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Synthesis, Characterization and Kinetics Studies of Block Copolymer Consist on N-vinyl-2-pyrrolidone and propylene oxide Catalysed by Maghnite-H⁺ (Algerian MMT)

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KEYWORDS

Maghnite, vinyl monomers; Ring opening polymerization; Block copolymers; N-Vinyl-2-pyrrolidone; propylene oxide; ¹H NMR; FTIR.

A B S T R A C T

Poly (N-vinyl-2-pyrrolidone) (PVP) is widely used in medicine due to its high biocompatibility but Poly (propylene oxide), its amorphous nature, retains its flexibility at low temperatures and impermeable to air, hydrocarbons is a useful material in a number of applications. In the present 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⁺ (Algerian MMT). This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers. Maghnite-H⁺, 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⁺), the temperature of reaction and the solvent were discussed.

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 amphophilic and may be synthetic or naturally occurring. The preparation of poly (N-venyl-2-perilidone-block- Propylene oxide) has gained noticeable interest and a

series of paper published by Siegel and Firestone in the late eighties (Firestone and Siegel, 1988 ; Siegel and Firestone, 1988). They investigated the influence of properties physical chemical and 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 Gndarrec *et al.*, 2004; Kobayashi *et al.*, 1983) and is including 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. Poly (propylene oxide), its amorphous nature, retains its flexibility at low temperatures and impermeable to air, hydrocarbons is a useful material in a number of applications (Liu *et al.*, 2001).

In the present 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.

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⁺ (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). Maghnite-H⁺, 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⁺ the temperature, and the solvent are discussed.

Techniques such as ¹H NMR, IR, were used to characterize the products of the reaction.

Materials and Methods

Reagents

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

Activation of Maghnite-Na⁺

Maghnite-H⁺ was prepared according to the process reported in our previous study (Harrane *et al.*, 2005). Raw-Maghnite- Na⁺ (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. The Table.1 show elementary compositions of Protons exchanged samples.

Characterization of catalyst (Maghnite-H⁺)

The x-ray powder diffraction profiles shown in Fig.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⁺”.The increase in basal spacing from 12.5 Å in “raw-Maghnite”, characteristic of a single

Table-1: Show chemical composition of Mag-H⁺(catalyst)

Sample	Chemical composition										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	As	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 ⁺	71.7	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11

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

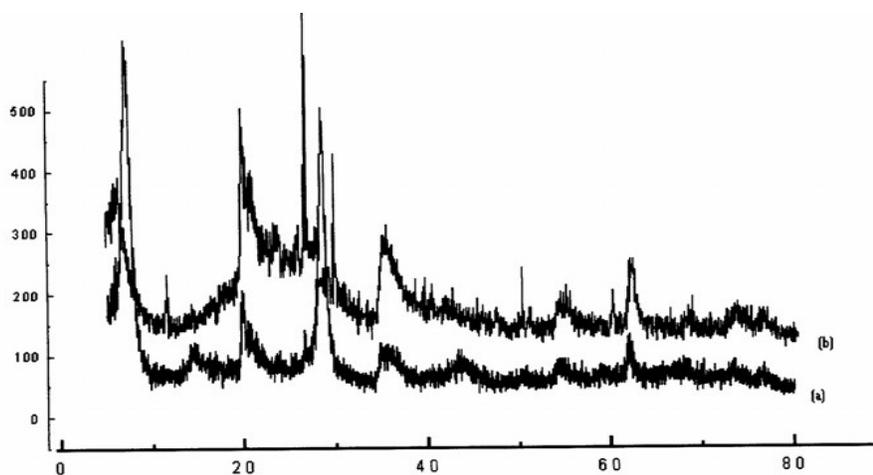
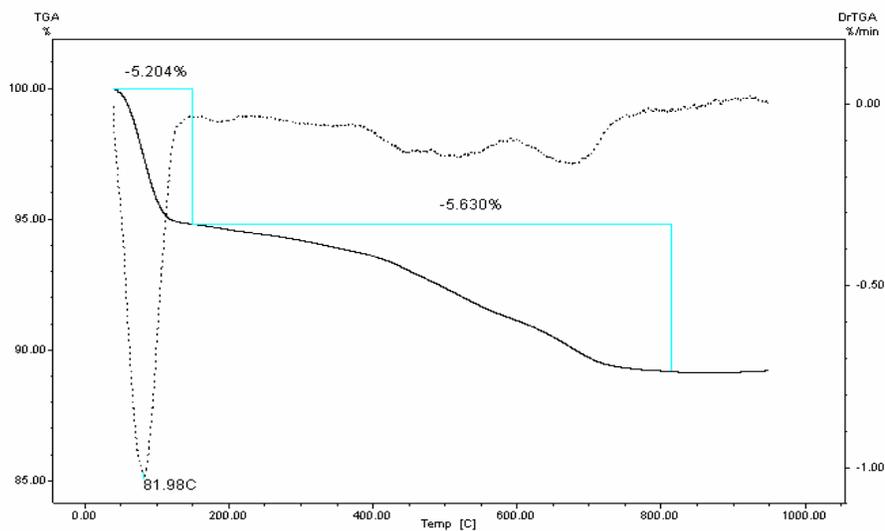


