ELSEVIER

Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 44 (2003) 4097–4100

polymer

www.elsevier.com/locate/polymer

Maghnite-H^+, an ecocatalyst for cationic polymerization of *N*-vinyl-2-pyrrolidone

R. Meghabar*, Affaf Megherbi, Mohammed Belbachir

Laboratoire de Chimie des Polymères, Département de Chimie, Faculté des Sciences, Université d'Oran Essenia,
BP 1524 El M'Nouar, 31000 Oran, Algeria

Received 28 February 2003; received in revised form 13 May 2003; accepted 15 May 2003

Abstract

The polymerization of *N*-vinyl-2-pyrrolidone catalyzed by the Maghnite-H^+ (Mag-H) was investigated. Mag-H is a montmorillonite sheet silicate clay, exchanged with protons. It was found that the cationic polymerization of *N*-vinyl-2-pyrrolidone (NVP) is initiated by Mag-H at 30 °C in bulk and in solution. The effect of the amount of Mag-H, the temperature and the solvent was studied. The polymerization rate increased with increase in the temperature and the proportion of catalyst, and it was larger in nitrobenzene than that in toluene. These results indicated the cationic nature of the polymerization. It may be suggested that the polymerization is initiated by proton addition to monomer from Mag-H.

Keywords: Cationic polymerization; Clay; *N*-Vinyl-2-pyrrolidone

1. Introduction

Over the past 50 years, *N*-vinyl-2-pyrrolidone polymers (PVP) have been extensively used, especially in the pharmaceutical, cosmetic, textile and food industry as well as for numerous technical applications.

In opposition to the free radical polymerization, the *N*-vinyl-2-pyrrolidone (NVP) polymerizes poorly by cationic mechanism, giving low molecular weight product [1,2]. Monomer and its oligomers forming stable complexes with the initiators, short-life propagating cations, chain transfer reaction, etc. [3] are often invoked to explain the failure to produce high degree of polymerization. However, the recently reported cationic polymerization of NVP was initiated by carbon black surface and electrochemically by anodic polymerization on a Pt surface leading to high molecular PVP [4–8].

Furthermore, the cationic initiators used to make polymers are expensive. They may be poisoned by products of the reaction or impurities present in the monomer feed, and contain heavy metals such as chromium, mercury, antimony, etc. that present environmental disposal problems for the user. Frequently, these initiators require the use of very high or very low temperature and high pressures during the polymerization reaction, thus the yield is often poor. The separation of the initiators from the polymer is not always possible. Therefore, the presence of toxic initiator presents problems in the manufacture of polymers used especially in medical and veterinary procedures.

Recently, Mukul et al. [9,10] have prepared new composites from montmorillonite and some heterocyclic polymers such as poly(*N*-vinylcarbazole) and polypyrrole. The cationic polymerization of *N*-vinylcarbazole and pyrrole were initiated directly by montmorillonite.

The purpose of this paper is to study the cationic polymerization of NVP by a montmorillonitic clay called Maghnite-H^+, a new non-toxic cationic catalyst for vinyl monomers [11,12]. Mag-H can be easily separated from the polymer product and regenerated by heating to a temperature above 100 °C [11]. The effect of some factors such as the amount of the Mag-H, the temperature or the dielectric constant of solvent, and the mechanism of initiation are discussed.

---

* Corresponding author. Tel.: +213-41332270; fax: +213-41510057.
E-mail address: rachidmeghabar@yahoo.fr (M. Rachid).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00400-2

2. Experimental

2.1. Preparation of the Maghnite-H$^+$

The preparation of the Mag-H was carried out by using a method similar to that described by Belbachir et al. [11]. Indeed, the raw-Maghnite (20 g) was crushed for 20 min using a Prolabo ceramic balls grinder. It was then dried by baking at 105 °C for 2 h. The Maghnite was then weighed and 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, until saturation was achieved over 2 days at room temperature, the mineral was washed with water until it became sulfate free and then dried at 150 °C.

2.2. Reagents

The monomer (Aldrich 99%) was purified by fractional distillation under reduced pressure. Methanol was dried over magnesium sulfate. Nitrobenzene was washed with dilute aqueous solution of sulfuric acid, dried over calcium chloride, and distilled under reduced pressure. Toluene was washed with concentrated sulfuric acid and water, refluxed over sodium, and distilled.

