

## Estimation of Heat of Formation ( $\Delta H_f$ ) for Hydroxy-Terminated Polybutadiene

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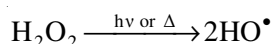
For estimation of heat of formation ( $\Delta H_f$ ) of hydroxy-terminated polybutadiene (HTPB), MNDO program was used. MNDO has restrictions in calculation large molecules, so we calculated  $\Delta H_f$  for segments and estimated it for mean chain of HTPB.

**Key Words:** Hydroxy-terminated polybutadiene, Heat of formation ( $\Delta H_f$ ), Polymer chain.

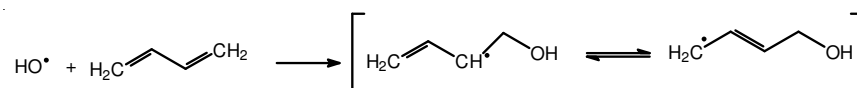
### INTRODUCTION

Heat of formation ( $\Delta H_f$ ) is an important thermodynamical property which gives the stability of materials. For calculating of this property, differential scanning calorimetry (DSC) was used. But for polymers, because they haven't sharp melting point and the results of DSC is incorrect<sup>1,2</sup>. For determination of  $\Delta H_f$ , the mechanism of polymer synthesis should be known. As shown below, polymerization of 1,3-butadiene<sup>3</sup> has three steps:

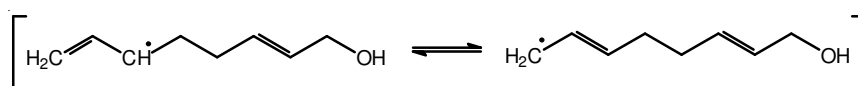
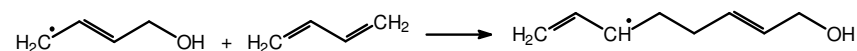
**Initiation step:** The  $H_2O_2$  is turned to OH radical by heat or light as show below:



OH radical can attack to monomer (1,3-butadiene) to make monomer radical:



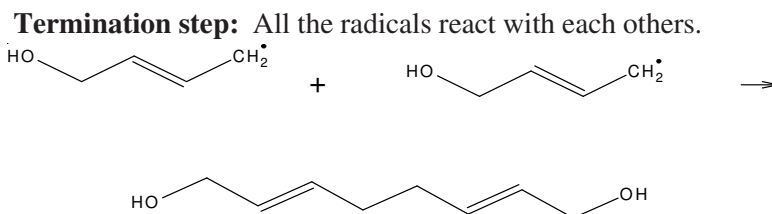
**Propagation step:** In this step all of reactant turns to radical species.



I

II

Resonance forms



## RESULTS AND DISCUSSION

In propagation step, the more radicals can react together. First of all, we calculated saturated hydrocarbon (homolog of methane) to determine accuracy of MNDO calculations. Then, the segments of HTPB were calculated by MNDO<sup>4</sup>. For simplicity, we use T for *trans* and C for *cis* and V for vinyl structure. The result of MNDO calculation for hydrocarbons and HTPB (monomer, dimer, trimer, tetramer and so on) are shown in Tables 1 and 2.

TABLE-1  
HEATS OF FORMATION OF IN TANDEM  
HOMOLOGUES OF METHYLENE

| Formula                         | Calculated $\Delta H_f$<br>(Kcal/mol) by<br>MNDO | Observed $\Delta H_f$<br>(Kcal/mol) from<br>CRC | Difference of $\Delta H_f$<br>for two homolog* |
|---------------------------------|--|---|--|
| CH <sub>4</sub>                 | -11.95   | -17.889   | -7.77  |
| C <sub>2</sub> H <sub>6</sub>   | -19.72   | -20.239   | -5.22  |
| C <sub>3</sub> H <sub>8</sub>   | -24.94   | -24.820   | -4.76  |
| C <sub>4</sub> H <sub>10</sub>  | -29.80   | -29.812   | -4.70  |
| C <sub>5</sub> H <sub>12</sub>  | -34.42   | -35.000   | -4.70  |
| C <sub>6</sub> H <sub>14</sub>  | -39.13   | -39.960   | -4.70  |
| C <sub>7</sub> H <sub>16</sub>  | -43.84   | -44.890   | -4.70  |
| C <sub>8</sub> H <sub>18</sub>  | -48.56   | -49.820   | -4.70  |
| C <sub>9</sub> H <sub>20</sub>  | -53.26   | -54.740   | -4.70  |
| C <sub>10</sub> H <sub>22</sub> | -57.98   | -59.670   | -4.70  |
| C <sub>11</sub> H <sub>24</sub> | -62.69   | -64.600   | -4.70  |

\*Difference between heats of formation of in tandem homologues of methylene that are calculated by MNDO.

