University of Oran1,Algeria

Theoretical and experimental study of the Chemical Modification of Poly(epichlorohydrin) by Grafting Menthol

Presented by :

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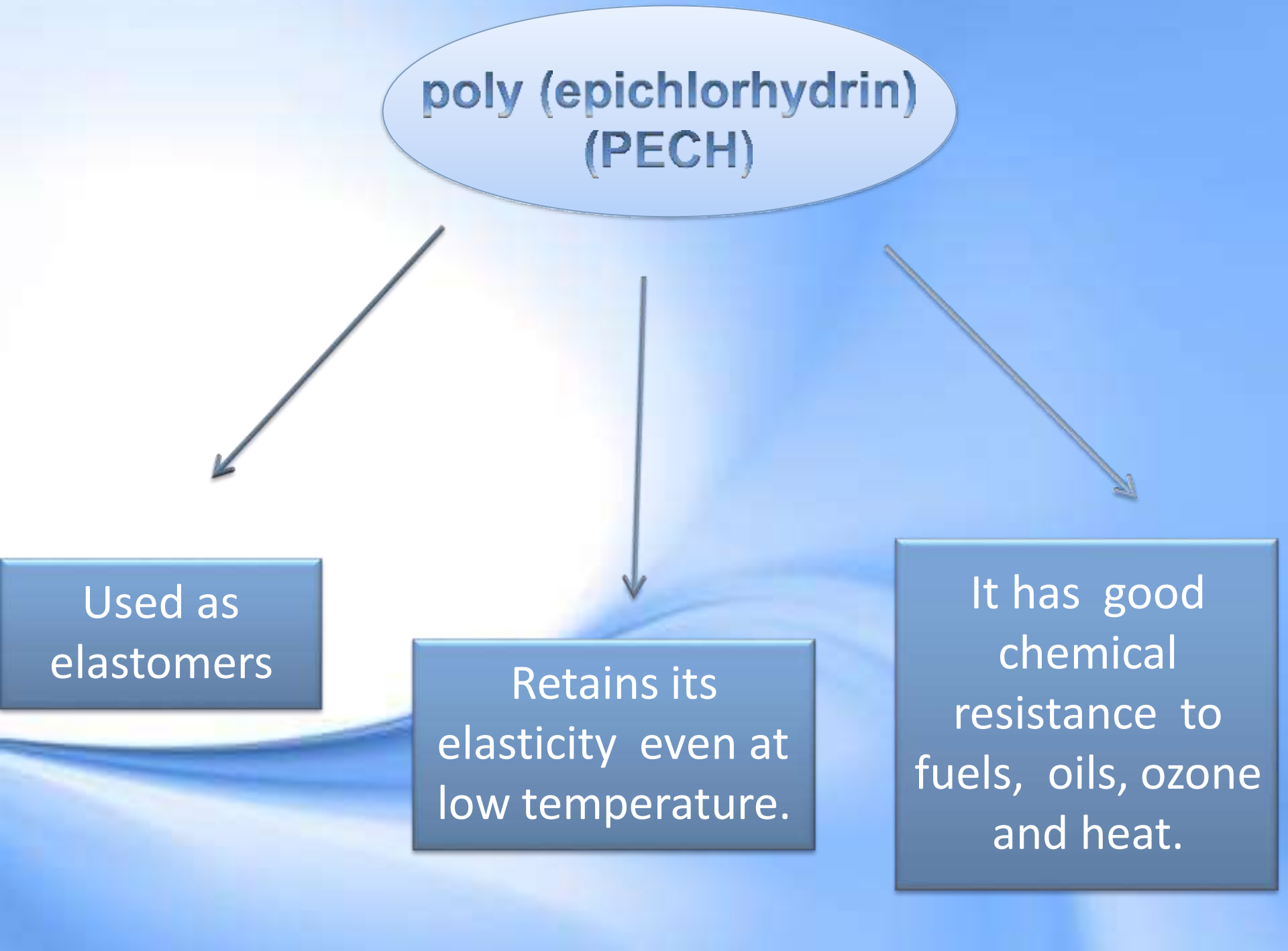
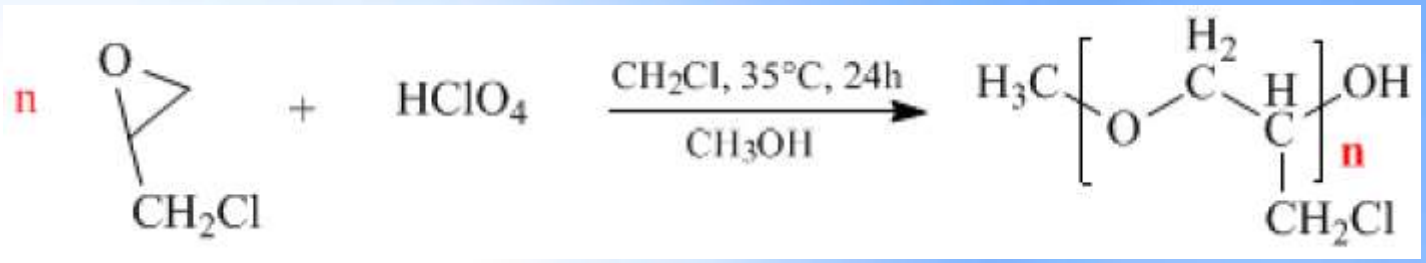
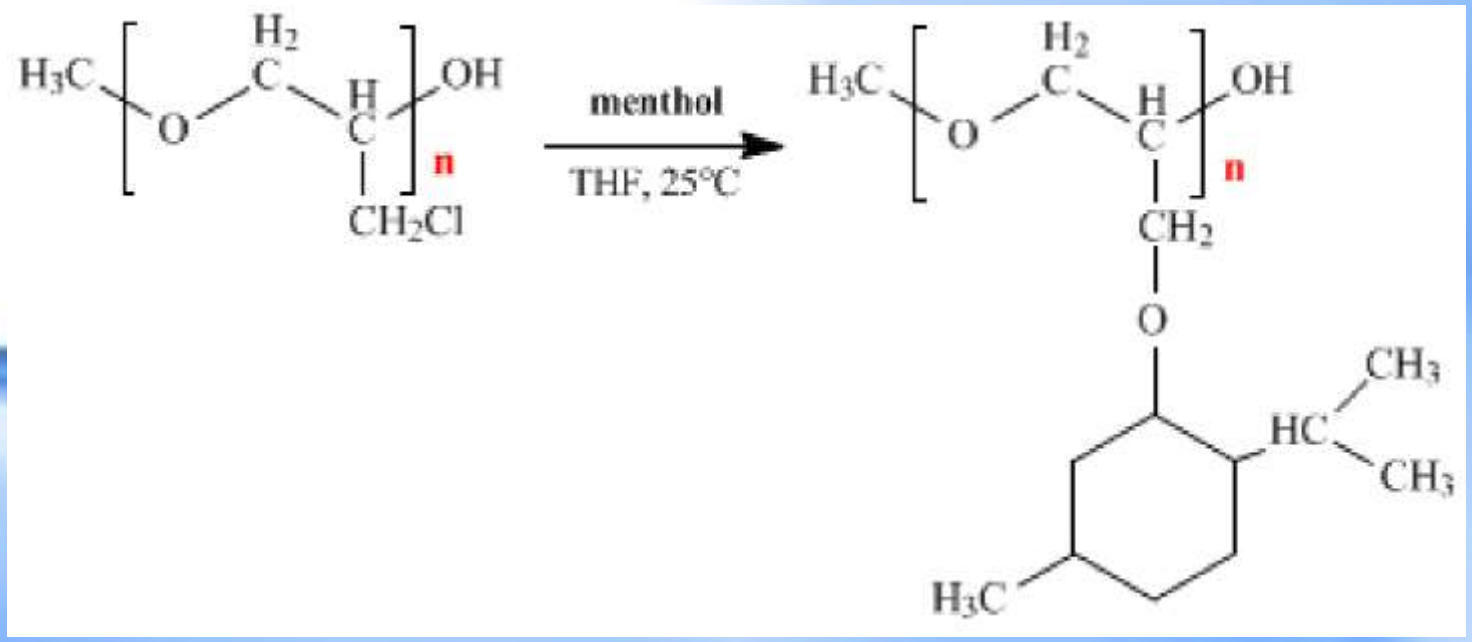
Introduction


