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Polymerization of n-butyl vinyl ether using Montmorillonite catalysts (Mag-H) as cationic initiating system

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ABSTRACT

In the present work poly(*n*-butylvinylether) were prepared successfully and cleanly by a one step process via cationic polymerization of *n*-butylvinylether (*n*-BVE) using an non-toxic cationic catalyst, known-as (Mag-H), Mag-H is a activated-montmorillonite sheet silicate clay exchanged with protons to produce Mag-H. The influences of the conditions in polymerization on the yield, composition, microstructure and molecular weight of polymer were thoroughly studied. The resulting monomer reactivity ratios creased with an increasing amount of Mag-H added. This finding suggests that Mag-H participates in the propagation step of the polymerization. The effects of reaction temperature, amount of Mag-H and reaction time on the yield and the intrinsic viscosity (η) were investigated. A typical reaction product of poly(*n*-BVE) was analyzed by infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy as well as by viscosimetry.

Keywords: *polymerization, cationic catalyst, n-butylvinylether, activated-montmorillonite.*

1. INTRODUCTION

Vinylethers [1] and derivatives have received revitalized interest due to their readiness to undergo complete polymerization by a cationic mechanism induced by photochemical [2], thermal and chemical methods and excellent properties of their corresponding polymers. They can also be polymerized in a controlled/living [3] manner to yield polymers with well defined and predetermined structures. Despite their high reactivity towards cationic initiators, vinyl ethers, however, do not undergo free radical homopolymerization because of the highly nucleophilic nature of the double bond caused by the alkoxy group present in the structure [4]. In the literature, it is often claimed that these monomers efficiently copolymerize with monomers that polymerize by a free radical mechanism. However, recent detailed studies [5] on the copolymerization activity of vinyl ethers revealed that these monomers exhibit very little tendency to undergo polymerization with acrylates and even less with styrenic monomers. On the other hand, vinyl ethers can undergo efficient copolymerization with electron-deficient vinyl monomers such as maleates and fumarates [6]. In this case, spontaneous thermal and photoinduced polymerizations is initiated via donor-acceptor complexes formed between the corresponding monomer components. Polymerization is one of the important techniques adopted in effecting systematic changes in the properties of the commercially important polymers. In the present work poly(*n*-BVA) were prepared successfully and cleanly via cationic transformation in one step. In this respect, it is even more interesting to use activated-

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montmorillonite (Mag-H) as catalyst to prepare *n*-BVA polymer by one step in bulk at 0°C and at 25°C. Mag-H, a new non-toxic catalyst can be easily separated from the polymer product and regenerated by heating to a temperature above 100°C [7]. (Mag) has both Bronsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly active catalysts for acid-catalysed reactions. 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 reactions polymerization [8, 9]. The purpose of this paper is also to study the polymerization of *n*-BVE and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called (Mag-H) [9-17]. The effect of some factors such as the amount of the Mag-H and effect of times are discussed. Montmorillonites have both brönsted and Lewis acid sites and when exchanged with cations having a high charges density, as protons, produce highly-active catalysts for acid-catalysed reactions [14]. 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 reactions of polymerization [15]. The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay (Mag-H) via *n*-BVE polymerization. The aim of this research is to extend the scope of other promising new field of polymer synthesis by the use of another catalyst system that has been shown to exhibit higher efficiency [18].

2. EXPERIMENTAL SECTION

2.1. Reagents. The preparation of the Mag-H 0.25M was carried out by using a method similar to that described by Belbachir and al. [7]. *n*-butylvinylether (*n*-BVE) (99%), tetrachloromethane (99%) were used as received.

2.2. Procedure and Polymer characterization. Polymerization was carried out in stirred flasks at 0°C and at 25°C. The catalyst was dried in a muffle at 120°C over night and then transferred to a vacuum desiccator containing P_2O_5. After cooling to room temperature under vacuum, the mineral was added to the *n*-BVE (2g) in stirred flask. At the required time, an aliquot of the reaction mixture was then taken in such manner as to exclude any clay mineral and slowly added to methanol with stirring. The precipitated polymer was filtered off and dried under vacuum and weighed. Intrinsic viscosity (η) measurements were performed at 35°C in toluene using a capillary viscometer SEMATECH (VISCOLOGIC TL1). The sample concentration was 1 mg/ml. ^{1}H-NMR spectra were recorded on an AM 300 FT Bruker instrument using deuterated chloroform as solvent, and tetramethylsilane (TMS) as internal standard. FT-IR measurements were performed using Alpha-FTIR-Spectrometer BRUKER optics Diamond ATR.

