

New Approach for the Polymerization of 2-Chloroethyl Vinyl Ether Using a Maghnite Clay as Eco-Catalyst

Malika Chabani,¹ Ahmed Yahiaoui,² Aïcha Hachemaoui,² Mohammed Belbachir¹

¹Laboratoire de Chimie des Polymères, Faculté des sciences, Université d'Oran, BP 1524 El-Menouer 31000 Oran, Algérie

²Laboratoire de chimie Organique, Macromoléculaire et des Matériaux (LCOMM), Faculté des Sciences et de la Technologie, Université de Mascara BP 763 Mascara 29000, Algérie

Received 22 February 2011; accepted 26 January 2011

DOI 10.1002/app.34242

Published online 10 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The polymerization of 2-chloro ethyl vinyl ether (CEVE) 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 2-chloroethyl vinyl ether is initiated by Mag-H+ at 20°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 of the temperature and the proportion of catalyst, and it was higher in dichloromethane than that in toluene. It may be suggested that the polymerization is initiated by proton addition to monomer from Mag-H+. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1800–1806, 2011

Key words: cationic polymerization; clay; 2-chloroethyl vinyl ether

INTRODUCTION

Since the first example of cationic polymerization of vinyl ethers was discovered with use of the combination of hydrogen iodine as an initiating system,¹ a variety of binary initiating systems consisting of a protonic acid and a Lewis acid have been reported to induce the living polymerizations of cationically polymerizable vinyl monomers.^{2–6}

The polymerization of 2-chloroethyl vinyl ether (CEVE) was initiated by $\text{CH}_3\text{CHIOR}/\text{ZnI}_2$ at low temperature in solution.

Nuyken and coworkers⁸ synthesized a series of poly (substituted vinyl ether) based on the living sequential copolymerization of 2-chloroethyl vinyl ether and isobutyl vinyl ether. The obtained block copolymers are modified by nucleophilic substitution of the chlorine in the poly(2-chloroethyl vinyl ether) (PCEVE) block. With this method a variety of amphiphilic polyvinyl ether-based polymers becomes accessible.

The use of acid-treated clays as a solid source of protons in number of industrial significant reactions continues because they constitute a widely available, inexpensive solid source of protons, e.g., they have been employed as cracking catalysts until the 1960s,⁹ and are still currently used in industrial processes,

such as the alkylation of phenols¹⁰ and the dimerization and polymerization of unsaturated hydrocarbons.¹¹ Montmorillonites have both Brønsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly-active catalysts for acid-catalyzed reactions.¹² Intercalated organic molecules are mobile and can be highly polarized when situated in the space between the charged clay layers. These exchanged Montmorillonites have been successfully used as catalysts for the reaction of polymerization.¹³

There is, to date, no information on the polymerization of CEVE with clay catalyst. In continuation of our studies on environmentally benign methods using solid supports,^{14,15} we report for the first time the synthesis of PCEVE via cationic polymerization by an acid exchanged Montmorillonite called Maghnite-H (Mag-H+), a new non toxic cationic catalyst for vinyl monomers.¹⁶ Mag-H+ can be easily separated from the polymer product and regenerated by heating to temperature higher than 100°C.

The effects of different synthesis parameters, such as the amount of Mag-H+, monomer, temperature, solvent, are discussed, together with the mechanism of polymerization.

EXPERIMENTAL

Materials

CEVE was commercially supplied (Fluka) and distilled twice over calcium hydride before use. Polymerization solvents (toluene, CH_2Cl_2) were purified

Correspondence to: A. Yahiaoui (yahmeddz@yahoo.fr).

Contract grant sponsor: National Agency for Development and Research of Algeria.

TABLE I
Elemental Composition of Proton-Exchanged Maghnite- H+ x Samples

Samples	Compositions (wt %)											Monomer conversion ^{a%}
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	As	LOI	
Raw -Mag	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	0.05	11	00
M1	70.75	14.67	1.05	0.30	1.01	0.49	0.78	0.16	0.75	0.04	10	25.5
M2	71.00	14.60	1.00	0.30	0.98	0.39	0.78	0.16	0.55	0.04	10.2	34
M3	71.58	14.45	0.95	0.29	0.91	0.35	0.77	0.15	0.42	0.03	10.1	53
M4	71.65	14.20	0.80	0.28	0.85	0.30	0.77	0.15	0.39	0.01	10.6	74
M5	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	0.01	11	90
M6	73.20	13.85	0.70	0.27	0.78	0.20	0.76	0.13	0.31	0.02	9.78	29
M7	75.31	13.52	0.71	0.26	0.78	0.18	0.75	0.13	0.32	0.01	8.03	18

Loss on ignition (LOI).

