Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Gritsenko, T. M.(1975) 'Polycondensation Stoichiometry', Journal of Macromolecular Science, Part A, 9: 3, 373 — 396
To link to this Article: DOI: 10.1080/00222337508065862
URL: http://dx.doi.org/10.1080/00222337508065862

J. MACROMOL. SCI.—CHEM., A9(3), pp. 373-396 (1975)

Polycondensation Stoichiometry

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ABSTRACT

Some examples demonstrate the feasibility of interpreting the results of polycondensation from stoichiometry. Utilizing only the consequences of stoichiometric principles, it is possible to draw conclusions of the basic principles of forming polymers in the polycondensation process and to substantiate the physical meaning of a number of averaged values used during calculations. The results confirm the relationships found earlier by means of other methods and make it possible to draw significant conclusions with respect to the character of the process and the peculiarities of the products obtained.

INTRODUCTION

The fundamental difference between the reactions on which the principle of the polycondensation method of obtaining polymers is founded and the reactions of organic and nonorganic synthesis is based, in general, on the fact that multifunctional (as a minimum, bifunctional) compounds are involved in polycondensation. This multifunctionality may either be due to the molecules of the original reagents or it may occur under the influence of certain factors in the reaction system [1]. This difference results in the formation, during the reaction, of particles with sizes which greatly exceed the sizes of the molecules of the original reagents, this fact being one of the principal specific features of the process. These particles may appear when sufficiently strong bonds of any chemical nature are formed between the molecules of the original reagents or their multifunctional fragments.

According to the method of formation of the polymer chains, polycondensation can be characterized in general by the fact that the reactions between the functional groups of molecules of the original reagents, which cause the formation of bonds between them, occur in accordance with the probability laws relevant to all the reactive groups found in the reaction zone. When this happens it is not important whether the reactions between the functional groups are additive reactions or substitution reactions; in other words, whether the low-molecular product of the functional group interaction is separated or not, since the basic principles which govern the formation of the polymer or oligomer chains remain unchanged.

In polycondensation the formation of each new bond between the particles of the original reagents requires the disappearance of the corresponding, strictly definite quantity (as a rule, two) of functional groups, therefore the formation of a polymer or oligomer particle should conform to certain stoichiometric principles.

In this article an attempt is made to study polycondensation from a stoichiometric position as one way of expressing the conservation of matter law. When doing so, it should be borne in mind that during such a study we finally come to the utilization of the results of the balance of reacting and forming particles and of their functional groups. The deductions made will give an averaged picture while the quantitative characteristics will have the meaning of number-average values.

BASIC SYMBOLS

N	Avogadro's number
N_A^0, N_B^0	original quantities of moles of reagents A and B, respectively
f_A, f_B	functionality of reagents A and B, respectively
x	extent of reaction (conversion) relative to all the functional groups taken for the reaction
x_A, x_B	extent of reaction (conversion) for the functional groups of reagents A and B, respectively
$q = N_A^0/N_B^0$	molar ratio of the original reagents

$Q = N_A{}^0 f_A / N_B{}^0 f_B$	ratio of the functional groups of the original reagents ($Q = qf_A/f_B$)
M_A, M_B	molecular weights of reagents A and B, respectively
n	quantity of molecules in the polycondensate
$\overline{P}_n$, $\overline{M}_n$	number-average degree of polycondensation and molecular weight of the polycondensation product, respectively

GENERAL COMMENTS

In our study we shall proceed from the obvious fact that if we take definite limited quantities of the original reagents, then the degree of polycondensation and the corresponding molecular weight of the polycondensation product will not increase indefinitely and may only tend toward limits determined by the original quantities available:

$$P_{lim} = (N_A{}^0 + N_B{}^0)\,N \tag{1}$$

and

$$M_{lim} = (M_A N_A{}^0 + M_B N_B{}^0 - g)\,N \tag{2}$$

where g is the quantity of the separated low-molecular product, determined by multiplying the quantity of the moles of pairs of the reacted functional groups by its molecular weight. When additive reactions for polycondensation are used, $g = 0$.

It is possible to find definite analytical expressions for the average degree of polycondensation and the molecular weight in the case when, by some means, the number of particles in the system is found.

If the number of particles is equal to n, then

$$\overline{P}_n = \overline{P}_{lim}/n \tag{3}$$

and

$$\overline{M}_n = M_{lim}/n \tag{4}$$

If we know the functionality of these particles, then n can be found by the quantity of the unreacted functional groups. The formation during polycondensation of intramolecular cycles is equivalent to a partial or total loss of functionality, and in these cases in order to evaluate the number of particles it is essential to introduce other methods which are independent of stoichiometry [2].