2.3. Preparation of Catalyst (Mag-H). The clay mineral sample was washed with distilled water to remove impurities; the raw-montmorillonite (20g) was crushed for 20min using a Prolabo ceramic balls grinder. Then, it was dried at 423K for 2h and stored in tightly stoppered glass bottles for later use, after this sample was activated in acid acidic-montmorillonite (Mag-H) by the procedure of Belbachir et al. [7]. Briefly, this procedure consists on refluxing 20g of clay in 200mL of 0.25M H_2SO_4 for 3h. The resulting acidic activated clay was centrifuged and washed with water several times until it was free of SO_4^{2-} and the pH of the washing was 6.8. Finally the sample was dried at 378K in air until constant weight. This acid activation also removes sodium from its composition [19, 20]. The sediments were washed three times with distilled water. The chemical composition of the two different clay minerals (raw and Mag-H) is included in Table 1.

Table 1: Composition (wt%) of raw-montmorillonite (M) and acidic-montmorillonite (Mag-H)

Composition (Wt %)	SiO_2	Al_2O_3	MgO	Fe_2O_3	K_2O	TiO_2	Rb_2O	ZrO_2	SO_3	ZnO	CaO	Na_2O	P_2O_5	Cl
M	76.30	12.75	1.91	2.81	2.31	0.14	0.02	0.01	0.11	0.02	0.02	2.58	0.33	0.71
Mag-H	74.62	17.88	2.87	1.78	2.60	0.12	0.05	0.01	0.08	–	–	–	–	–

Table 2 : Effect of the amount of Mag-H catalyst on the polymerization with *n*-BVE

Mag-H (%)		0.01	0.03	0.05	0.07	0.1	0.2	0.3	0.4	0.5
Yield (%)	*25 (°C)*	9	17	45	94	96.5	96	97	97	97
	0 (°C)	5	12	40	85	91	95	97	97	97
Viscosity x 10^{-2} ($dl.g^{-1}$)	*25 (°C)*	2.975	2.841	2.521	2.383	2.247	2.104	1.856	1.659	1.529
	0 (°C)	2.452	2.251	2.014	1.972	1.758	1.545	1.502	1.487	1.479

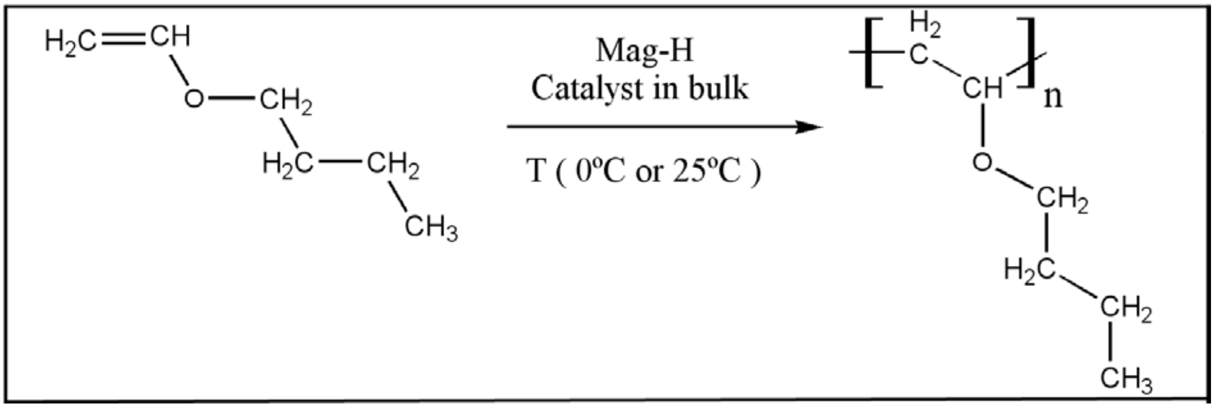

Figure 1: Polymerization of *n*-Butyl Vinyl Ether by Mag-H catalyst

3. RESULTS SECTION

3.1. Polymerization of n-BVE. The *n*-BVE is well known to be polymerized by Dichloroalane [22] or by $AlCl_3/LiAlH_4$ [23]. The cationic polymerization of *n*-BVE was examined in the presence of Mag-H powder in bulk at different temperatures (0°C and 25°C) (Figure 1). The IR spectrum of the polymer (Figure 2) showed bands due to poly(*n*-BVE) : peaks at 1374 and 1460 cm^{-1} (C-C stretching within the ring), at 804 (out of plane C-H bending vibrations); at 2866 and 2941 (symmetrical stretching bands $-CH_2-$), and other band at 1088 and 1231 cm^{-1} for ether group. The structure of the poly(*n*-BVE) was determined by ^{1}H-NMR. Figure 3 shows the chemical shifts at 3.53 and 3.44 ppm for the protons of ether group, that at 1.37, 1.53 and 1.83 ppm for the protons of ($-CH_2-$) of polymer and the signal of the typical protons of the methyl groups ($-CH_3$) sequences are observed at 0.91 ppm. These spectra all indicate the presence of *n*-BVE segments in the polymer.