poly (epichlorhydrin)
(PECH)
Used as elastomers
Retains its elasticity even at low temperature.
It has good chemical resistance to fuels, oils, ozone and heat.

➢ Synthesis of poly (epichlorhydrin) (PECH):



➢ Chemical modification of poly (epichlorhydrin) by grafting menthol:



at B3lyp/6-311++G** level of calculation :

- Determination of geometries.
- Determination of energies.
- Calcul of different reactivity indices.
- Determination of different stationary states of reaction path: optimization and characterization.
- In : gas phase and in Solution.

Results

Table 1 : Main geometric parameters of the Epichlorhydrin

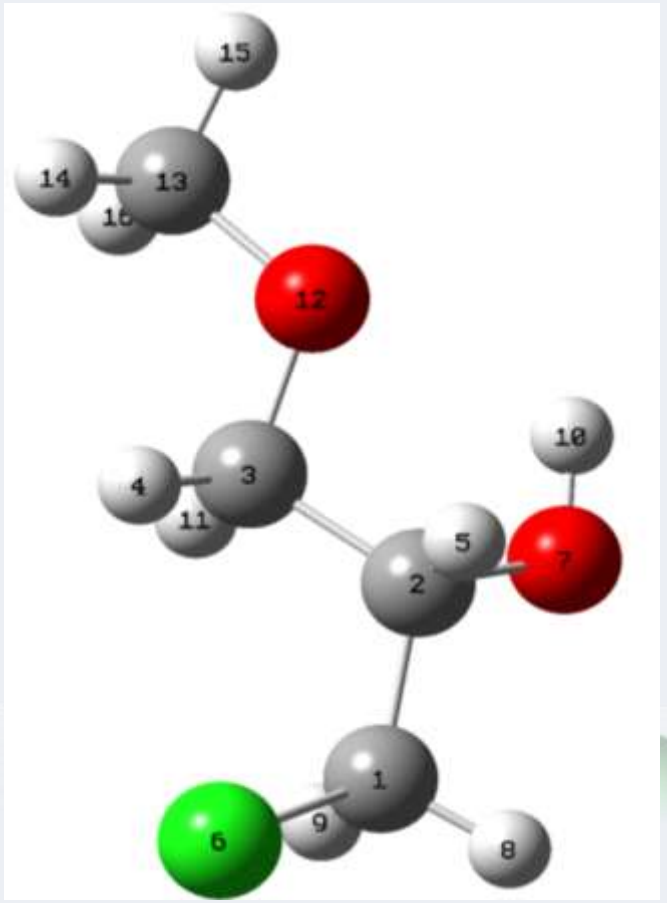
Optimized structure	Geometirc parameters	
	**Atomes**	**Lenght (A°)**
	Cl1-C2	1.790
	C2-C3	1.517
	C3-O4	1.418
	C3-C5	1.519
	C5-O6	1.418
	O6-C7	1.417
	C7-C8	1.515
	C8-O9	1.424
	C2-H10	1.089
	C2-H11	1.091
	C3-H12	1.098
	Atomes	**Angle (°)**
	O4-C3-C2	111.89
	Cl1-C2-C3	109.93
	C2-C3-C5	110.37
	C5-O6-C7	111.63
	C7-C8-O9	106.38
	H10-C2-C3	110.58
	H12-C3-C5	108.98
	H13-C4-C3	106.69
	Cl1-C2-C3-C5	-197.90

Table. 2 : Main geometric parameters of Menthol

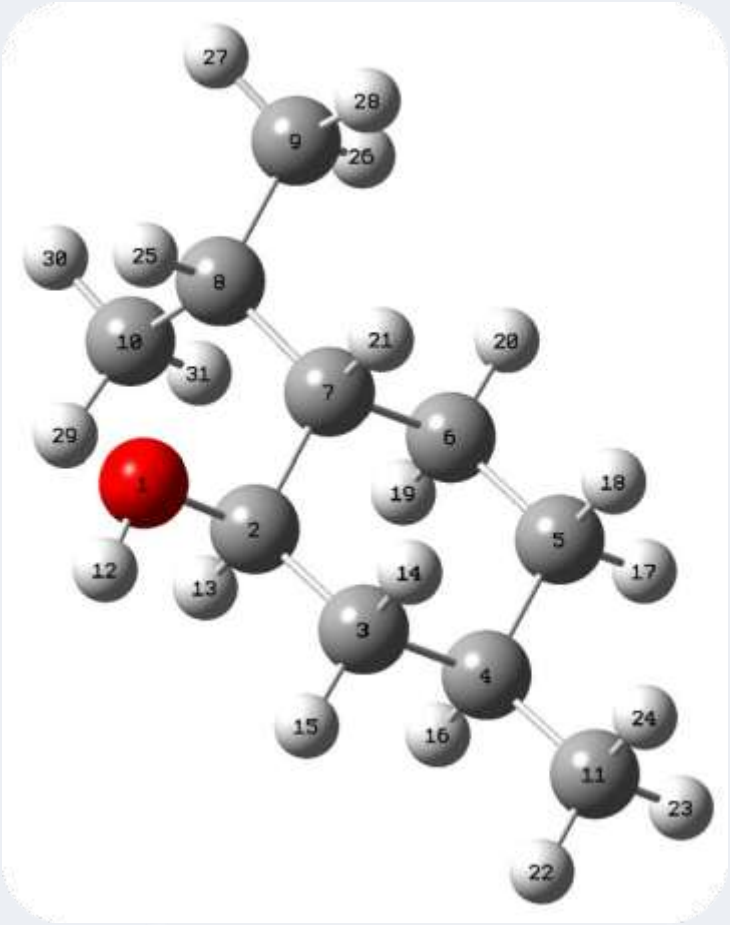
Optimized structure	Geometirc parameters	
	Atomes	Lenght (A°)
	O1-C2	**1.431**
	C2-C3	**1.526**
	C3-C4	**1.531**
	C5-C6	**1.531**
	C6-C7	**1.535**
	C7-C8	**1.542**
	C8-C9	**1.532**
	C8-C10	**1.531**
	C4-C11	**1.528**
	O2-H12	**0.963**
	C2-H13	**1.102**
	Atomes	Angle (°)
	O1-C2-C3	**107.49**
	C3-C4-C11	**111.27**
	C2-C3-C5	**110.37**
	C7-C8-C10	**113.50**
	C7-C8-O9	**106.38**
	H12-C1-C2	**107.00**
	H13-C2-C3	**108.48**
	H25-C8-C9	**106.02**
	H12-O1-C2-C7	**-173.20**

