

Piperazine Polymerization Catalyzed by Maghnite-H⁺

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Abstract

New polymers polypiperazines were synthesized in the presence of a non-toxic catalyst Maghnite-H⁺ from the addition of dihalogenated compounds such as 1,6-dichlorohexane and 1,2-dibromopropane to piperazine, after the comparative study of the polymerizations without and with this catalyst. The yields of the synthesis induced by Maghnite-H⁺ are high compared with those of the uncatalyzed reactions. In our case, the effect of reaction time on the yield was studied by carrying out a series of experiments by maintaining the quantities of the reagents and varying the time t. On the other hand, polymerizations of piperazine are realized by maintaining the amounts of monomer, the time duration and varying the amount of Maghnite-H⁺ in order to control the influence of the amount of this catalyst on the yield of the bulk polymerization of the piperazine. By constation, the yield grows either with the increase of reaction time, or by increasing the quantity of the catalyst. All products synthesized during the addition of dihalogenated compounds to piperazine were characterized by FT-IR spectroscopy (Perkin Elmer System), ¹H-nuclear magnetic resonance (NMR) and ¹³C nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer.

Keywords: Piperazine; Dihalogen; Addition; Maghnite-H⁺; Polypiperazine

Introduction

Piperazines are precursors of many polymers at high-value such as poly (methyl-para-piperazine-hydroxybenzoic acid), polyethylenes polypiperazines, polypiperazine phosphonamides, poly (iodideperfluorohexylpiperazine) etc. The importance of its use [1-3] is due to the chelating properties of tertiary nitrogen and to the presence of a stable cycle at six-ring.

These polypiperazines have various applications. They are used as resins for trapping copper ions in industrial reactors high-pressure [4], flocculation agents and polyamines synthesis products [5], linkers for diblock or triblock synthesis [6], pervaporation, ultrafiltration and reverse osmosis membranes [7].

The condensation of the piperazine with allyl chloride catalysed by Maghnite-H⁺ was carried out by Hachemaoui to prepare allyl chloride [8]. It has also synthesized ammonium iodides by adding the diiodinated compounds to the piperazine [9]. On the other hand, the grafting of this monomer on a halide was done by Benhamou [10] at ambient temperature and in the presence of tetrahydrofuran. The new non-toxic initiator Maghnite-H⁺ [11-16] has been used to prepare and study several kinds of polymers.

Experimental Part

Materials

In our case we have carried out the addition of dihalogenated compounds on piperazine such as 1,6-dichlorohexane and 1,2-dibromopropane in the presence of Maghnite-H⁺. The choice of reaction with catalyst was made after obtaining good yields (Tables 1 and 2). We have carried out a series of experiments by maintaining the quantities of the reagents and varying the time t (Figures 1 and 2). The molecular structure of products of all reactions of piperazine with dihalogenated compounds was characterized by FT-IR spectroscopy (Perkin Elmer System), ¹H-nuclear magnetic resonance (NMR) and ¹³C nuclear magnetic resonance (NMR) measurements were carried out on

Time (hours)	0.5	1.0	1.5	2.0	2.5	3.0
Yield (%) (a)	17	38	56	65	73	76
Yield (%) (b)	20	42	66	75	82	84

Table 1: Effect of time on the yield of piperazine polymerization with 1,6-dichlorohexane without (a) and with catalyst (b).

Time (hours)	0.5	1.0	1.5	2.0	2.5	3.0
Yield (%) (a)	12.8	22	39	60.9	64	66
Yield (%) (b)	14	24	44	67.1	69.5	72

Table 2: Effect of time on the yield of piperazine polymerization with 1,2-dibromopropane without (a) and with catalyst (b).

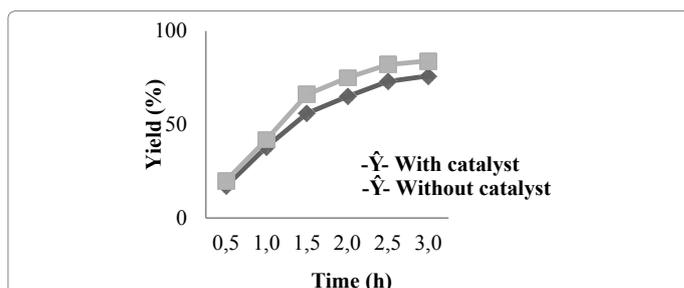


Figure 1: Effect of time on the yield of piperazine polymerization with 1,6-dichlorohexane without (a) and with catalyst (b).

