

Theoretical and Experimental Study of the Chemical Modification of Poly(epichlorohydrin) by Grafting Menthol †

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Abstract: Functional polymers, a significant class of compounds with diverse applications, are synthesized by incorporating functional groups into polymer matrices. Poly(epichlorohydrin) (PECH) is a pivotal polymer due to its reactive chloromethyl group, which readily enables its transformation into various functional polymers. Our study is focused on theoretically unraveling the mechanism behind modifying PECH through menthol grafting. We optimized and characterized various stationary states using Density Functional Theory (DFT) at the B3LYP/6-311++G** level. These calculations were conducted in both gas phase and a solution environment (THF). To anticipate the specific sites within our polymer that would be subject to grafting, we calculated various reactivity indices at the same computational level.

Keywords: Poly(epichlorohydrin); chloromethyl; grafting; Density Functional Theory

1. Introduction

Functional polymers are produced by the integration of the identical or different functional groups into a polymer matrix. These polymers have attracted a lot of interest due to their numerous applications in recent years, such as in electrical [1,2] and electronic science [3,4], biotechnology [5,6], biochemistry [7,8], biomedical [9–11] (carriers of active ingredients) as well as the agricultural field [12] (biocidal functions).

They constitute an important class of compounds with great activity in different fields. Indeed, the control of their structures from the point of view of their functionality has recently aroused great enthusiasm. Various applications, such as textiles, automobiles, optics and drug molecules, illustrate the great versatility that these materials offer in booming fields. The ability to polymerize heterocyclic monomers essentially depends on the size of the ring, the nature of the heteroatom which contains it as well as the nature of the substituent around the rings. Indeed, several studies have been carried out in this context [13–15]. It is important to modify the structure of a polymer according to tailor-made characteristics designed for target applications. Most research efforts have been reserved for attempts to transform functional polymers into products for the environmental and biological field. This technique has experienced very significant development in recent years, particularly in the field of industry, we can cite for example cellulose [16], which after chemical modification, can lead to a large class of polymers. This chemical modification of polymers presents essential advantages in the world of polymers such as the immobilization of macromolecular chains on polymer surfaces, the adjustment of the polarity of polymers and the preparation of three-dimensional networks.

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These polymers obtained after chemical modification either by substitution reactions [17], elimination [18], reduction [19], oxidation [20], alkylation [21] or grafting [22], can be classified as monofunctional polymers (comprising a functional group at the end of the chain) or difunctional (telechelic) polymers (comprising functional groups at both ends of the polymer) or even multifunctional polymers (comprising functional groups, identical or different, all along its polymer chain).

In this context, our contribution is in fact twofold: on the one hand, experimental: preparation of three-membered heterocyclic polymer poly(epichlorohydrin), as precursor polymer, by cationic method by activated monomer, followed by a chemical modification of this lastly by the technique of grafting with menthol, and on the other hand theoretical study: elucidation of the reaction mechanism of this chemical modification by reproducing in the same condition as best as possible the obtained experimental results.

2. Methodology of Calculations

All theoretical calculations were carried out using the Gaussian 09 program [23] with the (DFT) method [24,25], at the B3LYP/6-311++G** level [26]. An IRC calculation [27,28] was carried out. Given that the reaction occurs experimentally in an aprotic polar solvent (THF), the effect of the latter was taken into account implicitly in our calculations using Tomasi's PCM [29]. In order to understand chemical reactivity trends of the reactants, reactivity indices such as chemical potential μ , and chemical hardness η for each reacting species have been calculated at the same level of theory [30].

3. Results and Discussion

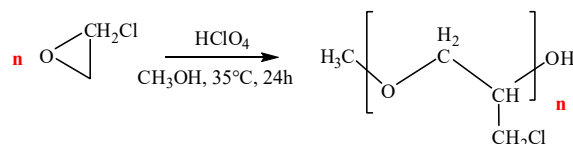
3.1. Experimental Study

Materials: epichlorohydrin (ECH) monomer was purchased from Aldrich and distilled under reduced pressure; methanol were distilled on the day of experiment, perchloric acid, menthol

Measurements: FT-IR spectra was obtained on ALPHA FT-IR mark "Bruker" bearing the Module "Platinumdiamond ATR single reflection ATR", at room temperature in the range of 400–4000 cm^{-1} .

3.2. Synthesis of Poly(epichlorohydrin) (PECH)

The cationic mass polymerization by ring opening of epichlorohydrin was carried out by activated monomer, the reaction is initiated by perchloric acid (HClO_4) in the presence of methanol (CH_3OH) [31], at a temperature of 35 °C, under atmosphere of nitrogen and under magnetic stirring for 24 h, according to the reaction Scheme 1.