Table. 3 : Main geometric parameters of the Monomer

Optimized structure	Geometirc parameters	
	Atomes	Lenght (A°)
	O37-C17 O37-C23 C17-C2 C2-O14 C18-C23 C1-O13 O13-C6 C17-H16 C17-C15 C23-H31 O14-H48	1.423 1.436 1.520 1.433 1.534 1.415 1.415 1.095 1.094 1.097 0.969
	Atomes	Angle (°)
	O37-C17-C2 C17-C2-O14 C17-O37-C23 O37-C23-C22 H16-C17-C2 H15-C17-C2 H48-O14-C2 H31-C23-C18 C23-O37-C17-C2	105.24 109.77 115.29 112.21 109.52 109.47 104.49 108.27 169.55

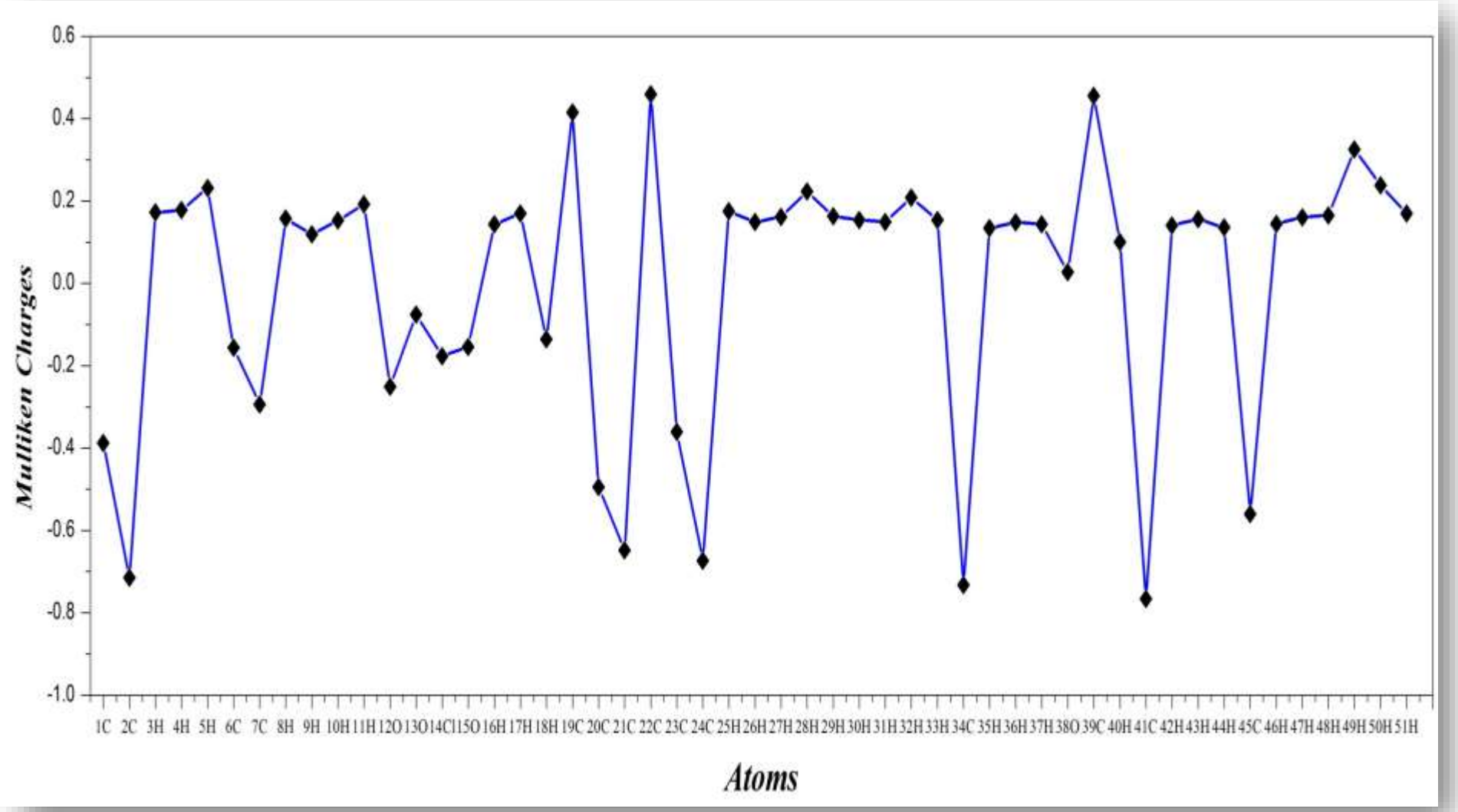


Fig.1: Mulliken charge distrubution of the Monomer.