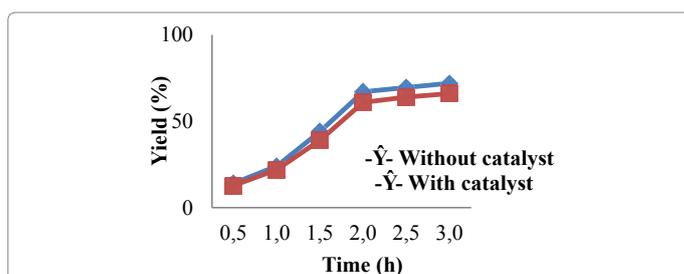


Figure 2: Effect of time on the yield of piperazine polymerization with 1,2-dibromopropane without (a) and with catalyst (b).

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a 300 MHz Bruker NMR Spectrometer, in CDCl₃, Tetramethylsilane (TMS) was used as the internal standard in these cases.

Polymer preparation

Reaction of piperazine with 1,2-dichloropropane: 2 g of dry Maghnite are introduced into a two-necked flask, and 2.74 ml (3×10^{-2} mol) of piperazine are added, with stirring at room temperature for 20 to 30 minutes. 0.974 ml (10^{-2} mol) of 1,2-dichloropropane are poured, the mixture is left stirring for 2 hours. The reaction crude is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried using a rotary evaporator. The product obtained is white with a yield of 96%.

Reaction of piperazine with 1,2-dibromopropane: 2 g of dry Maghnite are introduced into a two-necked flask, and 2.74 ml (3×10^{-2} mol) of piperazine are added, with stirring at room temperature for 20 to 30 minutes. 1.045 ml (10^{-2} mol) of 1,2-dibromopropane are poured, the mixture is left stirring for 2 hours. The reaction crude is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried using a rotary evaporator. The product obtained is white in a yield of 80%.

Reaction of piperazine with 1,6-dichlorohexane: 2 g of dry Maghnite are added to a two-necked flask, and 0.913 ml (10^{-2} mole) of piperazine are added with stirring at room temperature for 20 to 30 minutes. 1.45 ml (10^{-2} mol) of 1,6-dichlorohexane are poured, the mixture is left stirring for 2 hours. The reaction crude is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried using a rotary evaporator. The product obtained is viscous, and of a light yellow color with a yield 87%.

Reaction of piperazine with 1,6-dibromohexane: 2 g of dry Maghnite are introduced into a two-necked flask, and 2.74 ml (3×10^{-2} mol) of piperazine are added, with stirring at room temperature for 20 to 30 minutes. 1.54 ml (10^{-2} mol) of the 1,6-dibromohexane are poured, the mixture is left stirring for 2 hours. The reaction crude is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried using a rotary evaporator. The product obtained is light yellow in color with a yield of 72%.

Reaction of piperazine with dichloromethane: 2 g of dry Maghnite are introduced into a two-necked flask and 2.74 ml (3×10^{-2} mol) of piperazine are added, with stirring at room temperature for 20 to 30 minutes. 0.974 ml (10^{-2} mol) of 1,2-dichloropropane are poured, the mixture is left stirring for 2 hours. The reaction crude is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried using a rotary evaporator. The product obtained is white with a yield of 80%.

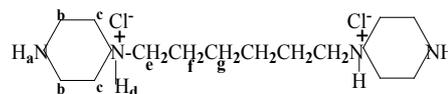
Reaction of Piperazine with dibromomethane: 2 g of Maghnite are introduced into a two-necked round-bottomed flask, dried in an oven for 24 hours, allowed to cool to room temperature and then 2.739 ml (3×10^{-2} mol) of piperazine are added, and after stopping the heating, 7.376×10^{-2} ml (10^{-2} mol) of dibromomethane are added. The mixture is left stirring for 2 hours. The crude reaction product is washed with chloroform; the Maghnite is recovered by simple filtration on filter paper. The filtrate is then dried with rotary evaporator; a residue is obtained which is washed. The yield is 60%.