If the ratio of the original reagents is such that the formation in the system of only macromolecule with a limiting degree of polycondensation becomes theoretically possible, then application of the concept of polydispersity is lost. We can presume that in those cases when, for some reason or other, the reactive volume may be divided into a number of more or less independent regions (spontaneously, for example, during the association phenomena or by some artificial method), in each of which a macromolecule can be formed, the resulting molecular weight distribution in the polymer will correspond to the weight distribution of these regions.

Owing to the fact that during the polycondensation in a general case the reactive mixture, during the reaction and after its completion, contains molecules of oligomers and unreacted original reagents besides the polymer molecules, we shall henceforth use the term "polycondensate" to designate the reaction product.

LINEAR POLYCONDENSATION

A condition generally required for the formation of linear molecules in the polycondensate is the bifunctionality of all the original reagents, i.e.:

$$f_A = f_B = 2 \qquad (5)$$

In order to make it possible in principle to form one linear macromolecule of the limiting degree of polycondensation from all the available quantities of the original reagents, it is necessary that only two unreacted functional groups should remain in the reaction system.

This is possible in three cases.

1. $\underline{N_A^0 = N_A^0 \ (q = 1)}$

Here one unreacted functional group of each original reagent remains. Thus the limiting extent of reaction for forming a linear polymer should be equal to

$$x_{\lim} = (N_A^0 N f_A + N_B^0 N F_B - 2)/(N_A^0 N f_A + N_B^0 N f_B) = 1 - 1/2N_A^0 N = 1 - 1/2N_B^0 N \qquad (6)$$

2. $N_A^0 > N_B^0$ $(q > 1)$

Here two unreacted functional groups should remain. They belong to Reagent A, i.e.,

$$N_A^0 N f_A - N_B^0 N f_B = 2$$

hence

$$N_A^0 - N_B^0 = 1/N \qquad (7)$$

3. $N_A^0 < N_B^0$ $(q < 1)$

Here two unreacted functional groups should remain. They belong to Reagent B, i.e.,

$$N_B^0 N f_B - N_A^0 N f_A = 2$$

hence

$$N_B^0 - N_A^0 = 1/N \qquad (8)$$

Expressions (5)-(8) are conditions under which there is a theoretical possibility of forming from the entire mass of the original reagents the only macromolecule with a linear structure.

For the case q = 1, the quantity of molecules of the polycondensate will be determined only by the extent of the reaction. At n molecules, which corresponds to 2n unreacted functional groups, the extent of reaction will be

$$x = (N_A^0 N f_A + N_B^0 N f_B - 2n)/(N_A^0 N f_A + N_B^0 N f_B) = 1 - n/2N_A^0 N =$$

$$1 - n/2N_B^0 N \qquad (9)$$

(compare with Eq. 6).

For the same case, Eq. (1) will be

$$P_{\text{lim}} = 2N_A^0 N = 2N_B^0 N \qquad (10)$$

From Eqs. (9) and (10) we have

$$x = 1 - n/P_{lim} \tag{11}$$

and from Eqs. (11) and (3) we find

$$\overline{P}_n = 1/(1 - x) \tag{12}$$

Expression (12) is identical to the one derived earlier by other methods [3, 4], only here x may change from 0 to x_{lim} (according to Eq. 6) and $\overline{P}_n$ from 1 to P_{lim} (according to Eq. 1 or 10).

For the cases $q \neq 1$ the quantity of molecules of polycondensate will depend both on the extent of reaction and on a chosen ratio of the original reagents. Let us examine the case $q > 1$. Here the reaction may be completed but the remaining unreacted part will be a part of the functional groups, belonging to Reagent A, according to which and, consequently, according to the total quantity of all the functional groups of the original reagents, the reaction will not be completed. The quantities of the reacted functional groups of Reagents A and B will be equal:

$$x_A N_A^0 Nf_A = x_B N_B^0 Nf_B$$

or taking into account Eq. (5),

$$N_A^0 x_A = N_B^0 x_B \tag{13}$$

Dividing both parts of Eq. (13) by N_B^0, we find

$$qx_A = x_B \tag{14}$$

At the same time it is possible to equate the total quantities of the reacted functional groups expressed in terms of the total extent of the reaction and in terms of the extent of the reaction according to the functional groups of each species:

$$x_A N_A^0 Nf_A + x_B N_B^0 Nf_B = x(N_A^0 Nf_A + N_B^0 Nf_B)$$

or taking into account Eq. (5),

$$N_A^0 x_A + N_B^0 x_B = (N_A^0 + N_B^0)x \tag{15}$$

Dividing both parts of Eq. (15) by N_B^0, we have

$$qx_A + x_B = (q + 1)x \tag{16}$$

From Eqs. (14) and (16) we can find that

$$x = 2x_B/(q + 1) = 2qx_A/(q + 1) \tag{17}$$

(at $q = 1$, $x = x_A = x_B$).