Fig . 2 : Representation of frontier orbitals (HOMO-LUMO)

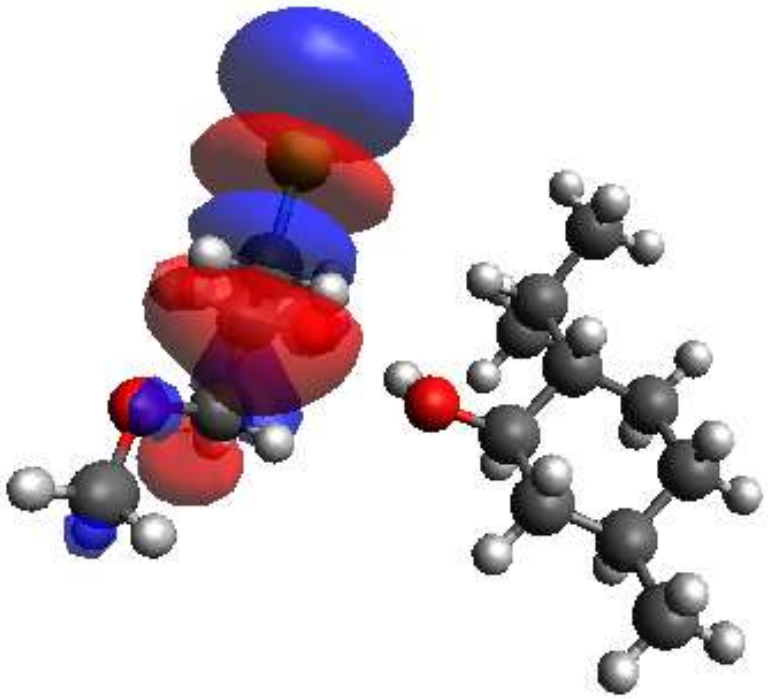
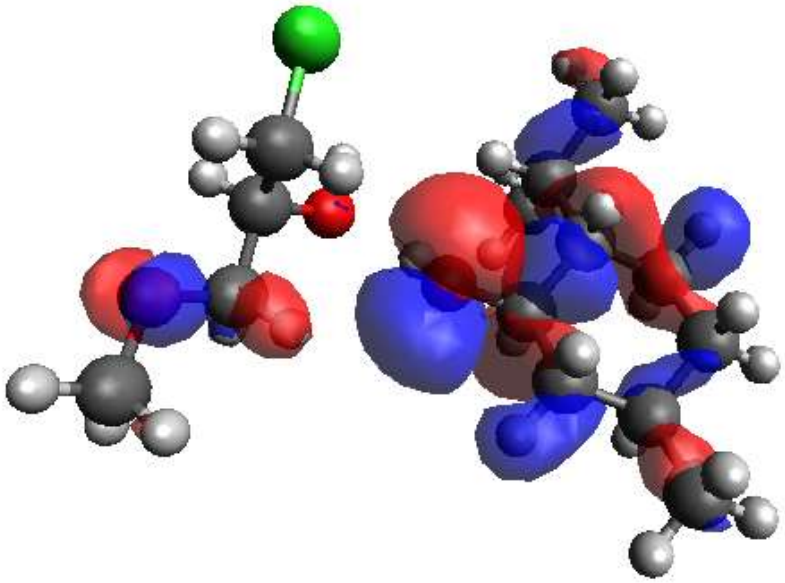
HOMO	LUMO
	

Table 4: Energy of the HOMO and LUMO frontier orbitals (E_{HOMO} and E_{LUMO}), chemical potential (μ), hardness (η),and eletrophicity (ω) (in eV).

