# Synthesis of Copolymer from 1,3,5-Trioxane and 1,3-Dioxolane Catalyzed by Maghnite-H$^+$

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**ABSTRACT:** Copolymers (polyoxymethylene) were prepared by cationic copolymerization of 1,3,5-trioxane (TOX) with 1,3-dioxolane (DOX) in the presence of Maghnite-H$^+$ (Mag-H$^+$) in solution. Maghnite is a Montmorillonite sheet silicate clay, with exchanged protons to produce Mag-H$^+$. Various techniques, including $^1$H-NMR, $^{13}$C-NMR, FT-IR spectroscopy, and Ubbelohde viscometer were used to elucidate structural characteristics properties of the resulting copolymers. The influence of the amount of catalyst, of dioxolane (DOX), temperature, solvent, and time of copolymerization on yield and on intrinsic viscosity of copolymers was studied. The yield of copolymerization depends on the amount of Mag-H$^+$ used and the reaction time. We also propose mechanisms involved in the synthesis of copolymer (polyoxymethylene). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2820–2827, 2010

**Key words:** Maghnite-H$^+$; polyoxymethylene; 1,3,5-trioxane; 1,3-dioxolane; copolymerization

## INTRODUCTION

Polyoxymethylene, which has a recurring unit of oxymethylene, is called polyacetal resin, and is a useful engineering plastic to replace metal. There are two routes for the production of polyacetal resin. One route is the polymerization of formaldehyde (acetal homopolymer),[1–6] and the other method is copolymerization of trioxane with cyclic ethers or acetals (acetal copolymer), preferably with 1,3-dioxolane[7–10] or ethylene oxide.[11–28]

The copolymerization of trioxane is of considerable industrial importance, because the acetal copolymer has better thermal properties and superior resistance to alkali than homopolymer and it is a commercially useful engineering plastic.

The properties of acetal copolymers depend on the comonomer composition and also on the sequence distribution of the constituent comonomers. Various investigators have presented two methods for determining the comonomer content: gas chromatography[29,30] and NMR spectroscopy.[31–33]

The ring-opening copolymerization of TOX can be initiated by Lewis acid such as BF$_3$O(Et)$_2$, TiCl$_4$,[34] and CH$_3$COClO$_4$.[35] Penczek and coworkers[36] studied the solution copolymerization of TOX and a small amount of DOX initiated by BF$_3$O(n-Bu)$_2$ and found that the unstable fraction content of the copolymer increased with increasing conversion, indicative of a higher reactivity of DOX than that of TOX toward the copolymerization.

However, there is a newly discovered mechanism for the copolymerization of TOX and DOX, using BF$_3$O(Et)$_2$ as catalyst in the presence of nanosilica, the copolymerization give a polymer with two or more consecutive DOX units in an oxymethylene main-chain sequence,[37] which differ from the previous results of Yamasaki.[38] However, the macromolecular chain of acetal/silica nanocomposite had only one DOX unit in an oxymethylene main-chain.[37]

Recently, an Algerian proton exchanged Montmorillonite clay called Maghnite-H$^+$(Mag-H$^+$), a new non toxic cationic initiator, was used as a catalyst for cationic polymerization of a number of vinylic and heterocyclic monomers.[39–42]

In the present work, we present a new approach to synthesis a copolymer of TOX by the cationic copolymerization of TOX with DOX in solution catalyzed by Mag-H$^+$ (Fig. 1). This catalyst can be easily separated from the copolymer product and regenerated by heating at a temperature above 100°C.[39]

The results of FT-IR spectroscopy and $^1$H-NMR and $^{13}$C-NMR spectrometry indicated that the polymerization product was acetal copolymer. From the NMR results, we discuss the sequence distribution of oxymethylene and oxethylene units in the macromolecular chain of acetal copolymer.