The limiting value of x (in the present case it is better to use the term "maximum") is realized when $x_B = 1$:

$$x_{max} = 2/(q + 1) \tag{18}$$

and the maximum value of x_A according to Eq. (14) is equal to

$$x_{max} = 1/q$$

At $x_B = 1$ the rest of the unreacted functional groups of Reagent A will be

$$N_A^0 Nf_A - N_B^0 Nf_B = 2NN_B^0 (q - 1)$$

The quantity of molecules of the polycondensate will be equal to

$$n = NN_B^0 (q - 1) \tag{19}$$

We transform Eqs. (1) and (2) into

$$P_{lim} = NN_B^0 (q + 1) \tag{20}$$

and

$$M_{lim} = NN_B^0 (qM_A + M_B - g/N_B^0) \tag{21}$$

The maximum average degree of polycondensation and molecular weight, corresponding to $x_B = 1$ from Eqs. (20) and (19) and from Eqs. (21) and (19) as per Eqs. (3) and (4) will be equal to

$$\overline{P}_{n\,\max} = (q + 1)/(q - 1) \tag{22}$$

$$\overline{M}_{n\,\max} = (qM_A + M_B - g/N_B{}^0)/(q - 1) \tag{23}$$

Expression (22), identical to the one obtained earlier [5], characterizes the entire mass of the polycondensate. The quantity of unreacted Reagent A in the polycondensate, the average degree of polycondensation of which is determined by Eq. (22), can be found by a known method [6] and then the degree of polycondensation of the remaining mass of the polycondensate will be $(3q - 1)/(q - 1)$.

From Eq. (22) it follows that any odd value of $\overline{P}_{n\,\max}$, being equal to $2\mu + 1$, the ratio of the quantities of the moles of Reagents A and B per 1 mole of the polycondensate should be equal to $(\mu + 1)/\mu$.

For an arbitrary value of x_B, the remaining unreacted functional groups of Reagents A and B will be

$$N_A^0 N f_A (1 - x_A) + N_B^0 N f_B (1 - x_B)$$

and taking into account Eqs. (5) and (14), this value will be equal to

$$2NN^0_B (q + 1 - 2x_B)$$

The quantity of molecules of the polycondensate will be equal to half of this value:

$$n = NN^0_B (q + 1 - 2x_B) \tag{24}$$

Then from Eqs. (20) and (24) and from Eqs. (21) and (24) we find

$$\overline{P}_n = \frac{1}{1 - 2x_B/(q + 1)} = \frac{1}{1 - 2qx_A/(q + 1)} = 1/(1 - x) \tag{25}$$

and

$$\overline{M}_n = \frac{qM_A + M_B - g/N_B^0}{q + 1}\,\overline{P}_n \tag{26}$$

Thus in linear polycondensation the average degree of polycondensation, expressed in terms of the extent of the reaction for all the functional groups, does not depend on the ratio of the original reagents;

however, if we express it in terms of the extent of the reaction for the functional groups of the original reagents taken separately, then it depends on the ratio of the original reagents (refer to Eq. 25). The extent of the reaction for all the functional groups of the original reagents may vary from 0 to $x_{max} = 2(q + 1)$ (refer to Eq. 18). The multiplier $(qM_A + M_B - g/N_B^0)/(q + 1) = (N_A^0M_A + N_B^0M_B - g)/(N_A^0 + N_B^0)$ in the equation for determining the number-average molecular weight (Eq. 26) has a physical meaning for the averaged molecular weight of a unit used to determine the actual weight ratios of the polycondensate fractions [7]. The average molecular weight, independent of the extent of the reaction in the terms in which it is expressed, depends on the ratio of the original reagents, except for the case when $M_A = M_B$ (in which case the nature of the dependence is the same as for the average degree of polycondensation).

BRANCHED POLYCONDENSATION

Polycondensates which contain branched molecules can be formed only in those cases when f_A and f_B are more than 2 or one of them is equal to 2 and the other one is more than 2. In this case the polymers (oligomers) obtained can range from those ideally branched to three-dimensional network ones.

By "ideally branched molecule" we shall understand a particle in which there is not a single closed cycle at the expense of the reactions of the functional groups.

The average degree of polycondensation and molecular weight can also be found by dividing the corresponding limiting values by the number of polycondensate molecules. However, in contrast to linear polycondensation, the number of molecules in the polycondensate is somewhat more difficult to determine here since the number of ends of the polymer particles is more than two, and with an increase in the degree of polycondensation the functionality of the polymer (oligomer) molecules likewise increases.

Here it is probably expedient to proceed from the most common case, viz:

$$N_A^0f_A \neq N_B^0f_B$$

Let us take $N_A^0f_A > N_B^0f_B$ and try to determine the ratios between N_A^0 and N_B^0 necessary for the formation of the ideally branched product. It is evident that at the completion of the reaction for the functional groups of Reagent B ($x_B = 1$), unreacted functional groups belonging to Reagent A will be left on the product molecules.