^a Mag-H+/CEVE: 3 %(w/w) *T* = 20°C, reaction time 3 h.

by usual methods and distilled at least twice over calcium hydride before use.

Raw-Maghnite, Algerian Montmorillonite clay, was procured from Bental (Algerian Society of Bentonite).

Preparation of the Mag-H+

Mag-H+ was prepared according to the process reported in our previous study.¹⁶ Raw-Mag (montmorillonite clay) (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 Mag was then weighed and placed in an Erlenmeyer flask together with 500 mL of distilled water. The Mag/water mixture was stirred using a magnetic stirrer and combined with different concentrations of sulfuric acid solution to obtain various forms of "Mag-H+ × M" catalyst. When saturation was achieved over two days at room temperature, the mineral was washed with distilled water until no sulfate ions were indicated present in the filtrate using BaCl₂. The Mag-H+ was then dried at 105°C and then finely ground and. The concentrations 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35M of sulfuric acid treatment solutions were used to prepare catalyst samples: "M1," "M2," "M3," "M4," "M5," "M6," and "M7," respectively.

Catalyst characterizations

Samples for X-Ray Fluorescence (XRF) analysis were prepared using the LiB₄O₇ fusion method. The resulting beads were analyzed on a Philips PW 2400 XRF spectrometer. Loss on ignition (LOI) was determined by heating the sample at 1000°C for 60 min and recording the % weight loss.

Polymerization procedure

Polymerizations were carried out under dry nitrogen at 20°C in bulk in a flask equipped with a modified

two-way Teflon stopcock. The procedure was identical in both cases, involving addition of catalyst to the stirred bulk CEVE. Prior to use, Mag-H+ was dried at 120°C overnight and then transferred to a vacuum desiccator containing P₂O₅ to cool to room temperature overnight. An example reaction is detailed here. After charging the reaction vessel with 9.4 mmol of CEVE in bulk or solution (methylene chloride or toluene as a solvent), 0.01 g of Mag-H+ (1% w/w) was added. At the required time, an aliquot of the reaction mixture was then taken in such manner as to exclude clay mineral. At the end of the reaction, the resulting mixture was dissolved in dichloromethane, filtered to remove the clay. The unreacted monomer and solvent in the reaction mixture were removed by rotary evaporation. The polymer mixture was dried under vacuum (1 Torr) at ~40°C for two days, and the yield was measured by gravimetry.

Polymer characterization

¹H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR spectrometer equipped with a probe BB05 mm, in CDCl₃. Tetramethylsilane (TMS) was used as the internal standard in these cases. Intrinsic viscosity [η] measurements were performed at 20°C in dichloromethane using a capillary viscometer SEMATECH (VISCOLOGIC TL1). The sample concentration was 1 mg/mL. Average molecular weights and molecular weight distributions of the different polymers were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 × 7.5 mm²) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm³), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 mL/min at 35°C. Poly(ethylene oxide)

TABLE II
Comparison in the Composition (in %) of American, French, and Maghnia (Algerian) Bentonites

	Wyoming (USA) ¹⁹	Vienne (Frensh) ¹⁸	Raw-Maghnite (Algeria)	Maghnite-H ⁺ (Algeria)
SiO ₂	50.04	57.49	69.39	71.70
Al ₂ O ₃	20.16	20.27	14.67	14.03
Fe ₂ O ₃	0.68	2.92	1.16	0.71
FeO		0.19		
CaO	1.46	0.23	0.30	0.28
MgO	0.23	3.13	1.07	0.80
K ₂ O	1.27	0.28	0.79	0.77
Na ₂ O	Tr	1.32	0.5	0.21
TiO ₂		0.12	0.16	0.15
SO ₃			0.91	0.34
As			0.05	0.01

standards (483–580.10³ g/mol) were used to calibrate the SEC.