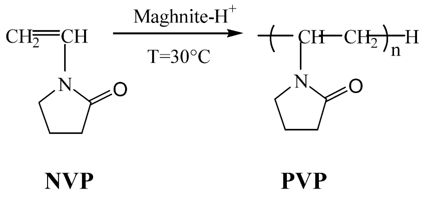
2.3. Polymerization procedures

2.3.1. Kinetics procedure

The polymerization of NVP was carried out in a heterogeneous system. Each mixture was prepared with 4.5 mmol of NVP and 0.05 g of Mag-H and were introduced in several (6–8) sealed tubes. The mixture was stirred with a magnetic stirrer under dry nitrogen. After a definite period of time, a quantity of methanol was then added and the content was dried in vacuo to eliminate Mag-H. In the next step, a given quantity of phenol was added as an external standard, and the solution was analyzed using high pressure liquid chromatography HPLC (standard spherisorb ODS column, mean diameter of particles: 5 μm, column length: 25 cm; eluant: methanol; $\lambda = 254$ nm). The consumption curve of the monomer is plotted.

2.3.2. Molecular weights

The purification of polymer was carried out as follows: a large amount of methanol was added to the mixture of the reaction which was filtered to eliminate Mag-H. The unreacted monomer and methanol were then pumped off at 60–80 °C and the polymer (PVP) was put into a vacuum desiccator because of its high hygroscopicity.



Scheme 1.

The viscosimetric molecular weights were calculated from the intrinsic viscosity measured in methanol at 30 °C, on a capillary viscosimeter, Viscologic TI.1, version 3-1 Semantec, by the following equation [13]

$$[\eta] = 23.10^{-3}\bar{M}_v^{0.65}$$

3. Results and discussion

3.1. Polymerization of NVP by Mag-H

The *N*-vinyl-2-pyrrolidone is well known to be polymerized by protonic acid such as boron trifluride etherate [14–16]. The cationic polymerization of NVP was examined in the presence of Mag-H powder in bulk at 30 °C (Scheme 1). The results are shown in Table 1 and Fig. 1. The proof for this polymerization obtained by ^{1}H NMR spectroscopy (Brucker AC 200, solvent: $CDCl_3$), is shown in Fig. 2.

3.2. Effect of the amount of Mag-H on the polymerization

Fig. 3 shows the effect of the amount of Mag-H on the polymerization rate of NVP. Indeed, using various amounts of Mag-H, 5, 10, 20, and 50% by weight, the polymerization of NVP was carried in bulk at 30 °C. The polymerization rate increased with the amount of Mag-H, in which the effect of Mag-H as a cationic catalyst of NVP is clearly shown. Similar results are obtained by Harrane et al. [12] in the polymerization of isobutylene by Mag-H, which polymerizes only by cationic process [17].

3.3. Effect of temperature on polymerization

In the presence of Mag-H, the polymerization of NVP in bulk was carried out at 30, 35, 60, and 80 °C and the effect of temperature on polymerization was examined. The results

Table 1
Polymerization of NVP initiated by Maghnite-H$^+$

Time (h)	1	2	3	4	5	6	10	15
Conversion (%)	07.87	12.17	15.32	18.89	29.54	45.78	58.65	61.14

NVP, 4.5 mmol ; Mag-H, 0.05 g; 30 °C.

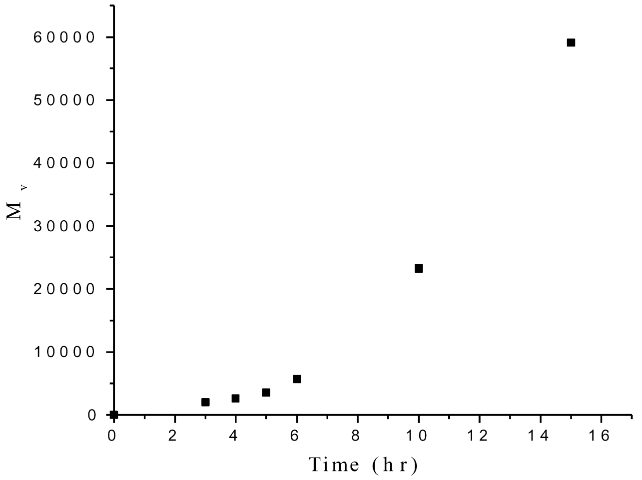


Fig. 1. Viscosimetric molecular weights of PVP catalyzed by Mag-H, 0.05 g; NVP: 4.5 mmol; 30 °C.

are shown in Fig. 4. The rate of polymerization was found to increase with the temperature of the polymerization.

The rate of polymerization at 30 °C, however, was the small. A similar effect was shown in the polymerization of NVP initiated by γ-poly(glutamic acid) [18]. At the temperature of 30 °C, we obtain high masses ($M_v = 59,100$) at weak conversion rate. On the other hand at 80 °C, although the conversion rate is high (90%), the viscosimetric mass remains low ($M_v = 5996$).