If we presume that every ideally branched molecule is formed by a molecules of Reagent A and b molecules of Reagent B, then the problem first consists of finding the ratio between a and b.

The structure of the ideally branched molecule can be presented as follows: Units from Molecule B are joined stepwise to a unit from Molecule A, then units from A, and then units from B, etc. to the last end units of A. Here, besides the first unit from molecule A, there will be (f_B - 1) units of A for each joined unit of B (in all b) and the degree of polycondensation and molecular weight can be presented as

$$\overline{P}_n = a + b = 1 + b + b(f_B - 1) = bf_B + 1 \qquad (27)$$

and hence

$$a = b(f_B - 1) + 1 \qquad (28)$$

and

$$\begin{aligned}\overline{M}_n &= M_A + bM_B + b(f_B - 1)M_A - g \\ &= [b(f_B - 1) + 1]M_A + bM_B - g \qquad (29)\end{aligned}$$

From Eq. (29) it can also be seen that the ratio between a and b corresponds to Eq. (28). The same ratio between a and b is likewise obtained with another order of the imaginary construction of the ideally branched polymer (oligomer) molecule.

If all the quantities of the original reagents are transformed into one polymer molecule, then

$$a = N_A{}^0N, \qquad b = N_B{}^0N \qquad (30)$$

Substituting Eq. (30) into Eq. (28) gives

$$N_A{}^0 - N_B{}^0(f_B - 1) = 1/N \qquad (31)$$

If from the total quantities of the original reagents n molecules of the polycondensate are formed, then as an average each of them will have

$$\bar{a} = N_A{}^0N/n, \qquad \bar{b} = N_B{}^0N/n \qquad (32)$$

Substituting Eq. (32) into Eq. (28) gives

$$N_A^0 - N_B^0(f_B - 1) = n/N \tag{33}$$

Expression (33) determines the quantity of moles of an ideally branched product which can be formed from N_A^0 and N_B^0 moles of Reagents A and B at $N_A^0 f_A > N_B^0 f_B$.

The expressions for the average degree of polycondensation and molecular weight can be found from Eq. (1), (2), and (33):

$$\overline{P}_n = \frac{N^0_A + N^0_B}{N_A^0 - N_B^0(f_B - 1)} \tag{34}$$

and

$$\overline{M}_n = \frac{M_A N_A^0 + M_B N_B^0 - g}{N_A^0 - N_B^0(f_B - 1)} \tag{35}$$

The denominators in Eqs. (34) and (35), according to Eq. (31), cannot be less than 1/N since physically not less than one molecule of the product can be formed, and therefore

$$N_A^0 > N_B^0(f_B - 1) \tag{36}$$

This is the basic condition of the principle possibility of forming an ideally branched polymer at $N_A^0 f_A > N_B^0 f_B$.*

Similarly it is also possible to obtain the conditions for the possibility of forming an ideally branched polymer at $N_A^0 f_A < N_B^0 f_B$:

$$N_B^0 > N_B^0(f_A - 1) \tag{37}$$

Proceeding from Eqs. (36) and (37), it is also possible to give a general representation of the conditions under which the formation

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*For the bifunctional reagents of a strictly linear polymer.

of ideally branched polymers at the completion of the reaction becomes impossible in principle, i.e.:

$$(f_B - 1) \leq N_A^0/N_B^0 \leq 1/(f_A - 1) \quad (38)$$

This region of ratios between N_A^0 and N_B^0 will be called the region of "forbidden" reagent ratios for the formation of ideally branched polymers.

From the existance of this region it follows that if the initial ratios of the reagents are such that they are found inside this forbidden region, then the polymer which is formed at the completion of the reaction is a cross-linked polymer, in which case the formation of the three-dimensional network begins at the separate growing macromolecules until the reaction is fully completed and, thus, the total network of the polymer can be formed of separate macromolecules which became networks by themselves; i.e., it can represent a rather irregular structure in which more closely-spaced segments of the network are interconnected with comparatively widely spaced cross-links. The last conclusion, formed for ideal conditions, holds even more for real systems in which the possibility of the formation of intramolecular cycles—primary network nuclei—is determined by the inevitable competition of the cyclization reaction and the continuation of the polymer chain, which is already well-known.