Results and Discussion

Polymer characterization NMR ¹H and ¹³C and IR

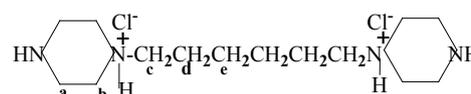
Characterization of product (3) ¹H NMR: An investigation was devoted to the analysis of the polymer (3) by ¹H NMR spectroscopy at 300 MHz (Table 3).

Formule



Characterization of product (3) ¹³C NMR: An investigation was devoted to the analysis of the polymer (3) by ¹³C NMR spectroscopy (Table 3a).

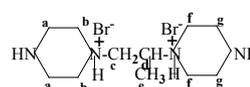
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Characterization of product (3) IR: Results of product (3) analysis by IR is explained in Table 3b.

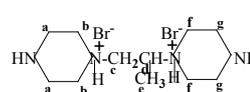
Characterization of product (2) ¹H NMR, ¹³C NMR and IR: An investigation was devoted to the analysis of the polymer (2) by ¹H NMR spectroscopy at 300 MHz (Table 3c).

Formule



Characterization of product (2) ¹³C NMR: An investigation was devoted to the analysis of the polymer (3) by ¹³C NMR spectroscopy (Table 3d) (Figures 3-7).

Formule



Polymer characterization IR

Polymer characterization of product (1): ¹H NMR (300 MHz, CHCl₃); δ in ppm = 4.1(H_c, H_j), 2.7(H_d, H_h), 2.5(H_a, H_k), 2.3(H_i, H_l), 1.3(H_e, H_l), 0.92(H_g) (Figure 8).

¹³C NMR (300 MHz, CDCl₃); δ in ppm = 40(C_a, C_g), 47(C_b, C_c), 30(C_d, C_f), 24(C_e) (Table 3e).

Proton type	a	b	c	d	e	f	g
δ in ppm	2.4	1.75	3.5	2.6	1.5	1.35	0.9

Table 3: Results of product (3) analysis by ¹H NMR spectroscopy.

Carbon type	a	d	b	c	e
δ in ppm	44.5	32	52.5	68.2	26

Table 3a: Results of product (3) analysis by ¹³C NMR spectroscopy.

Bond type	N-H	C-C	N-H
v vibration of bond in cm ⁻¹	3394 Elongation vibration	521.07 and 457.87 two peaks	1008 deformation Vibration

