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One step for the synthesis of epichlorhydrin-styrene copolymers

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ABSTRACT

In the present work poly(epichlorhydrin-co-styrene) copolymers were prepared successfully and cleanly by a one step process via cationic copolymerization of epichlorhydrin(ECH) with styrene (St) in heterogeneous phase using “Maghnite-H^+” (Mag-H^+) as catalyst in bulk, Maghnite is a montmorillonite sheet silicate clay exchanged with protons to produce Maghnite-H^+. Temperature is varied between 20 and 70 °C. 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(ECH-co-St) was analyzed by infra red spectroscopy (IR) and nuclear magnetic resonance spectroscopy as well as by viscosimetry.

Keywords: *Maghnite-H^+, epichlorhydrin, styrene, clay, montmorillonite, copolymerization.*

1. INTRODUCTION

Copolymerization is one of the important techniques adopted in effecting systematic changes in the properties of the commercially important polymers. In the present work Poly(epichlorhydrin-co-styrene) copolymers were prepared successfully and cleanly via cationic transformation in one step. Usually, they are prepared by two steps process via cationic-to-radical transformation at 70°C. At first epichlorhydrin(ECH) was polymerized using HBF_4 as catalyst and reacted with the sodium salt of 4,4'-azo-bis(4-cyanopentanoic acid)(ACPA) to yield poly(epichlorhydrin) (PECH) possessing thermally labile *azo* group. PECH-macroazoinitiator was then used to initiate the thermal radical block copolymerization of styrene [1]. In this respect, it is even more interesting to use “Maghnite-H^+” as catalyst to prepare (epichlorhydrin-styrene) copolymers by one step in bulk at room temperature. 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 [2]. Maghnite 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 [3,4]. The purpose of this paper is also to study the copolymerization of epichlorhydrin(ECH) with styrene

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(St) and examines the catalytic activity of an Algerian proton exchanged montmorillonite clay called “Maghnite-H$^+$” [3-17]. The effect of some factors such as the amount of the Mag-H$^+$ and effect of temperature are discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. The preparation of the ‘‘Maghnite-H$^+$ 0.25M’’ (Mag-H$^+$) was carried out by using a method similar to that described by Belbachir and al [1]. Epichlorhydrin (99%), methanol (99%) were used as received. Styrene was purified by stirring over CaH_2 for about 24 h and then distilled under reduced pressure over CaH_2 and was finally stored under nitrogen atmosphere.

2.2. Procedure and Polymer characterization. Copolymerizations were carried out in stirred flasks at differents Temperatures between 20 and 70 °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 Epichlorhydrin (0,083 mol), Styrene (0,083 mol) mixture preliminary kept 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 copolymer 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 and ^{13}C-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.

3. RESULTS SECTION

3.1. Characterization of products. The IR spectrum of the copolymer (Figure.1) showed bands due to PSt: peaks at 1431,67 ; 1556,17 and 1619,72 cm^{-1} (C-C stretching within the ring), at 700,99 and 744,88 (out of plane C-H bending vibrations); at 2874,70 and 2959,98 (symmetrical stretching bands –CH_2-) and 3017,37 cm^{-1} (aromatic C-H stretching), and others bands due to PECH at 1086,38–1198,89 cm^{-1} for C–O–C, at 630,68 cm^{-1} for C–Cl. Similar results are reported elsewhere [1,18,19].