Let us assume then that at $N_A^0 f_A > N_B^0 f_B$ the reaction is not completed, i.e., a polycondensate is obtained at some arbitrary value of x_B. If at the completion of the reaction n molecules of the polycondensate are formed, then at one unreacted group from Reagent B there will be n + 1 molecules, two groups of n + 2, and if $N_B^0 Nf_B(1 - x_B)$ functional groups of Reagent B do not react, then the quantity of the molecules of the product will be

$$n_{x_B} = n + N_B^0 Nf_B(1 - x_B) = N_A^0 N - N_B^0 N(f_B x_B - 1) \quad (39)$$

The number-average degree of polycondensation and molecular weight from Eqs. (1), (2), and (39), in accordance with Eqs. (3) and (4), will be equal to

$$\overline{P}_n = \frac{N_A^0 + N_B^0}{N_A^0 - N_B^0(f_B x_B - 1)} \quad (40)$$

and

$$\overline{M}_n = \frac{M_A N_A^0 + M_B N_B^0 - g}{N_A^0 - N_B^0 (f_B x_B - 1)} \tag{41}$$

In the same manner as from Eqs. (36) and (37), from Eqs. (40) and (41) we can formulate the required condition for the formation of an ideally branched product:

$$N_A^0 > N_B^0 (f_B x_B - 1); \quad N_B^0 > N_A^0 (f_A x_A - 1) \tag{42}$$

And as from Eq. (38), from Eq. (42) we obtain:

$$(f_B x_B - 1) \leq N_A^0 / N_B^0 \leq 1/(f_A x_A - 1) \tag{43}$$

Expression (43) gives the conditions under which the formation of an ideally branched polymer is "forbidden" in the incomplete reaction. In comparing Eq. (43) with Eq. (38), we find that for an incomplete reaction the region of the forbidden ratios for the formation of ideally branched products of polycondensation becomes narrower.

Comparing Eqs. (40) and (41) with Eqs. (34) and (35), we see that the product $f_i x_i$ can be considered as the effective functionality of the reagent in a given incomplete reaction.

Just as in the linear polycondensation, here also a question may arise of the connection between the extent of reaction expressed both in terms of the total quantity of the functional groups and in terms of the quantities of the functional groups of Reagents A and B.

From the fact that the quantities of the reacted functional groups of reagents are equal to one another,

$$x_A N_A^0 f_A = x_B N_B^0 f_B$$

we have

$$q f_A x_A = f_B x_B; \quad Q x_A = x_B \tag{44}$$

At the same time

$$x_A N_A^0 f_A + x_B N_B^0 f_B = x(N_A^0 f_A + N_B^0 f_B) \tag{45}$$

Let us divide Eq. (45) by N_B^0 or by $N_B^0 f_B$:

$$qf_A x_A + f_B x_B = (qf_A + f_B)x \quad \text{or} \quad Qx_A + x_B = (Q + 1)x \tag{46}$$

From Eqs. (44) and (46) we find

$$x = 2f_B x_B/(qf_A + f_B) = 2qf_A x_A/(qf_A + f_B) \tag{47}$$

and

$$x = 2x_B/(Q + 1) = 2Qx_A/(Q + 1) \tag{48}$$

We can now also express the average degree of polycondensation and molecular weight in terms of the ratios of the reagents of the reacting groups.

For example, for the case $N_A^0 f_A > N_B^0 f_B$ let us divide the numerator and denominator in the right-hand part of Eq. (40) by N_B^0, and after some transformations we shall have

$$\overline{P}_n = \frac{1}{1 - f_B x_B/(q + 1)} = \frac{1}{1 - qf_A x_A/(q + 1)} = \frac{1}{1 - x(qf_A + f_B)/2(q + 1)} \tag{49}$$

But if we divide the numerator and denominator in Eq. (40) by $N_B^0 f_B/f_A$, we shall then have

$$\overline{P}_n = \frac{1}{1 - f_A x_B/(Q + f_A/f_B)} = \frac{1}{1 - Qf_A x_A/(Q + f_A/f_B)}$$

$$= \frac{1}{1 - xf_A(Q + 1)/2(Q + f_A/f_B)} \tag{50}$$

Similar operations can be carried out with Eq. (41), and the number-average molecular weight can be expressed in terms of the ratios of the original reagents or their functional groups depending on extent of reaction, both for all the functional groups and for the functional groups of each of the reagents taken separately.

THEORETICAL GEL POINT

Let us now proceed to the solution of the question: At what extent of the reaction at different functionalities and different original ratios of the reagents can the only ideally branched molecule of a polymer be formed in principle, i.e., the question of the theoretical gel point.

