Original Research Article

Characterization and DFT studies of cis, trans and vinyl derivatives of 1,4-butadiene using C_{20} in different temperatures

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ABSTRACT

In this research of cis, trans and vinyl monomeric derivatives of 1,4-butadiene were studied using C20 in different temperatures by Functional density theory (DFT). To this purpose, the materials were firstly optimized geometrically, then the calculations of the thermodynamic parameters were performed on all of them. In the following, changes in parameters of energy such as specific heat capacity, enthalpy, entropy and Gibbs free energy, which were calculated per molecular weight, molecular volume to and surface, which were measured in this probe, were evaluated with respect to each other.

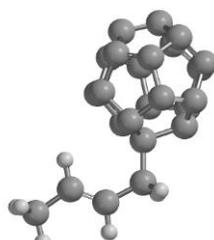**Keywords**: Cis, Trans and Vinyl, 1,4- butadiene monomers, C20, density functional Theory Method

Introduction

Polybutadiene was first polymerized in 1910 by a Russian scientist, Sergey Vasilevich Livado. He invented a process (1926) for preparing butadiene from methanol and in 1928T he applied sodium catalyst for butadiene polymerization. Regarding the discovery, the Soviet Union was the first country which succeed in producing polybutadiene in the late 1930s. Germany and America were among the countries that assessed highly the probe and development of polybutadiene production. After the Second World War in the mid-1950s, major developments in catalyst design (especially the Ziegler Nata catalyst) led to the production of new and optimized types of most polymers, including polybutadiene. Polybutadiene is one of the primary elastomers or rubbers that were designed. A high percentage of produced polybutadiene is applied for the preparation of rubbers and tires, and a smaller percentage is used as an additive to other rubbers to improve their mechanical strength. Polybutadiene can be polymerized by three different methods, in which case, cis, trans, and vinyl isomers are obtained. The characteristics of polybutadiene vary depending on the percentage of these three isomers. For instance: polybutadiene with high percentage of cis isomer is called High Cis Polybutadiene which possess a high elasticity, and is very prevalent. While polybutadiene with high percentage of trans isomer is called High Trans Polybutadiene, a crystalline plastic with any useful application. The annual production of this polymer in 2001 was more than 2.1 million tons, which takes the second place in consumption level after STR butadiene rubber (SBR) or (Styrene Butadiene Rubber) [1-3].
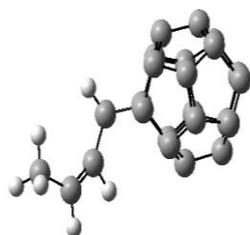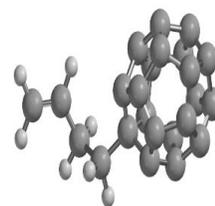
Cis- Bu C20   Trance-Bu C20   Vinyle-Bu C20

Figure 1: Cis, Trans, and Vinyl Monomers Produced by composting 1,4- Butadiene and C20

Table 1: Some chemical characteristics calculated for cis, trans and vinyl monomers at the surface of B3lyp/6-31g.

	Temperature=298.15K , pressure=1 atm		
	Cis-Bu C20	**Trance-Bu C20**	**Vinyle-Bu C20**
	C24H7	**C24H7**	**C24H7**
ENERGY(au)	-900.769899	-900.749731	-900.746818
E HOMO(eV)	-10.23	-10.24	-10.22
E LUMO (eV)	-3.39	-3.18	-3.15
Dipole Moment (Debye)	2.27	5.77	1.94
Weight(amu)	295.320	295.320	295.320
Volume(A^3)	289.98	288.42	288.75
Area (A^2)	261.03	257.28	259.14
Polarizibility	63.28	63.10	63.13
ZPE (KJ/mol)	659.14	663.11	663.87
H° (au)	-900.507755	-900.485954	-900.483095
CV (J/mol)	204.73	204.05	200.51
S° (J/mol)	420.19	423.37	416.85
G° (au)	-900.555472	-900.534031	-900.530432