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

Reaction path of grating menthol onto poly (epichlorohydrin)

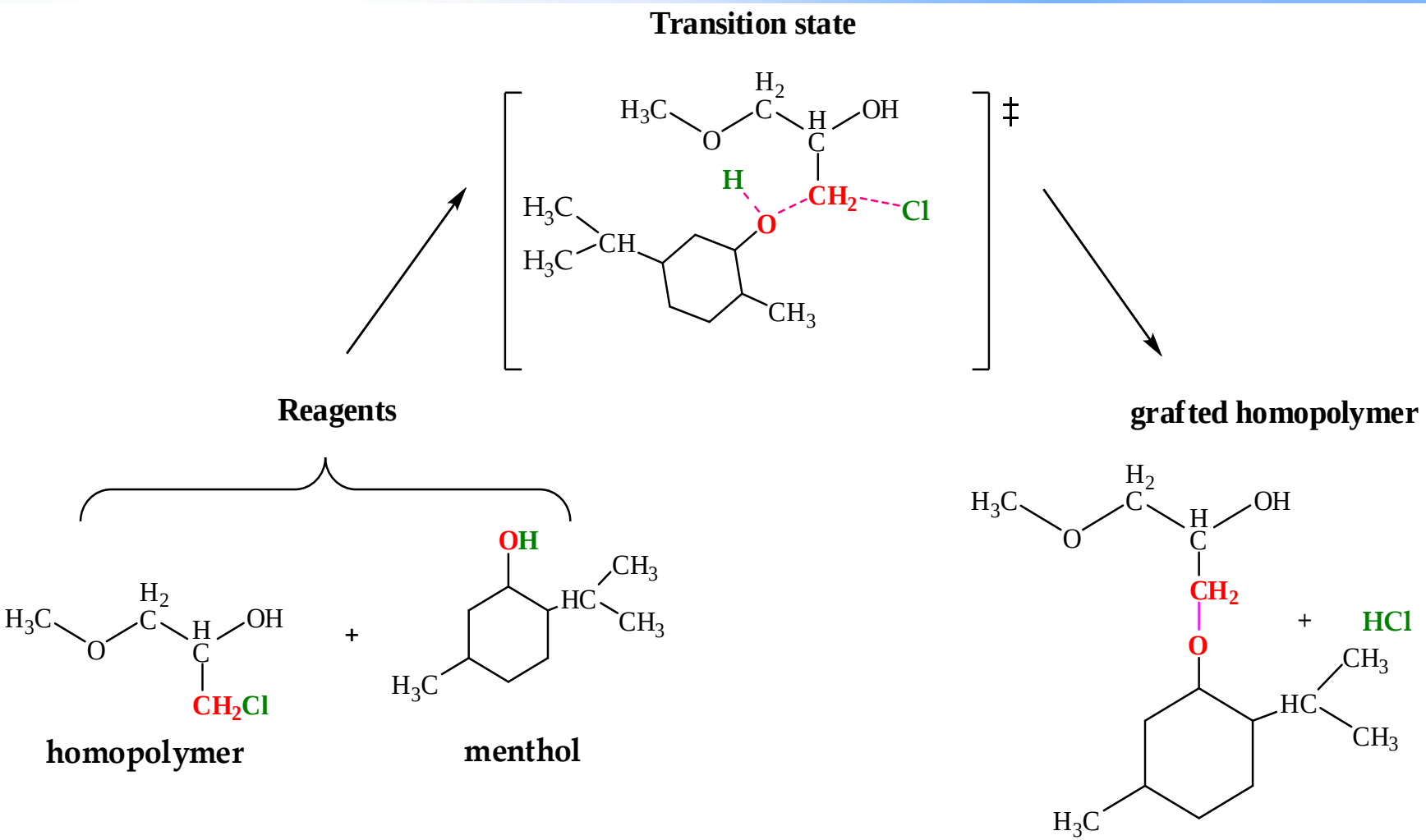
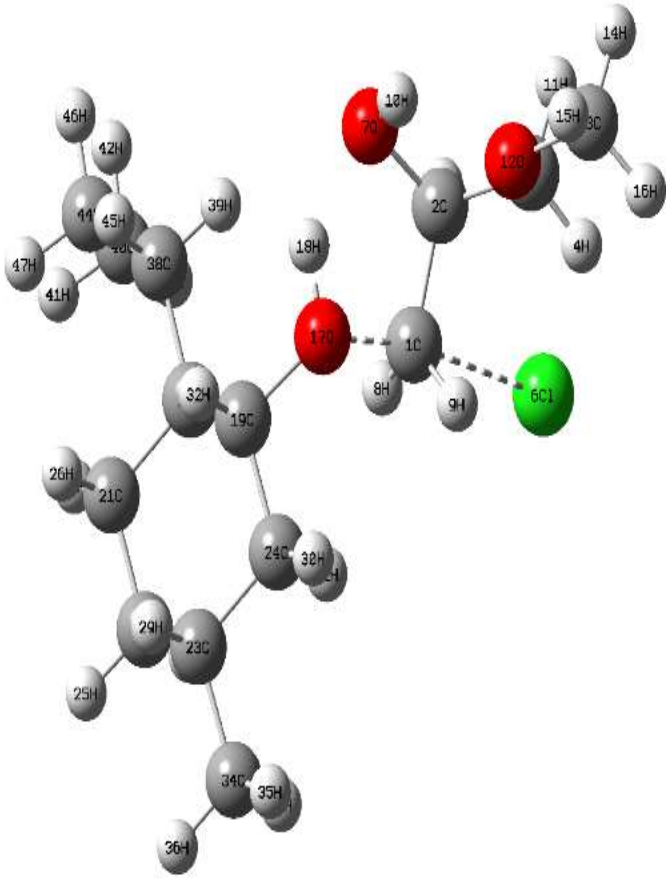


Table. 5 : Main geometric parameters of the transition state.