Figure.2 TGA curves of a Maghnite–Na+ obtained in nitrogen atmosphere at heating rate of 10°C/min



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. Show the weight losses (%) versus temperature (°C) curves for pure Maghnite–Na⁺, The TGA of pure Maghnite–Na⁺ show two stages of weight loss. The first weight loss in Na⁺-Mag below 100 °C is a result of the release of free water. The second weight loss 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⁺ shows a high thermal stability.

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

Polymerization procedures

The product was prepared by bulk polymerization in an Erlenmeyer flask of 100 ml. By mixture of 4.5g of (N-vinyl-2-pyrrolidone), 2.32g of (propylene oxide) and 5% of Maghnite-H⁺. The mixture was stirred with a magnetic stirrer at room temperature for 4 hours. At the end of the reaction a quantity of ethanol was then added to eliminate Maghnite-H⁺ 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 hours.

Measurements

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

Measurement of ¹H NMR spectra is conducted in CDCl₃ solution under ambient temperature on a Bruker Vance 300 MHz instrument, operating at 300 MHz (¹H). The TMS as the internal zero reference. The ¹H NMR spectra were recorded.

The intrinsic viscosity [η] 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.

Purification of the products

Purification and removal of unreacted monomer and low molecular weight polymers were carried out by dissolving the product in dichloromethane (CH₂Cl₂) 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 copolypolymer was filtered and dried under vacuum. It was finally kept in refrigerator until use.

Result and Discussion

The present study is also concerned with polymerization and examines the catalytic

activity of Algerian proton exchanged montmorillonite clay. These exchanged montmorillonite have been 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 (Scheme.1).

Fig.1. shows the spectra for copolymer. The N-vinyl-2-pyrrolidone carbonyl vibration C=O occurs at around 1672 cm⁻¹. The characteristic vibration of C-O-C band is observed respectively at 1000 cm⁻¹. A weak absorbance around 3475 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 experimental part section. Sample was withdrawn, purified and analysed by ¹H NMR spectroscopy.

In Fig. 2 the corresponding spectra of the prepared block copolymer (NVP-OP) is shown. With the appearance of the necessary proton peaks and to confirm the structure of product (Fechine *et al.*, 2004; Birte *et al.*, 2002). The different peaks of product were regrouped in Table.3.

Fig.3 shows 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 ° C with a weight loss of 13.41% of the sample which corresponds to the NVP monomer, this 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 ° C with a weight loss of 5.114% is the poly (PO) linear, then decomposition at 304, 64 ° C, the weight loss is 4.472%, which due to the presence of poly (OP) cyclic, the main decomposition step is about 461 ° C with 61.516% mass loss of the sample corresponds to the formed block copolymer poly(NVP-block-OP).