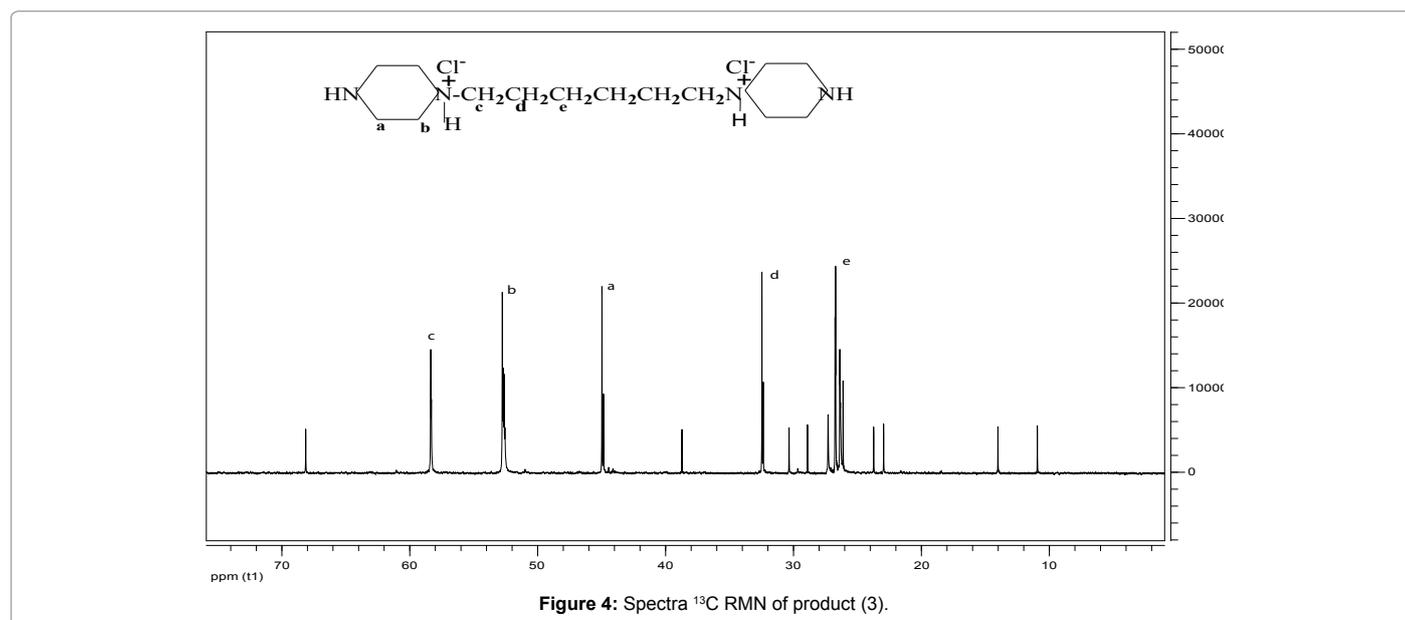
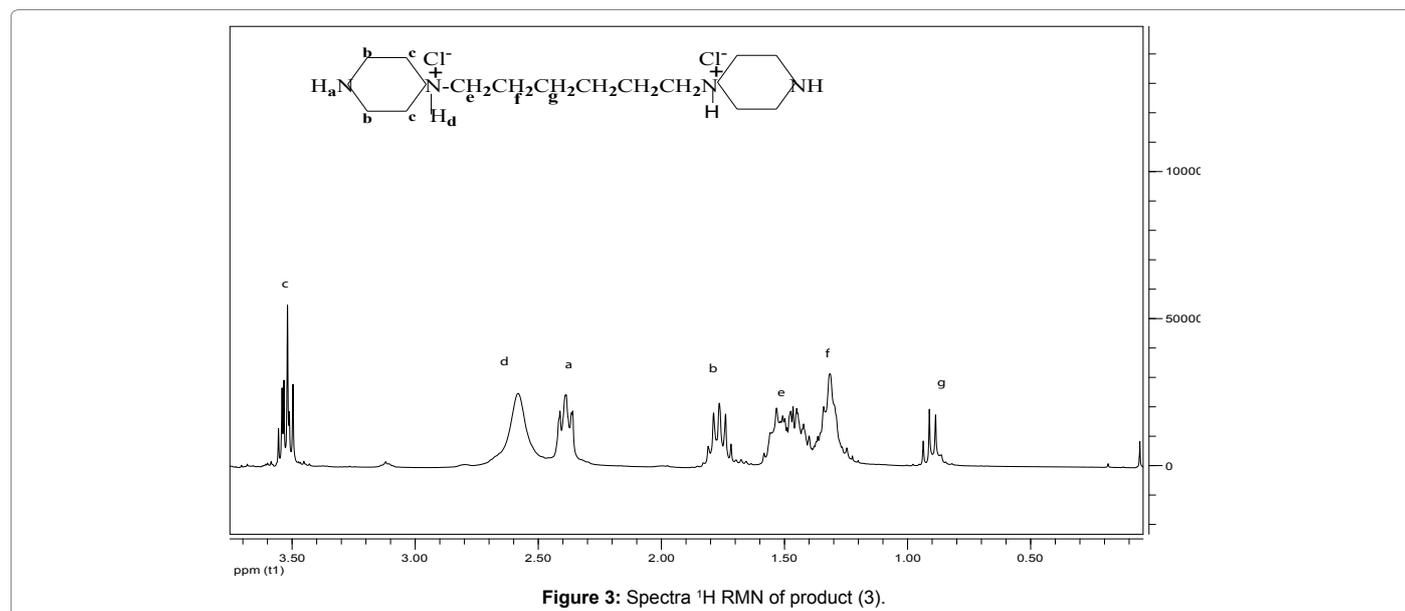
Table 3b: Results of product (3) analysis by IR.

