

A new strategy for synthesis of microspheres of amphiphilic block copolymer based on epichlorhydrin and n-vinyl-2-pyrrolidone induced by an ecologic catalyst clay layered called maghnite-H⁺ (Algerian MMT)

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ABSTRACT

Biodegradable copolymer microsphere of poly(epichlorhydrin-co-NVP) was synthesized by a ring-opening polymerization process of epichlorhydrin and n-vinyl-2-pyrrolidone. The copolymerization of epichlorhydrin (ECH) and n-vinyl-2-pyrrolidone (NVP) catalyzed by maghnite-H⁺ (mag-H⁺) was investigated. The effect of some factors such as the amount of the catalyst (maghnite-H⁺), the temperature of reaction and the solvent were discussed. It was found that the copolymerization rate increased with increase in the temperature and the proportion of catalyst, and it was larger in nonpolar solvents. The product was characterized by various technique characterization such as FTIR and 1H-NMR.

Keywords: Epichlorhydrin, n-vinyl-2-pyrrolidone, amphiphilic block, maghnite-H⁺, microspheres, H-NMR spectroscopy, ring opening polymerization.

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INTRODUCTION

In recent years, polymers based on epichlorhydrin and N-vinyl-2-pyrrolidone have received increasing attention (Georgiev et al., 1992; Gao et al., 1997). Polymerization of this monomer via ring opening of the epoxy group has been subjected only in few papers (Kamada et al., 2000). Epichlorhydrin is a colourless liquid with a characteristic chloroform-like odour that is manufactured using chlorine, propylene and milk of lime as raw materials. Epichlorhydrin is used in the production of polyamide resins for ion exchange (Harper et al., 1991), the water treatment and paper industries (Valero et al., 1999), flame retardants, quaternary amines and in the production of Zeospan, a speciality polyether rubber used in automobiles (Dey and Ray, 2003). N-Vinyl-2-pyrrolidone (NVP) is either caustic stabilized with 0.1% NaOH, or amine stabilized with 10 ppm N,N'-disec-butyl-paraphenylene diamine (Kim et al., 2002). NVP is a slightly to moderately yellow heterocyclic (Lou et al., 2001), reactive vinyl monomer made from the reaction of

acetylene and 2-pyrrolidone (Yang et al., 2005). The inherent properties of high polarity, low toxicity, water solubility, chemical stability and pseudo-cationic activity are imparted to its homopolymers and copolymers (Matsushima et al., 2000).

Montmorillonites have both Brönsted and Lewis acid sites and when exchanged with cations having a high charge density, such as protons, they produce highly-active catalysts for acid-catalysed reactions (Zeng et al., 2002). Modified (activated) clays also have been used in other applications. These applications include adsorbents, rheological control agents, paints, grease, cosmetics, personal care products, oil well drilling fluids, etc (Brindley and Brown, 1980). Among the clay minerals, smectites, especially montmorillonite, have been extensively used to prepare organoclays because of its excellent properties, such as high cation exchange capacity, swelling behavior, adsorption properties and large surface area (Hasegawa et al., 2000). According to

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

Belbachir et al. (2001), Maghnite-Na⁺ and Maghnite-H⁺ have been prepared and used in an industrial scale. These clay minerals swell in water into a manner similar to smectites, and have interlayer charge densities higher than that of smectites (Garcia-Lopez et al., 2002). Unlike natural clay minerals, they have high crystallinity, controllable composition and fewer impurities (Benharrats et al., 2003). For these reasons, the use of such modified Maghnite as host materials is expected to be more advantageous than the use of raw natural clay minerals (Maghnite-Na⁺) (Breen et al., 1995). Biodegradable polymers should non-toxic, capable of maintaining good mechanical integrity until degraded, and capable of controlled rates of degradation (Belbachir and Bensaoula, 2006). The goal is not to illicit the immune response, and the products of degradation also need to be non-toxic. Biodegradable polymers have been extensively investigated for temporary therapeutic applications such as surgical sutures, bone fracture internal fixation devices, drug delivery systems, as well as tissue engineering scaffolds (Ge et al., 2002). In recent years, some researches have focused on using new modified natural clays as catalysts or initiators for polymerization of vinylic and hetero-cyclic monomers (Albertsson and Eklund, 1994 ; Storey et al., 2001; Harrane et al., 2002). In the present study, epichlorohydrin (ECH) copolymerized with PVP was targeted, which would combine the advantages of PECH and PVP to broaden the field of application. The properties of block copolymers depend on the comonomer composition and also on the sequence distribution of the constituent comonomers. In this work, we would like to report a new and efficient ecologic catalyst which is a protonated organically-modified nanoclay (Maghnite-H⁺) in order to prepare microsferes amphiphilic block copolymer based on (epichloridrin and N-vinyl-2-pirolidone) (Benahmed et al., 2001). The product is very soluble in comments organics solvant such as chloroform, dichlorometane. and can be extracted from the reaction media easily. Techniques such as ¹H NMR, IR, were used to characterize the products of the reaction.