Kinetics studies

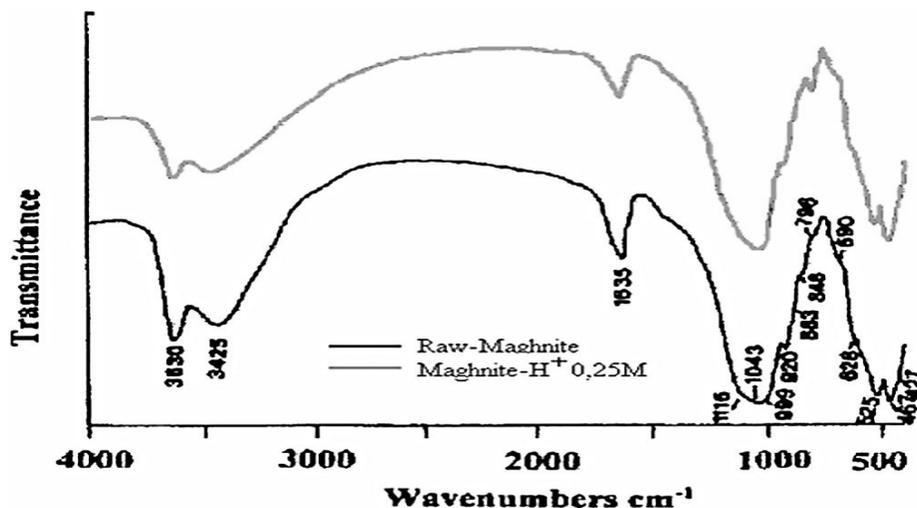
Effect of reaction time

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

The reaction was monitored at various times to study the yield and the intrinsic viscosity of the copolymer with reaction time. The results are given in Table.1.

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 fig.3.and fig.4. The intrinsic viscosity [η] 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.

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



Scheme.1 Schematic representation of the synthesis of (NVP-OP) copolymer block catalysed by Maghnite-H+.

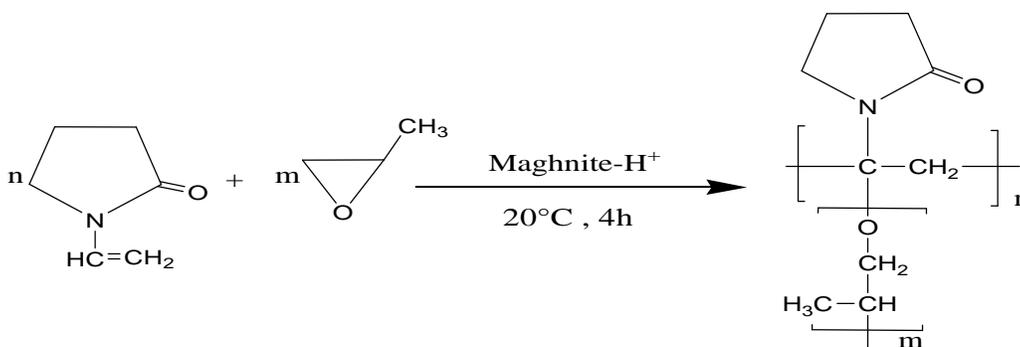


Figure.1 IR spectrum of poly (NVP-OP) polymerized with Maghnite-H+ at room temperature