Proton type	a, k	b, j	c, i	d, h	e, f	g
δ in ppm	1.9	0.8	2.75	2.35	1.2	0.75

Table 3c: Results of product (2) analysis by ¹H NMR spectroscopy.

Carbon type	a, d, g, e	b, c, f
δ in ppm	48	77

Table 3d: Results of product (2) analysis by ¹³C NMR spectroscopy.



IR (KBr); ν in cm^{-1} = 3382.07 (an average band due to the N-H elongation vibration), 1007.25 (an intense peak due to the C-C valence vibration).

Polymer characterization of product (4): ¹H NMR (300 MHz, CHCl_3); δ in ppm=1.35(H_g), 3.3(H_d), 2.5(H_a), 1.8(H_b), 3.6(H_c), 1.6(H_e , H_f)

¹³C NMR (300 MHz, CDCl_3); δ in ppm=31(C_a , C_d), 57(C_b), 75(C_c), 31(C_e)

IR (KBr) ν in cm^{-1} =3632.60 (an average band due to the N-H elongation vibration), 1014.73 (intense peak due to the C-C valence vibration).

Polymer characterization of product (5): ¹H NMR (300 MHz, CHCl_3); δ in ppm = 1.35 (H_d), 1.95(H_b), 2.9(H_c), 1.7 (H_a , H_e)

¹³C NMR (300 MHz, CDCl_3); δ in ppm = 75 (C_a , C_b , C_c)

IR (KBr); ν in cm^{-1} = 3380.60 (an average band due to the N-H

elongation vibration), 1014.73 (intense peak due to the C-C valence vibration), 3632.60 (an average band due to the N-H deformation vibration).

Polymer characterization of product (6): ¹H NMR (300 MHz, DMSO); δ in ppm=1.3(H_d), 1.77(H_a , H_e), 0.9(H_b), 2.9(H_c)

¹³C NMR (300 MHz, DMSO deutérié); δ in ppm=49 (C_a , C_b , C_c)

IR (KBr); ν in cm^{-1} = 3632.50 (an average band due to the N-H elongation vibration), 1101.36 (an intense peak due to the C-C valence vibration).

Effect of the amount of Maghnite-H⁺ on the yield of the piperazine polymerization

In order to control the influence of the amount of the catalyst on the yield of the bulk polymerization of the piperazine, we have carried out a series of experiments by maintaining the amounts of monomer

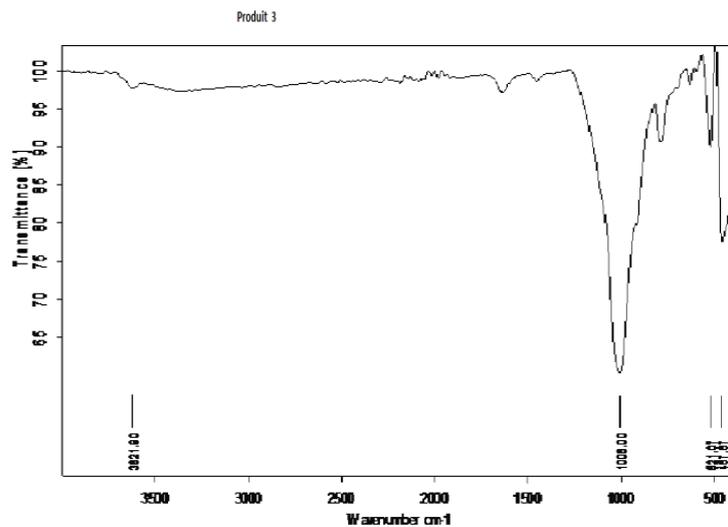


Figure 5: Spectra IR.