EXPERIMENTAL

Materials

(a) The monomers (NVP, ECH) (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).

(b) Dichloromethane (DCM) was washed successively with conc. sulfuric acid, distilled water, 5% aqueous Sodium hydroxide, and distilled and dried over anhydrous calcium chloride. DCM was distilled (bp 40°C) from calcium hydride and stored.

(c) Methanol was used as received.

(d) 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 M sulfuric acid treatment solutions were used to prepare "H-Maghnite 0.05 M", "H-Maghnite 0.10 M", "H-Maghnite 0.15 M", "H-Maghnite 0.20 M", "H-Maghnite 0.25 M", "H-Maghnite 0.30 M" and "H-Maghnite 0.35 M" respectively. "H-Maghnite XM", the acid form of "raw-Magnate", is prepared by shaking the raw material (raw- Na-Maghnite) with a solution of sulfuric acid at room temperature until saturation is achieved over a two day period, The cation-exchanged clay was filtered, resuspended in deionized water continuously until no sulfate ions were detected in the filtrate by BaCl₂; isolated by filtration; dried in an oven at 105°C and then finely ground. The clay cation exchange capacity (CEC) was found to be 84 mEq/100 g of dried clay.

RESULTS AND DISCUSSION

Preparation of catalyst (maghnite-H⁺)

Maghnite-H⁺ were prepared by a method similar to that described by Belbachir et al. (2001). 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 150°C. Table 1 show elementary compositions of protons exchanged samples.

Catalyst structure

Various methods of analysis, such as MAS NMR, show that "Maghnite" is a montmorillonite sheet silicate clay (Yahiaoui et al., 2003). The elementary analysis of

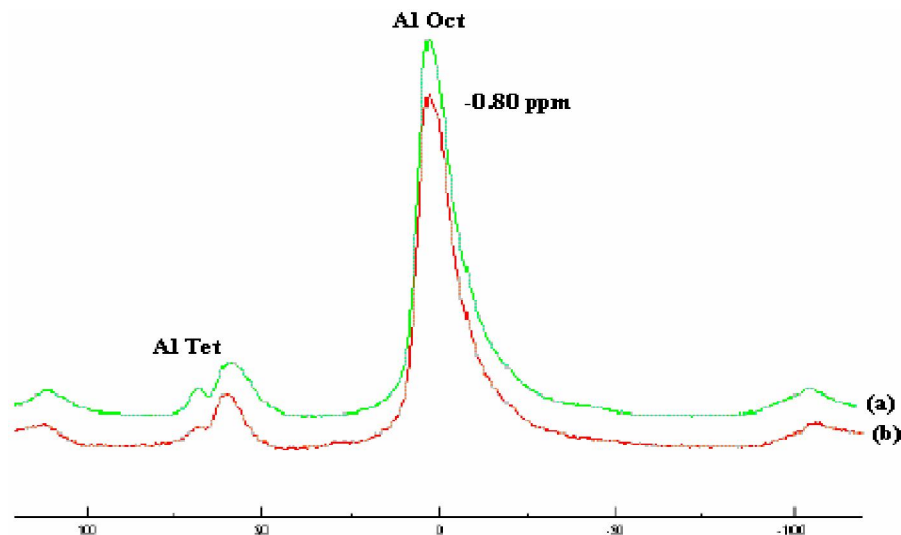


Figure 1. ^{27}Al MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite" 0.25 M.

