Calculation of heat of polymerisation: group-contribution method

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Abstract :

Heat of Polymerisation of a polymeric system is largely dependent on its monomer. So depending upon the structure of the monomer, the prediction of the heat of polymerisation can be done. In the present study the structural features of the monomer, that is undergoing polymerisation reaction, has been assumed to be responsible for the heat of polymerisation. To calculate the heat of polymerisation of a particular reaction, Group-Contribution method (GC-method) has been used. Certain values (S_R value) have been assigned for the different structural units, present in the monomers. The S_R values have been obtained by correlating of the heat of polymerisation of a large number of polymers. Addition of the S_R values corresponding to the structural units of the monomer will give the heat of polymerisation of that particular reaction. This GC-method is applicable where liquid monomers form condensed polymers. This empirical method gives quite satisfactory results in calculating the heat of polymerisation for a large number of polymeric systems.

1. Introduction :

Heat of Polymerisation (ΔH_P) of a polymerisation reaction is the enthalpy change that takes place during the formation of the polymer from its monomer. Most of the polymerisation reactions are exothermic (ΔH_P=-ve).There are several experimental methods available among which the Combustion method, Direct reaction calorimetry and Thermodynamic equilibrium techniques are generally used. But prediction of the heat of polymerisation for a polymer can be done by some theoretical or empirical methods, without actually doing the experiments. Calculation of the heat of polymerisation by theoretical and empirical methods have been done in the past by several workers. First Flory[1] and then Prosen et al.[2] have presented a theoretical method of calculation from the heat of hydrogenation. The heat of polymerisation, in Flory's method, comes from the parallel reaction of hydrogenation, which involves a change from trigonal to tetrahedral

hybridisation of the carbon atoms. Joshi[3] and co-workers have developed a method for estimating the enthalpies of formation and polymerisation from bond-energy calculation for the several individual polymers by extending the Somayajulu-Zwolinski generalised bond-energy scheme. Calculation, based on the group-contributions, to determine the free enthalpy of polymerisation was first attempted by Anderson et al. (1944) subsequently followed up Bremner and Thomas (1948), Souders et al. (1949) and by Franklin (1949). The method of group-value contribution was elaborated by Van Krevelen and Chermin (1951). The essence of calculation in these different methods lie in the relative stability of the monomers with respect to the polymers. Based on the stability of monomer, more precisely on the structure of the monomer a Group-Contribution method (GC-method) has been developed in the present study for calculating the heat of polymerisation. The magnitude of the heat of polymerisation depends to a large extent on the stability of the monomer which in turn depends on its structure and constitution.

2. Details of Calculations :

From the First law of thermodynamics and considering only pressure-volume work,

$$\Delta H_P = \Delta E - P\Delta V.$$
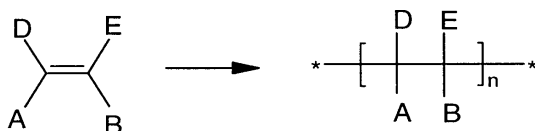
For negligible volume change,

$$\Delta H_P = \Delta E.$$

So the heat of polymerisation (ΔH_P) largely depends upon the internal energy change of the molecules. The relative stability of the monomer and the polymer governs the magnitude of the heat of polymerisation. This empirical method has been developed taking into account the structure and constituents of the monomer. In the present study some particular values (S_R values) have been assigned against the different structural parts of the monomer (ie. the functional groups, side-chains, different atoms and groups). This method can be termed as a Group-Contribution method where the group-values (S_R values) have been fixed against different structural units. The S_R values have been assumed to represent the fractional heat of polymerisation contributed by particular units present in the monomer. Simple addition of S_R values, according to the structural units present in the monomer, gives its heat of polymerisation with a negative sign. Depending on the structural units presents in the monomer, the heat of polymerisation will be different for different monomers.

The S_R values have been obtained from the correlation of the heat of polymerisation data of a large number of polymeric systems, obtained from the several theoretical and experimental methods. As these values are obtained empirically, it is not possible to describe the way of determination of the S_R values for a certain polymer individually. There are generally two types of polymers for which the S_R values are given. One of this type is compounds having olefinic double-bonds or unsaturation and the other type is carboxylic acids and its derivatives. In these two types of compounds double-bonds are present which are responsible for polymerisation. It has been observed that for a certain common value (S_R value) of olefinic double-bond, the heat of polymerisation of almost all of the polymers can be correlated. Same trend has been
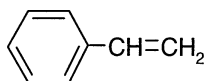
followed for carboxylates also, where the double-bond between C and O have been assigned a common value which will be applicable to a large number of carboxylates.