The effects of different synthesis parameters such as the amount of Mag-H$^+$, comonomer DOX, and eventually the mechanism are discussed.
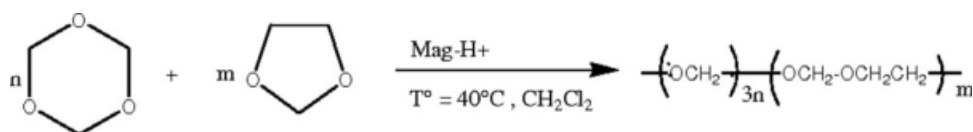
**Figure 1** Schematic representation of the synthesis of copolymer (TOX–DOX).

## EXPERIMENTAL

### Preparation of Mag-H$^+$

Pristine Maghnite is activated with a sulfuric acid solution to give a Maghnite exchanged with protons, called Mag-H$^+$. In an Erlenmeyer flask, crushed raw Maghnite (30 g) was dispersed in a volume of distilled water (120 mL). The mixture was stirred using a magnetic stirrer for 2 h at room temperature. Then, a solution of sulfuric acid $0.5M$ (100 mL) was added. The solution thus obtained was maintained for 2 days under stirring and then the mineral was filtered off and washed several times with distilled water upto pH 7. After filtration, the Mag-H$^+$ was dried in an oven for 24 h, at 105°C and was then crushed.

### Reagents

1,3,5-Trioxane (98%), 1,3-dioxolane (96%), dichloromethane, and acetone were purchased from Aldrich and used as received. Raw-Maghnite: Algerian Montmorillonite clay, was procured from "BENTAL" (Algerian Society of Bentonite).

### Polymer preparation

Copolymerizations were performed in dichloromethane at 40°C. The procedure was identical in both cases, involving addition of catalyst to the stirred solution containing TOX and DOX in dichloromethane.

Before use, Mag-H$^+$ was died in a muffle at 105°C overnight. An example reaction is detailed here. After charging the reaction vessel with TOX (6 g, 1 mol) solution in dichloromethane (10 mL) and DOX (2.22 g, 0.03 mol), the catalyst (10% by weight, 0.06 g) was added at a copolymerization temperature, e.g., 40°C. At the end of the reaction (4 h), the resulting mixture was filtered to remove the clay (Mag-H$^+$) and a insoluble polymer composed almost entirely of TOX units (POM), which precipitated as a fine powder during the early stages of polymerization, then poured into ether to precipitate the soluble polymeric product (copolymer TOX–DOX) in cold acetone. The precipitates were characterized by $^1$H-NMR, $^{13}$C-NMR, and IR (FT-IR) analysis.

## INSTRUMENTATION

To determine the chemical structure of the products, measurements of $^1$H-NMR and $^{13}$C-NMR were carried out on a BRUKER 300 MHz in CDCl$_3$ with Tetramethylsilane as the internal standard in these cases.

IR absorption spectra of the copolymers as thin films KBr pellets were accorded with an ATI- Matson FTIR Spectrometer.

Intrinsic viscosity (η) measurements were performed in Dichloromethane at 25°C, using a capillary viscosimeter viscologic TI.1, version 3-1 Semantec.

X-ray diffraction (XRD) patterns for Mag-H was obtained on a Philips analytical X-ray diffractometer (Cu anode, 35 kV, 20 mA).

## RESULTS AND DISCUSSION

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.[43] 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.[44]

The present study is also concerned with polymerization and examines the catalytic activity of an Algerian proton exchanged Montmorillonite clay called "Maghnite" via cationic copolymerization of 1,3,5-trioxane (TOX) with 1,3-dioxolane (DOX). The aim of this research is to extend of other new field of polymer synthesis by the use of another catalyst system that has been shown to exhibit higher efficiency.

### Structural analysis

$^1$H-NMR results of copolymer (TOX/DOX):

The polyoxymethylene copolymer (TOX–DOX) is composed of oxymethylene units ($-$OCH$_2-$, or M) and ethylene oxide (EO) units ($-$OCH$_2$CH$_2-$, or E).

The $^1$H-NMR spectrum of copolymer is shown in Figure 2. Various distributions of oxymethylene (M) and ethylene oxide (E) units are observed in the resulting copolymers are observed, the results are presented in Table I.