RESULTS AND DISCUSSION

The purpose of this paper is the synthesis of poly(2-chloroethyl vinyl ether) (PCEVE) by bulk polymerization of 2-chloroethyl vinyl ether catalyzed by Maghnite-H⁺. The interesting aspect of this chemistry is the environment friendly nature of the reaction because it does not imply the disposal of metal catalysts.^{15,16}

It can be seen that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite. Acid treatment of "Raw-Maghnite" causes reduction in octahedral content (Al₂O₃) resulted in an increase in the proportion of silica (SiO₂) (Table I).

It is necessary to report that the best value of monomer conversion was obtained with "Mag-H + 0.25M," in which there is a complete saturation of Montmorillonite with protons without destruction of catalyst structure.^{13,17} For this reason we have used this sample for all kinetic studies.

Table II shows the various types of montmorillonites studied, we can see that Maghnite has 11.9% more SiO₂ than that from Wyoming and 19.35% than

from Montmorillon (Vienne, French).¹⁸ When treated with sulfuric acid, this difference is even greater; 14.21% and 21.66% as compared with Wyoming¹⁹ and Vienne clay, respectively. Maghnite contains 5.60% and 5.49% less Al₂O₃, than the Wyoming and Vienne clays, respectively.

Cationic polymerization of CEVE by Mag-H+

The cationic ring-opening polymerization of CEVE was examined in the presence of Mag-H⁺ as a catalyst at 20°C for 1 h. The results are shown in Table III and Figure 2. The proof for this polymerization obtained by ¹H NMR spectroscopy is shown in (Fig. 1).

The spectrum (Fig. 1) showed different peaks,²⁰ the methylene groups of the main chain as large signal in the range of 1.5–2 ppm, the methylene groups (CH₂Cl) and the methylene and methine groups (CH₂O and CHO-) in the range of 3.4–4 ppm, the terminal methyl groups at 1.2 ppm. Besides these well-known resonances, analysis shows at 4.9 ppm the characteristic resonance of the protons borne by the terminal double bond.

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

Amount of catalyst (Mag-H⁺/CEVE) was an important factor of polymerization. Figure 2 showed the effect of amount of catalyst on the polymerization rate of CEVE. We can see from Table III, that the polymerization rate increased with the amount of Mag-H⁺, in which the effect of Mag-H⁺ as a cationic catalyst for CEVE polymerization is clearly shown. 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. Similar results were obtained by Meghabar et al.²¹ in the polymerization of *N*-Vinylpyrrolidone by Mag-H⁺, which polymerizes only by cationic process.

In contrast, as depicted in Figure 3 and Table III, the viscosity and the molecular weight are inversely proportional to the amount of Mag-H⁺. This finding is in good agreement with the proposal that Mag-

TABLE III
Polymerization of CEVE Induced by the Mag-H+ for 60 min

Catalyst	Solvent	Amount of catalyst	Yield (%)	\bar{M}_n	\bar{M}_w/\bar{M}_n
Mag-H+	Bulk	1%	34	3800	2.30
Mag-H+	Bulk	2%	63	2870	2.68
Mag-H+	Bulk	3%	70	2080	2.45
Mag-H+	CH ₂ Cl ₂	1%	27.72	4370	2.05
Mag-H+	Toluene	1%	22.25	4100	2.15
1st recovered Mag-H+	Bulk	1%	31	3700	2.35