To make it more simple, let us start with the case $N_A^0 f_A = N_B^0 f_B$. Here, as was shown above, $x = x_A = x_B$. Theoretically only one molecule may be formed if Eq. (39) is valid at $n_{x_B} = 1$, i.e.,

$$1 = N_A^0 N - N_B^0 N(f_B x_B - 1)$$

but since here $x_B = x = x_g$, then

$$1 = N_A^0 N - N_B^0 N(f_B x_g - 1)$$

Let us substitute N_B^0 with an equal value of $N_A^0 f_A/f_B$:

$$1 = N_A^0 N - N_A^0 N f_A (f_B x_g - 1)/f_B \qquad (51)$$

The solution of Eq. (51) relative to x_g yields

$$x_g = 1/f_A + 1/f_B - 1/N_A^0 N f_A \qquad (52)$$

Neglecting the last term in Eq. (52), which is small relative to others, we find

$$x_g = 1/f_A + 1/f_B \qquad (53)$$

If $f_A = f_B = f$, then

$$x_g = 2/f \qquad (54)$$

The last expression is identical to the one derived earlier [8]. By using Eqs. (53) and (54) it is possible to determine the average functionality of the system of Reagents A and B:

$$2/f_m = 1/f_A + 1/f_B$$

Hence

$$f_m = 2f_A f_B/(f_A + f_B) \tag{55}$$

It should be remembered that this average functionality pertains only to the case $N_A^0 f_A = N_B^0 f_B$.

If, however, $N_A^0 f_A > N_B^0 f_B$, then proceeding from Eq. (39), where $x_B = x_{Bg}$:

$$1 = N_A^0 N - N_B^0 N(f_B x_{Bg} - 1)$$

we have

$$x_{Bg} = N_A^0/N_B^0 f_B + 1/f_B - 1/N_B^0 N f_B = (q + 1)/f_B - 1/N_B^0 N f_B \tag{56}$$

Neglecting the last term in Eq. (56), we have

$$x_{Bg} = (q + 1)/f_B \tag{57}$$

or

$$x_{Bg} = Q/f_A + 1/f_B - 1/N_B^0 N f_B \tag{58}$$

and neglecting the last term in Eq. (58):

$$x_{Bg} = Q/f_A + 1/f_B \tag{59}$$

But, according to Eqs. (47) and (48),

$$x_{Bg} = x_g(qf_A + f_B)/2f_B = x_g(Q + 1)/2 \tag{60}$$

Substituting Eq. (60) into Eqs. (57) and (59):

$$x_g(qf_A + f_B)/2 = q + 1; \qquad x_g(Q + 1)/2 = Q/f_A + 1/f_B$$

Hence

$$x_g = 2(q + 1)/f_A(q + f_B/f_A) = 2(q + 1)/f_B(qf_A/f_B + 1) \tag{61}$$

$$x_g = 2(Q + f_A/f_B)/f_A(Q + 1) = 2(Qf_B/f_A + 1)/f_B(Q + 1) \tag{62}$$

At $f_A - f_B = f$, as is seen from Eqs. (61) and (62),

$$x_g = 2/f$$

i.e., at equal functionality of Reagents A and B, the gel point, expressed in terms of the extent of the reaction for all the functional groups, does not depend on the ratio of the original reagents.

From Eqs. (61) and (62) it is also possible to find the expressions for the average functionality f_m of the system of Reagents A and B taken in unequivalent quantities:

$$2/f_m = 2(q + 1)/f_A(q + f_B/f_A) = 2(Q + f_A/f_B)/f_A(Q + 1)$$

$$f_m = (qf_A + f_B)/(q + 1) = (Q + 1)/(Q/f_A + 1/f_B) \tag{63}$$

Here the question is if there is a real possibility of reaching the required (in accordance with the calculation) degree of completion of the reaction since, according to Eqs. (47) and (48),

$$x_{max} = 2f_B/(qf_A + f_B) = 2(Q + 1) \tag{64}$$

We may determine the value of q (or Q) at which we can still hope for the possibility of realizing gelation. It can be found from the condition

$$x_g < x_{max}$$

$$2(q + 1)/f_A(q + f_B/f_A) \leq 2f_B/(qf_A = f_B)$$

Substituting the value of q, we have

$$N_A{}^0 \leq N_B{}^0 (f_B - 1) \tag{65}$$

By carrying out similar deductions for the case $N_A{}^0 f_A < N_B{}^0 f_B$, we have

$$N_B{}^0 \leq N_A{}^0 (f_A - 1) \tag{66}$$

Combining Eqs. (66) and (65),

$$(f_B - 1) \geq N_A{}^0 / N_B{}^0 \geq 1(f_A - 1) \tag{67}$$

Expression (67) is identical to Eq. (38), limiting the region of the forbidden ratios of the reagents for forming the ideally branched polymers. Thus, as was to be expected, we may hope in principle to obtain gelation by working only in that region of the ratios of reagents which is forbidden for the formation of the ideally branched polymers (polycondensates).

RELATION BETWEEN NUMBER-AVERAGE MOLECULAR WEIGHT AND CONTENT OF FUNCTIONAL GROUPS IN THE POLYCONDENSATE

For the case of the completed reaction it is not difficult to find the relationship between the number-average molecular weight of the polycondensate and the content of the residual functional groups in it.

