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Density functional theory based study of the heat of polymerization of olefins

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Density functional theory (DFT) at the B3LYP/6-31G level was used to compute the heat of polymerization of six olefins, namely, polypropylene (PP), 1,2-polybutadiene (1,2-LPB), poly-2-chloro-butadiene (CR), polyisoprene (IR), poly(isoprene-3,4) and poly(isoprene-1,2), by taking into account the previously determined system error. By comparing the calculated results to experimental data available in the literature for the first four polymers, the relative errors were found to be 0%, 1.66%, 2.04% and 1.20%, respectively, demonstrating that the method employed is able to calculate the heat of polymerization of olefins with reasonable accuracy and reliability. Based on the findings, the heats of polymerization for the other two polymers poly(isoprene-3,4) and poly(isoprene-1,2) were predicted to be -44.71 kJ·mol^{-1} and -50.67 kJ·mol^{-1}, respectively.

Keywords: Heat of polymerization, Density Functional Theory (DFT), B3LYP/6-31G, Olefins

INTRODUCTION

Heat of a polymerization reaction represents the enthalpy change during the formation of the polymer from its monomer.

Such thermodynamic data are a fundamental property in chemistry, e.g., allowing feasibility studies of polymerization reactions before performing an experiment and also optimization of the polymerization processes in terms of heat transfer and other operational parameters [1]. Therefore, there has been continuous effort in determining, either experimentally or theoretically, the heat of polymerization for different polymerization reactions. Experimentally, it can be measured with a range of methods through, e.g., direct reaction calorimetry, combustion method, and thermodynamic equilibrium techniques [2]. Although there has been increasing number of reports about experimental data, there are still numerous substances for which no thermodynamic data are available, and one of the key causes is associated with the complexity of experimental setups required to obtain thermodynamic data [3]. In that respect, theoretical and computational approaches provide valuable tools as complementary or alternative methods. For example, the density functional theory (DFT), associated with Gaussian software package, has proven to be an effective approach to compute and estimate thermodynamic characteristics of a wide range of reactions [4-9], including polymerizations [10-19].

To predict the heats of formation, Keshavarz *et al*. used recently developed density functionals such as ωB97X-D and M06-2X in comparison with B3LYP for estimating the gas phase heats of formation, $\Delta_f H°$(g), and the condensed phase heat of formation, $\Delta_f H°$(c) of polycyclic saturated hydrocarbons [20]. Chi *et al.* studied the heats of formation, specific enthalpies of combustion, detonation performances, and electronic structure at B3LYP/6-311 G** level for a series of polydinitroaminocubanes [21]. Based on the computations for a series of polyisocyanoadamantanes also at the DFT-B3LYP level, Zhao *et al.* estimated the heats of formation and strengths of group interactions for 19 polyisocyanoadamantanes [22]. Lee *et al*. used DFT to calculate the thermodynamic properties of polychlorinated dibenzo-p-dioxins and also investigated the intramolecular Cl-Cl repulsion effects and their thermochemical implications [23]. In our previous work, we computed the heat of polymerization of polyethylene with DFT at the B3LYP/6-31G level and, by comparing to the experimental results, estimated the system error which was further taken into account for the calculation of the heat of polymerization of 1,3-polybutadiene [24]. Based on that, the aim of the present studies was to further study the heats of polymerization of a series of polyolefins in order to develop a reliable and efficient method for the calculation of heats of polymerization for other polymers of interest. The heats of polymerization of four polyolefins were computed and compared with published experimental data. The heats of polymerization of further two polyolefins were then predicted with the method validated.

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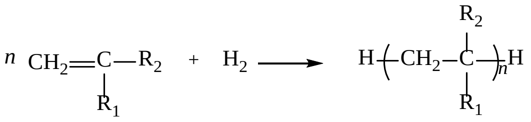
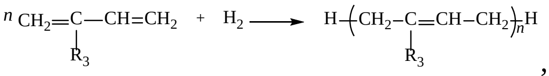
COMPUTATIONAL DETAILS

The computations were performed using DFT at the B3LYP/6-31G level with a Gaussian 3 program package [25]. The geometry of each molecule was optimized first, and the standard enthalpies of formation of all molecules were calculated in order to obtain the heat of polymerization. The chemical reactions of the polymerization of olefins are generally represented by equations (1) and (2).



$$n\,CH_2{=}C(R_1){-}R_2 + H_2 \longrightarrow H{-}\!\left(CH_2{-}C(R_1)(R_2)\right)_n\!{-}H \quad ,\ (1)$$



$$n\,CH_2{=}C(R_3){-}CH{=}CH_2 + H_2 \longrightarrow H{-}\!\left(CH_2{-}C(R_3){=}CH{-}CH_2\right)_n\!{-}H \quad ,\ (2)$$

Six polymers were examined and the corresponding side chains or groups are presented in Table 1.

