

Copolymerization of Styrene Tetrahydrofuran-catalyzed by the Maghnite H⁺

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Abstract: The copolymers are mixed materials synthesized from two polymers blended in optimized percentages. The objective of this study is to use the maghnite H⁺ as cocatalyser in the presence of monomers to obtain a copolymer polytetrahydrofuran- styrene by polymerization. The obtained results RX, RMN, IR and DSC confirmed the copolymerization of monomers and their stability. The studies done, such as the effect of the amount of catalyser and the amount of acetic anhydride on the syntheses of polytetrahydrofuran and polystyrene have proved the effectiveness of the Maghnite.

Key words: Copolymerization • X-rays diffraction • infra-red • RMN and DSC

INTRODUCTION

Many works, realised since fifty years, have shown that clays possess catalytic properties [1,2]. In this regard, one can cite, among other things, testing of the use of clay catalysts in the cracking of petroleum products made by Milliken and al. (1950) [3].

Kessaissia and al (1978) [4] have worked on the catalytic properties of local montmorillonite. These latter are exploited in the formation of amino acids and in their polymerization into polypeptides. Tests of polymerization of styrene, Methyl methacrylate on the surfaces of certain clay minerals have been made by Solomon and al. (1965 - 1968) [5-6] on attapulgite, kaolin, montmorillonite and others.

In 1987, Njopwouod and al. [7] have studied the catalytic action of Cameroonian clays on the polymerization of styrene.

Recently Mr. Belbachir and al. [8] have studied the polymerization of several heterocyclic and vinyl monomers using bentonite of Maghnia (the Maghnite) activated by sulfuric acid 0.23M.

In this work we have bentonite of Maghnia for the polymerization and copolymerization of the system which aims to answer some questions.

Does the Maghnite catalyze the reactions of polymerization and copolymerization?

Does it have the same efficiency as protic acids, Lewis acids, benzoyl peroxides, hydroperoxide of

ditertiobutyle? What is the initiation mode, cationic or radical? We will try to answer all these questions through this study.

This work is entirely devoted to experimentation, we will present: the polymerization of styrene, the polymerization of tétrahydrofuran and copolymerization of styrene and tétrahydrofuran. The characterizations of the samples obtained by the techniques of spectroscopy IR, DRX, DSC and the RMN of the proton.

We will describe the results obtained in the polymerization and copolymerization of tetrahydrofuran and styrene initiated by activated bleaching earth. Initially, we synthesized the polytetrahydrofuran, polystyrene and copolymers: poly (THF-co-St), by optimizing the parameters which allow us to obtain higher yields of polymers and copolymers, then, we have characterized it.

MATERIAL AND METHODS

Products Used: Acetic anhydride (CH₃CO)₂O, styrene and the tetrahydrofuran, marketed by BIOCHEM, the THF has the following characteristics: $d = 0.886-0.889$, $T_{eb} = 65-66.5^{\circ}\text{C}$, $PM = 72.17 \text{ g / mol}$. The styrene (C₈H₈ vinylbenzen) has the following characteristics: $d = 0.9060$, $T_{eb} = 145.14^{\circ}\text{C}$, $PM = 104.14 \text{ g / mol}$. The Maghnite provided by the company ENOF has a bleaching power: 95-100%, acidity in HCl: 0.06%, density: 0.05.

Chemical Activation: the acidification (Maghnite H⁺)

The catalyst used is the Maghnite, also known as the activated bleaching earth (TDA). The acid activation of the bleaching earth is made as follows:

- With a weight of 30 g of bleaching earth, a quantity of 120 ml of distilled water is added.
- The mixture (bleaching earth + distilled water) is left in suspension by mechanical stirring and at room temperature, at which 100 ml of a solution of
- H₂SO₄ (0.23 M) will be added after thirty minutes. The stirring is maintained for forty-eight hours.
- After two days, the bleaching earth is filtered by rinsing it several times with distilled water.
- After filtration, the activated bleaching earth is dried in an oven for twenty-four hours at a temperature of 105°C (Fig.2).
- Finally, the grinding stage for twenty minutes and storing away from the air and moisture.

Polymerization of THF: We add to 10 g of THF, 1.6 g of acetic anhydride (16% in weight of monomer) and the TDA, in a varying quantity, in a flask.

Preliminary reactions have allowed to optimize the amount of acetic anhydride in the reactional mixture, the rate chosen for the remaining of our work is 16% by weight of monomer (molar ratio THF / Acetic Anhydride = 8.84), the value that allows an optimal conversion rate [9-11].

