

## Synthesis and Characterization of n-Butyl Vinyl Ether Copolymer

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### INTRODUCTION & AIM

The use of acid-treated clays as solid proton sources in various industrially significant reactions has continued because they are abundant, inexpensive, and efficient heterogeneous catalysts. Historically, they were used as cracking catalysts until the 1960s and are still currently employed in several industrial processes, such as the alkylation of phenols and the dimerization and polymerization of unsaturated hydrocarbons.

Montmorillonites possess both Brønsted and Lewis acid sites, and when exchanged with cations of high charge density, such as protons, they form highly active catalysts for acid-catalyzed reactions. Intercalated organic molecules are mobile and can become highly polarized within the interlayer space of charged clay sheets. These exchanged montmorillonites have been successfully applied as catalysts in various polymerization reactions.

Vinyl ethers constitute a large family of monomers, generally derived from acetylene and the corresponding alcohols. Their polymerization proceeds exclusively via a cationic mechanism. Since the first report of the cationic polymerization of vinyl ethers initiated by hydrogen iodide [1], numerous binary initiating systems combining a protonic acid and a Lewis acid have been developed to achieve living cationic polymerizations of vinyl monomers [2–3].

The aim of this research is to extend the scope of polymer synthesis by employing an alternative catalyst system that exhibits higher efficiency and environmental compatibility. In continuation of our program to develop environmentally benign catalytic methods using solid supports [4–5], this study investigates the catalytic activity of an Algerian proton-exchanged montmorillonite clay, known as Maghnite (Mag-H<sup>+</sup>), in the living cationic polymerization of n-butyl vinyl ether (nBVE) to produce poly(n-butyl vinyl ether)-block-polystyrene (PnBVE-b-PS). In contrast to conventional homogeneous catalysts, Mag-H<sup>+</sup> can be easily separated from the reaction medium and regenerated for reuse. The effects of the relative amounts of Mag-H and solvent on the polymerization process were also examined.

### METHOD

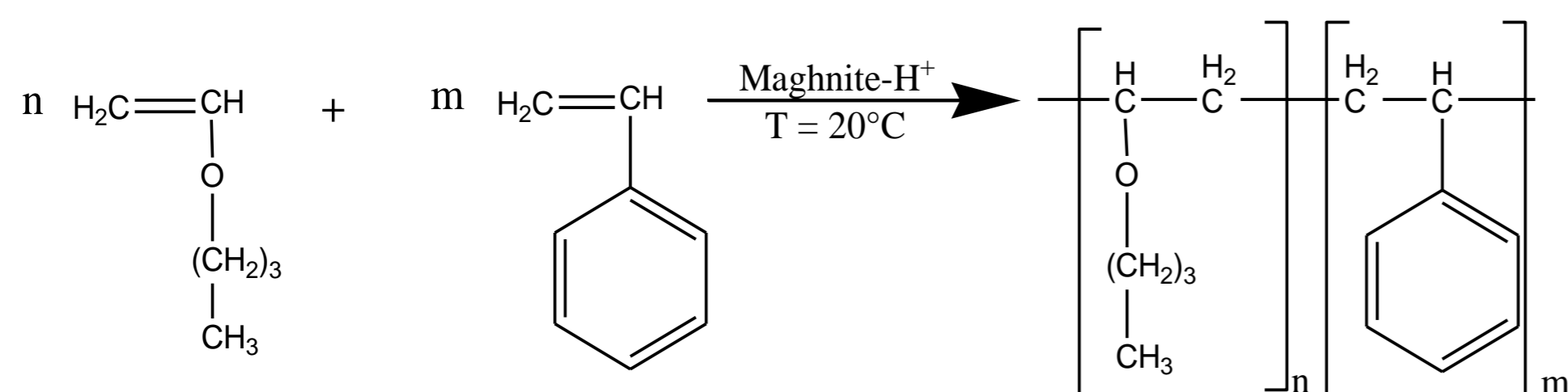
The clay, which has been used as catalyst, is supplied by a local company (ENOF Maghnia (Western of Algeria). First, montmorillonite (Mag-H) was prepared by shaking the clay in a solution of 0.25M sulfuric acid until saturation was achieved (After 2 days at room temperature). The cation-exchanged clay was then recovered by filtration, and again suspended in deionized water. The Mag-H was dried at 105°C, and then finely ground.