Calculations and results

The computational investigation of cis, Trans and vinyl monomers obtained from mixing 1, 4- butadiene and C20, was studied using density functional theory. The operation was performed applying the Gaussian 98 and Gauss view soft wares. The compounds were initially optimized by the DFT method in the basic series (6-31g); then IR technique was applied to calculate thermodynamic parameters related with the process. All computations are exerted on the surface of B3lyp/6-31g at 297 K and atmospheric pressure. Investigation of the results from the calculations showed that by increasing molecular volume and molecular surface area (in monomers with the same molecular weights) in derivative obtained from mixing cis 1,4-butadiene and C20, the specific heat capacity is increased compared to the derivatives obtained from the trans and vinyl monomers and, of course, its internal energy is decreased (Fig 2-4)[4-6].

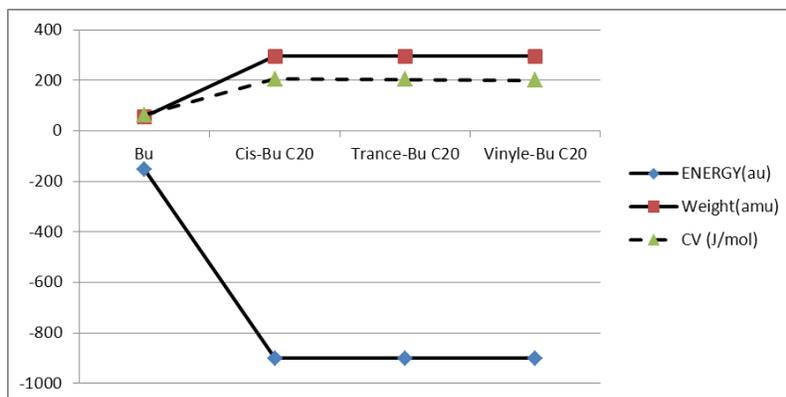## Calculate and check the values of enthalpy changes

Figure 2: comparison of molecular weight, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20
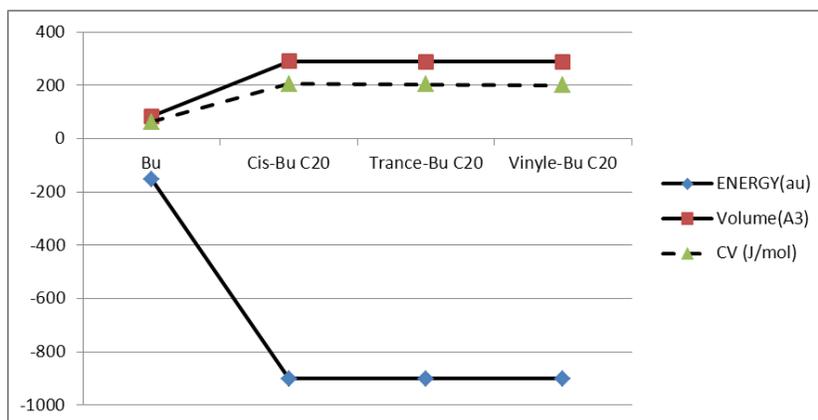

Figure 3: : comparison of molecular volume, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20
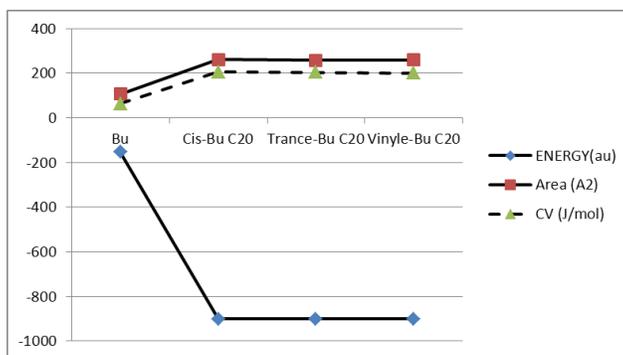
Figure 4: comparison of molecular surface area, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20
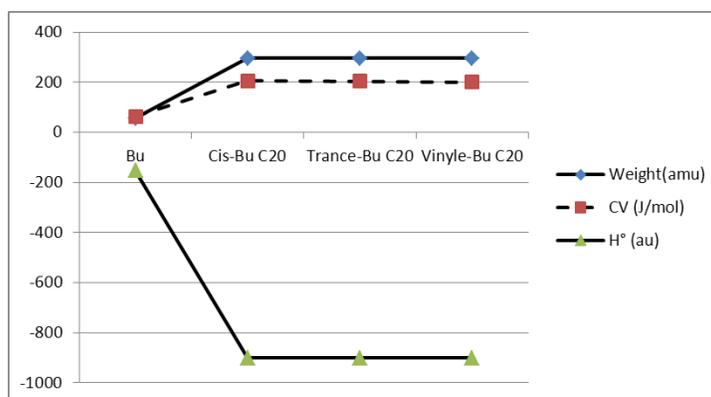