The quantities of TDA vary from 0.5 to 2.5% compared to the weight of monomer, the reactions were performed under magnetic stirring, at T = 30 ± 2 ° C for a reaction time equal to 6 h. The TDA is recovered by filtration. The polymer is precipitated in an excess methanol by cooling.

Polymerization of Styrene: We In a flask, 1 g of treated Maghnite dried overnight in an oven, is added to 20 g of treated styrene. The reactional mixture was placed under medium magnetic stirring (Fig. 1), the reactional crude is washed several times with dichloromethane. The clay was recovered by filtration through sintered or filter paper. The filtrate is then poured drop by drop into an excess of methanol, polystyrene precipitate, it is then recovered by filtration.

Synthesis of the Copolymer Poly (THF-co-St): The copolymerization is in weight. The reactional mixture composed of MaghniteH⁺, THF, Acetic anhydride and styrene is placed in a flask of 100ml then immersed in an oil bath preheated to 40°C. The device is under magnetic stirring during 6 h.

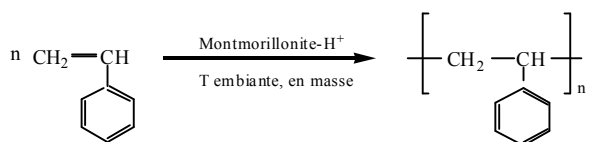


Fig. 1: Reactional scheme of the polymerization of styrene

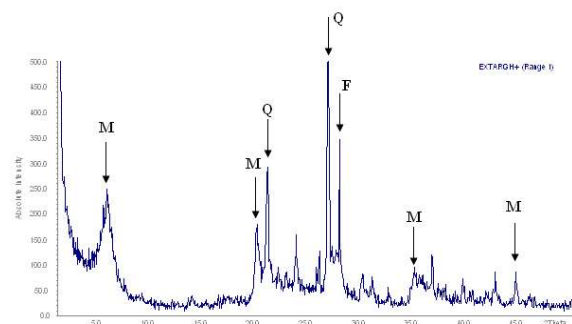


Fig. 2: Spectrum of X-ray diffraction of the Maghnite (0.23M)

Table 1: The copolymer elaboration of experimental conditions

Mass ratio THF/St (g)	30/70	40/60	50/50
wt of Styrene (g)	10	10	10
Wt of THF (g)	2.97	4.61	6.92
wt of Catalyst (g)	0.69	0.74	0.86
yield (%)	42	10	3

The addition of acetic anhydride is needed in the reaction of the copolymerization of THF with the styrene. When the reaction time passes, the reactional mixture was placed in 20 ml of THF to remove all traces of monomers. Next, the mixture is filtered to remove the catalyst. The resulting product was precipitated in methanol by cooling. The recovered product is dried in the open air and then weighed.

The mass ratios THF/St used are resumed in the Table1.

RESULTS AND DISCUSSION

The X-ray diffraction on powder, using the stripe K α of copper, was used in order to verify the belonging of the Maghnite to the family of montmorillonite clays and to see the changes that took place after having activated the bleaching earth using sulfuric acid (0.23 M). The diffractograms of the Maghnite are represented by Figure 2. On this latter intense stripes are observed around $\theta = 6.05$ ($d = 14.6 \text{ \AA}$) as well as a series of peaks of different intensities.

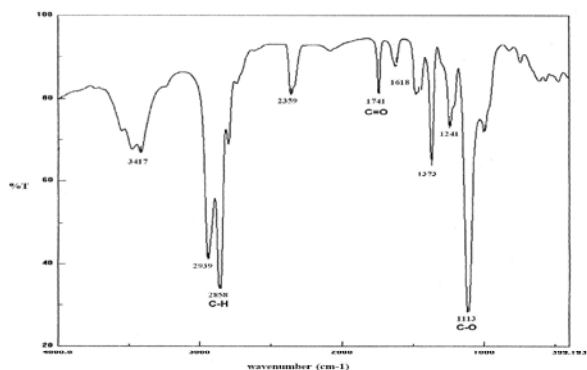


Fig. 3: IR spectrum of PTHF.