#### Synthesis of Block Copolymers :

Block copolymers were prepared following a typical copolymerization reaction (Figure 1), the PnBVE-b-PS was carried out in a heterogeneous system. Each mixture was prepared with PnBVE and 24 mol of styrene, and were introduced in several sealed tubes. The mixture was stirred with a magnetic stirrer under dry nitrogen.

The required amounts of relevant monomer styrene (St) and macroinitiator poly(n-butylvinyl ether) (PnBVE).

After reacting for various time periods, the copolymers were purified of polymer was carried out as follows: a large amount of dichloromethane was added to the mixture of reaction which was filtered to eliminate Maghnite-H<sup>+</sup>. The copolymers were then precipitated by the addition of a ten-fold excess of methanol. The copolymers were then dried in vacuo for 24h.



**Figure 1 :** living cationic polymerisation of nBVE to produce PnBVE-b-PS by Mag-H catalyst

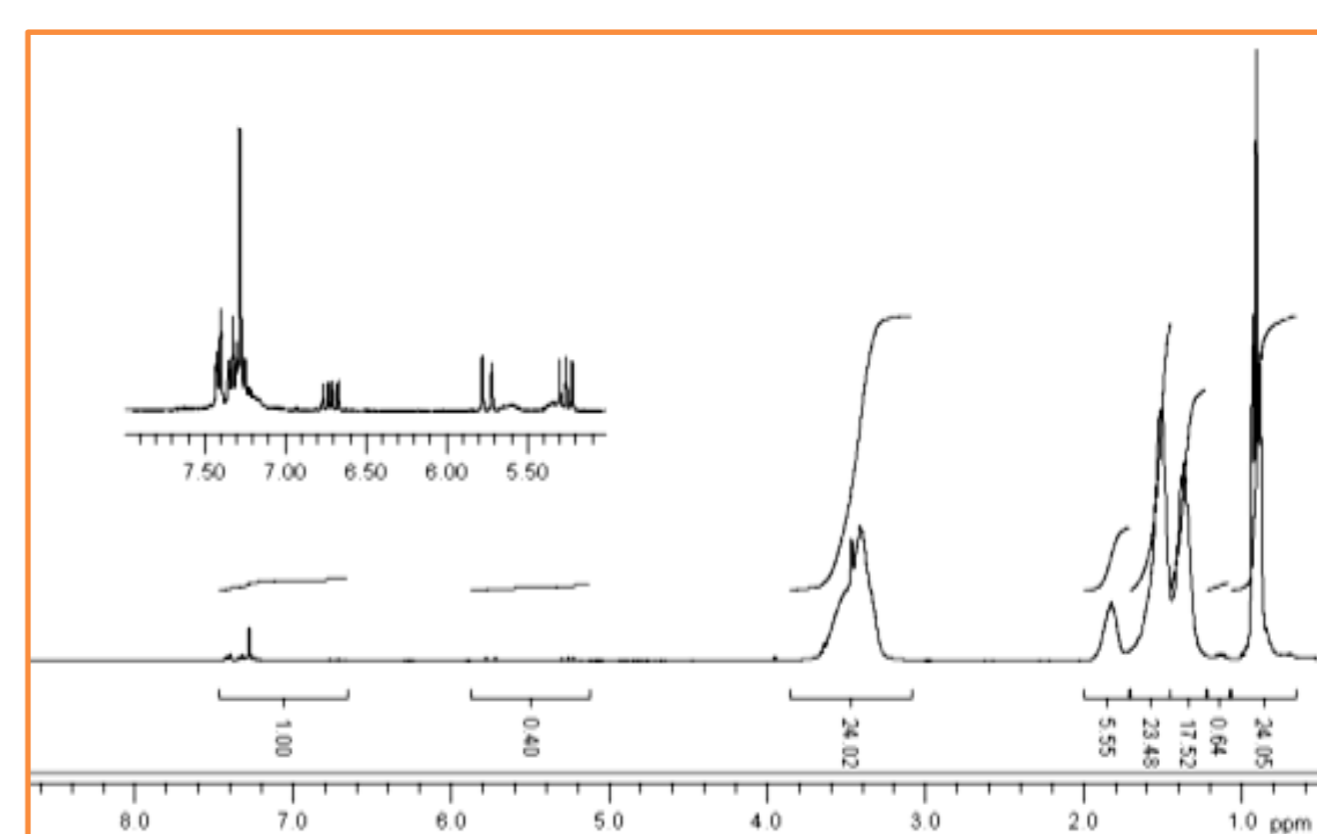
### FUTURE WORK / REFERENCES

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### RESULTS & DISCUSSION

The spectrum is represented in the Figure... . Firstly, chemical shifts in PnBVE spectrum are observed at around 3.53 and 3.44 ppm for the protons of the ether group, shifts at 1.37, 1.53 and 1.83 ppm indicate the protons of (-CH2-) and the methyl groups (-CH3) are observed at 0.91 ppm.

<sup>1</sup>H NMR analysis shows that PnBVE and styrene are indeed copolymerized: PnBVE peaks are present in the NMR spectrum of the copolymer, in addition to the presence of new peaks attributed to polystyrene at 6.44 and 4.44.