Scheme 1. Reaction scheme of the cationic polymerization of epichlorohydrin by activated monomer.

The cationic polymerization reaction was carried out in a three neck distilling flask, connected to a nitrogen supply. In order to prevent the solvent from being carried away by the nitrogen flow, a refrigerant is used to cool and condense the solvent vapors and to avoid any variation in the concentration of the reaction medium. The reaction is maintained under magnetic stirring and at a fixed temperature. The synthesis device is represented by Figure III.1 below. Into the three-necked distilling flask we introduce, successively, the methanol, the epichlorohydrin, and the perchloric acid, the latter is added drop by drop. At the end of the reaction, the crude product is precipitated in cyclohexane at

room temperature. The polymer is obtained with a gross yield by weight of 92%. The experimental conditions of the ring opening polymerization are summarized in Table 1.

Table 1. Experimental conditions and yield by weight of the synthesis of poly(epichlorohydrin) at T = 35 °C, in 24 h.

Reagents	n (mol)	V (mL)	C (mol/L)	Weight (%)
ECH	0.127	10	0.0127	92
HClO ₄	0.0002	0.0120	0.1600	
MeOH	0.004	0.23	0.017	

3.3. Characterization of Obtained Polymer

The FTIR spectrum of the monomer and the polymer obtained are, respectively, represented in Figures 1 and 2.

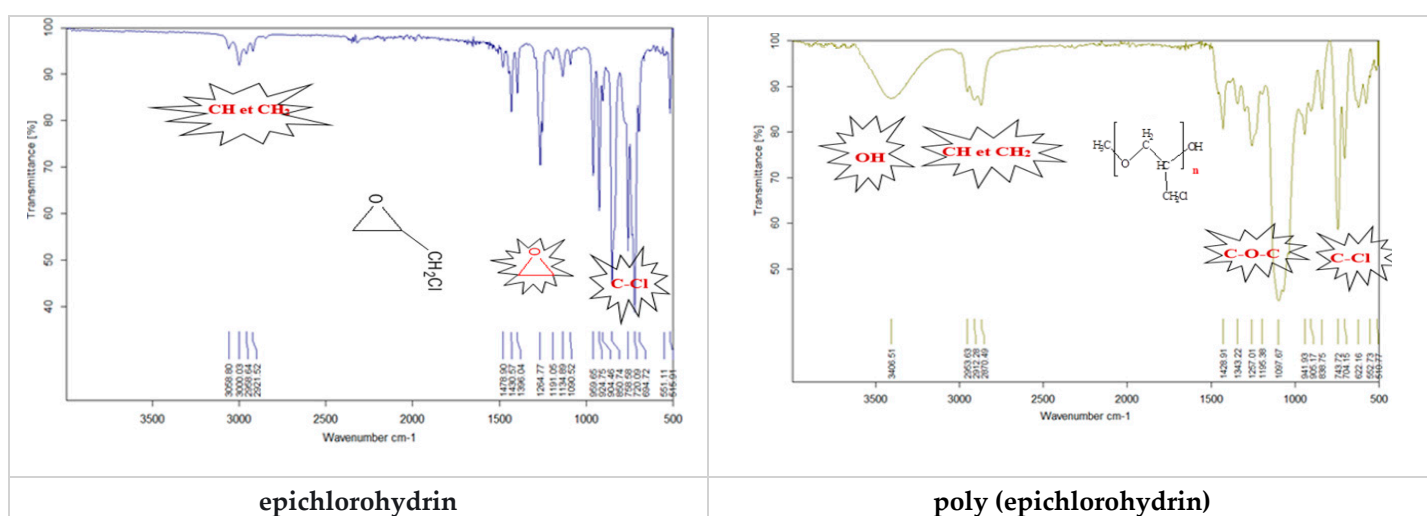


Figure 1. FTIR spectrum.