The chemical shifts of oxymethylene M in triads is not constant and depends on the neighboring units. The methylene proton signal of oxymethylene unit is observed at 5 ppm, which is assigned to copolymer MMM sequence. The signal resulting from the

H(-OCH$_2$-)$_{3n}$-(OCH$_2$-OCH$_2$CH$_2$)$_m$-OH

M     M     E
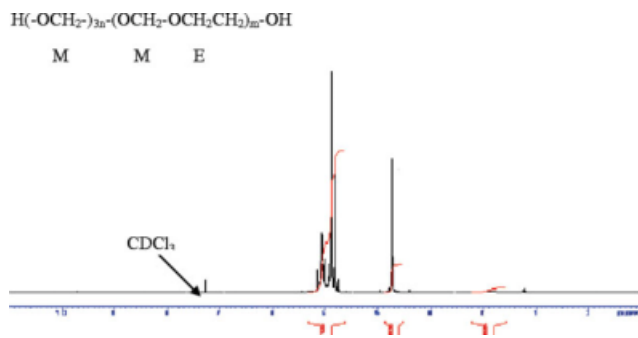


**Figure 2** $^1$H-NMR Spectrum (300 MHz) of copolymer (Solvent, CDCl$_3$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1,3-dioxolane monomer is observed at 3.73 ppm and 4.81 ppm. The first signal can be assigned to the ethylene oxide unit in the copolymer MEM sequence and the second signal can be assigned to the methylene proton of oxymethylene unit located between two consecutive ethylene oxide units: EME. The resonance peak occurring at 4.91 ppm corresponds to the methylene proton of oxymethylene in the copolymer MME/EMM sequence. Similar results are obtained by Guangqin et al.[45] The same results are also obtained with the copolymerization of TOX and DOX, using BF$_3$O(Et)$_2$ as catalyst in the presence of nanosilica.[37]

In the NMR spectrum of the copolymer (TOX–DOX), the peak of hydroxyl groups at 1.9 ppm is obvious (Fig. 2).

The $^{13}$C-NMR spectrum of the copolymer is shown in Figure 3.

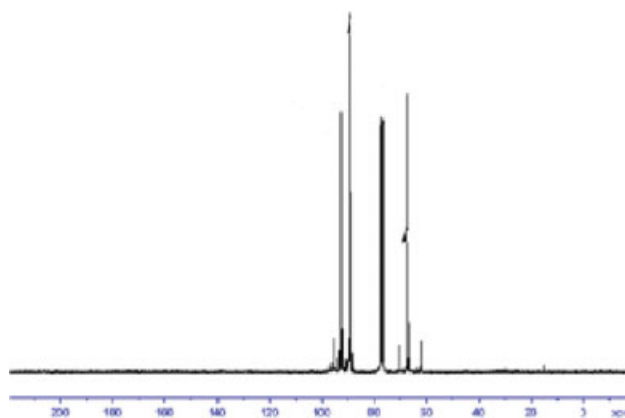$^{13}$C-NMR spectroscopy is much more suitable for structural studies. The Signals observed in the spectrum can be assigned to the various distributions of oxymethylene (M) and ethylene oxide (E) units in the copolymer (TOX–DOX). Some assignment results are given in Table II. The chemical shifts of oxymethylene (M) in pentad sequences is not constant and depends on the neighboring units.

The results obtained are comparable to the results of $^{13}$C-NMR spectrum of copolymer (TOX–DOX) synthesized in CDCl$_3$, using a shift reagent, 1,1,1,2,2,3,3-heptafluor-7,7-dimethyl-4,6-octadionatoeuropium (Eu(fod)$_3$).[46]

Figure 4 shows the IR absorption spectra of copolymer (TOX–DOX).