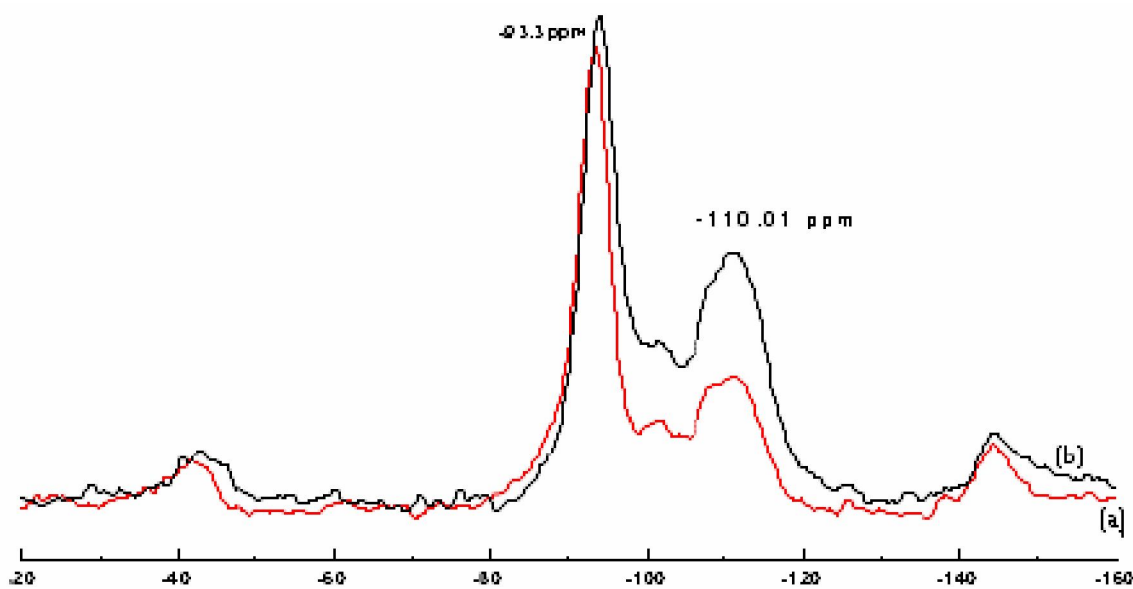


Figure 2. ^{29}Si MAS NMR spectra of (a) "Raw-Maghnite" and (b) "H-Maghnite 0.25 M".

selected samples obtained using XRF and comonomer conversions obtained from the reaction of 0.41 g (5%) of each sample with 3.71 g of Epichlorhydrin and 4.5 g of N-vinyl-2-pyrrolidone for 4 h in a bulk polymerization at 20°C.

It is necessary to report that the best value of Epichlorhydrin and N-vinyl-2-perilidone conversion is obtained with "H-Maghnite 0.25 M". We thus selected this sample to study the effect of catalyst proportions and temperature on Epichlorhydrin and N-vinyl-2-perilidone polymerization. Acid treatment of "Raw-Maghnite" caused a reduction in octahedral Al_2O_3 content with an increase in the proportion of silica (SiO_2) observed. The

copolymer yield decrease implies that the Maghnite original structure was not preserved (destroyed) after acid treatment at a concentration ≥ 0.25 M.

The ^{27}Al MAS NMR spectra of both Raw-Maghnite and H-Maghnite-0.25 M (Figure 1) show Aluminum in two tetrahedral environments, with resonances centered at 60 and 68 ppm, in addition to the main contribution from the octahedral aluminum at 2.9 ppm. These values and assignments concur with those published in the literature (Johnson et al., 1992; Farmer, 1974).

The ^{29}Si MAS NMR spectra for the Raw-Maghnite and H-Maghnite 0.25 M are shown in Figure 2. The dominant