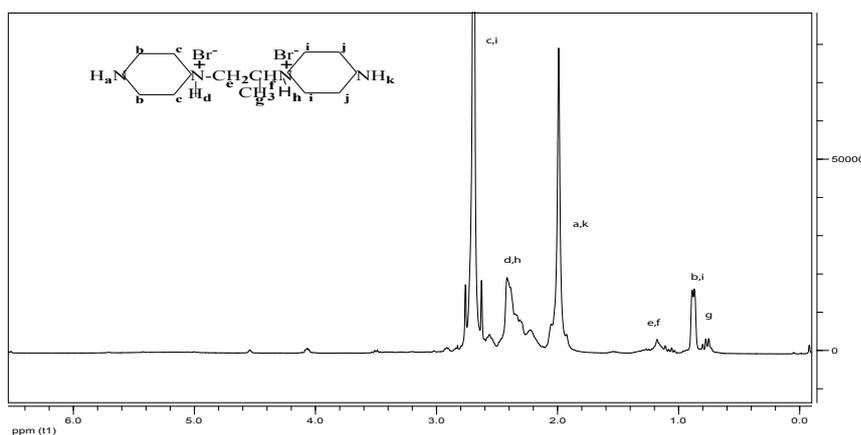


Figure 6: Spectra ¹H RMN of product (2).

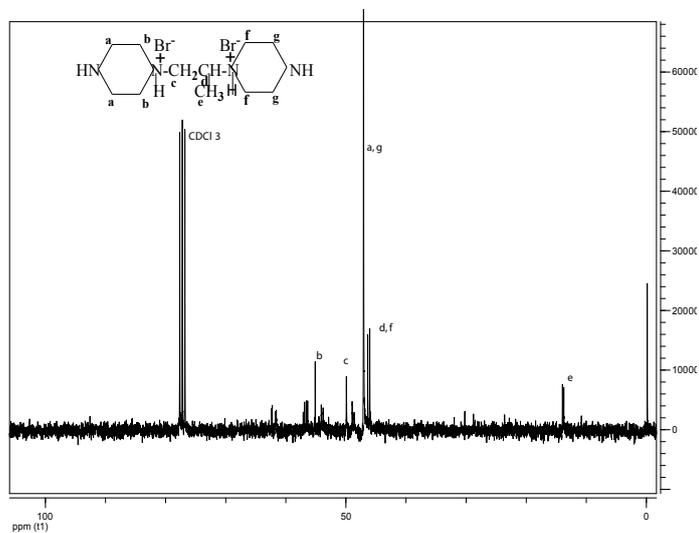


Figure 7: Spectra ¹³C RMN of product (2).

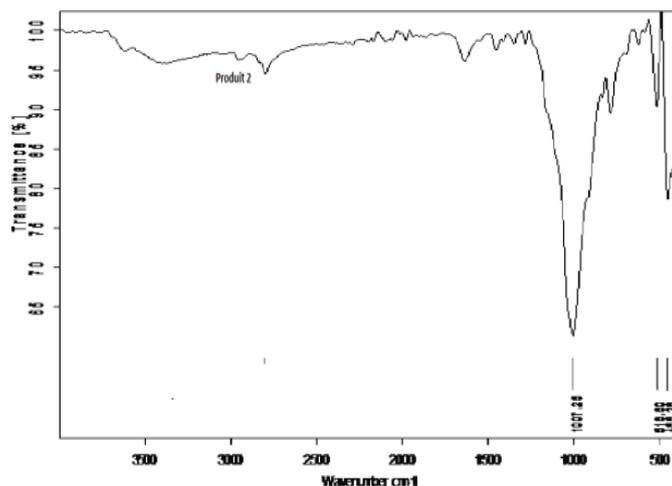


Figure 8: Spectra IR of product (2).

Bond type	N-H	C-C
ν vibration of bond in cm^{-1}	3250-3420 cm^{-1}	1007.25 cm^{-1}

Table 3e: Results of product (2) analysis by IR.

The amount of Maghnite-H ⁺ (g)	0.5	1	1.5	2	
Yield (%)	(a)	68	75	78	96
	(b)	60	66	72	87
	(c)	55	59	65	80
	(d)	50	54	61	72

Table 4: Influence of the amount of Maghnite-H⁺ on the yield of the polymerization reaction of piperazine, -with the 1,2-dichloropropane (a).; -with the 1,6-dichlorohexane (b).; -with the 1,2-dibromopropane (c).; -with the 1,6-dibromohexane(d).