Figure 5: comparison of molar enthalpy, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20
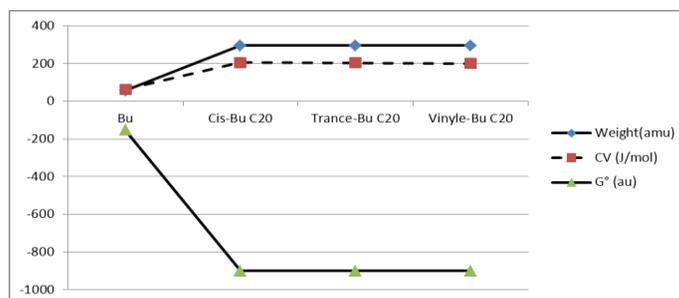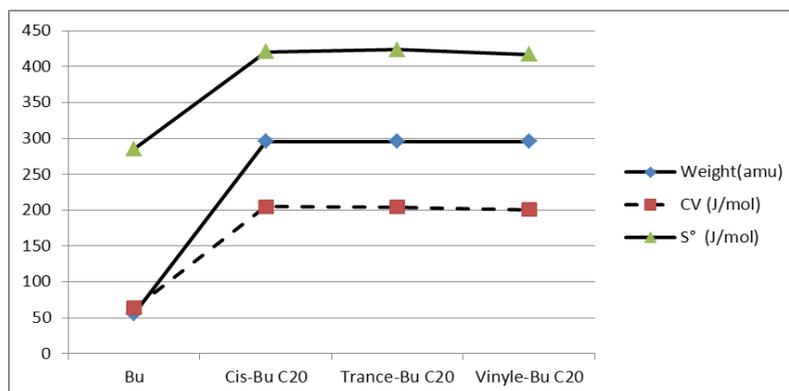

Figure 6: comparison of molar Gibbs free energy, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20

Figure 7: comparison of molar entropy free energy, internal energy and specific heat capacity of cis, trans and vinyl monomers obtained from mixing 1,4- butadiene and C20

Also, the investigation of calculation results showed that by increasing the volume and molecular surface area the specific heat capacity in the derivative obtained from cis 1,3-butadiene is higher than that of its derivatives obtained from different fullerenes, but, by increasing the volume and molecular surface area, the molar enthalpy and the molar Gibbs free energy is decreased (Fig 5-6). Also, the study of molar entropy indicated that increasing the molecular volume and molecular surface area in the derivative obtained from cis 1,3-butadiene does not show a clear trend compared to the other derivatives (Fig 7) [7-8].

Conclusion.

Comparison of the partial incremental trend of the specific heat capacity as increasing the volume and molecular surface area in the derivative obtained from mixing cis and C20, indicates their coordination to each other.

We know that the specific heat capacity CV is the amount of heat that per unit mass needed to promote the temperature by one degree Celsius. Obviously, the higher energy of the material, the less specific heat capacity of its CV. Therefore, it is concluded that by increasing the molecular volume and molecular surface of molecules obtained from nano derivatives with the same carbon number and area

are higher, the product possesses less energy-efficient. (table 1). Comparison of values of other thermodynamic parameters investigated in this study proved the results.

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