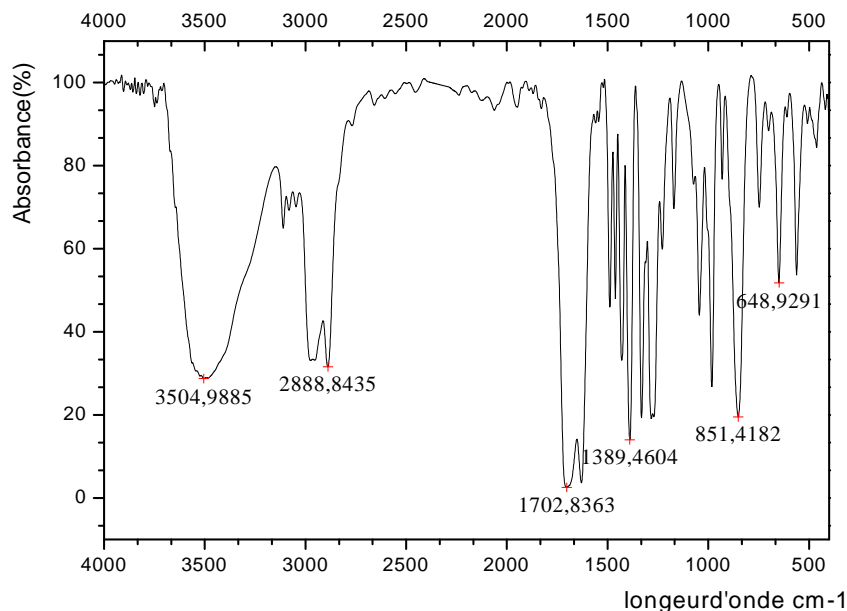


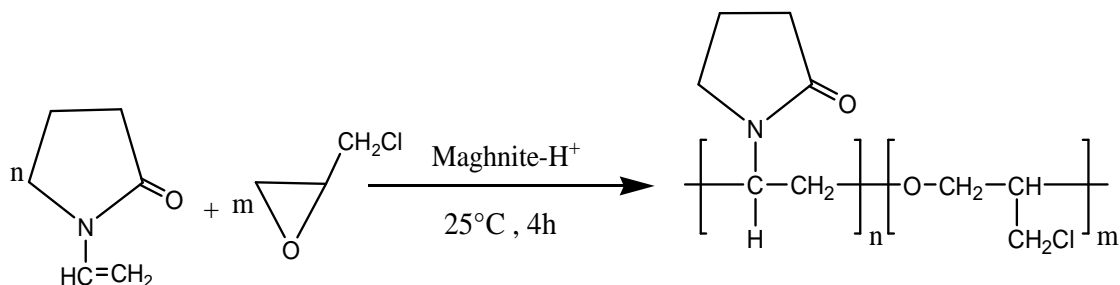
Figure 3. IR spectrum of poly (Epichloridrin-co-NVP) polymerized with Maghnite- H^+ at room temperature.

resonance at -93.5 ppm corresponds to Q 3 (OAI) units, that is, SiO_4 groups crosslinked in the tetrahedral sheets with no aluminum in the neighboring tetrahedral (Moeke, 1974). The resonance at -112 ppm corresponds to three-dimensional (3D) silica with no aluminum present and is generally labeled Q 4(OAI) (Yahiaoui et al., 2003; Yahiaoui et al., 2003; Benvenuti, et al., 1997).

Procedure and product characterization

The poly(epichlorhydrin-co-N-Vinyl-2-pyrrolidone) copolymers was prepared by bulk polymerization in an Erlenmeyer flask of 125 ml. 4.5 g of (N-vinyl-2-

pyrrolidone), with 3.71 g of epichlorhydrin and 0.41g (5%) of catalyst (Maghnite- H^+). The catalyst was dried in a muffle oven at $120^\circ C$ over night and then transferred to a vacuum desiccator containing P_2O_5 . The mixture was stirred with a magnetic stirrer at room temperature for 4 h. At the end of the reaction the resulting mixture was filtered to remove the clay and then slowly added to methanol with stirring and then the polymer was dried under vacuum at room temperature for 24 h. 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 $40^\circ C$ for 5 h.

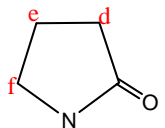
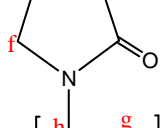
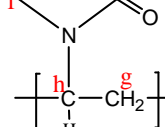
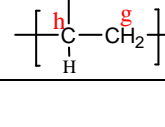
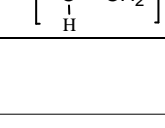