The heat of polymerization of olefins is expressed as

$$\Delta H_{polymer} = \frac{1}{n}H_{polymer} - H_{monomer} - \frac{1}{n}H_{H} \quad ,\quad (3)$$

RESULTS AND DISCUSSION

With the Gaussian 03 program the H values of PP, 1,2-LPB, CR, IR, poly(isoprene-1,2) and poly(isoprene-3,4) with different degree of polymerization were calculated. a_n (in hartree) represents the mean of H with a degree of polymerization n. The values of a_n for different olefins polymerization are summarized in Table 2.

Further analysis on data shown in Table 2 revealed that for each polymer a can be represented by

$$a_n = a_{n-1} + a_1 - a'_0 + b_{n-1} = na_1 - (n-1)a'_0 + \sum_{i=1}^{n-1} b_i \quad \text{when } n > 1,\quad (4)$$

where a_0 is the enthalpy of monomer, and b is a constant (in hartree). The best fitting values of b for each polymer are summarized in Table 3.

It can be seen from Table 3 that for PP the value of b_n has insignificant variation when n varies from 1 to 14, thus their mean value may be used. That also applies to the other five polymers. It indicates that n is negligible for computing their heats of polymerization if n is low ($n < 22$). When n increases ($n >> 22$) the heat of polymerization can be determined to be the convergence value of a_n($n \to \infty$)taking into account the system error of SE = -0.0004 hartree which was obtained for computing the heat of polymerization of ethylene using the same method [24].

Thus,

$$\lim_{n\to\infty}\Delta H_{polyolefin} = \lim_{n\to\infty}\left[\frac{1}{n}a_n - \frac{1}{n}a'_0 - a_0\right] + SE =$$
$$\lim_{n\to\infty}\left\{\frac{1}{n}\left[na_1 - (n-1)a'_0 + (n-1)b\right] - \frac{1}{n}a'_0 - a_0\right\} + SE$$
$$= \lim_{n\to\infty}\left[a_1 - a'_0 + \frac{n-1}{n}b - a_0\right] + SE$$
$$= a_1 - a'_0 + b - a_0 + SE \quad ,\ (5)$$

By inserting data from Tables 2 & 3 into equation (5), heats of polymerization for the six polymers were calculated. The results are summarized in Table 4. For comparison, experimental data for the first four polymers, obtained from the literature, are also shown.

By comparing the calculated results and experimental data available for the four polymers, absolute errors were found to be 0.00 kJ·mol^{-1}, 1.44 kJ·mol^{-1}, 1.62 kJ·mol^{-1}and 0.87 kJ·mol^{-1}, and relative errors - 0%, 2.10%, 2.04%, and 1.20%, respectively. It was demonstrated that the use of the DFT B3LYP/6-31G method can provide good agreement between computed and experimental results with a low computational cost, which can be further applied for more complex molecular systems. Based on that, it was employed to predict the heats of polymerization for other two polymers poly(isoprene-3,4) and poly(isoprene-1,2) which were found to be -44.71 kJ·mol^{-1} and -50.67kJ·mol^{-1}, respectively. The prediction may be compared and validated by further experimental work.

Table 1. Six polymers with various side chain groups (R_1, R_2 and R_3).

Polymer	R_1	R_2	R_3
Polypropylene (PP)	CH_3	H	
1,2-polybutadiene (1,2-LPB)	CH=CH_2	H	
Poly-2-chloro-butadiene (CR)			Cl
Polyisoprene (IR)			CH_3
Poly(isoprene-3,4)	CH_2=C-CH_3	H	
Poly(isoprene-1,2)	CH=CH_2	CH_3	

Table 2. Values of *a* with different degree of polymerization

	PP	1,2-LPB	CR	IR	3,4-polyisoprene	1,2-polyisoprene
a_0	-117.794734	-155.866934	-615.452433	-195.145478	-195.145478	-195.145478
a_1	-119.006746	-157.071514	-616.662688	-196.353608	-196.34544	-196.347412
a_2	-236.830172	-312.960675	-1232.185366	-391.522469	-391.508378	-391.512622
a_3	-354.653582	-468.849173	-1847.666046	-586.691365	-586.671314	-586.677827
a_4	-472.476986	-624.737217	-2463.145597	-781.860233	-781.834251	-781.843037
a_5	-590.300398	-780.625639	-3078.623159	-977.029127	-976.997186	-977.008238
a_6	-708.123816	-936.514442	-3694.101793	-1172.198001	-1172.160122	-1172.173446
a_7	-825.947223	-1092.402896	-4309.624445	-1367.366872	-1367.323056	-1367.338652
a_8	-943.776214	-1248.291347	-4925.147118	-1562.535728	—	-1562.503856
a_9	-1061.594052	-1404.179761	-5540.669762	—	—	-1757.669061
a_{10}	-1179.417458	-1560.068178	-6156.192427	—	—	—
a_{11}	-1297.24087	-1715.956593	-6771.715036	—	—	—
a_{12}	-1415.064287	-1871.845091	—	—	—	—
a_{13}	-1532.887702	—	—	—	—	—
a_{14}	-1650.711114	—	—	—	—	—
a_{15}	-1768.534528	—	—	—	—	—

Note: The heat of formation of hydrogen a'_0 = -1.162033 hartree.