Consider a typical polymerisation reaction :

Consider the assigned S_R values for the different parts of the monomer ie.-A,-B,-D,-E and the double-bonded framework to be $S_R^1, S_R^2, S_R^3, S_R^4, S_R^5$ respectively. Then the heat of polymerisation with a negative sign for this reaction is ($S_R^1 + S_R^2 + S_R^3 + S_R^4 + S_R^5$). In the following section is presented S_R values for various structural units and atoms, which give agreeable values for the heat of polymerisation when the above method is used.
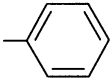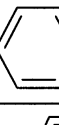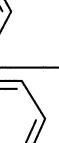
For a typical monomer like styrene,

The S_R values for the one double bond, three -H atoms and one -Ph rings are -24.2, 3x11 (=33) and 7.6 respectively. So the $-\Delta H_p$ obtained by this GC-method is(-24.2 +33.0 +7.6) =16.4.This is the heat of polymerisation with a negative sign when liquid styrene is undergoing polymerisation reaction to form condensed polymer at 25°C.

Table-1 : The S_R values for different structural units or atoms.

Monomer Units	S_R Value
$C=C$	−24.2
$C=O$	−0.7
−OH	7.9
$-N^+(\!\!\begin{smallmatrix}O\\O\end{smallmatrix}$	12.9
−C≡N	9.5
−F	15.8

$-Cl$	8.3
$-H$	11.0
$-CH_3$	11.3
$-CH_3$ (in the same C with $-CH_3$)	2.6
$-CH_3$ (in the same C with $-CH_2-CH_3$)	3.6
$-CH_3$ (in the same C with)	2.9
$-CH_3$ (in the same C with $-Cl$)	10.1
$-CH_3$ (in the same C with $-C\equiv N$)	6.2
$-CH_3$ (in the same C with $\diagdown C=O$)	-10.3
$-CH_3$ (alpha to $\diagdown C=O$)	6.0
$-CH_3$ (cis to $-CH_3$)	10.1
$-CH_3$ (trans to $-CH_3$)	9.6
$-CH_2-CH_3$	11.2
$-CH_2-CH_3$ (alpha to $\diagdown C=O$)	1.8
$-CH_2-CH_2-CH_3$	11.1
$-CH_2-CH_2-CH_2-CH_3$	11.0
$-CH_2-CH_2-CH_2-CH_2-CH_3$	11.0
$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	11.0
	7.7
$-CH_2$	1.5
$-O-CH_3$	10.6
$-O-CH_2-CH_3$	10.7
$-O-CH_2-CH_2-CH_3$	10.8
$-O-CH_2-CH_2-CH_2-CH_3$	10.9

Group	Value
$-O-CH_2-CH_2-CH_2-CH_2-CH_3$	10.9
$-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	10.9
$-O-CH\begin{smallmatrix}CH_3\\\\CH_3\end{smallmatrix}$	11.2
$-O-CH_2-CH\begin{smallmatrix}CH_3\\\\CH_3\end{smallmatrix}$	11.2
$-O-CH=CH_2$	19.4
$-O-\bigcirc$ (benzene ring)	9.2
$-O-CH_2-\bigcirc$ (benzene ring)	10.3
$-O-\bigcirc$ (cyclohexane ring)	9.1
$-O-CH_2-CH_2-OH$	8.9
$-O-CH_2-CH-OH$ with CH_3	9.0

3. Results and Discussion:

The Group-Contribution method gives the heat of polymerisation value for the polymerisation reaction where the liquid monomer forms a condensed polymer at 25°C. 'Condensed' refers to the state of the polymer after polymerisation ie. here the volume of the liquid monomer is reduced during the polymerisation. Basically, the standard state of polymer is "liquid-condensed"(lc). Although there is some temperature effect on the heat of polymerisation, it is not so large and so has not been considered in this method. The results therefore work best at 25°C, but are sufficiently accurate for a reasonable temperature range around it.

Table-2 : Data for the heat of polymerisation of some polymers, calculated by the GC-method in comparison with that observed in different experimental and theoretical methods.