At $N_A{}^0 f_A > N_B{}^0 f_B$ the quantity of the residual functional groups belonging to Reagent A at completion of the reaction will be

$$(N_A{}^0 f_A - N_B{}^0 f_B) N$$

while the quantity of their moles will be equal to

$$N_A{}^0 f_A - N_B{}^0 f_B \tag{68}$$

the total weight of the polycondensate being

$$N_A{}^0 M_A + N_B{}^0 M_B - g \tag{69}$$

If the molecular weight of the functional groups of Reagent A is equal to m_A, then from Eqs. (58) and (69) we find the following expression for the percentage content of these functional groups:

$$\varphi_A = 100m_A(N_A^0 f_A - N_B^0 f_B)/(N_A^0 M_A + N_B^0 M_B - g) \tag{70}$$

The problem for the case $N_A^0 f_A < N_B^0 f_B$ is solved similarly. Here the percentage content of the functional group remaining from Reagent B in the polycondensate at completion of the reaction will be equal to

$$\varphi_B = 100m_B(N_B^0 f_B - N_A^0 f_A)/(N_A^0 M_A + N_B^0 M_B - g) \tag{71}$$

Let us multiply Eqs. (35) and (70) by parts and solve relative to M_n:

$$\overline{M}_n = \frac{N_A^0 f_A - N_B^0 f_B}{N_A^0 - N_B^0(f_B - 1)} \; \frac{100m_A}{\varphi_A} = F_A \frac{100m_A}{\varphi_A} \tag{72}$$

Similarly for the case $N_A^0 f_A < N_B^0 f_B$:

$$\overline{M}_n = \frac{N_B^0 f_B - N_A^0 f_A}{N_B^0 - N_A^0(f_A - 1)} \; \frac{100m_B}{\varphi_B} = F_B \frac{100m_B}{\varphi_B} \tag{73}$$

Factors F_A and F_B in Eqs. (72) and (73) characterize the average functionality of the polycondensate particles formed in the completed reaction at $N_A^0 f_A > N_B^0 f_B$ and $N_A^0 f_A < N_B^0 f_B$: respectively, in the region of not forbidden original reagent ratios for the formation of ideally branched molecules of the product.

INFLUENCE OF FORMATION OF INTRAMOLECULAR CYCLES

Let us assume now that in the reaction between A and B the ideally branched product is not formed and on the average z closed cycles occur per each of its molecules.

In this case it is likewise possible to proceed from the expressions of Types (28) and (30), but the ratio between a and b will be different. Carrying out, just as before, an imaginary construction of a polymer particle for the case $N_A{}^0 f_A > N_B{}^0 f_B$, and taking into account that the formation of z intramolecular cycles is accompanied by a reduction of the quantity of the molecules of Reagent A incorporated in this particle by z, we can write:

$$\overline{P}_n = 1 + b + b(f_B - 1) - z = bf_B + 1 - z = A + b \tag{74}$$

and

$$\overline{M}_n = M_A + bM_B + b(f_B - 1)M_A - zM_A - g = [b(f_B - 1) + (1 - z)]\, M_A + bM_B - g \tag{75}$$

From Eqs. (74) and (75) it is seen that

$$a = b(f_B - 1) + (1 - z) \tag{76}$$

If all the quantities of the original reagents are transformed into one polymer molecule, then substituting Eq. (30) into Eq. (76) will yield

$$N_A{}^0 N = N_B{}^0 N(f_B - 1) + (1 - z) \tag{77}$$

If, however, n polycondensate molecules are formed, then by substituting Eq. (32) into Eq. (76) we shall have

$$N_A{}^0 N = N_B{}^0 N(f_B - 1) + (1 - z)n$$

or

$$n = \frac{N_A{}^0 N - N_B{}^0 N(f_B - 1)}{1 - z} \tag{78}$$

Dividing Eqs. (1) and (2) by Eq. (78) we shall have

$$\overline{P}_n = \frac{N_A^0 + N_B^0}{N_A^0 - N_B^0(f_B - 1)}(1 - z) \tag{79}$$

and

$$\overline{M}_n = \frac{M_A N_A^0 + M_B N_B^0 - g}{N_A^0 - N_B^0(f_B - 1)}(1 - z) \tag{80}$$

Thus, at the appearance of intramolecular cycles in z quantity per particle, on the average the average degree of polycondensation and molecular weight will differ from the corresponding values for an ideally branched product by a factor of (1 - z).