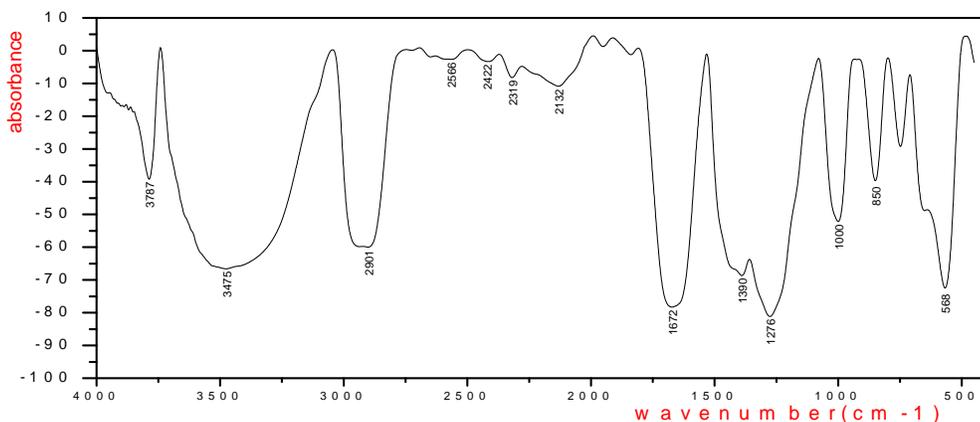


Table.2 Different peaks of the ¹H NMR spectrum of copoly (NVPD-OP) observed

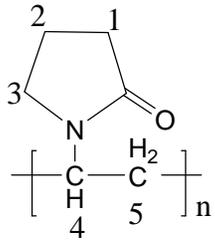
Nature of protons	displacement (pmm)
—CH ₃	1.1
—CH ₂ —O	3.5
—CH—O	3.4
	1 : 2.4
	2 : 1.65
	3 : 3.14
	4 : 3.7
	5 : 2

Figure.2 ¹H NMR spectrum of poly (NVP-OP) polymerized with Maghnite-H⁺ at room temperature.

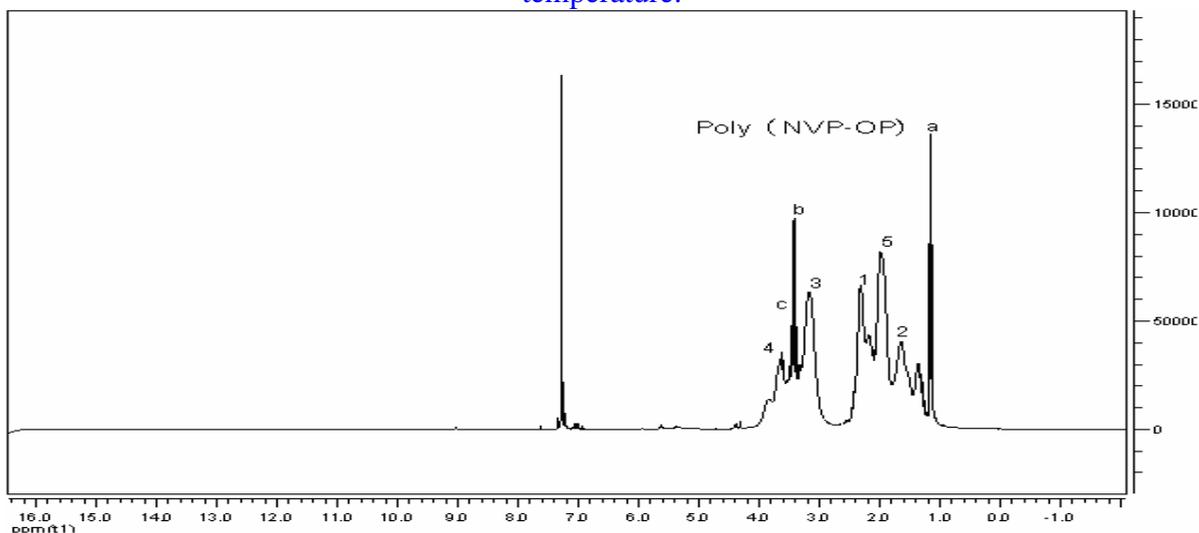


Figure.3 TGA and TDA curves of a pure poly(NVPblock-OP) obtained in nitrogen atmosphere at heating rate of 10°C/min.