Monomer	$-\Delta H_{P \text{ calculated}}$ (kcal/mole) at 25°C	$-\Delta H_{P \text{ observed}}$ (kcal/mole)
Acetaldehyde[4]	0.0	0.0 *
Acetone[4]	−5.9	-6.0 *
Acrolein[5]	19.1	19.1 **
Acrylic acid[5]	16.0	16.0 **
Acrylic acid, n-butyl ester[6]	19.0	19.1 *
Acrylic acid, ethyl ester[6]	18.8	18.8 *
Acrylic acid, methyl ester[7]	18.7	18.7 ***
Acrylonitrile[8]	18.3	18.3 *
1,3-Butadiene[9]	17.6	17.6 *
1-Butene[10]	20.0	20.0 *
cis-2-Butene[10]	17.9	17.9 *
trans-2-Butene[10]	17.0	17.0 *
2-Chloroprene[11]	16.2	16.2 *****
Ethylene,tetrafluoro-[12]	39.0	39.0 *
Ethylene,nitro-[13]	21.7	21.7 *
1-Hexene[10]	19.8	19.8 *
Isoprene[14]	17.9	17.9 *
Methacrolein[5]	14.1	15.6 **
Methacrylic acid[5]	11.0	10.1 **
Methacrylic acid, benzyl ester[15]	13.4	13.4 ***
Methacrylic acid, cyclohexyl ester[15]	12.2	12.2 ***
Methacrylic acid, ethyl ester[6]	13.8	13.8 *
Methacrylic acid, n-hexyl ester[6]	14.0	14.0 *
Methacrylic acid, β-hydroxyethyl ester[6]	12.0	11.9 *
Methacrylic acid, β-hydroxypropyl ester[6]	12.1	12.1 *
Methacrylic acid, isobutyl ester[16]	14.3	14.3 **
Methacrylic acid, isopropyl ester[16]	14.3	14.3 **
Methacrylic acid, methyl ester[11]	13.9	13.9 ***
Methacrylic acid, phenyl ester[15]	12.3	12.3 ***

Methacrylic acid, n-propyl ester[16]	13.9	13.7 **
Methacrylonitrile[5]	13.5	13.5 **
Methyl vinyl ketone[17]	14.1	17.7 **
Propylene[10]	20.1	20.1 *
Styrene[18]	16.4	16.4 ****
Styrene, α-methyl[19]	8.3	8.4 *
Vinyl acetate[7]	21.3	21.3 ***
Vinyl benzoate[16]	20.2	20.2 **
Vinyl chloride[20]	17.1	17.0 *
Vinylidene chloride[7]	14.4	14.4 ***
Vinyl propionate[16,17]	20.5	20.5 **

(∗ : 25° C, ∗∗ : 74.5° C, ∗∗∗ : 76.8° C, ∗∗∗∗ : 26.9° C, ∗∗∗∗∗ : 61.3° C.)

Some of the ΔH_P values, obtained by this GC-method, are given in the above table. As the S_R values are obtained by the correlation of the heat of polymerisation of a large number of polymers, these values can be applied for a new polymer. So by this GC-method, the heat of polymerisation of a large number of polymeric systems can be calculated and also that of a new polymer can be predicted.

4. Conclusions :

Heat of polymerisation of a large number of polymers (excluding the cyclic polymers) can be satisfactory calculated by the Group-contribution method. Although this is a totally empirical method and there is no clear-cut theoretical basis of determining the S_R values, the data obtained by this method is quite consistent to the values obtained by previous workers who have calculated the heat of polymerisation experimentally or theoretically for some specific systems. Flory's method, which assumes that there is no steric hindrance in the polymer, often gives deviation because of this assumption. The Joshi's bond-energy method works well only when the extension of the Somayajulu-Zwolinski bond-energy scheme is made for the structural energy differences arising from tacticity of the α-olefin polymers. So both these methods have some limitations because of which the ΔH_P of a large number of polymers can not be calculated by them. The method of calculation, given by Van Krevelen and Chermin, requires some structural correction due to structural influences on the group contributions. Moreover, this method gives the free enthalpy of formation($\Delta G_f^°$) ie. it does not give the heat of polymerisation directly. But the Group-contribution method (GC-method) that has been developed in the present study, directly gives the heat of polymerisation. It is also more general. The only limitation here is that the heat of polymerisation can be calculated for liquid monomers giving condensed polymers. Most of the polymerisation reactions, however, belong to

this class and hence the utility of this method. So practically ΔH_p can be calculated for large number of polymers by this GC-method. The importance and utility of this method (GC-method)lies in its generality and ease of working.

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