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Thermodynamic Aspects of Degradation with Particular Reference to Unsaturated Polyester Resins

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ABSTRACT

Like the concept of ceiling temperature, which allows the prediction of when a depolymerisation reaction can occur from the thermodynamic point of view, it is pointed out that degradation reactions other than depolymerisation can be treated in an analogous manner. Since, in many cases, the required thermodynamic data are not available, approximate values can be obtained by calculation from increments, which is valid for gas phase reactions. Likewise, an approximate correction for physical states other than gaseous can be introduced. Calculations on the basis of increments are particularly useful because the increments of parts of the molecule which are not involved in the reaction process do not occur explicitly in the calculation. Thus, for certain types of reaction, typical thermodynamic data can be obtained. In this paper thermodynamic data of some typical reactions which are of importance in the field of the thermal degradation of unsaturated polyester resins are calculated. The results are compared with experimental results obtained from previously published research in the field of polyesters.

INTRODUCTION

Thermodynamic considerations in polymerisation reactions were introduced by Dainton & Ivin.[1] They were able to explain by thermodynamic arguments why certain copolymers could not be obtained from their monomers. This became well known as the concept of the 'ceiling temperature'. The polymerisation reaction in general cannot take place exclusively above a certain temperature, but, depending on the signs of the

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thermodynamic parameters, there may be, in certain cases, a temperature, below which the polymer becomes unstable with respect to its monomer.[2] This temperature is sometimes referred to as the 'floor temperature' and the most common example concerns rubberlike sulphur, which may be formed at elevated temperatures but is not stable at room temperature. In other cases a polymer will never be formed from its 'hypothetical' monomer for thermodynamic reasons.

Since classical thermodynamics deals exclusively with equilibria, the concept underlying the ceiling temperature is not only valid for polymerisation reactions but can also be applied to the reverse reactions; namely, depolymerisation. In this paper, the qualitative statements above will be treated more rigorously in the language of formulae.

THEORY

The formation of a basic unit of polymer belonging to a chain of degree of polymerisation n from a monomeric unit may be represented as in eqn (1).

$$M \rightarrow (1/n)P \qquad (1)$$

The Gibbs free energy for this reaction is:

$$\Delta G_p = \Delta G(\text{polymer, state}) - \Delta G(\text{monomer, state}) \qquad (2)$$

where ΔG(polymer, state) is the free energy of formation of the polymer from its elements, and ΔG(monomer, state) is the free energy of formation of the monomer from its elements, in the physical state given.

The polymer can be formed either as a crystalline or amorphous solid, or in solution. The monomer can be in the gaseous, liquid or solid state or in solution. As already stated, this formalism is likewise valid for the reverse reaction and the Gibbs free energy for the process

$$(1/n)P \rightarrow M \qquad (3)$$

is simply

$$\Delta G_d = \Delta G(\text{monomer, state}) - \Delta G(\text{polymer, state}) \qquad (4)$$

Usually during pyrolysis the monomer will be ejected in the gaseous state and the polymer is in the condensed state or eventually in the molten state. Neglecting the temperature dependence of enthalpy and entropy (Ulich's approximation) the Gibbs free energy of formation of the monomer assuming ideal behaviour can be written as

$$\Delta G(\text{monomer, g}) = \Delta H^{\circ}(\text{monomer, g}) - T * \Delta S^{\circ}(\text{monomer, g}) + RT * \ln(p/p^{\circ}) \qquad (5)$$

The superscript '°' denotes standard conditions of enthalpy of formation (ΔH) and entropy of formation (ΔS).

Usually the depolymerisation reaction is of interest at ordinary pressures, i.e. standard pressures, and so the pressure correction can be neglected. Exceptions may be pyrolysis experiments *in vacuo* (TVA-technique) or some special situations like the equilibrium pressure of methyl methacrylate formed from PMMA at room temperature.