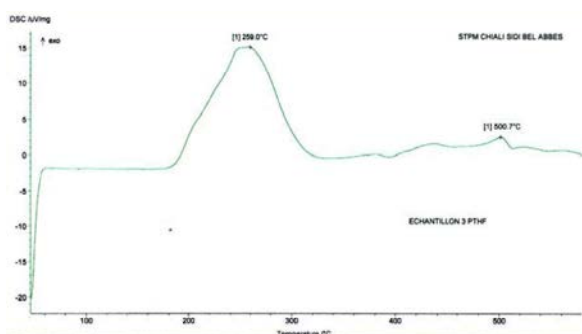


Fig. 4: DSC thermogram of PTHF

Caractérisation du Poly THF

IR Spectroscopy: Figure 3 shows the IR spectrum of the obtained polymer, which corresponds to the results RMN described in manuscript N. Ouis [9]. The absorption bands observed in the spectrum of PTHF, have already been identified in the literature and correspond to the carbonyl group (C = O) of ester at 1741 cm^{-1} , at the vibrations of the C-H connection of methyl group at 2858 cm^{-1} , the presence of the ether function C-O, is confirmed by the band located at 1113 cm^{-1} .

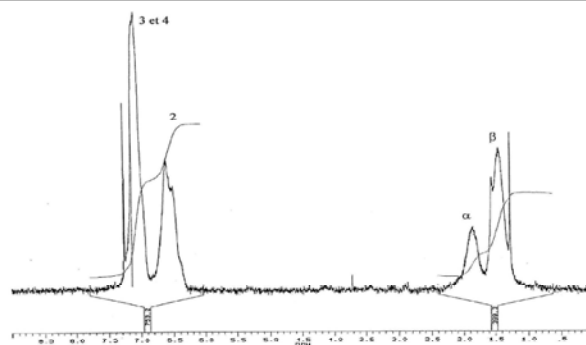
Differential Calorimetric Analysis (DSC): The study of polymers degradation can most often intervene on the factors which improve their thermal stability and also which allow to situate better their own domain of application.

We observe on the thermogram of PTHF (Fig. 4) the presence of an exothermic accident between 200 and 280°C, centered at 259°C attributed to the crosslinking of the polymer chains. From this peak, the curve exhibits a descent corresponding to the beginning of the decomposition of PTHF.

The study of the system THF- anhydride acetic - Maghnite shows that:

Table 2: Chemical displacements of different protons in the polystyrene (CDCl_3)

δ (PPM)	Attribution
6.9-7.25	1H ₄ +2H ₃
6.3-6.8	2H ₂
1.86	H α
1.3-1.65	2H β

Fig. 5: RMN ¹H spectrum of polystyrene.

- The Maghnite accelerates the polymerization of THF in the presence of acetic anhydride.
- The amount of Maghnite affects the yield.
- The molar ratio THF / acetic anhydride = 8.84 gives a yield of 50% of Poly THF.

Characterization of Polystyrene

RMN¹H: The polymer obtained was characterized by RMN¹H (200 MHz). The different protons observed and their chemical displacements are given in Table 2.

On the spectrum RMN¹H (Fig. 5), we also observe a singlet located at about 1.2 ppm which corresponds probably to the methyl of the end of the chain.

The other protons of the end of chain are confused with the protons of the polymer chain.

Moreover, the RMN¹H spectrum, have allowed us to calculate the molar weight of the polymer by comparing the integration of aromatic protons of the nucleus I_a located between 6.3 and 7.25 ppm to those of methyl protons I_m of chain end.

We then find an average weight of about 2100 ($I_a / I_m = 17$).

IR Spectroscopy: IR spectroscopy (Fig. 6) allows us to confirm the nature of the polymer by identifying characteristic bands of PS previously cited in the literature.

The benzene nucleus sign its presence at 3100 cm^{-1} in elongation, the deformations appear at $697\text{-}755\text{ cm}^{-1}$.

Table 2: Signals and chemical displacements of different protons present in the obtained product according to the RMN¹H (300 MHz) in solution in the CDCl₃

Indication	pattern	Nature of the proton	δ ppm	
			théo	exp.
a	St	Ph-CH-	1,6 -2,7	1,875
b		Ph-CH-CH ₂	1,2 -1,8	1,461
c		2H (en ortho du phényle)	6,0 -8,0	6,611
d,e		3H (en méta et en para du phényle)	6,0 -8,0	7,075
f,i	THF	-O-CH ₂ CH ₂ CH ₂ CH ₂ -O-	3,3 -4,0	3,448
g,h		-O-CH ₂ CH ₂ CH ₂ CH ₂ -O-	1,2 -1,8	1,645
j		-CH ₂ O-CO-CH ₃	3,9 -4,6	4,116
k	AA	-CH ₂ O-CO-CH ₃	1,8 -2,6	2,079

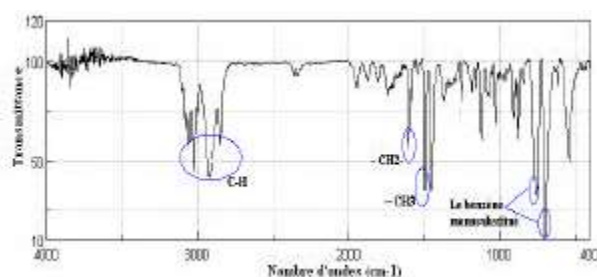


Fig. 6: IR spectrum of polystyrene.