**Figure 3** $^{13}$C-NMR spectrum (300 MHz) of copolymer (Solvent, CDCl$_3$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The spectra show strong characteristic peaks of acetal polymer around 991–933 and 1236–1122 cm$^{-1}$, which are assigned to the methylene —CH$_2$— rocking and skeletal stretching vibration, and C—O—C stretching vibration. The absorption band at 1122 cm$^{-1}$ results from asymmetric stretching vibration of C—O—C and bending vibration of O—C—O. The absorption peak at 1484 cm$^{-1}$ is due to the bending vibration of C—C. Other bands appear in the region of 2975–2919 cm$^{-1}$ which is assigned to C—H stretching vibration. The absorption band of the OH group stretching vibration appears at 3459 cm$^{-1}$. The same results are obtained by Egawa et al.[47]

Intensity versus 2θ scans of Maghnite (before and after polymerization: Fig. 5). The X-ray peaks of the fresh and the recovered Maghnite-H$^+$ did not change. This implies that the original structure was well preserved after polymerization and no delamination of the clay was observed.

## Effect of the amount of Mag-H$^+$

Figure 6 shows the effect of the amount of Mag-H$^+$, expressed by using various weight ratios Mag-H$^+$/ monomers, on the copolymerization rate of TOX with DOX. The copolymerization of TOX and DOX was carried at 40°C. The yield of copolymers increased with the amount of Mag-H$^+$. The output increases according to the quantity of Mag-H$^+$ up to

**TABLE I**
**$^1$H-NMR Chemical Shifts of Ethylene Oxide (E) and Oxymethylene (M) Units of Copolymer**

| Chemical shift (ppm) | Repeating unit of copolymer |
| --- | --- |
| 3.73 | MEM |
| 4.81 | EME |
| 4.91 | EMM = MME |
| 5.00 | MMM |

**TABLE II**
**$^{13}$C-NMR Spectra Assignment of the Peaks of Copolymer Due TOX Oxymethylene (M) an EO (E) Units**

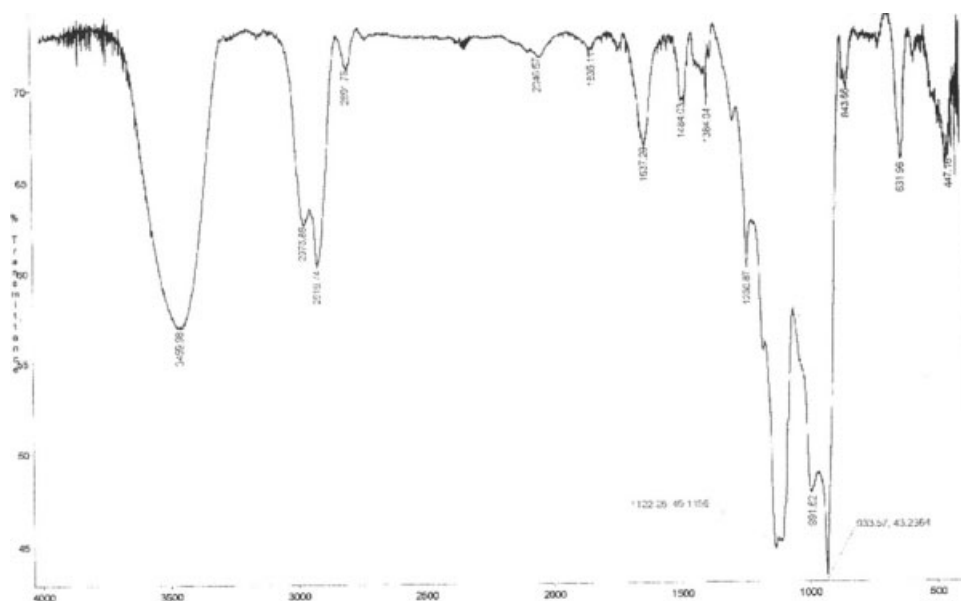| Chemical shift (ppm) | Repeating unit of copolymer |
| --- | --- |
| 95.57 | MEMEM |
| 93.28 | MMMEM |
| 92.13 | MEMME |
| 89.65 | MMMMM |
| 88.80 | EMMMM |
| 67.46 and 66.80 | EMEMM |

**Figure 4** FT-IR Spectrum of copolymer (TOX/DOX) recorded from thin films and KBr pellets.

the point optimal and reached 42% and which corresponds to 10% of Mag-H$^+$ beyond this value the yield decrease. This result shows the effect of Maghnite-H$^+$ as a cationic catalyst. Similar results are obtained by Belbachir and coworkers,[39,48–50] in the polymerization of isobutylene by Maghnite-H$^+$, which polymerizes only by cationic process.[51]

The low yield polymerization was not observed only with Maghnite-H$^+$ but also with triflic acid and other acid initiator: BF$_3$ complex derivatives[52] when the polymerization of TOX with DOX is realized in bulk, at 40°C.