Bond lengths(A°)

C_1Cl_6: 2.617

C_1O_{17} : 1.724

$O_{17}H_{18}$:1.003

C_1C_2 : 1.550

Angles (°) :

$O_{17}C_1$ Cl_6:170.4

$H_{18}O_{17}C_1$: 98.0

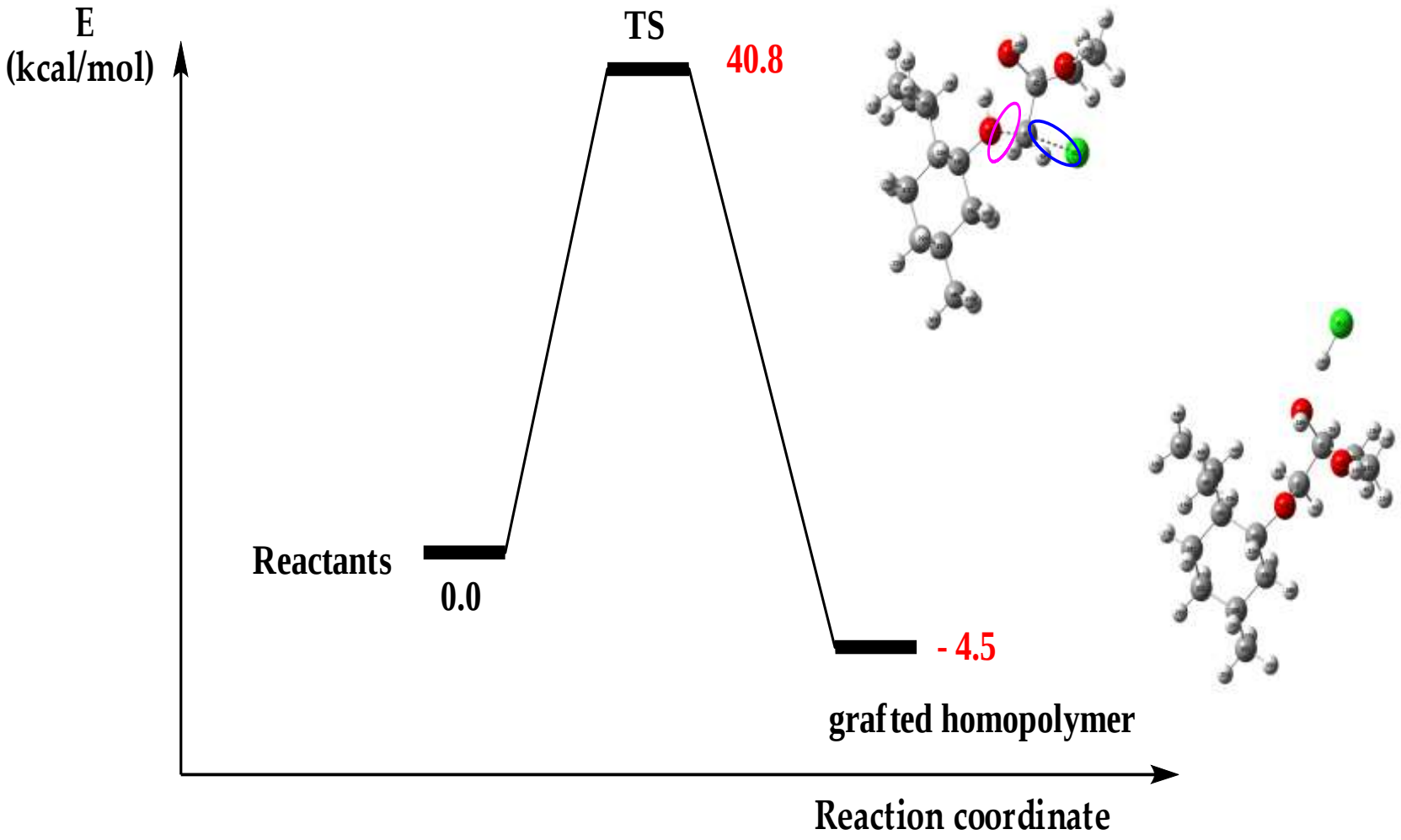


Fig.3: **Different stationnary points of the reaction path of grating menthol onto poly (epichlorhydrin), in gas phase.**

❖ Solvent effect on the reaction path is calculated by PCM model.