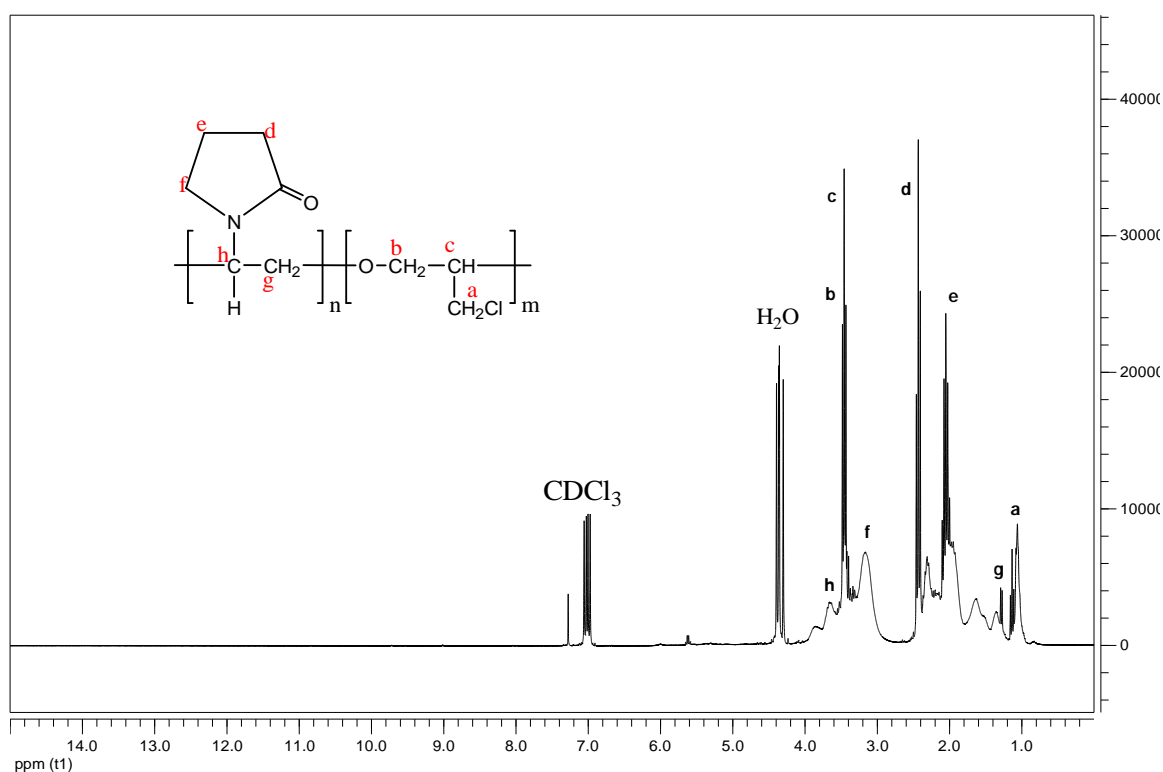
Schema 1. Ring opening polymerization of poly(epichlorhydrin-co-N-vinyl-2-pyrrolidone) by maghnite- H^+ .

Figure 3 shows the FTIR spectra for poly(epichlorhydrin-co-N-Vinyl-2-pyrrolidone) copolymer. A strong absorption at 1702 cm^{-1} associated with the carbonyl group appears for the copolymers. The characteristic vibration of C-O-C band is observed respectively at 1389 cm^{-1} . A weak

absorbance around 3475 cm^{-1} assigned to the hydroxyl group was observed (KBr), at 2888 cm^{-1} for C-H asymmetric stretching of aromatic structure. The following, at 851 cm^{-1} for C-Cl, results may present the preliminary information on such mechanistic aspects of the

Table 2. Chemical shift of copolymers protons.

Protons	Displacements (pmm)
a —CH ₂ Cl	a 3.67
b —CH ₂ O	b 3.50
c —CH	c 3.45
	d 2.42
	e 2.04
	f 3.20
	g 1.11
	h 4.03

**Figure 4.** ¹H NMR spectrum of a typical Poly(epichlorhydrin-co-NVP) in CDCl₃ at 25°C.

copolymerization (Hong-Quan et al., 2003).

The copolymer obtained was characterized by RMN1H (300 MHz, Solvent deuterated CDCl₃). The different protons observed and their chemical displacements are given in Table 2. On the spectrum 1HRMN (Figure 4), we also observe a singlet located at about 1.11 ppm which corresponds probably to the methyl of the end of the chain (g). The other protons of the end of chain are confused with the protons of the polymer chain (d, e) at 2.04 to 2.42 ppm. The proton signals of —CH₂Cl, —CH₂O and —CHO— groups are observed respectively at 3.67, 3.50 and 3.45 ppm (Demirbag and Cakmak, 1996).