### Effect of time on copolymerization

The results depicted graphically on Figure 7 shows that at the end of 240 min, copolymerization evolves/moves quickly and reaches a best performance of 69% at the end of 360 min, after this time it slows down gradually and the yield becomes almost constant.

The same results were obtained during the copolymerization of the TOX with DOX started by BF$_3$ in ethylene dichloride and at the temperature of 30°C, studied by Yeong et al.,[53] the yield polymerization reached 70%.
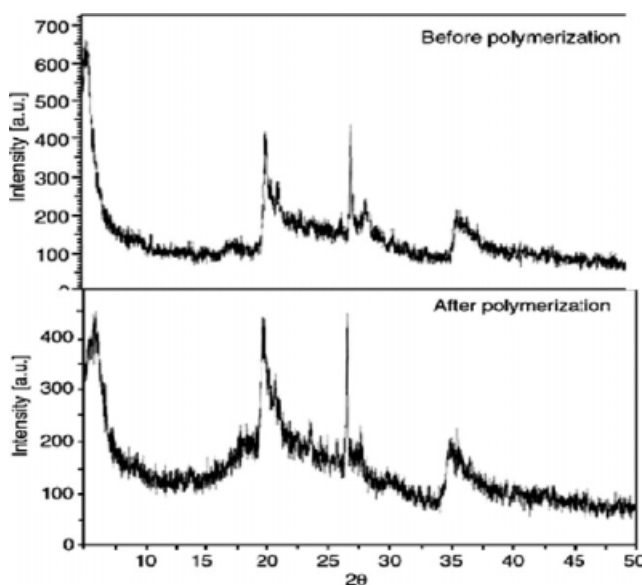
### Evolution of intrinsic viscosity according to time

The effect of copolymerization duration on the intrinsic viscosity was studied. As depicted in Figure 8, the intrinsic viscosity ($\eta$) decreases when the duration of copolymerization increases, this is due
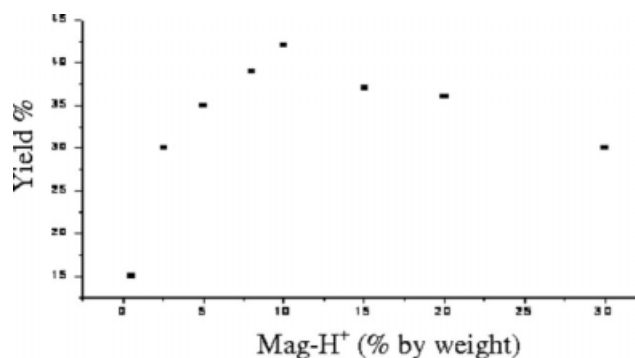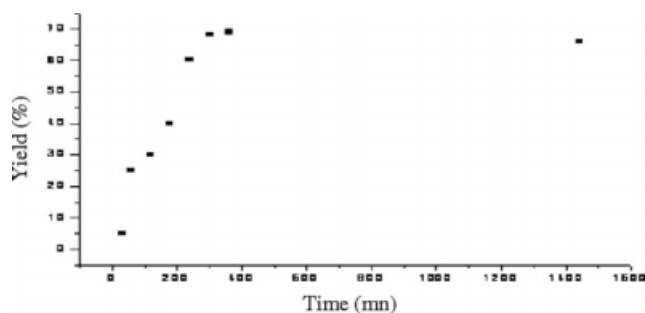


**Figure 5** XRD scans: Maghnite before polymerization and after polymerization.



**Figure 6** Effect of the amount of catalyst on the yield of formed copolymer (TOX/DOX) DOX (3 mol %) in dichloromethane at 40°C.

