Similar results were obtained by Ferrahi and Belbachir (2003, 2004) in the polymerization of isobutylene by Maghnite-H<sup>+</sup> which was polymerized only by the cationic process.

## Conclusion

In this study, the novel copolymer block (PVP-OP) was synthesized by cationic polymerization through the proton



exchanged montmorillonite clay "Maghnite-H<sup>+</sup>". This catalyst is an effective initiator for the polymerization of epoxies and vinyl polymers.

The catalytic activity as measured by the conversion rate and the molecular weight of the formed polymers depends on the catalyst proportion in the reaction medium and the reaction temperature. Poly (NVP-OP) was produced by a very simple procedure. Through simple filtering, the clay can be separated from the reaction mixtures. Moreover, this acidic clay is inexpensive, stable and non corrosive. The product was bloc copolymer, and as demonstrated by FTIR and 1H-NMR spectroscopy, the chain structure of the copolymer was finally characterized.

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