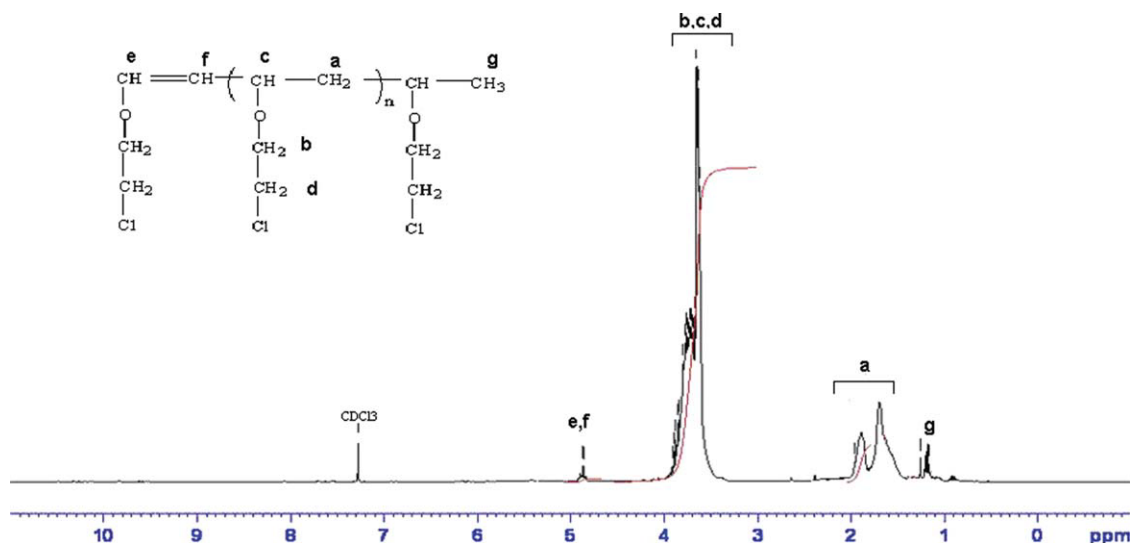


Figure 1 ^1H NMR spectrum (CDCl_3) of PCEVE polymerized with Maghite-H+, $T = 20^\circ\text{C}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

H^+ is present as the active initiator species since the number of those species should be related to their surface area. Kadakowa et al.,²² and Crivello and Fan²³ obtain similar results, in the polymerization of lactones by Sn-montmorillonite and cyclohexene oxide by Cobalt, respectively.

Effect of time on the polymerization

Figure 2 shows the conversion of monomer versus time for the polymerization of CEVE using Mag-H+ as catalyst. As the figure shows, polymerization takes place slowly and smoothly, reaching a yield of 88% after 180 min at 20°C in the presence of 3% of Mag-H+. The polymerization yield became constant at a time; this is probably the result of an increase in the medium viscosity.

The effect of polymerization duration on the intrinsic viscosity, as shown in Figure 3, has the same trend as that of yield.

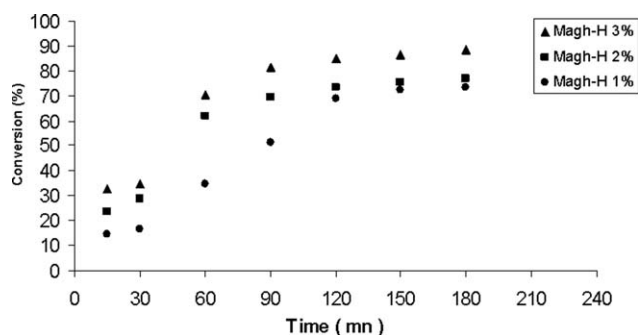


Figure 2 Effect of Mag-H+/monomer weight ratio on monomer conversion; CEVE: 9.4 mmol; 20°C in bulk.

After the polymerization, the Mag-H+ catalyst was removed from the reaction mixture by filtration. The recovered Mag-H+ was dried at 120°C for 3 h under reduced pressure, and used as the catalyst again for the polymerization of CEVE under the same conditions as above. The yield and $[\eta]$ values (Entry 6, Table III) were comparable with those shown in Entry 1 (Table III). For example, when the polymerization was carried out using the removed Mag-H+ under the conditions as in Entry 1, PCEVE was obtained in 31% yield. The \bar{M}_n value was 3700. These experimental results indicate that the catalytic activity did not decrease as compared with 1st run. Although the X-ray peak of the fresh and the recovered Maghite-H did not change. This implies that the original structure was well preserves after polymerization and no delamination of the clay was observed (Fig. 4).

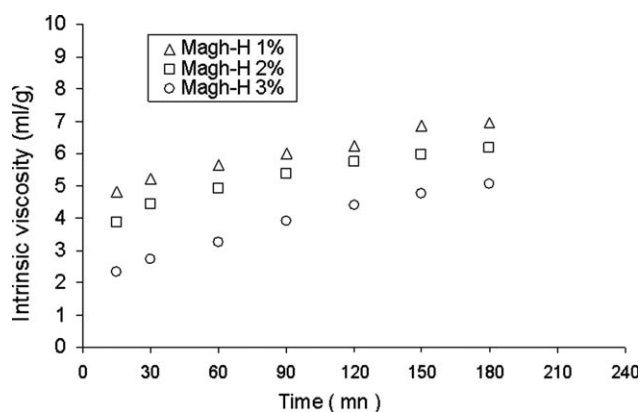


Figure 3 Effect of polymerization duration and amount of Mag-H+ on intrinsic viscosity of PCEVE (CVE: 9.4 mmol in Bulk at 20°C).