**Figure 7** Effect of copolymerization duration on yield of copolymer Mag-H$^+$ (10% by weight), DOX (20 mol %) in dichloromethane at 40°C.

probably to the reactions of intramolecular transesterification, i.e., "back-biting," which causes degradation and formation of cyclic oligomers and consequently may cause a decrease of the intrinsic viscosity. The same results are obtained by Fejgin et al.[54] when they polymerized TOX with DOX in the presence of BF$_3$ O (n-C$_4$H$_9$)$_2$.

The importance of chain transfer in the polymerization of TOX is illustrated by the fact that molecular weights of polymers can not be increased.

## Effect of the quantity of the 1,3-dioxolane on the yield

One varied the molar percentage of the 1,3-dioxolane compared to the TOX by maintaining the other parameters of synthesis constant: the duration of the reaction (4 h), the temperature is 40°C, and the quantity of Mag-H$^+$ is equal to 10%. The results obtained are presented in Figure 9. The graph corresponding shows that the output increases according to the molar percentage of DOX then it is stabilized. Similar results were obtained by copolymerization TOX with DOX in presence of BF$_3$ complex, the yield of copolymerization was reached between 65% and 77% with low molecular weight when the proportion of DOX
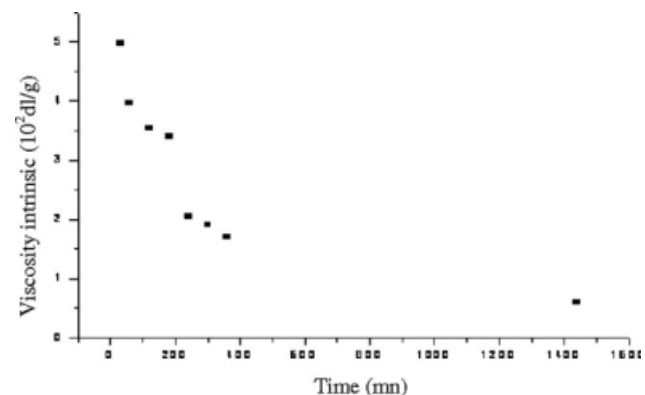


**Figure 8** Evolution of intrinsic viscosity according to time Mag-H$^+$ (10% by weight), DOX (20 mol %) in dichloromethane at 40°C.
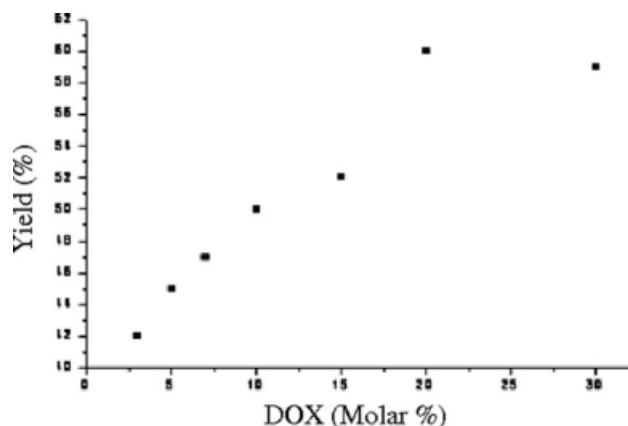
**Figure 9** Evolution of the yield according to the % Molar of the DOX Mag-H$^+$ (10% by weight) in dichloromethane at 40°C.

units increases above 2.5 mol %.[54] The rate of consumption of both comonomers (TOX, DOX) is not the same,[28,55] DOX is consumed much faster and the copolymer formed initially is considerably enriched by DOX units, and an insoluble polymer is formed composed almost entirely of TOX units.

## Effect of solvent on the copolymerization of the TOX with the DOX

As all the reactions were carried out in solution, it was interested to study the effect of solvent on the copolymerization of TOX with DOX. Under the experimental conditions depicted in Table III, we used a series of solvents having different ($\varepsilon$), "epsilon" is a sign of dielectric constant, at a temperature: 40°C with Mag-H$^+$ (10% by weight) and DOX (3% mol) for a time 4 h.