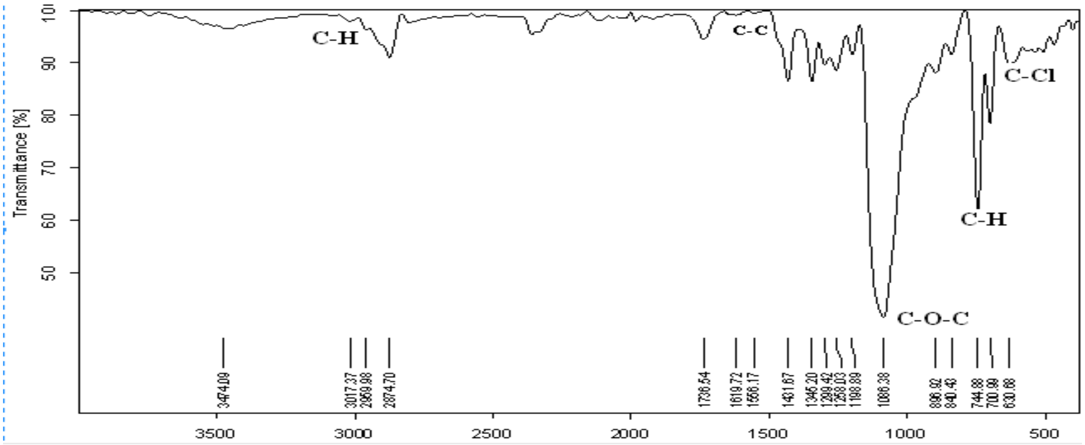

Figure.1: IR spectrum of Poly(epichlorhydrin-co-styrene).

The structure of the Poly(epichlorhydrin-co-styrene) was determined by ^{1}H-NMR. Figure 2 shows the chemical shifts at 7,23 and 7.33 ppm for the protons of benzene ring, that at 3.74 ppm for the protons of methylene groups of PECH and those at 1.26 ppm and 1.74 ppm for the methylene and methine groups of PSt. Thus these two spectra all indicate the presence of PECH segments and PSt segments in the copolymer, Similar results are obtained by Demirbag.A and Cakmak.I, Cunha. H. T. and Oliveira. C. M. F ,Hong-Quan.X and al [1,18,19].

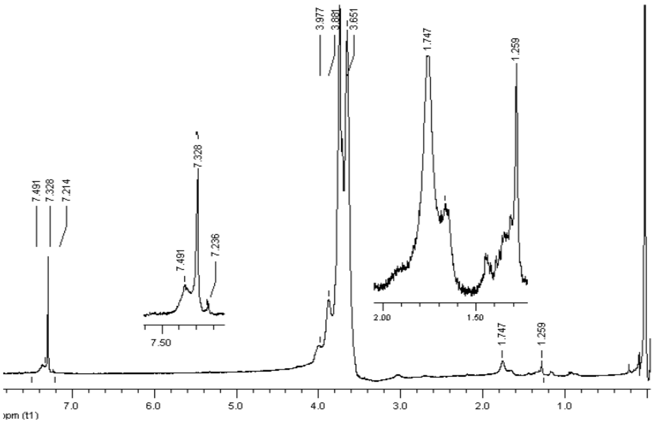

Figure 2: ^{1}H-NMR spectrum of Poly(epichlorhydrin-co-styrene).

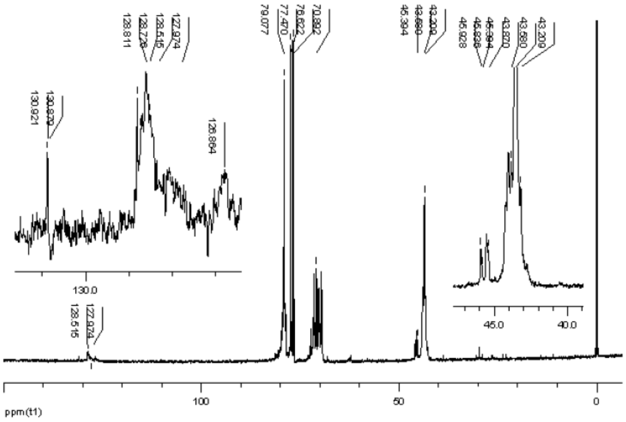

Figure 3: ^{13}C-NMR spectrum of Poly(epichlorhydrin-co-styrene).