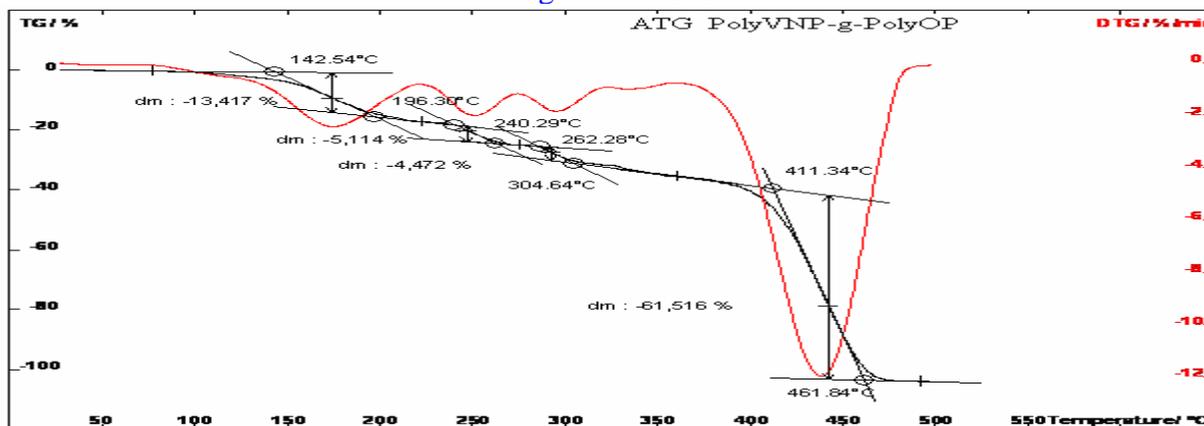


Table.3 Copolymerization of NVP with OP initiated by Maghnite-H⁺

Time (min)	Yield (%)	intrinsic viscosity(η)
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

Figure.3 Yield of reaction time of poly (NVP-OP) Catalyzed by Maghnite-H⁺, 4.5 g; NVP, 3.32g OP 5% of Maghnite-H⁺.

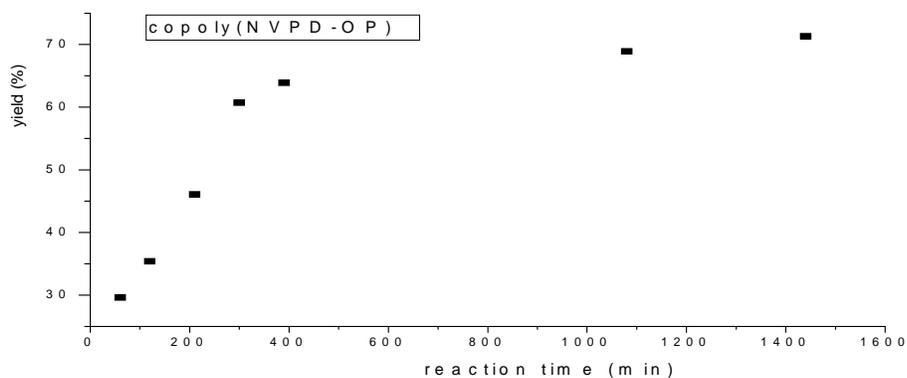


Figure.4 Intrinsic Viscosity mg/l of poly (NVP-OP) Catalyzed by Maghnite-H⁺, 4.5 g; NVP, 3.32g 5% of Maghnite-H⁺.

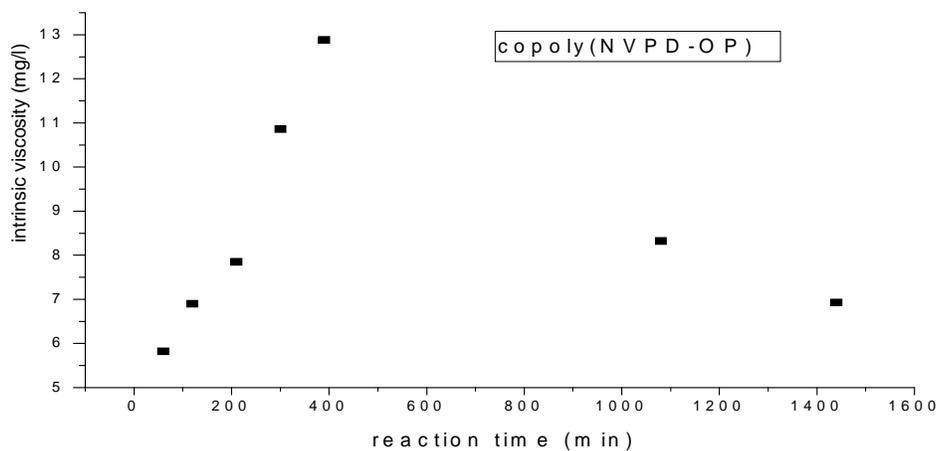


Table.4 Copolymerization of NVP with OP initiated by Maghnite-H⁺

Expriment	Catalyst (%)	Yield (%)	intrinsic viscosity(η)
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.5 Effect of Yield on the Maghnite-H⁺ amount