The results are shown in Figure 10. It can be seen that for the values of high dielectric constant ($\varepsilon$), no realizable copolymerization, whereas for lower values, the reaction is favoured. This result is due to catalyst structure, as all minerals clay, the Maghnite-H$^+$ shows an affinity over polar particles and in this case, adsorbed molecules of polar solvent reduce the contact between the monomers (TOX and DOX) and the "initiating active sites" and it doesn't lead to any copolymerization.

**TABLE III**
**Yield of the Experiments in Solution, in $T$ = 40°C, 10% of Mag-H$^+$ and 3 mol % of the DOX**

| Solvent | $\varepsilon$ | Yield (%) |
|---|---|---|
| DMF | 37 | – |
| CH$_3$OH | 33.7 | – |
| CH$_2$Cl$_2$ | 8.93 | 42 |
| CHCl$_3$ | 4.81 | 53.5 |
| Cyclohexane | 2.28 | 30.5 |
| CCl$_4$ | 2.24 | 23.5 |
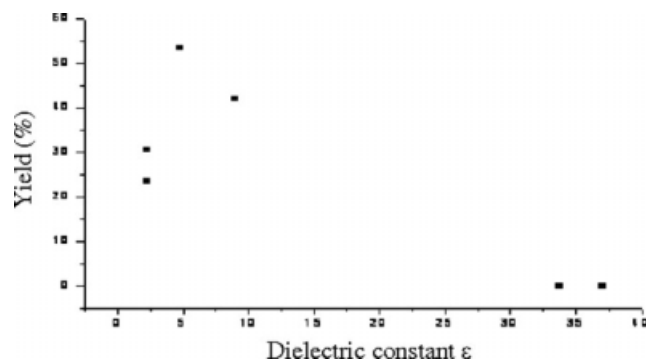
**Figure 10** Variation of the yield according to dielectric constant (ε) solvents used.

## Effect of the temperature on the yield

The temperature is an important factor in the initiation process and its influence was studied. We carried out copolymerization in solution and mass, at different temperatures (25, 30, 40, 50, and 60°C), for the same duration of 4 h in the presence of Mag-H$^+$ (0.23$M$) with 10% by weight and 3 mol % of DOX.

Figure 11 show that the copolymerization temperature has much influence on the yield of copolymers (TOX/DOX). The yield increased with the temperature, it reached a high yield (52%) at 60°C.

In the bulk process, molten TOX is polymerized in admixture with comonomer in the 60–120°C range, above the melting and below the boiling point of TOX. Several problems may occur during this bulk process. The heat of polymerization of TOX is close to 4.0 Kcal/mol[23] and this heat has to be removed.

## MECHANISM OF THE CATIONIC COPOLYMERIZATION OF TOX WITH DOX

Copolymerizations proceed by successive reactions between the functional groups of the monomers. According to the foregoing discussion and the results of product analysis, we may suggest the mechanism below for the resulting reaction of copolymerization induced by "Maghnite-H 0.25 M."

Protons carried by montmorillonite sheets of "Maghnite-H 0.25 M" induced the copolymerization. These montmorillonite sheets acts as counter-anions.

## Initiation

The first step in the copolymerization of TOX with DOX is the protonation of TOX and DOX by the Mag-H$^+$, the initiation reactions are determined by the relative reactivity of TOX and DOX toward the proton to form TOX-cyclic oxonium and DOX-cyclic oxonium as in reactions (1) and (2), respectively.
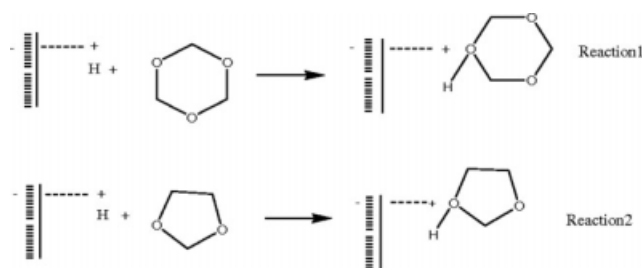
## Propagation