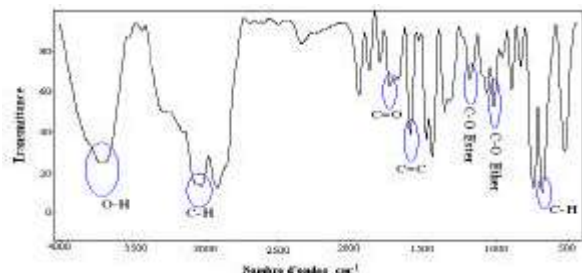


Fig. 7: IR spectrum of poly (THF-co-St).

The band located at 2921 cm⁻¹ is attributed to the stretching of the C - H connection in the groups of the ethylene and methylene. The peak located at 1480 cm⁻¹ is attributed to -CH₃ group at the chain end.

We also note the absence of the double connection C=C expected at 1680 cm⁻¹ and specific to the used monomer.

Characterization of the Obtained Copolymer THF-St

IR Spectroscopy: The analysis by infrared spectroscopy (Fig. 7) of the polymer (experiment: mass ratio = 30/70) shows the main functions present in the copolymer.

The ester function present in the acetate of the chain end, appears clearly in two areas: at 1735.79 cm⁻¹ for the group (C = O) and at 1185.89 cm⁻¹ for the function (CO).

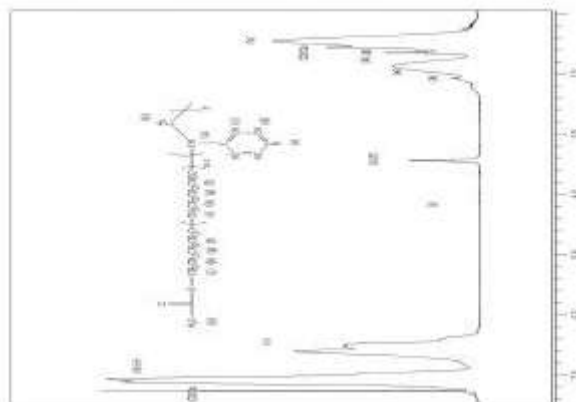


Fig. 8: RMN¹H spectrum (300 MHz) of poly (THF-co-St), solvent CDCl₃.

The phenyl of St appears in three absorption bands: one at 1596.99 cm⁻¹ for the (C = C), another at 3028.29 cm⁻¹ for (CH) and the last at 755.80 cm⁻¹ for the deformation in the plan of (CH).

The ether function appears clearly at 1070.79 cm⁻¹.

The large band at 3720.29 cm⁻¹ is attributed to the connection (OH), which is probably due to a bad drying of KBr used for this analysis.

RMN¹H: The interpretation summarized in Table 2 of Figure 8 confirms that the resulting product is poly (THF-co-St) by the presence of two motifs THF and styrene.

A mass ratio of THF / St = 30/70, gives a yield of 42% with 5% Maghnite and 16% acetic anhydride compared to the weight of THF.

CONCLUSION

After an extensive study on methods of preparing polymers and copolymers, a simple and profitable synthesis of polystyrene and polytetrahydrofuran, homopolymers and copolymers by heterogeneous catalysis have been proposed.

This method is different from that cited in the scientific literature by using a new ecocatalyst clay-based named Maghnite.

The studies done such as the effect of the amount of catalyst and the amount of acetic anhydride on the syntheses of polytetrahydrofuran and polystyrene have proved the effectiveness of the Maghnite.

The different parameters studied had little influence on the chaining in the polymers, it is likely, therefore, that the growing chains are found in a complex form.

The obtained results, though preliminary, permit an approach to understanding and explaining the mechanisms of polymerization initiated by the Maghnite.

On the other hand, it is desirable that the synthesis of heterocyclic and vinyl polymers by heterogeneous catalysis, initiated by the Maghnite, be followed by larger development, both for fundamental and economic interest, that it presents.

Finally, this study will surely allow the meeting of an industrial laboratory and our university team and this in the common goal of research.

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