The ^{13}C-NMR spectrum Figure 3 proves also the presence of both components in the copolymer and shows numerous resonances in the regions of 79,07, 43,68, and 69,50–72,13 ppm assignable to C-H, CH_2Cl, and CH_2 of PECH respectively, and others attributed to PSt at 130,88, 128,70, 127,03, 126,74 (aromatic carbons of PSt), 43,58-45,53 (aliphatic carbons of PSt).

3.2. Effect of the temperature on the copolymerization. Table 1 shows the experimental results for the copolymerization of ECH (0,083 mol) with styrene (0,083 mol) induced by "Maghnite- H$^+$ 0.25 M" proceed in bulk at different temperatures. It was found that Maghnite- H$^+$ by itself possesses good activity as catalyst for the copolymerization. The yield of copolymerization and the intrinsic viscosity reach maximum values around 40-60°C. On the other hand,with the increase in the reaction temperature above 50 °C the intrinsic viscosity and the yield of the obtained copolymers decrease progressively suggesting the possible occurrence of thermal degradation.

Table 1: Effect of reaction temperature on the polymerization

T(°C)	Yield (%)	[η](dl/g)^a
20	57,44	0,95
30	61,28	1,26
40	67,53	1,58
50	72,32	1,73
60	69,14	1,47
70	65,93	1,19

[ECH] = 0,083 mol; [St] = 0,083 mol; 5% of Maghnite-H$^+$ 0.25 M, Reaction time = 6 h, ^{a}Determined in toluene at 35 °C.

3.3. Effect of the amount of Mag-H$^+$ on the copolymerization. The effect of the amount of Maghnite-H$^+$ on the copolymerization was examined (Table 2). It can be noted that the yield increases with increasing "Maghnite- H$^+$ 0.25 M" proportion. Indeed, using various amounts of Mag-H$^+$, 2.5, 5 and 10 % by weight, the polymerization was carried in bulk at 50 °C. The polymerization rate increases with the amount of Mag-H$^+$, In contrast, the intrinsic viscosity (η) is inversely proportional to the amount of Mag-H$^+$, in which the effect of Mag-H$^+$ as a catalyst is clearly shown. This phenomena is probably the result of number of "initiating active sites" responsible of inducing polymerization, this number is prorata to the catalyst amount used in reaction. Similar results are obtained by Belbachir and al [13-17].

Table 2: copolymerization using different amount of Maghnite- H^+

Maghnite-H^+ 0.25M (%)	Yield(%)	[η](dl/g)^a
2,5	46,58	1,87
5	72,32	1,73
10	89,66	1,49

[ECH] = 0,083 mol; [St] = 0,083 mol, Reaction time = 6 h, T=50°C, ^{a}Determined in toluene at 35 °C

3.3. Effect of the reaction time on the copolymerization. Polymerization using 5 % of Maghnite-H^+ 0.25 M was carried in bulk at 50 °C and the reaction was monitored at various times. The results are given in Table 3 shows the evolution of the yield and the intrinsic viscosity of the copolymer with reaction time. The intrinsic viscosity increases with polymerization time. On the other hand, the yield increases with the time and it can be noted that initially the polymerization proceeds very slowly; this can be considered as an induction period (4 h). At the end of this period.the polymerization process becomes faster.

Table 3: Kinetic evolution of the copolymerization of ECH with styrene catalyzed by Maghnite-H^+ 0.25 M.

Time(h)	Yield(%)	[η](dl/g)^a
2	32,16	0,63
3	37,91	0,85
4	43,73	1,07
5	61,95	1,42
6	72,32	1,73

[ECH] = 0,083 mol; [St] = 0,083 mol; 5% of Maghnite-H^+ 0.25 M, T=50°C, ^{a}Determined in toluene at 35 °C.

4. CONCLUSIONS

In conclusion, it was proved that Mag-H^+ can be used to induce the copolymerization of epichlorhydrin with Styrene. The products were obtained by a very simple procedure via cationic transformation in one step at room temperature. 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 copolymers was confirmed by ^{1}H-NMR,^{13}C-NMR, and IR.

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