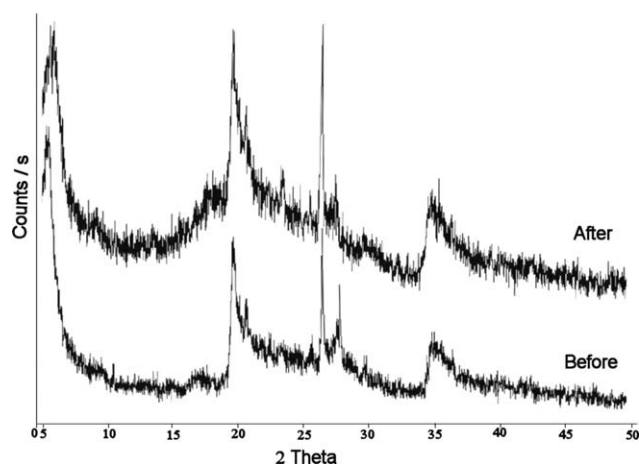


Figure 4 X-ray diffraction patterns of fresh and recovered Maghnite-H+.

Effect of temperature on the polymerization

Using CEVE and 1% [Mag-H+/CEVE] (w/w), the polymerization was carried out at different temperatures 0, 10, and 20°C and the effect of temperature on polymerization was studied. In the absence of Mag-H+ no polymerization could be detected. In the presence of Mag-H+, however, the polymerization was initiated. Figure 5 shows that polymerization temperature has much influence on the yield of PCEVE. The yield increased with the temperature rising from 0 to 20°C and reached a high yield of 88% at 20°C.

As Figure 6 shows, the intrinsic polymer viscosity decrease, depending on the polymerization temperature, in the following order: 0°C > 10°C > 20°C. This is because increasing the temperature causes an increase in the rate of chain transfer reaction of the growing polymer cation (inter and intramolecular).^{24,25}

Effect of solvent on the polymerization

The polymerization of CEVE was carried out in toluene ($\epsilon = 2.38$, $\mu = 0.43$ D) and dichloromethane ($\epsilon =$

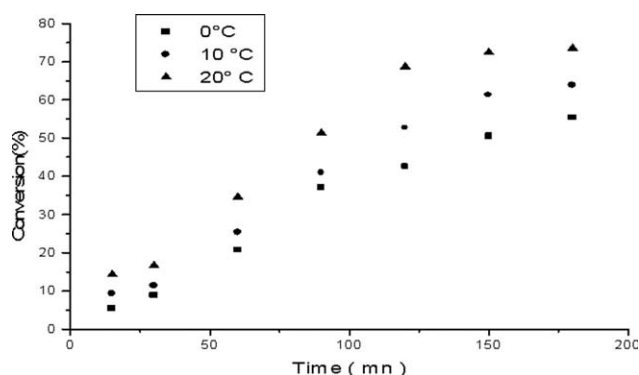


Figure 5 Temperature effect on the PCVE yield (CVE: 9.4 mmol, 1% of Mag-H+ in bulk).

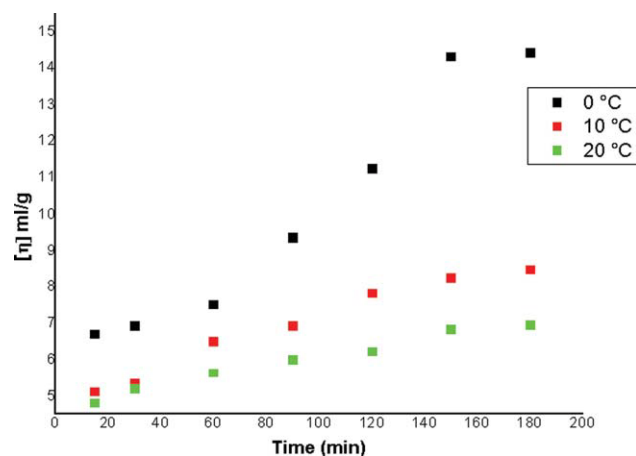


Figure 6 Temperature effect on the intrinsic viscosity of PCEVE (CEVE: 9.4 mmol, 1% of Mag-H+ in Bulk). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

8.93, $\mu = 1.5$ D) and the effect of solvent on the polymerization of CEVE was studied.