Thus for pure polymer in the condensed state the Gibbs free energy with the approximation above can be written as

$$\Delta G(\text{polymer}, a) = \Delta H^\circ(\text{polymer}, a) - T * \Delta S^\circ(\text{polymer}, a) \qquad (6)$$

The index '*a*' denotes the amorphous state. In the general case some additional corrections, e.g. for melting, etc., can be made to meet the physical state in which the polymer is actually depolymerising. An example for polystyrene is given in Table 1. Some data concerning the heat and entropy of polymerisation are given in the literature, but not in the states which are of interest here. However, utilising thermodynamic cycles, it is possible to calculate the thermodynamic data which are of particular interest. This is

TABLE 1

Enthalpies and Entropies for Some Important Reactions Concerning Polystyrene

(a)

Reaction	ΔH° [*J/mol*]	$-\Delta S^\circ$ [*J/(mol.K)*]
Styrene(l) → polystyrene(s)	−70 000	+104
8 C(s) + 4 H_2(g) → styrene(l)	+104 000	+328
8 C(s) + 4 H_2(g) → styrene(g)	+147 000	+223
7 C(s) + 4 H_2(g) → toluene(g)	+50 000	+240
Polystyrene(s) → polystyrene(l) (calculated at 240°C[3,4])[a]	+8 400	−16

(b) The following may be calculated from the above data:

Reaction	ΔH° [*J/mol*]	$-\Delta S^\circ$ [*J/(mol.K)*]
Polystyrene(s) → styrene(g)	+113 000	−209
8 C(s) + 4 H_2(g) → polystyrene(s)	+34 000	+432
Heat of formation calculated from combustion data of polystyrene	+37 000	—
Polystyrene(s) → toluene(g) + C(s)	+16 000	−192

[a] For crystalline polystyrene.

done in the lower section of Table 1. The ceiling temperatures can be calculated from the data given in Table 1. To have a deeper feeling of how the ceiling temperature is defined here, the Gibbs free energy may be expressed as in eqn (7).

$$\Delta G = \Delta G^\circ + RT * \ln(K) \tag{7}$$

K is the so-called thermodynamic equilibrium constant. Thus under equilibrium conditions, $\Delta G = 0$. Thus, setting $\Delta G^\circ = 0$ for calculating the ceiling temperature or, more generally, the equilibrium temperature, means that eqn (7) is evaluated under conditions where the thermodynamic equilibrium constant is unity.

Table 1 shows that the contribution of fusion to the thermodynamic parameters is comparatively small. As well as information about the equilibrium temperature, it can be directly deduced from Table 1 whether the reaction under consideration is endothermic or exothermic.

In addition to the depolymerisation reaction, the decomposition of polystyrene into gaseous toluene and char is also evaluated. From the point of view of the original concept of ceiling temperature, polystyrene is regarded as a copolymer of toluene and coal. This is not important for synthetic purposes, but is a possible degradation path. It can easily be verified that this particular reaction can occur below room temperature, although it does not occur—obviously for kinetic reasons. In addition, this reaction is much less endothermic than the depolymerisation reaction.

The degradation of polystyrene into toluene and char can be generalised in the following manner:

$$\text{Polymer 1(solid)} \rightarrow \text{Polymer 2(solid)} + \text{Product(g)} \tag{8}$$

As explained below, it will be of some interest to deal with polymers in their hypothetical gaseous states. So the vaporisation of the polymers has to be taken into consideration.

$$\text{Polymer(solid)} \rightarrow \text{Polymer(g)} \tag{9}$$

In eqns (8) and (9) the particular physical state of the polymer is not given explicitly. For more detailed considerations 'solid' must be replaced by 'crystalline' or 'amorphous' or 'fused' etc., and equations similar to the phase transition in eqn (9) must be added. The Gibbs free energy for the vaporisation of the polymer is:

$$\Delta G_{\text{vap}}(\text{polymer}) = \Delta G(\text{polymer, g}) - \Delta G(\text{polymer, solid}) \tag{10}$$

So the Gibbs free energy for the reaction in eqn (8) can be written as:

$$\begin{aligned}\Delta G = {} & \Delta G(\text{polymer 2, g}) - \Delta G(\text{polymer 1, g}) \\ & + \Delta G(\text{product, g}) - \{\Delta G_{\text{vap}}(\text{polymer 2}) - \Delta G_{\text{vap}}(\text{polymer 1})\}\end{aligned} \tag{11}$$