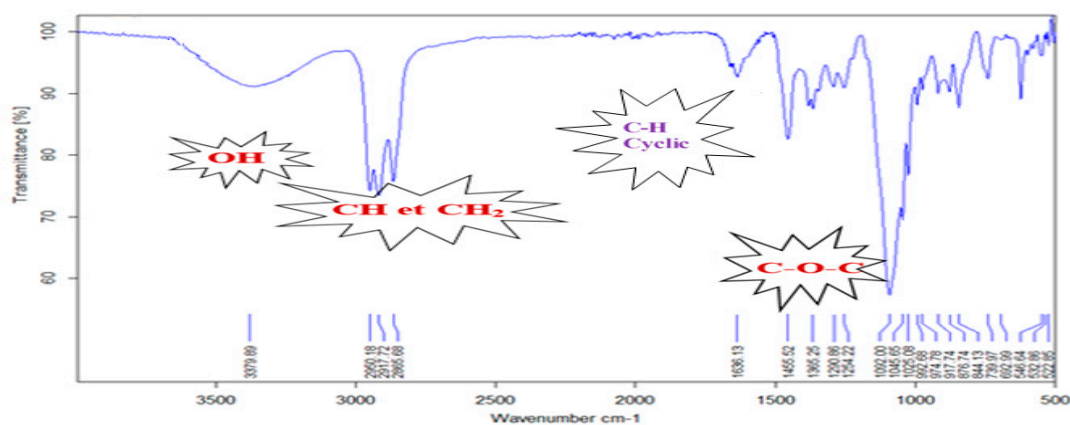


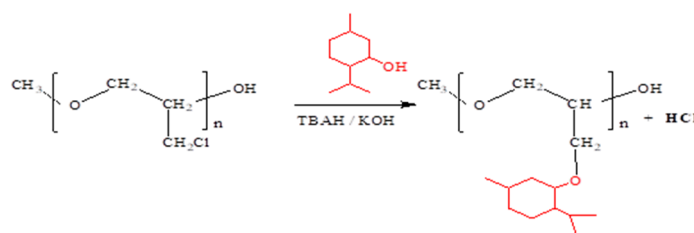
Figure 2. IR spectrum of poly(epichlorohydrin) modified by menthol grafting.

The FTIR spectrum of the monomer epichlorohydrin illustrated in Figure 1 shows the main characteristic bands in this case, an intense band at 904 cm⁻¹ characteristic of oxirane and an intense band at 720 cm⁻¹ which characterizes the C-Cl bond. Furthermore, the FTIR absorption spectrum of the synthesized polymer reveals the presence of the main bands which characterize the expected polymer. The FTIR spectrum (**poly (epichlorohydrin)**), allows us to first observe the disappearance of the characteristic band of oxiranes located at 904 cm⁻¹, and the appearance of a new absorption band at 1097 cm⁻¹

characteristic of the ether function (C-O-C), and an elongation band located at 3406 cm^{-1} characteristic of the hydroxyl groups (OH) located at the end of the homopolymer chain and those of the adsorbed water. These results allow us to assume that cationic ring-opening polymerization in the presence of methanol leads to the formation of poly(epichlorohydrin) with a hydroxyl end.

3.4. Chemical Modification of Poly(epichlorohydrin) by Grafting Menthol

The preparation of multifunctional polymers can be carried out by chemical modification of the homopolymers [32,33]. These multifunctional polymers can serve as carriers for active ingredients [34]. For our part, we tried to graft active ingredients such as menthol, a biodegradable natural product, onto poly(epichlorohydrin) (Scheme 2).



Scheme 2. Reaction scheme of the chemical modification of poly(epichlorohydrin) by menthol grafting.

Chemical modification of poly(epichlorohydrin) was carried out using the phase transfer method. The homopolymer is dissolved in THF and at $25\text{ }^{\circ}\text{C}$, is brought into contact with menthol and an aqueous solution of KOH and TBAH, with magnetic stirring. The experimental conditions for this reaction are summarized in Table 2.

Table 2. Experimental conditions for the chemical modification of poly(epichlorohydrin).

Reagents	m (mg)	V (mL)	Weight (%)
PECH	1.28	--	
MENTHOL	0.2	--	
KOH	28.05	20	62
TBAH	0.43	--	
THF	--	20	

3.5. Characterization of Obtained Polymer

The product obtained was characterized by IR absorption spectroscopy. The FTIR spectrum is illustrated in Figure 2.

From the Figure 2 we notice that the disappearance of the characteristic band of the CH_2Cl group observed in the FTIR spectrum of homopolymer at 743 cm^{-1} . On the other hand, we note the appearance of a new absorption band at 1455 cm^{-1} which characterizes the deformation of the cyclic C-H bonds belonging to the menthol cycle grafted onto the poly(epichlorohydrin) as well as the vibration of the C-O-C bond at 1092 cm^{-1} .

This result allows us to conclude that menthol was grafted onto the poly(epichlorohydrin) homopolymer using the phase transfer method, thus leading to the formation of the multifunctional polymer.

3.6. Prediction of the Nucleophilic and Electrophilic Character of the Reagents

The reaction is governed by LUMO control, since LUMO gap is smaller (0.2792 u.a.) than the HOMO gap (0.3478 u.a.). Therefore, the interaction to be considered as a priority is that which develops between HOMO of menthol (nucleophile) and LUMO of homopolymer (electrophile).

The electronic chemical potentials μ , hardness η , electrophilicity indices ω and nucleophilicity indices N , of the reagents, are presented in Table 3.