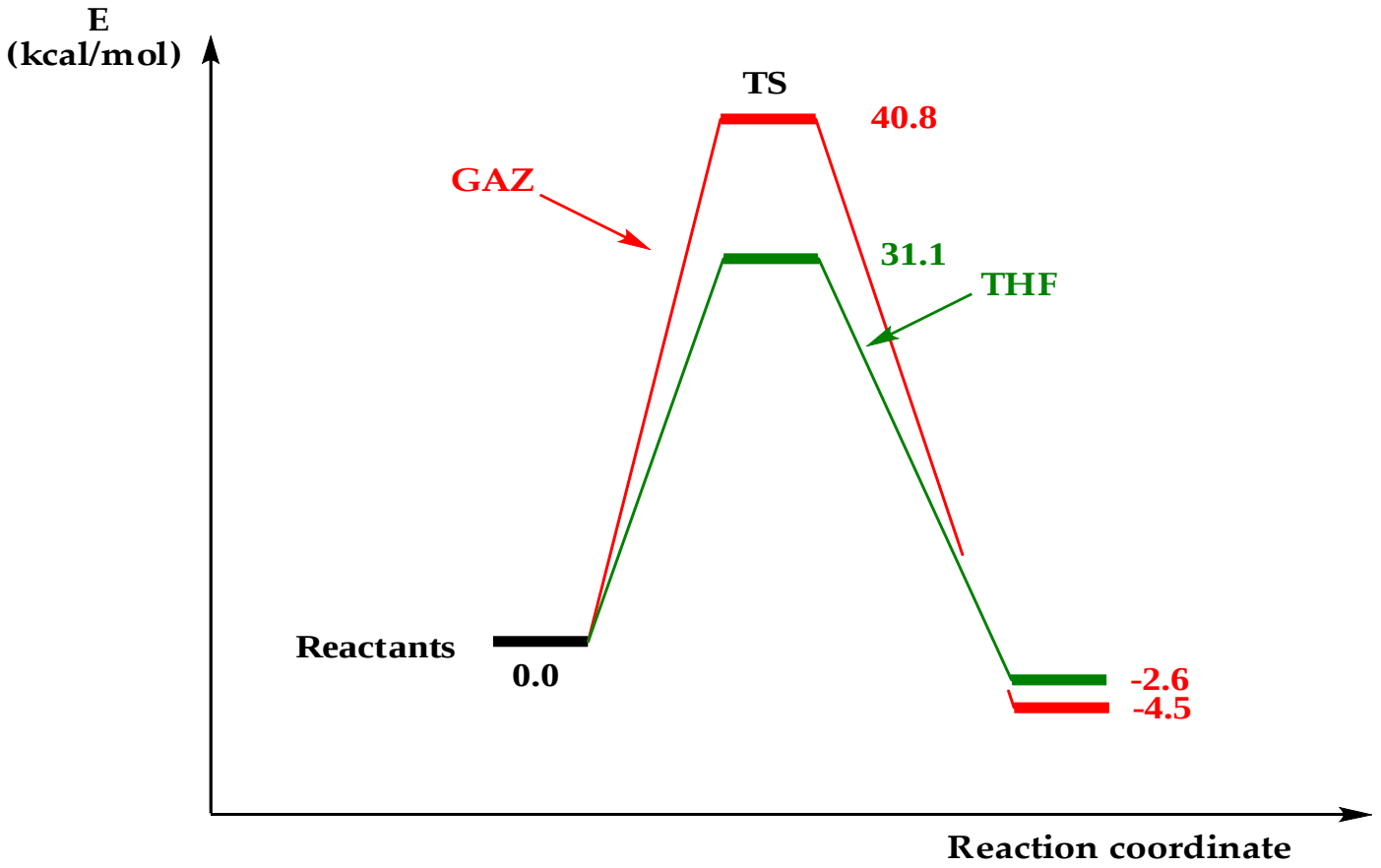


***Fig . 4*: Energy diagram of the chemical modification of the homopolymer modified by menthol in THF.**

Conclusion

✓ The prposed mechanism for the reaction of grating menthol onto poly (epichlorhydrin) is a mechanism of nucleophilic substitution SN2 of the chloromethyl group.

✓ This reaction is carried out according to a one-step were one transition state were localized.

➢In our best level of calculation, we concluded that:

✓ The polymer formed with a greater HOMO energy which is equal to – 7.1578 eV.

✓The calculated chemical hardness values indicate that the compound has a good stability and goood stability and good hardness.

✓A small LUMO/HOMO gap indicates that the compound is softer and more reactif.

✓The value of the ionization potential indicates clearly that the compound is very stable.

THANK YOU FOR YOUR ATTENTION