Kinetics studies

Effect of the amount of catalyst (mag-h+) on copolymerization

Figure 5 shows the effect of the amount of Mag-H+, expressed by using various weight ratios Mag-H+/monomer, on the polymerization rate. The polymerization was carried out in bulk. As shown in Figure 5, a yield of 70 wt% was reached for 10 wt% of Mag-H+, and the use of a lower or higher amount of clay caused a decrease of the yield of the reaction. Similar

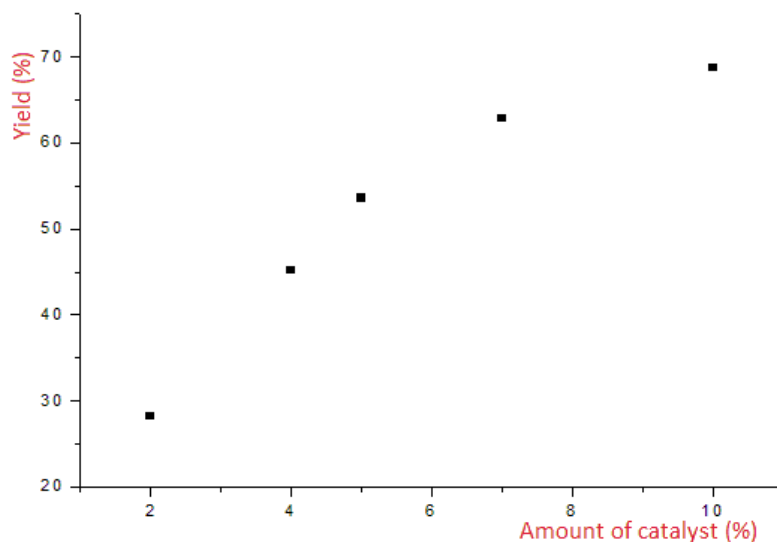


Figure 5. Effect of the amount of the catalyst on co-polymerization of Epichlorhydrin (3.71 g), with N-Vinyl-2-pyrrolidone (4.5 g).

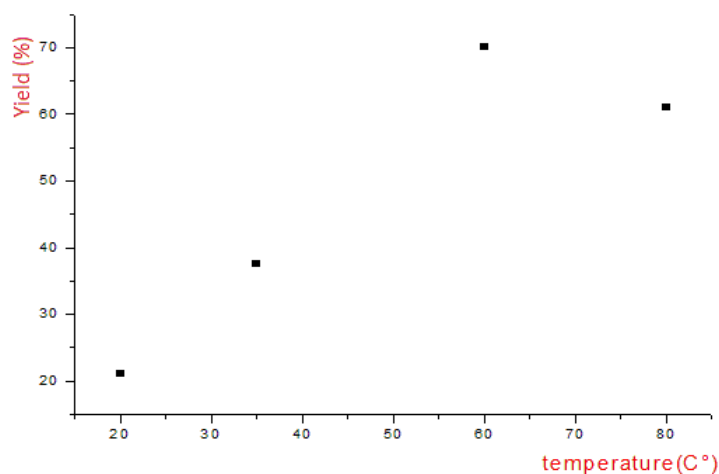


Figure 6. Effect of temperature on the yield of copolymer (Epichlorhydrin-co-N-Vinyl-2-pyrrolidone).

results are obtained by Yahiaoui et al. (2003). In the polymerization of epichlorhydrin, and Ferrahi and Belbachir (2004, 2005) in propylene oxide and cyclohexene oxide by Mag-H⁺ and the polymerization of styrene by montmorillonite, respectively. This phenomenon is probably the result of the number of 'initiating active sites' responsible of inducing polymerization, this number is prorating to the catalyst amount used in reaction.

Effect of temperature on copolymerization proces

The effect of temperature on the copolymerization of N-vinyl-2-pyrrolidone (4.5 g) with epichlorhydrin (3.71 g)

initiated by maghnite-H⁺ (5% by weight) for 5 h, is shown in Figure 6. The copolymerization yield reach maximum value around 60°C. On the other hand, with the increase in the reaction temperature above 60°C, the molecular weight of the obtained copolymer decrease progressively, suggesting the possible occurrence of thermal degradation (Meghabar et al., 2003). On the basis these results, subsequent copolymerizations were carried out at 60°C.