Table 3. Best fitting of *b* values for different olefins

	PP	1,2-LPB	CR	IR	3,4-polyisoprene	1,2-polyisoprene
b_1	0.021287	0.020320	0.022023	0.022714	0.020469	0.020169
b_2	0.021303	0.020983	0.022021	0.022679	0.020471	0.020174
b_3	0.021309	0.021437	0.022026	0.022707	0.020470	0.020169
b_4	0.021300	0.021058	0.022019	0.022681	0.020472	0.020178
b_5	0.021295	0.020678	0.022017	0.022701	0.020471	0.020171
b_6	0.021306	0.021028	0.021997	0.022704	0.020473	0.020173
b_7	0.021300	0.021030	0.022018	0.022719	—	0.020175
b_8	0.021297	0.021066	0.021989	—	—	0.020174
b_9	0.021307	0.021064	0.02201	—	—	—
b_{10}	0.021301	0.021066	0.021954	—	—	—
b_{11}	0.021295	0.020983	—	—	—	—
b_{12}	0.021298	—	—	—	—	—
b_{13}	0.021301	—	—	—	—	—
b_{14}	0.021299	—	—	—	—	—
AV	0.021300	0.020974	0.022007	0.022701	0.020471	0.020172

Table 4. Comparison of calculated results with experimental data of heats of polymerization

Polymer	Calculated results		Experimental data / kJ·mol^{-1}	Relative error / %
	hartree	kJ·mol^{-1}		
PP	-0.032679	-85.80	-85.80 [26]	0
1,2-LPB	-0.025686	-67.44	-68.58 [27]	2.10
CR	-0.029606	-77.73	-79.35 [27]	2.04
IR	-0.026397	-71.93	-72.80 [26]	1.20
poly(isoprene-3,4)	-0.016029	-44.71		
poly(isoprene-1,2)	-0.018301	-50.67		

NB. 1 hartree = 2625.5 kJ·mol^{-1} [28]

There is generally a range of factors which can have effects on the accuracy of the results obtained by this method, such as polarity of side chain groups, where more accurate results may be computed for determining the heat of polymerization of polymers with straight chains or small groups. Approximation is also necessary with DFT and algorithm (e.g., numerical limit analysis) in most cases. In addition, the effect of reaction conditions such as temperature, pressure and solvation can cause variation in the heat of polymerization [29] which, in turn, can result in further discrepancy between computational and experimental data.

CONCLUSIONS

In the present study, the heat of polymerization of six olefins was calculated using the DFT B3LYP/6-31G method by taking into account the previously estimated system error. The calculated heats of polymerization for four polymers, namely, polypropylene, 1,2-polybutadiene, poly-2-chloro-butadiene and polyisoprene, were compared with experimental results available in the literature, showing relative errors of 0%, 2.10%, 2.04% and 1.20%, respectively. Based on the results presented, it can be verified that the method employed was able to calculate heat of polymerization of olefins with reasonable accuracy and reliability. That method was further used to predict the heats of polymerization for the other two polymers poly(isoprene-3,4) and poly(isoprene-1,2) to be -44.71 $kJ\cdot mol^{-1}$ and -50.67 $kJ\cdot mol^{-1}$, respectively.

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ИЗСЛЕДВАНЕ НА ТОПЛИНАТА НА ПОЛИМЕРИЗАЦИЯ НА ОЛЕФИНИ С ПОМОЩТА НА ТЕОРИЯТА НА ПЛЪТНОСТНИЯ ФУНКЦИОНАЛ (DFT)

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(Резюме)

Използвана е теорията на плътностния функционал (DFT) на ниво B3LYP/6-31G за да се изчисли топлината на полимеризация на шест олефина, а именно: полипропилен (PP), 1,2-полибутадиен (1,2-LPB), поли-2-хлоро-бутадиен (CR), поли-изопрен (IR), поли(изопрен-3,4) и поли(изопрен-1,2), отчитайки предварително натрупаната грешка. При сравнението на изчислените резултати с достъпните експериментални данни за първите четири полимера се оказва, че относителната грешка е съответно 0%, 1.66%, 2.04% и 1.20%, което показва че методът позволява изчисляването на топлината на полимеризация на олефини с разумна точност и надежност. На тази основа топлините на полимеризация за останалите два полимера поли(изопрен-3,4) и поли(изопрен-1,2) са определени съответно на -44.71 $kJ\cdot mol^{-1}$ и -50.67 $kJ\cdot mol^{-1}$.