A General Equation in Polycondensation

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SYNOPSIS

In polycondensation, we define $\bar{F}$ and $\bar{f}$ to be the true and effective average functionalities of the reaction system, respectively. The value of Q relates to the functionality and quantity of the nonbifunctional monomer. If there is monofunctional monomer in the reaction system, the value of Q may be less than 0. If the ring-closure reaction in a system can be neglected, the relation among the molecular weight, the component of the reaction system, and the reaction extent of functional groups can be represented by the following equation: $P = (\bar{F} - Q - 2/\bar{x}_n)/\bar{f}$. The equation may be used in line, branching, and cross-linking polycondensations without any restrictional conditions. According to Carothers, the gelation point P_c can be estimated by the following equation: $P_c = (\bar{F} - Q)/\bar{f}$. All relations among the molecular weight of the polymer, the component of the reaction system, and the reaction extent of the functional group can be replaced by the new equation. Only the Flory equation that is used to estimate P_c cannot be replaced by the new equation.

INTRODUCTION

In polycondensation, it is very important to grasp the relation among the molecular weight of the polymer (or degree of polymerization), the component of the reaction system, and the reaction extent of functional groups. The relative equations have been established in various forms,[1-3] but none can be used without restriction. The equations found in different books are presented in different forms according to reaction conditions; there is no equation that can describe the polycondensation with no experimental or functionality restriction. The focus of this paper is to introduce a new general equation of polycondensation that represents all the equations but the Flory equation that estimates the gelation point in polycondensation.

DEMONSTRATION

As a simple demonstration, assuming a polycondensation system that is composed of several kinds of monomers, if Nai stands for the initial mol concentration of one of the monomers that has the same

functional group a and if fai is the functionality of the monomer, then Nbi stands for the initial mol concentration of one of the monomers that has the same functional group b and fbi is the functionality of the monomer ($i = 1, 2, 3 \cdots$, the index of monomers having the same functional group). P is the extent of the reaction of a kind of functional group and, in the case of unequal mol of groups a and b, P is the reaction extent of the functional group that is less. In addition, if the ring-closure reaction in the system can be neglected, the mol number of all resident groups of the system is

$$\sum Nai\, fai + \sum Nbi\, fbi - 2P \sum Nai\, fai \quad \text{or}$$

$$\sum Nbi\, fbi + (1 - 2P) \sum Nai\, fai \quad (1)$$

noting that the mol number of functional group a is supposed less than or equal to that of b.

In the system, the number of all molecules is

$$\frac{\sum Nai + \sum Nbi}{\bar{X}_n} \quad (2)$$

where $\bar{X}_n$ is the average number of structure units in a molecule. The average number of residual functional groups in a molecule can be represented in the following form:

$$\frac{\sum Nai(fai - 2) \sum Nbi(fbi - 2)}{\sum Ni + \sum Nbi} \bar{X}_n + 2 \quad (3)$$

The last "2" is the number of end groups of a molecule.

Then, supposing

$$Q = \frac{\sum Nai(fai - 2) + \sum Nbi(fbi - 2)}{\sum Nai + \sum Nbi} \quad (4)$$

Eq. (5) can be easily obtained:

$$\frac{\sum Nai + \sum Nbi}{\bar{X}_n}$$
$$= \frac{\sum Nbi\,fbi + (1 - 2P) \sum Nai\,fai}{\bar{X}_n Q + 2} \quad (5)$$

Both sides of eq. (5) represent the number of molecules in a system. If we define

$$\bar{F} = \frac{\sum Nai\,fai + \sum Nbi\,fbi}{\sum Nai + \sum Nbi}$$

and

$$\bar{f} = \frac{2 \sum Nai\,fai}{\sum Nai + \sum Nbi}$$

(supposing the total number of functional group a is less than or equal to that of group b). Equation (6) is easily derived from eq. (5):

$$P = \frac{\bar{F} - Q - 2/\bar{X}_n}{\bar{f}} \quad \text{or} \quad \bar{X}_n = \frac{2}{\bar{F} - Q - p\bar{f}} \quad (6)$$

Equation (6) represents the relation among the molecular weight of the polymer, the component of the reaction system, and the reaction extent of functional groups. It can be used not only in time polycondensation, but also in branching and cross-linking polycondensation without any restriction conditions.

RESULTS AND DISCUSSION

According to Carothers,[4] the gelation point P_c in cross-linking polycondensation is the critical extent of the reaction when $X_n \to \infty$. Therefore, eq. (6) can be changed into the following form to estimate the gelation point P_c:

$$P_c = \frac{\bar{F} - Q}{\bar{f}} \quad (7)$$

Several polycondensation systems have been taken to test eqs. (6) and (7); the results obtained are shown in Table I for comparison with those from previous equations that can be found in many books.[1-3]

It can be seen that these results are in conformity. The advantage of the new equation is obvious. All equations so far established in polycondensation can

Table I Comparison of Results of Eq. (6) with Those from Previous Equations

Reaction System	$\bar{F}$	$\bar{f}$	Q	Results from Eq. (6)	Results from Previous Equations
$Na1 = Nb1$ $fa1 = fb1 = 2$	2	2	0	$\bar{X}_n = \dfrac{1}{1-p}$	$\bar{X}_n = \dfrac{1}{1-P}$
$Na1/Na1 = 0.9$ $fa1 = fb1 = 2$	2	1.895	0	$\bar{X}_n = \dfrac{1}{1-0.95P}$	$\bar{X}_n = \dfrac{1}{1=0.95P}$
$Na1 = Nb1 = 1$ $Na2 = 0.1$ $fa1 = fb1 = 2$ $fa2 = 1$	1.95	1.82	0.05	$\bar{X}_n = \dfrac{1}{1-0.91P}$	$\bar{X}_n = \dfrac{1}{1-0.91P}$
$Na1 = 0.707$ $Na2 = 0.195$ $Nb1 = 1$ $fa1 = fb1 = 2$ $fa2 = 3$	2.10	2.10	0.10	$P_c = 0.95$ $(\bar{X}_n \to \infty)$	$P_c = 0.95$ (Ref. 4)

be replaced by the new equation without any restriction of functionality and number of monomers present in a reaction system. Only the Flory equation that is used to estimate the gelation point P_c cannot be replaced by the new equation. It is very evident that the new eq. (6) makes our work more convenient.

REFERENCES

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