Conclusion

The dispersion characteristics of organoclay based on poly(epichlorhydrin-co-N-vinyl-2-pyrrolidone)- ontmorillonite

(Mag-H+) organoclay were prepared via solution intercalation method. After an extensive study on methods of preparing copolymers, a simple and profitable synthesis of poly(epichlorhydrin-co-N-Vinylpyrrolidone) copolymers by heterogeneous catalysis have been proposed. The different parameters studied had little influence on the chaining in the copolymers, it is likely, therefore, that the growing chains are found in a complex form. On the other hand, it is desirable that the synthesis of heterocyclic and vinyl polymers and copolymers by heterogeneous catalysis, initiated by the Maghnite, be followed by larger development, both for fundamental and economic interest, that it presents. Finally, the interpretation of structure, morphology and conformation confirms that the resulting product is poly (ECH-co-NVP) by the presence of two motifs ECH and NVP.

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REFERENCES

- Albertsson AC, Eklund M, 1994. Synthesis of copolymers of 1,3-dioxan-2-one and oxepan-2-one using coordination catalysts. *J Polym Sci Part A: Polym Chem*, 32:265-279.
- Belbachir M, Bensaoula A, 2006. Composition and method for catalysis using bentonites, US patent, No. 7, 094-823 B2.
- Belbachir M, Bensaoula A, 2001. Maghnite-H+, an ecocatalyst for cationic polymerization A. *US Patent*. 6274527B1.
- Benahmed A, Ranger M, Leroux J-C, 2001. Novel polymeric micelles based on the amphiphilic diblock copolymer poly (N-vinyl-2-pyrrolidone)-block-poly (D, L-lactide). *Pharm Res*, 18: 323-328.
- Benharrats N, Belbachir M, Legran AP, D'espinoze de la Caillerie JB, 2003. ²⁹Si and ²⁷Al MAS NMR study of the zeolitization of kaolin by alkali leaching. *Clays Miner*, 38:49-61.
- Benvenuti F, Galletti AMR, Carlini C, Sbrana G, Nannini A, Bruschi P, 1997. Synthesis, structural characterization and electrical properties of highly conjugated soluble poly(furan)s. *Polymer*, 38:4973-4982.
- Breen C, Madejová J, Komadel P, 1995. Characterisation of moderately acid-treated, size-fractionated montmorillonites using IR and MAS NMR spectroscopy and thermal analysis. *J Mater Chem*, 5(3):496-474.
- Brindley GW, Brown G, 1980. *Crystal Structures of Clay Minerals and their X-ray Identification*, Mineralogical Society, London.
- Demirbag A, Cakmak I, 1996. Synthesis of epichlorhydrin-styrene block copolymers via cation-to-radical transformation process. *Macromolecular Reports*, A33(SUPPL. 2), 127.
- Dey RK, Ray AR, 2003. Synthesis, characterization, and blood compatibility of copolymers of polyamidoamines and N-vinyl pyrrolidone. *J Appl Polym Sci*, 90:4068-4074.
- Farmer VC, 1974. *Infrared Spectra of Minerals*, V.C. Farmer, Ed.; Mineralogical Society: London, p.331.
- Ferrahi MI, Belbachir M, 2004. Preparation of poly(oxybutyleneoxymaleoyl) catalyzed by a proton exchanged montmorillonite clay. *Molecules*, 9 :968-977.
- Ferrahi MI, Belbachir M, 2005. Synthesis of cyclic polyesters of poly(oxybutylene oxymaleoyl). *J Polym Res*, 12:167-171.
- Gao JY, Dubin PL, Muhoberac BB, 1997. Measurement of the binding of proteins to polyelectrolytes by frontal analysis continuous capillary electrophoresis. *Anal Chem*, 69:2945-2951.
- Garcia-Lopez D, Picazo O, Merino JC, Pastor JM, 2002. Polypropylene – clay nanocomposites: effect of compatibilizing agents on clay dispersion. *Eur Polym J*, 39:945-950.
- Ge H, Hu Y, Jiang X, Cheng D, Yuan Y, Bi H, Yang C, 2002. Preparation, characterization, and drug release behaviors of drug nimodipine-loaded poly(epsilon-caprolactone)-poly(ethylene oxide)-poly(epsilon-caprolactone) amphiphilic triblock copolymer micelles. *J Pharm Sci*, 91:1463-1473.