Difference between heats of formation ( $H_f$ ) of in tandem homologues of methylene in CRC tables is -4.96 Kcal/mol. This is very close to differences of  $H_f$  for methylene<sup>5,6</sup> that are calculated by MNDO. For determination of  $H_f$  for undecane as a material with unknown  $H_f$ , we estimated that butane (C<sub>4</sub>H<sub>10</sub>) has theoretical  $H_f$  (calculated by MNDO) -29.8 Kcal/mol and the differences between heats of formations of C<sub>5</sub>H<sub>12</sub> and C<sub>4</sub>H<sub>10</sub> is -4.7 so as eqn. 1:

$$H_f = (F \times G) + B \quad (1)$$

TABLE-2  
HEAT OF FORMATION OF *cis*, *trans* AND VINYL SEGMENTS OF  
1,3-BUTADIENE BY MNDO

| Molecules | Abbreviation | Heat of formation (Kcal/mol) |
|-----------|--------------|------------------------------|
|           | T            | -47.74                       |
|           | TT           | -43.18                       |
|           | TTT          | -37.17                       |
|           | C            | -46.52                       |
|           | CC           | -40.28                       |
|           | CCC          | -32.35                       |
|           | V            | -42.49                       |
|           | VV           | -28.26                       |
|           | VVV          | -7.87                        |

where F = difference between heats of formations of two in tandem from butane to undecane and its value is -4.7 Kcal/mol, G = number of molecules between butane and undecane, B = heat of formation of butane.

$$\begin{aligned} H_f &= [7 \times (-4.7)] + (-29.812) \\ &= -62.72 \text{ Kcal/mol} \end{aligned}$$

For calculating of error per cent in calculating of heat of formation, we subtract heat of formation of undecane (that shown in CRC tables) from heat of formation of it (calculated by MNDO). Then the result must be divided by heat of formation of undecane (calculated by MNDO), as shown below:

$$\begin{aligned} \% \text{ Error} &= -64.60 + 62.69/62.69 \times 100 \\ &= 3.047 \% \end{aligned}$$

## Conclusion

In HTPB, we have three structures for chain polymer with double bonds. Some of them are *cis*, *trans* or vinyl and per cent of them isn't same. So, we calculated the heat of formation for monomer (1,3-butadiene), dimer and trimer. Because MNDO program can calculate 35 atoms (Table-2). So difference between monomer-dimer, dimer-trimer, that have *cis*, *trans* or vinyl, will be calculated and then multiple it in polymerization degree of HTPB (43.1), then result must be added to heat of formation of monomer(1,3-butadiene). By using eqn. 1:

$$H_f = (F \times G) + B$$

where F = number of *cis* isomer in one mean chain of HTPB, G = polymerization degree of HTPB, B = heat of formation for *cis* isomer of monomer (1,3-butadiene).

$$\begin{aligned} \text{For } cis \text{ isomer: } H_f &= (F \times G) + B \\ &= (-7.09 \times 43.1) + (-46.52) = -352.88 \text{ Kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{For } trans \text{ isomer: } H_f &= (F \times G) + B \\ &= (-5.29 \times 43.1) + (-47.74) = -276.3 \text{ Kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{For } vinyl \text{ isomer: } H_f &= (F \times G) + B \\ &= (-17.31 \times 43.1) + (-42.49) = -790.46 \text{ Kcal/mol} \end{aligned}$$

In a chain of HTPB polymer, the percent of *cis*, *trans* and vinyl is 57.5, 24.72 and 17.78, respectively. So the heat of formation of a chain of HTPB is the sum of the heat of formations for each isomer that multiplied by its per cent.

$$\begin{aligned} \text{Heat of formation of HTPB} &= (H_f \text{ cis} \times \text{cis } \%) + (H_f \text{ trans} \times \text{trans } \%) \\ &\quad + (H_f \text{ vinyl} \times \text{vinyl } \%) \\ &= (-276.3 \times 0.575) + (-352.88 \times 0.2472) + (-790.45 \times 0.1778) \\ &= -386.65 \text{ Kcal/mol} \end{aligned}$$

Heat of formation of HTPB in literature was calculated for one individual sample is 388.15 Kcal/mol.

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