It is important to note that in this particular case the 'vaporisation terms' have different signs and may, in the most favourable case, cancel completely. In the literature only a few data regarding enthalpies of vaporisation are given. However, in general we expect that the vaporisation terms are small in comparison with the terms concerning formation, since the latter reflect chemical reactions whereas vaporisation is a physical process. On the basis of these two arguments it seems likely that the reaction in eqn (8) can be expressed in terms only of gaseous state thermodynamic parameters. The type of reaction given in eqn (8) seems to be of some importance in pyrolysis reactions. A common example is the ejection of hydrogen chloride from poly(vinyl chloride) in the course of thermal treatment.

Calculation of heats of formation by increments

The unusual idea of expressing the enthalpy and entropy of formation of polymers in the gaseous state immediately becomes less unusual, when it is realised that the heats and entropies of formation can be calculated from increments according to the method of Van Krevelen.[5] This is particularly useful, because only a restricted set of experimental thermodynamic data is available in the literature. Using Van Krevelen's method, thermodynamic data are calculated from increments of chemical groups with further corrections; for example, for conjugated double bonds or rings. The standard values are believed to be valid in the range of 300–600 K. For example, the enthalpies and entropies of formation of tetrahydrofuran can be calculated from the following group contributions: four $—CH_2—$, one —O— and one five membered ring.

The polymerisation reaction of styrene can be formulated as follows:

$$—CH{=}CH_2 \rightarrow {>}CH—CH_2— \qquad (12)$$

It is not necessary to put the group contribution of the phenyl residue into the calculation of the heats of formation since this contribution appears on both sides of the equation and will finally cancel. Thus the concept of increments cannot explain differences due to substituents. A big advantage, however, is the fact that due to this particular feature certain types of reactions can be evaluated easily without the need to know the complete chemistry of the other parts of the system. A further example is explained in detail below. The ejection of carbon dioxide from a polyester linkage can be depicted as in eqn (13):

$$—COO— \rightarrow CO_2 \qquad (13)$$

There is no need to write the reaction as in eqn (14):

$$—CH_2—COO—CH_2— \rightarrow CO_2 + —CH_2—CH_2— \qquad (14)$$

since the $—CH_2—$ increments will cancel.

Because these reactions are in general referring to a particular reaction type, they will be referred to as 'typical' reactions.

RESULTS

Some standard enthalpies and entropies of formation have been calculated for typical reactions which are of importance in the degradation of unsaturated polyesters. The particular reactions are shown in Table 2. No corrections have been made for different physical states.

The three different decarboxylation reactions are shown; namely, ejection of carbon dioxide from an ester group, from an aliphatic acid group which is not substituted in the alpha-position, and from an aromatic acid group. These reactions in general have exothermic character and are endoentropic; this means they are possible in all cases.

Different behaviour exists in the decarbonylation reaction, the ejection of carbon monoxide. This reaction is strongly endothermic and due to the entropy term is only possible above *c.* 500°C. Dehydration of an aliphatic alcohol is possible above the freezing point.

For the depolymerisation reaction it is possible to estimate the effect of changes of the physical state. According to Van Krevelen[5] some 7–17 kJ/mol should be added to the value of the enthalpy and some 15–40 kJ/(mol . K) should be subtracted from the entropy term. These values would fit the experimental values better (*c.f.* Table 1). The ceiling temperature, however, remains essentially unaffected.