- Georgiev G, Konstantinov C, Kabaivanov V, 1992. The role of the charge-transfer complex during the copolymerization of N-vinylpyrrolidone and maleic anhydride. *Macromolecules*, 25, 6302-6308.
- Harper GR, Davies MC, Davis SS, Tadros TF, Taylor DC, Irving MP, Waters JA, 1991. Steric stabilization of microspheres with grafted polyethylene oxide reduces phagocytosis by rat Kupfer cells in vitro. *Biomaterials*, 12:695-699.
- Harrane A, Meghabar R, Belbachir M, 2002. A protons exchanged montmorillonite clay as an efficient catalyst for the reaction of isobutylene polymerization. *Int J Mol Sci*, 3(7):790-800.
- Hasegawa N, Okamoto H, Kawasumi M, Kato M, Tsukigase A, Usuki A, 2000. Polyolefin-clay hybrids based on modified polyolefins and organoclay. *Macromol Mater Eng*, 280/281:76-79.
- Hong-Quan X, Shao-Bo P, Jun-Shi G, 2003. Ring-opening copolymerization of epoxy-terminated polystyrene macromer with epichlorohydrin and study on properties of the copolymers. *Eur Polym J* 39 :715-724.
- Johnson SD, Anderson JM, Marchant RE, 1992. Biocompatibility studies on plasma polymerized interface materials encompassing both hydrophobic and hydrophilic surfaces. *J Biomed Mater Res*, 26:915-935.
- Kamada H, Tsutsumi Y, Yamamoto Y, Kihira T, Kaneda Y, Mu Y, Kodaira H, Tsunoda SI, Nakagawa S, Mayumi T, 2000. Antitumor activity of tumor necrosis factor- α conjugated with polyvinylpyrrolidone on solid tumors in mice. *Cancer Res*, 60:6416- 6420.
- Kim JC, Song ME, Park SK, EJ Lee, MJ Rang, HJ Ahn, 2002. Synthesis and characterization of nonionic 1-vinyl-2-pyrrolidinone/methacryloxy silicone copolymers: effects of molecular weight of silicone and crosslinking density, *J Appl Polym Sci*, 85:2244-2253.
- Lou X, Garrett KL, Rakoczy PE, Chirila TV, 2001. Synthetic hydrogels as carriers in antisense therapy: preliminary evaluation of an oligodeoxynucleotide covalent conjugate with a copolymer of 1-vinyl-2pyrrolidinone and 2-hydroxyethyl methacrylate. *J Biomater Appl*, 15(4):307-320.
- Matsushima S, Takasu A, Inai Y, Hirabayashi T, Era S, Sogami M, Kinoshada Y, 2000. Saturation transfer ratio in magnetic resonance imaging. A novel physical parameter for evaluation of the hydrophilicity of synthetic copolymer gels. *Polym J*, 32(10):828-833.
- Meghabar R, Megherbi A, Belbachir M, 2003. Maghnite-H+, an ecocatalyst for cationic polymerization of N-vinyl-pyrrolidone. *Polymer*, 44 :4097-4100.
- Moeke HHW, 1974. *Infrared Spectra of Minerals*, V.C. Farmer, Ed.; Mineralogical Society: London, p.365.
- Storey RF, Mullen BD, Melchert KM, 2001. Synthesis of novel hydrophilic poly(ester-carbonates) containing pendent carboxylic acid groups. *J Macromol Sci Pure Appl Chem*, 38:897-917.
- Valero V, Buzdar AU, Theriault RL, Azarnia N, Fonseca GA, Willey J, Ewer M, Walters RS, Mackay B, Podoloff D, Booser D, Lee LW, Hortobagyi GN, 1999. Phase II trial of liposome-encapsulated doxorubicin, cyclophosphamide, and fluorouracil as first-line therapy in patients with metastatic breast cancer. *J Clin Oncol*, 17:1425-1434.
- Yahiaoui A, Belbachir M, Hachemaoui A (2003). An acid exchanged montmorillonite clay-catalyzed synthesis of polyepichlorhydrin. *Intl J Mol Sci*, 4 :548-561.
- Yahiaoui A, Belbachir M, Hachemaoui A, 2003. Cationic polymerization of 1,2-epoxypropane by an acid exchanged montmorillonite clay in the presence of ethylene glycol. *Int J Mol Sci*, 4:572-585 .
- Yang Q, Xu ZK, Dai ZW, Wang J, Ulbricht M, 2005. Surface modification of polypropylene microporous membranes with a novel glycopolymer. *Chem Mater*, 17:3050-3058.
- Zeng QH, Wang DZ, Yu AB, Lu GQ, 2002. Synthesis of polymer-montmorillonite nanocomposites by in situ intercalative polymerization. *Nanotechnology*, 13:549-553.