When analyzing Eqs. (79) and (80) we are faced with an interesting case, viz., $z = 1$. In this case $\overline{P}_n$ or $\overline{M}_n$ would not be equal to zero, which would be an absurdity, for it would be necessary that the denominators in Eqs. (79) and (80) would also be transformed into zero. Then $\overline{P}_n = \infty$ and $\overline{M}_n = \infty$, i.e., if on the average there is one cycle per one molecule in the polycondensate, the molecular weight cannot be found by an analytical calculation. At $z > 1$ the denominator should change its sign, i.e., then the ratio of the reagents should pass into the forbidden region for the formation of ideally branched products. In this region of ratios of the reagents the growing macromolecules should actually be the primary nucleus for the three-dimensional network.

For the case $N_A^0 f_A < N_B^0 f_B$, Eqs. (79) and (80) will be written as

$$\overline{P}_n = \frac{N_A^0 + N_B^0}{N_B^0 - N_A^0(f_A - 1)}(1 - z) \tag{81}$$

and

$$\overline{M}_n = \frac{M_A N_A^0 + M_B N_B^0 - g}{N_B^0 - N_A^0(f_A - 1)}(1 - z) \tag{82}$$

It is easy to show that during the formation of the polycondensation product containing intramolecular cycles, the relationship between the average degree of polycondensation and molecular weight and the content of the residual functional groups will also be changed, and Eqs. (72) and (73) will be transformed as follows.

For the case $N_A^0 f_A > N_B^0 f_B$:

$$\overline{M}_n = 100m_A(1 - z)\frac{N_A^0 f_A - N_B^0 f_B}{N_A^0 - N_B^0(f_B - 1)} = F_A \frac{100m_A}{\varphi_A} \tag{83}$$

and for $N_A^0 f_A < N_B^0 f_B$:

$$\overline{M}_n = 100m_B(1 - z)\frac{N_B^0 f_B - N_A^0 f_A}{N_B^0 - N_A^0(f_A - 1)} = F_A \frac{100m_B}{\varphi_B} \tag{84}$$

Here the average functionality of the polycondensate particles will differ from the case of an ideally branched product by the factor (1 - z).

It is probably expedient in this section to study once more the question of the theoretical gel point. It is evident that the formation of one intramolecular cycle corresponds to the reaction between two functional groups belonging to the same growing particle. This means that if in an ideally branched particle z cycles do not appear in the gel point, then 2z functional groups have not reacted.

If, as we have assumed, $N_A^0 f_A = N_B^0 f_B$, then at the extent of the reaction corresponding to the theoretical gel point x_g, the residual unreacted groups will be

$$2z = 2N_A^0 N f_A(1 - x_g)$$

Hence

$$x_g = 1 - z/N_A^0 N f_A \tag{85}$$

On the other hand, if the only molecule of a polymer consists of a molecules of A and b molecules of B, then according to Eq. (30),

$$a = N_A^0 N; \qquad b = N_B^0 N$$

and according to Eq. (77),

$$N_A^0N = N_B^0N(f_B - 1) + (1 - z)$$

Hence

$$z = 1 + N_A^0N(f_A - f_A/f_B - 1) \tag{86}$$

Substituting Eq. (86) into Eq. (85):

$$x_g = 1/f_B + 1/f_A - 1/N_A^0Nf_A$$

i.e., the same as Eq. (53).

If the whole system has been transformed into one molecule of a polymer, then according to Eq. (85):

$$2z = 2N_A^0f_A(1 - x_g)$$

If there are two particles, then two more unreacted groups are added; if three, four more; i.e., every new pair of unreacted groups corresponds to an extra particle of the polycondensate. That means that at $(z + \sigma)$ pairs of unreacted functional groups the quantity of the particles will be $(\sigma + 1)$. Therefore, in the case of ideally branched particles we can write

$$2(z + \sigma) = 2N_A^0Nf_A(1 - x) \tag{87}$$

Substituting z from Eq. (86) into Eq. (87), we have:

$$x = 1/f_A + 1/f_B - (\sigma + 1)/N_A^0Nf_A \tag{88}$$

(at $\sigma = 0$, Eq. 88 is transformed into Eq. 52).

From Eq. (88) it is seen that in the region of the gelation, very large changes in the quantity of the particles in the polycondensate $(\sigma + 1)$ have very little effect on the extent of reaction and vice versa. At an almost constant extent of reaction, close to the gel point, it is possible to have a sufficiently high quantity of particles and, consequently, a wide range of variation in their average degree of polycondensation and molecular weight.

CONCLUSION

By examining examples of the utilization of the stoichiometric approach to the study of the polycondensation process, we have obviously not exhausted all its possibilities. Apparently it is expedient to modify the forms of this approach to make them applicable to some real systems, depending upon the concrete problems which are to be solved. It is possible that this method will be useful when examining the reactions in polycondensation multicomponent systems when the original reagents are of different functionality or are mixtures of single-type reagents containing fractions of different functionalities.

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Accepted by editor September 10, 1974
Received for publication November 8, 1974