From the various distributions of oxymethylene (M) and ethylene oxide (E) units obtained from the results of RMN$^1$H and $^{13}$C. This may be explained as follows, during the chain propagation period the increasing chain of oxymethylene attacks DOX as shown in reaction (3), another possibilities about the structure of the copolymer (TOX/DOX) is the increasing chain of DOX with TOX monomers (reaction 4).
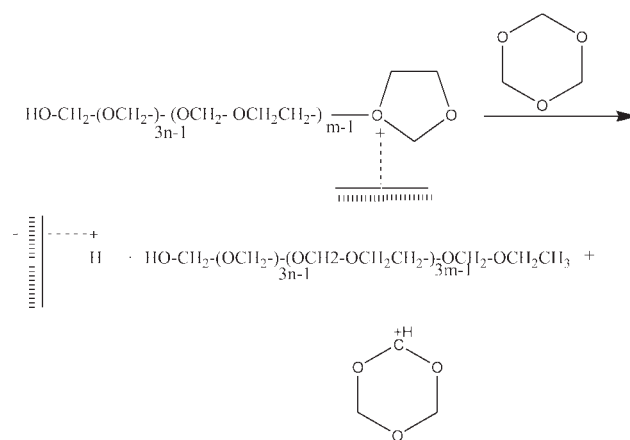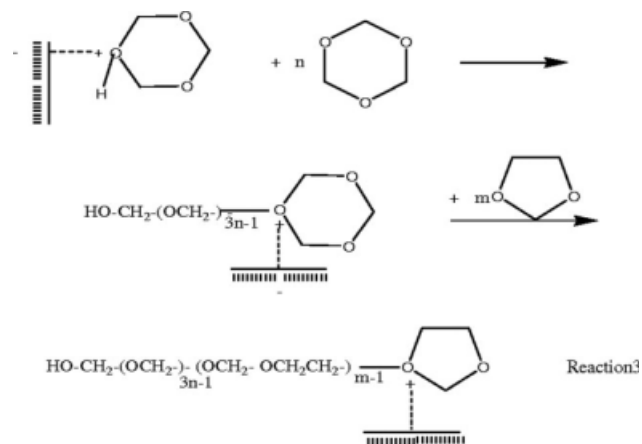


It is admitted that the propagation is done by the successive addition of each monomer on the macrocation of the increasing chain reaction (3).
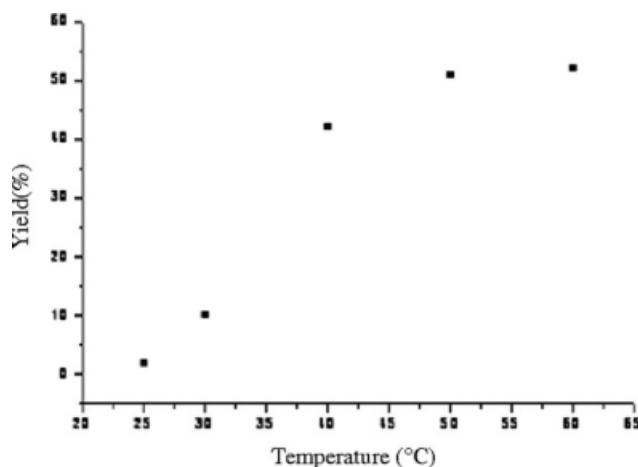
**Figure 11** Temperature effect on the copolymer (TOX/DOX) yield Mag-H$^+$ (10% by weight), DOX (3 mol %) in dichloromethane at 40°C.

## Reaction of transfer

It is supposed that there is a reaction of transfer of chain to the monomer and the absence of the reaction of termination in this kind of cation copolymerization per opening of cycle of the two monomers reaction (4).

## CONCLUSION

The present work shows that the preparation of copolymer (TOX/DOX) can be induced in heterogeneous phase by proton-exchanged Montmorillonite clay "Mag-H$^+$."

The catalytic activity of this catalyst (measured by the conversion) and the intrinsic viscosity of the formed copolymers depend on the proportion of catalyst in the reaction medium, the solvent and the temperature of reaction.

Copolymers (TOX/DOX) were produced by a very simple procedure, just by filtering, the clay can be separated from the reaction mixtures, and acidic clay is inexpensive, stable, and non corrosive.

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