3.4. Effect of solvent on the polymerization

The polymerization of NVP was carried out in toluene ($\varepsilon = 2.24$, $0 < \mu < 2$ D) and nitrobenzene ($\varepsilon = 34.8$, $\mu > 25$ D) and the effect of solvent on the polymerization of NVP was studied. The results are shown in Fig. 5. The rate of polymerization in nitrobenzene was found to be much larger than that in toluene. The chain transfer of growing polymer cation to monomer takes place more easily in nitrobenzene than in toluene. Similar results was found, by Tsubokawa et al. [18–20], in the cationic polymerization of *N*-vinylcarbazole initiated successively by γ-poly (glutamic acid), carbon fibber and carbon black.

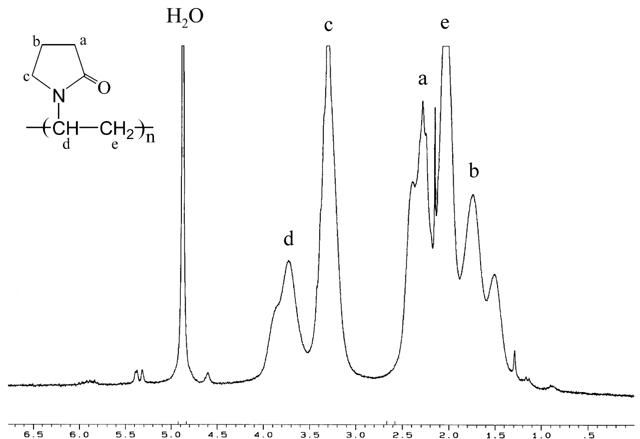


Fig. 2. ^{1}H NMR-spectra ($CDCl_3$) of PVP polymerized with Mag-H, $T = 30$ °C.

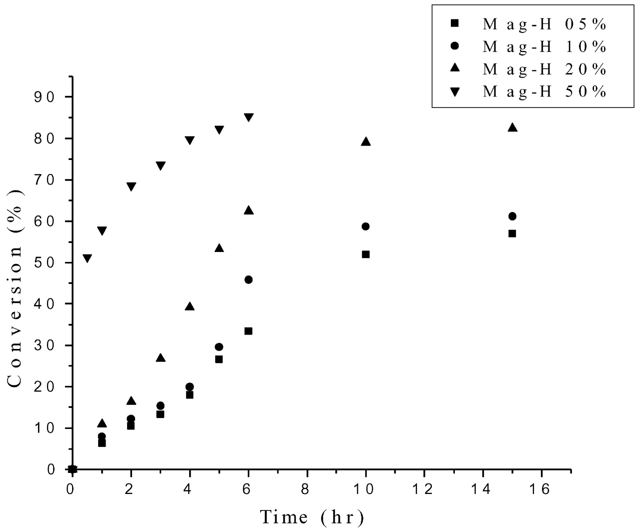


Fig. 3. Effect of the amount of the catalyst on polymerization of NVP; NVP, 4.5 mmol; 35 °C.

3.5. Mechanism of polymerization

The polymerization of NVP is considered to be initiated by proton addition from Mag-H to NVP and the Maghnite takes place as counter-ion. Propagation and termination then take place by conventional cationic mechanism. Termination occurs by proton transfer to monomer and/or to initiator produced by unsaturation as shown in the reaction scheme (Eqs. (1)–(3)).

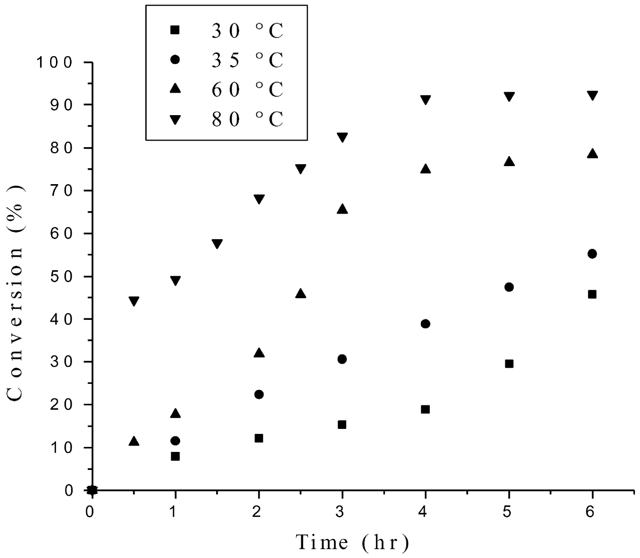


Fig. 4. Effect of temperature on the polymerization of the NVP; catalyzed by Mag-H, 0.05 g; NVP, 4.5 mmol.