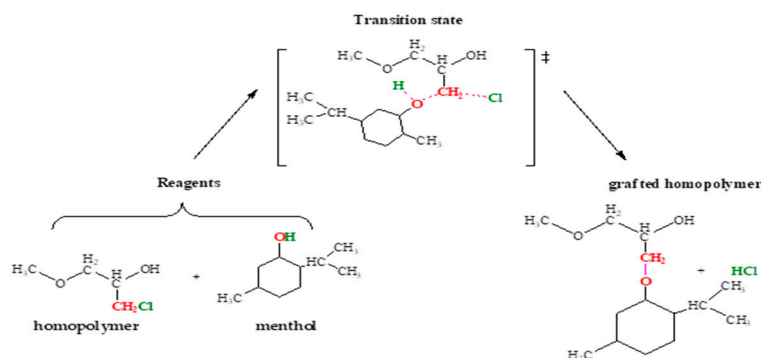
Table 3. Energy of the HOMO and LUMO frontier orbitals (E_{HOMO} and E_{LUMO}), chemical potential (μ), hardness (η), and electrophilicity (ω) (in eV), calculated at B3LYP/6-311++G**.

Reagents	E_{HOMO}	E_{LUMO}	μ	η	ω	N
Homopolymer	-0.2726	0.0234	-7.0992	8.0547	3.1285	-17.6535
Menthol	-0.25588	0.0752	-5.9387	9.0100	1.9571	-17.1783

The results presented in Table 4 shows that the chemical potential μ of the homopolymer (-7.0992 eV) is lower than that of menthol, implying that charge transfer will take place from menthol to the homopolymer and menthol is less electrophilic than the monomer. In other words, menthol is more nucleophilic than the homopolymer.

3.7. Energy Profile of the Reaction

A nucleophilic substitution reaction has been experimentally proposed for this reaction of the chemical modification of the polymer poly(epichlorohydrin) (PECH) by menthol. However, we attempted to determine by theoretical means the order of this reaction. We were first concerned with determining the transition state between the homopolymer and menthol (Scheme 3).



Scheme 3. Reaction path of the reaction of the chemical modification of (PECH) by grafting of menthol.

The energy calculation of the transition state (E) and the activation barrier (E_a) was carried out at the B3LYP/6-311++G** level. The results are summarized in Figure 3.

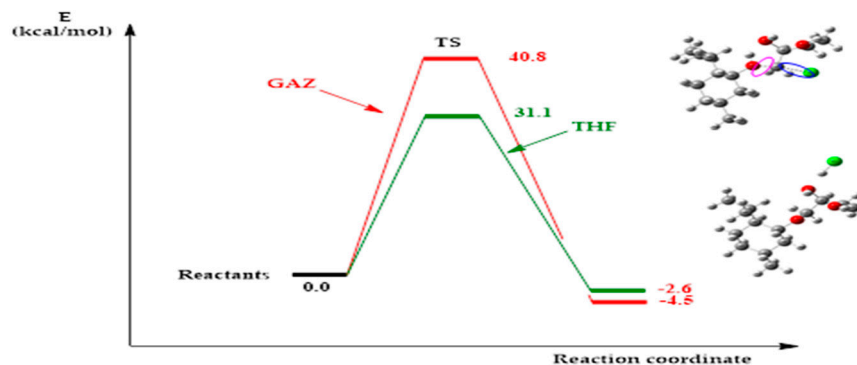


Figure 3. Energy diagram of the chemical modification of the homopolymer modified by menthol in THF, at the B3LYP/6-311++G** level.

The influence of solvent on the reaction rate is measured by the reduction in the activation energy barrier of ≈ 10 kcal/mol in THF compared to the gas phase, the measured

difference is significant in terms of kinetic. Indeed, this reaction is accelerated by the effect of the solvent.

The comparison of the calculated free enthalpies allows us to say that the reaction of the chemical modification of the homopolymer grafted by menthol is favored by the chosen solvent (THF), a factor favoring the S_N2 mechanism proposed by our calculations.

4. Conclusions

Cationic polymerization by ring opening allowed us to synthesize the homopolymer of epichlorohydrin. For this, we adopted the activated monomer process to minimize transfer reactions. The polymerization reaction is carried out in bulk. Furthermore, the homopolymer of poly(epichlorohydrin) served as a precursor for the synthesis of modified poly(epichlorohydrin). The chemical modification of the homopolymer is carried out by eventually substituting chlorine which exists along the polymer chain, with menthol. The homopolymer as well as the chemically modified polymer were characterized by Fourier transform infrared (FTIR). The FTIR spectra obtained confirm that these are indeed the expected polymers. The results of the theoretical study are in good agreement with those obtained experimentally and make it possible not only to predict the type of chemical modification reaction of this polymer which is a nucleophilic substitution, but also to determine its order (S_N2).

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