The dehydrogenation reaction in Table 2 can only occur to a significant extent in the case of non-aromatic systems at temperatures of *c.* 700°C. In the case of aromatic systems the values of enthalpy and entropy are comparatively small and eventual corrections may change the impression that dehydration is never possible. Inspecting the compilation of Grassie & Scotney[6] of pyrolysis products obtained from various polymers, one finds that in the case of polymers with aliphatic groups hydrogen is not given as a decomposition product (with one exception). This is consistent with what one would expect from the present prediction. But in the case of polymers with aromatic structures, in particular of those which decompose at high temperatures, hydrogen is reported, in most of the cases, as a minor product. It is interesting to consider the influence of the pressure dependence of the equilibrium temperature. The calculations are concerned with a pressure of gaseous products of one atmosphere. In the present case the entropy term is so small that a partial pressure in the range of a few millimetres is sufficient to reverse the temperature dependence of the Gibbs free energy (*c.f.* eqn 5).

Disproportionation can occur spontaneously. By disproportionation is

TABLE 2

Thermodynamic Data of Elementary Reactions

	Free enthalpy of formation (J/mol)
Decarboxylation	
$-COO- \rightarrow CO_2$	−57 500 − 118.T
$-CH_2-COOH \rightarrow -CH_3 + CO_2$	−25 500 − 127.T
$>C_{aro}-COOH \rightarrow >C_{aro}-H + CO_2$	−10 000 − 116.T
Decarbonylation	
$-COO- \rightarrow -O- + CO$	+106 000 − 136.T
Dehydration	
$-CH_2-CH_2-OH \rightarrow -CH=CH_2 + H_2O$	+38 000 − 138.T
Depolymerisation	
$>CH-CH< \rightarrow -CH=CH-$	+81 400 − 164.T
$>CH-CH_2- \rightarrow -CH=CH_2$	+85 700 − 154.T
Dehydrogenation	
$-CH_2-CH_2- \rightarrow -CH=CH- + H_2$	+120 000 − 128.T
$-CH=CH- \rightarrow -C\equiv C- + H_2$	+154 000 − 126.T
$2>C_{aro}-H \rightarrow 2>C_{aro}- + H_2$	+25 000 + 24.T
Disproportionation	
$>CH-CH_2- \rightarrow -CH_3 + C$	−21 300 − 127.T
$>C=CH-CH_2- \rightarrow -CH_3 + 2C$	−112 000 − 95.T
$-CH_2- \rightarrow C + H_2$	+22 000 − 102.T
$2C_{aro}-H \rightarrow 2C + H_2$	−25 000 − 52.T
Hydrogen Chloride Formation	
$>CCl- + H_2 \rightarrow >CH- + HCl$	−66 700 − 20.T
$>CHCl + H_2 \rightarrow >CH_2 + HCl$	−63 300 − 18.T
$=CCl- + H_2 \rightarrow =CH- + HCl$	−56 000 − 12.T
Ester → cycl. (5) Anhydride + (poly)-Ether	
$-OOC-COO- \rightarrow -OC-O-CO- + -O-$	+105 000 − 106.T
Ester → cycl. (5) Anhydride + cycl. (5)-Ether	
$-OOC-COO- \rightarrow -OC-O-CO- + -O-$	+125 000 − 206.T
Ester → cycl. (5) Anhydride + cycl. (3)-Ether	
$-OOC-COO- \rightarrow -OC-O-CO- + -O-$	+205 000 − 228.T
Ester → cycl. (5) Anhydride + Acetaldehyde	
$-OOC-COO- + -CH_2-CH_2- \rightarrow -OC-O-CO- + CH_3CHO$	+98 000 − 259.T
Ester → Acid + Olefin	
$-OOC-COO-CH_2CH_2- \rightarrow -OOC-COOH- + -CH=CH_2$	+49 000 − 134.T
Ether → Alcohol + Olefin	
$-CH_2CH_2-O- \rightarrow -OH + -CH=CH_2$	+49 000 − 156.T
HET-anhydride → HEX + MA-anhydride	+126 000 − 258.T

meant the decomposition of a certain species into two, one of them containing more hydrogen than the other.[7] This reaction, together with dehydration, is also of importance in organic geochemistry, as in the formation of coal from organic plant debris.[8] If these reactions could not proceed readily at ordinary temperatures, the formation of natural gas, crude oil and coal would not be possible.