Data in Table III show that polymerization carried out in solution lead to higher molecular weights and narrower MWDs (M_w/M_n). However, conversions in solution were smaller than the ones obtained in bulk polymerization. Law conversions in solution polymerization may be explained by “the initiating active sites” of Mag-H+ at the surface of Mag-H+.¹⁵

The rate of polymerization in dichloromethane was found to be much higher than that in toluene (Fig. 7). There is an effect of the dielectric constant of solvent (dichloromethane and toluene) on the conversion of monomer. The most polar solvent produces a polymer with the highest conversion yield. The chain transfer of growing polymer cation to

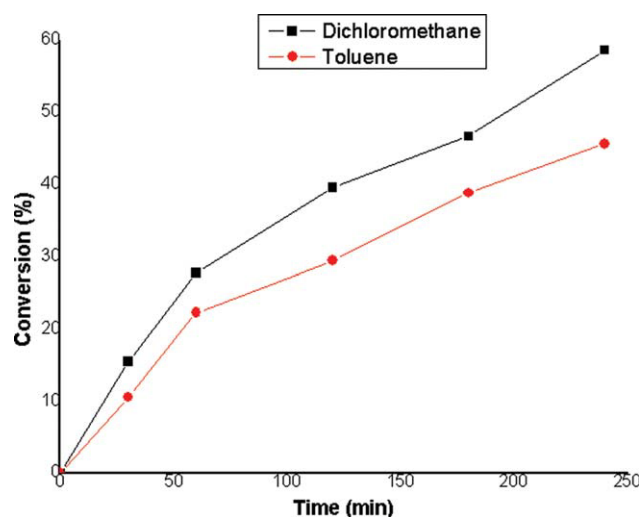
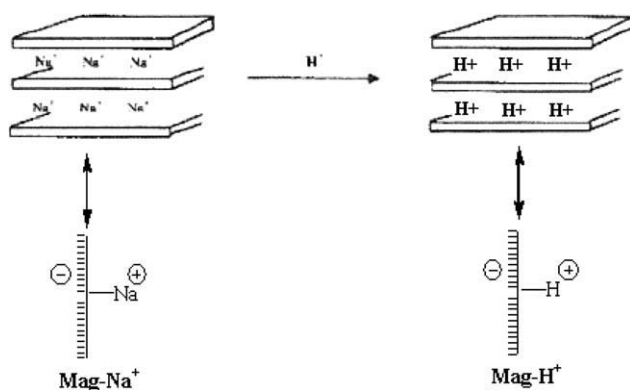


Figure 7 Effect of solvent on the polymerization of CEVE (1% of Mag-H+, [CEVE]: 0.94M, 20°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1 Schematic representation of Mag-Na^+ and Mag-H^+ .

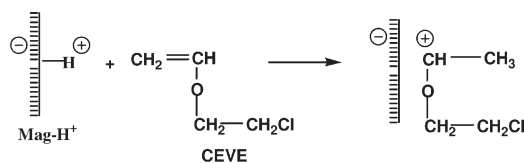
monomer takes place more easily in dichloromethane than in toluene. Similar results were found, by Tsubokawa et al.,²⁶ in the cationic polymerization of *N*-vinylcarbazole initiated successively by γ -poly(-glutamic acid), carbon fiber, and carbon black.

Mechanism of polymerization

Mag-H^+ is a proton-exchanged montmorillonite sheet silicate clay. The Montmorillonite lattice is composed of layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet.¹¹ CEVE polymerizes cationically by opening of the double bond in the monomer. According to the foregoing discussion and the results of product analysis, we may suggest a cationic mechanism for the resulting reaction of polymerization induced by Mag-H^+ . Protons carried by Montmorillonite sheets of Mag-H^+ (Scheme 1) induce the cationic polymerization. Propagation then takes place by a conventional cationic mechanism.