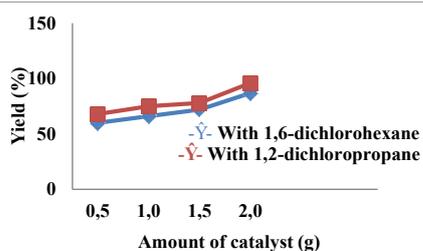


Figure 9: Influence of the amount of Maghnite-H⁺ on the yield of the polymerization reaction of piperazine, -with the 1,2dichloropropane (a). -with the 1,6-dichlorohexane (b).

and the time duration and varying the amount of Maghnite-H⁺ (Table 4; Figures 9 and 10).

Conclusion

This present work shows that piperazine polymerization was induced by proton exchanged montmorillonite clay called Maghnite-H⁺ with an important yield. These polypiperazine were produced by very simple procedure, through simple filtering, the clay was separated from reaction mixture.

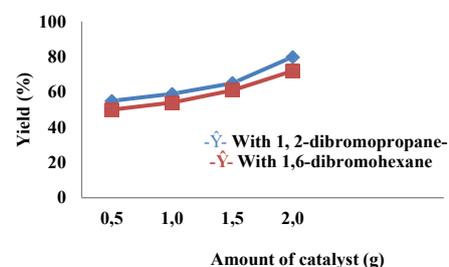


Figure 10: Influence of the amount of Maghnite-H⁺ on the yield of the polymerization reaction of piperazine, -with the 1,2-dibromopropane (c).; -with the 1,6-dibromohexane(d).

References

- Duquette LG, Garrou PE (1987) US Patent No. 4,684,729 to Dow Chemical Company, Midland, MI, USA.
- Lin LM, Sibert JF (1988) US Patent No. 4,734,203 to Nalco Chemical Company, Naperville, USA.
- Files T (1990) US Patent No. 4,906,376 to University of Victoria, Victoria, CA, USA.
- Nair CPR, Clouet G, Brossas J, Macromol J (1990) Sci Chem A 25: 1089.
- Boutevin B (1988) Advances in Polymer Science 94: 89.
- Credali Baruzzi G, Guidotti V (1978) U.S. Patent No. 4,129,559 to Montedison SPA, Milan, IT, USA.
- Hachemaoui A, Belbachir M (2005) Montmorillonite clay-catalysed synthesis of cyclic allylamines, Mendeleev Commun 15: 124-125.
- Hachemaoui A, Belbachir M, Yahiaoui A (2005) Asian J Chem 17: 755.
- Benhamou A, Belbachir M (2005) Grafting reaction of amines on PVC in the presence of Maghnite -H⁺. PhD Thesis.
- Stanke D, Hallensleben ML, Toppare L (1995) Graft-copolymers and composites of poly (methyl methacrylate) and polypyrrole. Synthetic metals 72: 89-94.
- Kizilyar N, Toppare L, Onen A, Yagci Y (1998) Conducting copolymers of polyepyrrole/polyhydrofuran. Polymer Bulletin 40: 639-645.
- Park YH, Kim KW, Jo WH (2002) Preparation and characterization of conducting poly (acryloyl chloride) -g- polypyrrole copolymer. Polymers for Advanced Technologies 13: 670-677.

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13. Tarkuc S, Sahin E, Toppare L, Colak D, Cianga I, et al. (2006) Synthesis, characterization and electrochromic properties of a conducting copolymer of pyrrole functionalized polystyrene with pyrrole. *Polymer* 47: 2001-2009.
 14. Kizilyar N, Toppare L, Onen A, Yagci Y (1999) Synthesis of conducting PPy/pTHF copolymers. *Journal of Applied Polymer Science* 71: 713-720.
 15. Jerome C, Martinot L, Louette P, Jerome R (2000) Synthesis of new pyrrole-g-epsilon-caprolactone copolymers. *Macromolecular Symposia* 153: 305-319.
 16. Belmokhtar A, Sahli N, Yahiaoui A, Belbachir M (2007) Polycondensation of pyrrole and benzaldehyde catalysed by Maghnite -H⁺. *Express Polymer Letters* 1: 443-449.