The formation of hydrogen chloride from organically bonded chlorine is always possible. To treat this reaction in isolation, however, is not reasonable, because it is known that hydrogen formation is not possible in most cases. The equation can be combined, however, with some dehydrogenation reaction in the scheme. The character of these reactions is exothermic. In separate experiments utilising differential thermal analysis techniques with chlorine-containing unsaturated polyester resins,[9] it turned out that the decomposition reaction became increasingly exothermic with increasing chlorine content. This conforms to the picture developed in this paper since hydrogen chloride was shown to be among the products of pyrolysis.[10] Elsewhere it was stated that polyester resins with increasing chlorine content degrade to yield more char and, instead of styrene as pyrolysis product, toluene will be formed.[11] It can be seen from the data in this paper that the depolymerisation reaction is much more endothermic than the disproportionation reaction. The differential thermal analysis traces also reflect this.

The combination of the formation of hydrogen chloride with the dehydration reaction of aromatic systems is of particular interest. The latter reaction is the formation of higher condensed aromatic systems as the precursor of soot. This combination results in an exothermic reaction, the free Gibbs energy of which is nearly independent of temperature.

Some polyester degradation reactions are also given in Table 2. The decomposition of the diol component to cyclic anhydride and various compounds is evaluated. It was somewhat unsatisfactory from the chemical point of view that the anhydride had to be built up from the contributions of carbonyl and carboxyl groups since anhydride was not given in Van Krevelen's system.[5] The degradation to a polyether can only occur at unreasonably high temperatures. The same is true for the degradation of a 1,2-diol-unit into an epoxide. But a cyclic ether with a five membered ring (tetrahydrofuran in the case of 1,4-butanediol[11]) can easily be formed. Also acetaldehyde can be formed from a polyester containing ethylene glycol.[12]

This is just what has been found experimentally. In previous degradation schemes, degradation via a polyether intermediate was depicted as one of the possible routes but it was stated that it was not clear whether this really occurs. In the meantime some low temperature pyrolysis experiments have been performed with subsequent analysis of the residue by means of infrared spectroscopy. The aim of these experiments was to find out whether an increased content of polyether structures could be detected. This was not the case. Further, by GC–MS studies, only trace amounts of presumably linear oligoethers could be identified. This is supported by thermodynamic considerations. Actually, if a substance is thermodynamically unstable, this does not mean that a degradation process does not occur via such an intermediate. It only means that it is improbable that one will be able to detect such a product.

In the last part of Table 2, the standard enthalpies and entropies for β-scission of an ester linkage and the analogous reaction for a polyether structure are presented. In addition, the retro-Diels–Alder reaction for a HET-acid unit is given (HET-acid was used in previous studies[11]). Even when the results are quite reasonable, it is not clear whether the concept of increments can be applied to bridged systems without introducing appreciable error.

CONCLUSIONS

In this paper some thermodynamic concepts have been considered, which allow one to obtain some idea of the conditions under which certain reactions can take place. A particular feature is the introduction of the concept of increments. Thus it is possible to make certain predictions, even when only fragmentary thermodynamic data are available on the particular substances. Because of the approximations made, conclusions must be drawn with care. Even when a particular reaction is possible thermodynamically there is no guarantee that this reaction will actually occur. A rule of thumb may be stated. A reaction will most likely proceed when a detailed mechanism can be worked out requiring a minimum of reasonable elementary steps.

On the other hand, it should be kept in mind that, even if a particular reaction is not allowed, it can occur if it is running concomitantly with another reaction, the combination of both being allowed.

It is common in organic chemistry to carry out an experiment, examine the results, and then establish the reaction mechanism. By means of thermodynamic considerations it is possible to get some idea of what else might happen. This may be valuable, for example, in the development of flame retardants. By taking into consideration the real degradation path of a particular polymer it is possible to consider what other degradation path could be more desirable for effective flame retardancy. The task is then to find a catalyst or a reactive additive, described as a ‘flame retardant’, which forces the degradation path in the desired direction. Needless to say, desirable but impossible degradation paths can be ruled out thermodynamically. There may also be some applications outside the scope of unsaturated polyester resins.

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