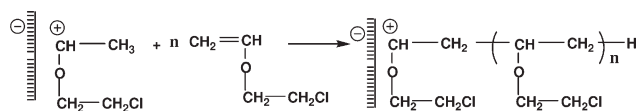
Initiation

Initiation involves the reaction between CEVE and Mag-H^+ and yields carbocation intermediate; the formation of this species is the rate determining step.



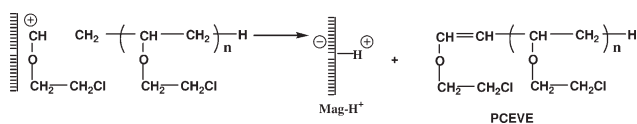
Propagation

The propagation step is the successive reaction of CEVE with the carbocation intermediate.



Termination

We suppose that there was formation of a double bond at the end of the chain of the CEVE by spontaneous transfer and regeneration of catalyst (Mag-H^+).



CONCLUSIONS

This work shows that the preparation of PCEVE can be induced in heterogeneous phase by proton exchanged Montmorillonite clay " Mag-H^+ ".

The catalytic activity of this catalyst (measured by the conversion) and the viscosity of the formed polymer depend on the proportion of catalyst in the reaction medium and the temperature of reaction. The polymerization was considered to be initiated by the proton addition from Mag-H^+ to monomer. PCEVE was produced by a very simple procedure: just by filtering, the clay can be separated from the reaction mixtures. The proton exchanged clay is inexpensive, stable, noncorrosive and may be recovered and reused.

References

- Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1984, 17, 265.
- Higashimura, T.; Sawamoto, M. *Adv Polym Sci* 1984, 62, 49.
- Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol Chem Macromol Symp* 1988, 13/14, 457.
- Sawamoto, M. *Prog Polym Sci* 1991, 16, 111.
- Sawamoto, M.; Higashimura, T. *Makromol Chem Macromol Symp* 1992, 60, 47.
- De Velde, P. V.; Goethals, E.; Du Prez, F. *Polym Int* 2003, 52, 1589.
- Nuyken, O.; Ingrish, S. *Makromol Chem Phys* 1998, 199, 711.
- Nuyken, O.; Ingrish, S. *Makromol Chem Phys* 1998, 199, 607.
- Thomas, C.L.; Hickey, J.; Stecker, G. *Ind Eng Chem* 1950, 42, 866.
- Kaplan, H. US Patent 1966, 3,287,422.
- Hojabri, F. *J Appl Chem Biotechnol* 1971, 21, 87.
- Ballantine, J. A.; Davies, M.; Purnell, J. H.; Rayanakorn, M.; Thomas, J. M. *J Chem Soc Chem Commun* 1981, 427, 4.
- Breen, C.; Madejova, J.; Komadel, P. *J Mater Chem* 1995, 5, 496.
- Yahiaoui, A.; Belbachir, M. *J Appl Polym Sci* 2006, 100, 1681.
- Yahiaoui, A.; Belbachir, M.; Hachemaoui, A. *Int J Mol Sci* 2003, 10, 572.

16. Belbachir, M.; Bensaoula, A. US Patent 2001, 690, 101.
17. Madejova, J.; Komadel, P. J Phys Chem B 1997, 10, 5324.
18. Damour, A.; Salvétat, D. Ann Chim Phys 1847, 21, 376.
19. Bentonite, U. Wyoming (USA), Analytical Data Reference, Clay Min, Report N° 7. Am Petro. Int. Project 49 1950.
20. Hashimoto, T.; Rahman, M. S.; Yamada, Y.; Kodaira, T., J. M. S. Pure Appl Chem A 1999, 36, 449.
21. Meghabar, A.; Megherbi, A.; Belbachir, M. Polymer 2003, 44, 2397.
22. Kadokawa, J.; Iwasaki, Y.; Tagaya, H. Green Chem 2002, 4, 14.
23. Crivello, J. V.; Fan, M. J Polym Sci, Part A Polym Chem 1992, 30, 1.
24. Inoue, S.; Aida, T. In Ring-opening Polymerization; Ivin, K. J.; Saegusa, T., Eds.; Applied Science Publishers: New York, 1984; Vol.1.
25. Goethals, E. J Pure Appl Chem 1976, 48, 335.
26. Tsubokawa, N.; Inagaki, M.; Kubota, H.; Endo, T. J Polym Sci Part A: Polym Chem 1993, 31, 3193.