3.2. Effect of the amount of Mag-H on the polymerization. The effect of the amount of Mag-H on the polymerization was examined (Table 2). It can be noted that the yield increases with increasing Mag-H proportion. Indeed, using various amounts of Mag-H between 0.01 and 0.5 % by weight, the polymerization was carried in bulk at 0°C and at 25°C. The polymerization rate increases with the amount of Mag-H, In contrast, the intrinsic viscosity (η) is inversely proportional to the amount of catalyst, in which the effect of Mag-H as a catalyst is clearly shown. This phenomenon is probably the result of number of “initiating active sites” responsible of inducing polymerization, this number is prorating to the catalyst amount used in reaction [11, 14-17].

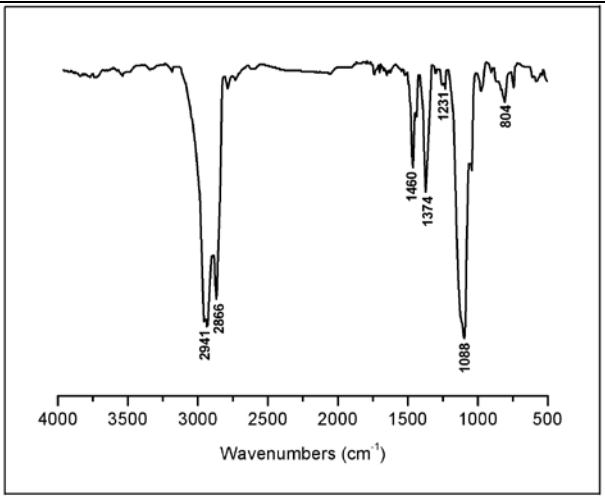

Figure 2: FT-IR transmission spectra of poly(*n*-BVE) obtained by Mag-H catalyst at room temperature

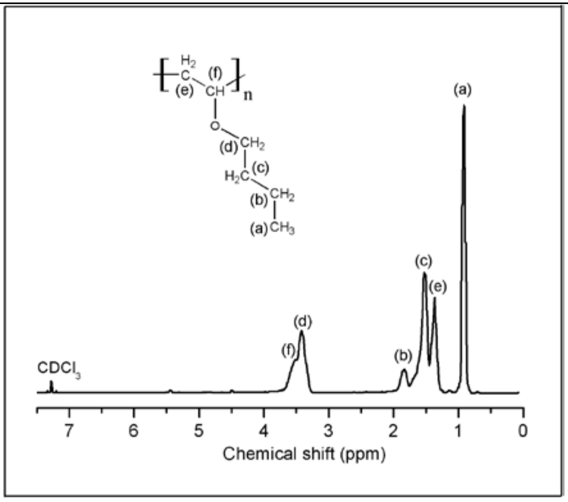

Figure 3: ^{1}H-NMR spectrum of poly(*n*-BVE) obtained by Mag-H catalyst at room temperature

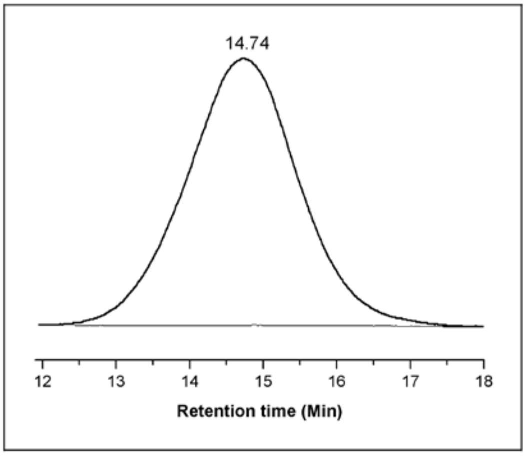

Figure 4: GPC traces of the poly(*n*-BVE) obtained by Mag-H catalyst at room temperature