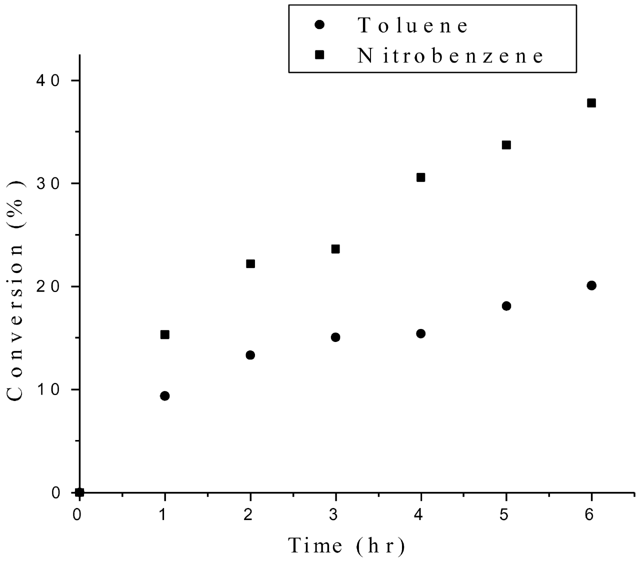
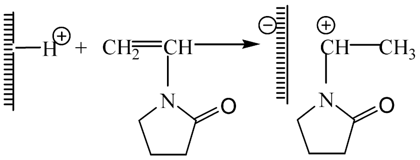


Fig. 5. Effect of solvent on the polymerization of NVP, catalyzed by Mag-H, 0.05 g; NVP, 4.5 mmol; solvent: 2 cm^3; 30 °C.

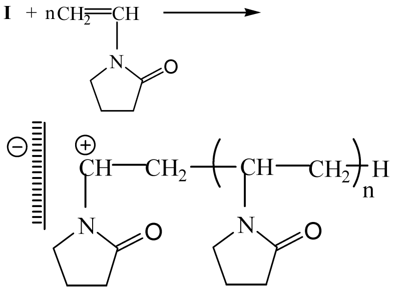
Initiation. Initiation is done between the initiator and a first molecule of the monomer to form the active species



(1)

Mag-H **NVP** **I**

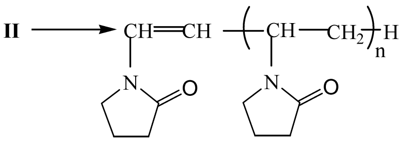
Propagation



(2)

II

Termination. We suppose that there was formation of a double bond at the end of the chain of the PVP by spontaneous transfer



(3)

4. Conclusions

The cationic polymerization of NVP was found to be initiated by Maghnite-H$^+$ powder in heterogeneous phase. The polymerization was considered to be initiated by the proton addition from Maghnite-H$^+$ to monomer and the propagation proceeds with Maghnite as counter-ion.

Acknowledgements

The research was supported in parts by the National Agency for Development and Research of Algeria. We thank the persons in charge for this agency.

References

[1] Haaf F, Sanner A, Strub F. Polym J 1985;17:143.
[2] Barabas ES. Concise encyclopedia of polymer, science and engeneering. New York: Wiley; 1990. p. 1236.
[3] Schade C. Private communication.
[4] Tsubokawa N, Takeda N, Kanamaru A. J Polym Sci, Polym Lett Ed 1980;18:625.
[5] Tsubokawa N, Takeda N, Iwasa T. Polym J 1987;13:1093.
[6] Tsubokawa N, Maruyama H, Sone Y. J Makromol Sci Chem 1988; A25:171.
[7] Tsubokawa N, Yoshikara T. Polym J 1991;23:177.
[8] Léonard-Stibbe E, Lécayon G, Deniau G, Viel P, Defranceschi M, Legeay G, Delhalle J. J Polym Sci, Part A: Polym Chem 1994;32: 1551.
[9] Mukul B, Suprakas SR. Polymer 1998;39(25):6423.
[10] Suprakas SR, Mukul B. Mater Res Bull 1999;34(8):1187.
[11] Belbachir M, Bensaoula A. US Patent, No 6,274,527 B1; 2001.
[12] Harrane A, Meghabar R, Belbachir M. Int J Mol Sci 2002;3:790.
[13] Levy GB, Frank HP. J Polym Sci 1955;17:247.
[14] Schildkencht CE, Zoss AO, Grosser F. Ind Engng Chem 1949;41: 2891.
[15] Lindemann MK. In: Mark HF, Gaylord NG, editors. Encyclopedia of polymer science and technology, vol. 14. New York: Wiley; 1971. p. 239.
[16] Vollmet B. Polymer chemistry, (translated by Immergut EH). Berlin: Springer; 1973. p. 45.
[17] Odian G. La polymerisation: principes et applications. New York: Ed. Technica; 1994. p. 222.
[18] Tsubokawa N, Inagaki M, Kubota H, Endo T. J Polym Sci, Part A: Polym Chem 1993;31:3193.
[19] Tsubokawa N, Maruyama H, Sone Y. Polym Bull 1986;15:209.
[20] Okhita K, Tsubokawa N, Noda M, Uchiyama M. Carbon 1977;15:194.