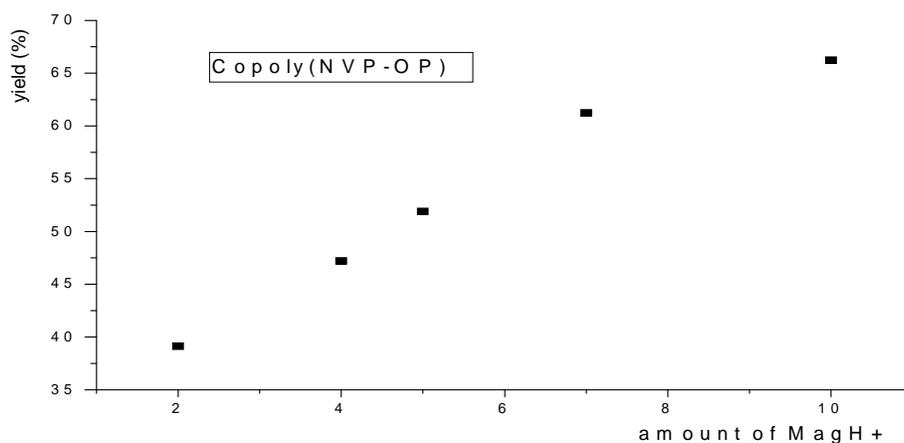
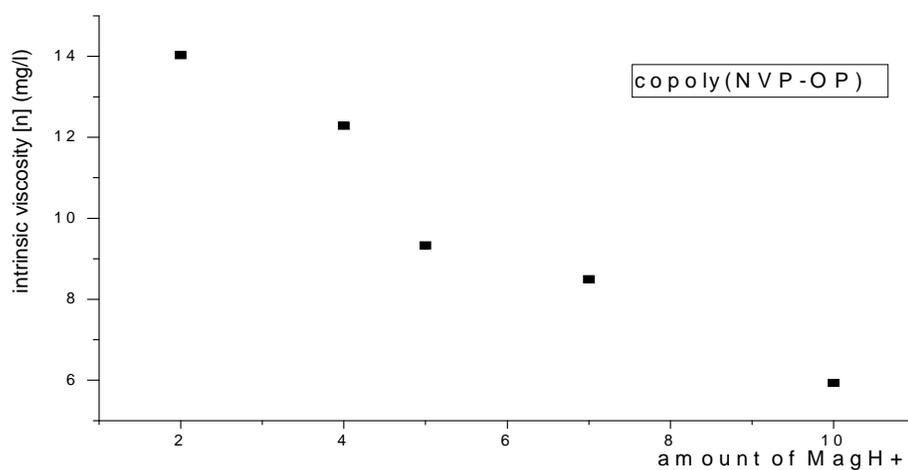


Figure.6 Effect of Intrinsic Viscosity mg/l on Maghnite-H⁺ amount



It was found that, the yield rate increased with copolymerization time of reaction, and at the end of 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 are obtained by Yahiaoui *et al.*, (2003); Odian La, (2007) and Njopwouo *et al.*, (1987) in the polymerization of epichlorohydrin and propylene oxide by Maghnite-H⁺ and the polymerization of styrene by montmorillonite-H⁺, respectively. And the polymerization of N-vinyl-2-pyrrolidone obtained by Harrane *et al.*, (2002)

Effect of the amount of Maghnite-H⁺ on the polymerization

The polymerization of N-vinyl-2-pyrrolidone with (OP) Indeed, using various amounts of Maghnite-H⁺, 2, 4, 5, 7, and 10% by weight, the polymerization was carried in bulk at room temperature for 2 hours.

Here, we can see from Table.3 and the figs.5, 6, that the yield of polymerisation increases with increasing Maghnite-H⁺ proportion, and decreases the intrinsic viscosity of the resulting copolymer. This result shows the effect of Maghnite-H⁺ 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 to the catalyst amount used in the reaction.

Similar results are obtained by Ferrahi *et al.*, (2003); Ferrahi and Belbachir, (2004) in the polymerization of isobutylene by Maghnite-H⁺ which polymerizes only by the cationic process.

In this study, the novel copolymer block (PVP-OP), was synthesized by cationic polymerization by proton exchanged montmorillonite clay "Maghnite-H⁺". 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 formed polymers depend 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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