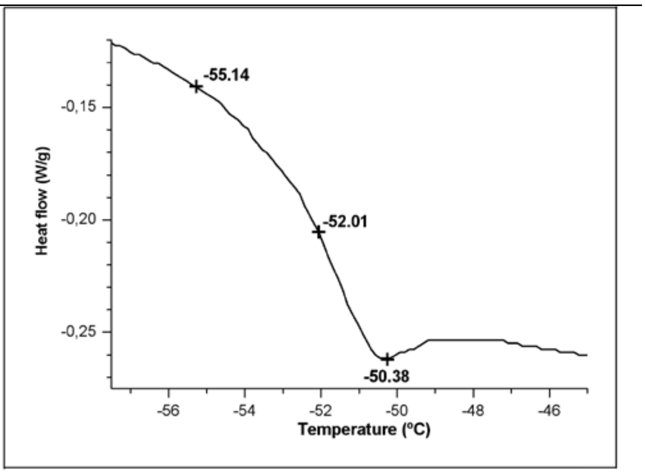

Figure 5: DSC traces of the poly(*n*-BVE) obtained by Mag-H catalyst at room temperature

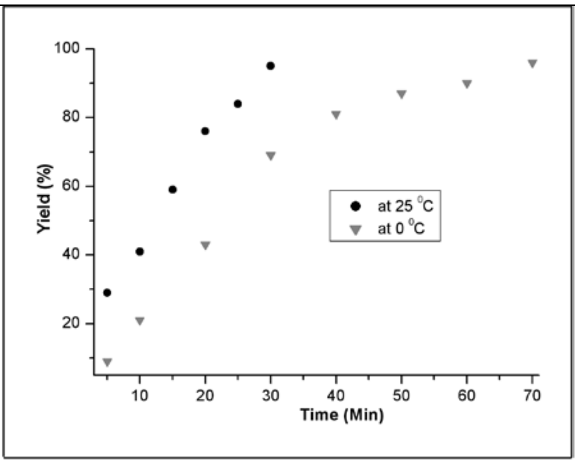

Figure 6: Effect of polymerization time on polymer yield poly(*n*-BVE) obtained by Mag-H catalyst

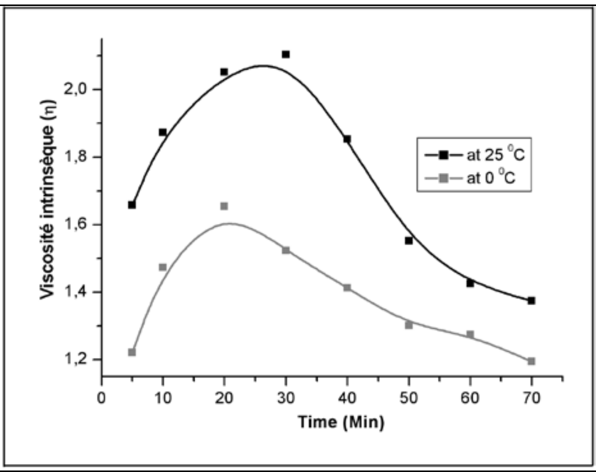

Figure 7: Effect of the reaction time of *n*-BVE by Mag-H catalyst on intrinsic viscosity

The GPC traces of poly(*n*-BVE) at 25ºC show a monomodal molecular-weight distribution (Figure 4). Differential Scanning Calorimetry (DSC) was used to determine the thermal glass transition temperatures for the polymer obtained by *n*-BVE with Mag-H. Figure 5. shows the DSC thermogram for the poly(*n*-BVE). The polymer had a Tg of -59°C [23], which compared to a Tg of -55.14°C for the poly(*n*-BVE) that was obtained made by Mag-H catalyst. We note that the Tg of poly(*n*-BVE) is marketed (Tg= -55°C).

3.3. Effect of the reaction time on the polymerization. The time-polymer yield curve at room temperature and 0 ºC are shown in Figure 6. The polymerization of *n*-BVE by Mag-H catalyst at room temperature is much more reactive than the synthesis at 0 ºC. After 30 minutes, the yield of the polymerization at room temperature is close to its maximum (97%), while the yield at 0 ºC of the polymer is increasing continually.

3.4. Effect of the polymerization time on the intrinsic viscosity. The effects of the reaction time of *n*-BVE by Mag-H catalyst on intrinsic viscosity (η) were examined as shown in Figure 7. The intrinsic viscosity increases as the reaction time increases from 5 to ~25 min reaching a maximum and after 30 min is decreasing to about one half in the run terminated after 70 min.

4. CONCLUSIONS

Butyl vinyl ether (*n*-BVE) was polymerized by using an non-toxic cationic catalyst. It was proved that Mag-H can be used to induce the polymerization of *n*-BVE. The products were obtained by a very simple procedure via cationic transformation in one step at room temperature and at 0ºC. Through simple filtering the clay can be separated from the reaction mixtures. Moreover this acidic clay is inexpensive, stable and non corrosive. The structure of polymer was confirmed by 1H-NMR and IR.

5. ACKNOWLEDGMENTS

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