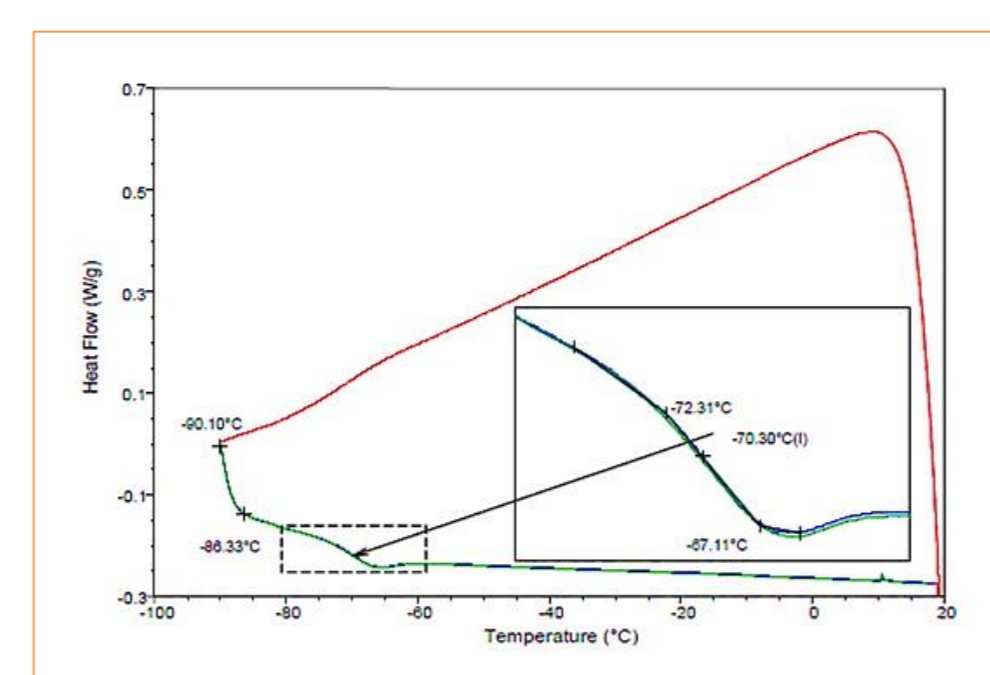


**Figure 2.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of block copolymer PnBVE-b-PS catalyzed by Mag-H.

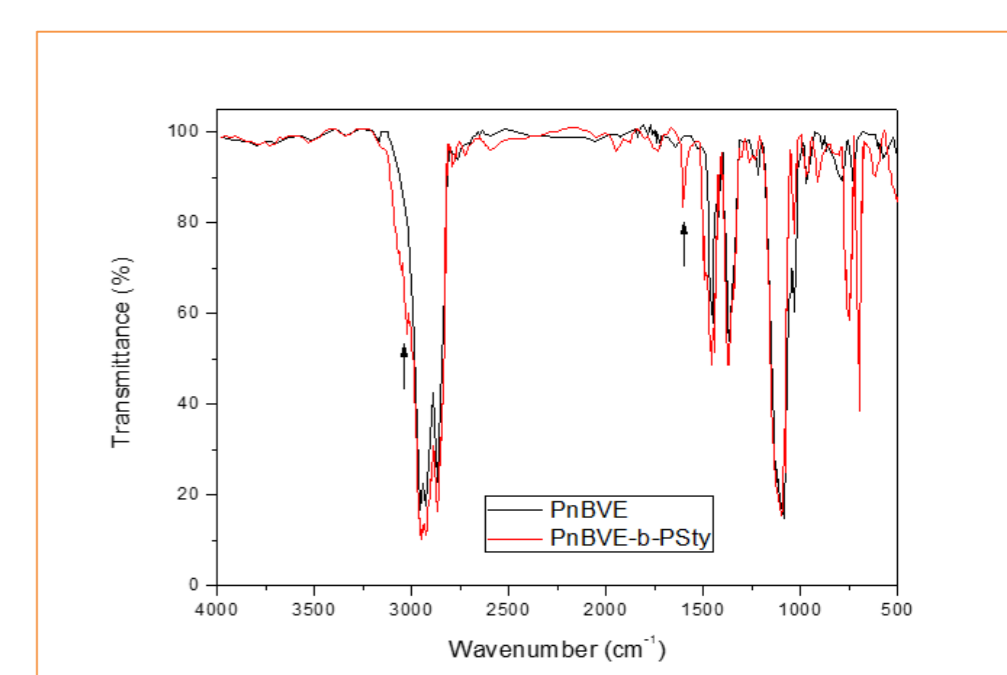
Differential Scanning Calorimetry (DSC) was used to determine the thermal glass transition temperatures (T<sub>g</sub>) of the copolymers obtained by cationic living polymerization.

Figure 3 presents DSC graph of PnBVE-b-PS prepared copolymer. The graph shows a single thermal glass transition temperature (T<sub>g</sub>) at - 70.30 °C indicating a good miscibility between the two blocks.

It is noted that the T<sub>g</sub> of poly(nBVE) was - 55.14 °C, as previously determined for this polymer catalyzed using Magh-H<sup>+</sup> [6] and T<sub>g</sub> of polystyrene is between 100 and 107 °C.



**Figure 3.** DSC of PnBVE-b-PS.



**Figure 4.** FTIR spectra of PnBVE and PnBVE-b-PS.

Figure 4 shows the FTIR spectra of PnBVE and PnBVE-b-PS. The FTIR spectrum of PnBVE (in black), used for comparison, shows bands at 2866 and 2941 cm<sup>-1</sup> (symmetrical stretching bands -CH<sub>2</sub>-), at 1374 and 1460 cm<sup>-1</sup> attributed to C-C stretching within the ring), at 804 (out of plane C-H bending vibrations); and other band at 1088 and 1231 cm<sup>-1</sup> for ether group.

When styrene is introduced into the copolymer, additional peaks appear: an aromatic C=C stretching around 1600 cm<sup>-1</sup> and an aromatic C-H bending out of plane between 700 and 900 cm<sup>-1</sup>, which are absent in pure poly(nBVE).

### CONCLUSION

Maghnite-H<sup>+</sup>, a proton exchanged montmorillonite clay, is an effective initiator for the living cationic polymerization of nBVE. This polymerization was found to be initiated by Maghnite-H<sup>+</sup> powder in heterogeneous phase. The polymerization was considered to be initiated by the proton addition from maghnite-H<sup>+</sup> to monomer and the propagation proceeds with maghnite as counterion.

In the polymerization, the solid catalyst was thought to act as an acid to generate cation species.

Actually, the efficiency of the polymerization reflected the Lewis acidity of maghnite-H<sup>+</sup>. Two main advantages were shown in the polymerization system using the solid acid maghnite-H<sup>+</sup>: The catalyst could be removed from the mixture of the products by simple filtration and recycled without a loss of catalytic activity.