Block length distribution in finite polycondensation copolymers

E. Sorta and the Late A. Melis
Snamprogetti S.p.A., Direzione Ricerca e Sviluppo, San Donato Milanese, Milan, Italy
(Received 7 April 1978; revised 22 May 1978)

A statistical theory has been developed which allows the homopolymeric block length to be obtained in a statistical copolymer with finite length. The results were tested numerically by a Monte Carlo method. Application to a class of copolyether–estereamides has been made.

INTRODUCTION

Some years ago polymer material technologists focussed their attention on so-called thermoplastic elastomers. Such elastomers are copolymers which yield two phases: the first, called the 'hard phase', can be formed by crystalline, paracrystalline or glassy amorphous material and impairs the dimensional stability of the second phase called the 'soft phase' responsible for the elastomeric behaviour. The monomers, which constitute the copolymer, are grouped in blocks as a consequence of sequential homopolymerization or statistical copolymerization. The homopolymeric block lengths and their distribution influence the copolymer properties[1]. It is generally assumed[2] that the hard and soft segments, in the case of polycondensation copolymers, are randomly distributed and in the case of a high degree of polymerization it is possible to introduce a statistical average degree of copolymerization. The finite nature of the chain length makes the definition of the degree of polymerization more difficult because it is necessary to take into account the termination probability. Up to this time only the fraction of macromolecules with a given number of blocks of specified length has been calculated[2] in finite macromolecules. In the present paper the average length of the homopolymeric blocks and their distribution in polymers with relatively low molecular weight has been calculated. The results, tested by the Monte Carlo method were applied to polyether–estereamide copolymers developed in our laboratory[3].

THEORETICAL

The copolymer was synthesized by random polymerization of two bifunctional monomers A and B having the same reactivity and initial molar concentrations X_A and X_B, respectively. The macromolecules, constituted by a set of A and B blocks, have the general formula:

$$\mathrm{I} \ldots \mathrm{A}_{x_i}\mathrm{B}_{y_i} \ldots \mathrm{T}$$

where I and T represent monomers (A or B) which reacted monofunctionally, A_{x_i} and B_{y_i} are the ith homopolymer blocks. Owing to the random distribution of the block lengths it is reasonable to attempt to define a statistical average degree of polymerization, $\bar{n}$, so that the general formula of the average macromolecule should be:

$$\mathrm{I}(\mathrm{A}_{\bar{k}_A}\mathrm{B}_{\bar{k}_B})_{\bar{n}}\mathrm{T}$$

where $\bar{k}_A$ and $\bar{k}_B$ are the average length of the A and B blocks. $\bar{k}_A$ and $\bar{k}_B$ can be calculated from the equations[4]:

$$\bar{k}_A = \frac{1}{1 - P_{AA}}; \quad \bar{k}_B = \frac{1}{1 - P_{BB}} \tag{1}$$

where P_{pq} is the conditional probability of the occurrence of a unit q, given that the preceding unit is p. In the case of infinite chain length[2]:

$$P_{AA} = X_A; \quad P_{BB} = X_B \tag{2}$$

To take into account the finite nature of the chain it is necessary to introduce the termination probability $P_T(P_{AT}$ or $P_{BT})$[5]. Expression (2) becomes:

$$P_{AA} = X_A(1 - P_T); \quad P_{BB} = X_B(1 - P_T) \tag{3}$$

In order to calculate P_{AA} and P_{BB} modified in this manner, it is convenient to build up a statistical model. Let us take two urns: the first one contains the initial monofunctional units A– or B–, generically indicated I; the second one contains the bifunctional units –A– and –B– as well as the terminal units –A and –B, the last two indicated generically by T. The relative amounts in the second urn are x_A, x_B and x_T for the –A–, –B– and T units with $x_A + x_B + x_T = 1$. The composition of the I and T units coincide with the initial monomer composition X_A and X_B. To build up a macromolecule it is necessary to draw out the initial unit I from the first urn, then A and B units from the second urn until a T unit is extracted. After any extraction the compositions in the urns do not change.

From the material balance the following relations are obtained:

$$x_A = (1 - x_T)X_A; \quad x_B = (1 - x_T)X_B \tag{4}$$

The transition probabilities P_{AA}, P_{BB}, P_{AB}, P_{BA}, P_{AT} and P_{BT} depend on the second urn composition and these expressions result:

$$P_{AA} = P_{BA} = x_A$$

$$P_{BB} = P_{AB} = x_B$$

0032–3861/78/101153–04$02.00

$$P_{AT} = P_{BT} = x_T$$

The average chain length (equation 1) becomes:

$$\bar{k}_A = \frac{1}{1-x_A}; \quad \bar{k}_B = \frac{1}{1-x_B} \tag{5}$$

Owing to the distribution of the chain lengths it is possible to obtain the following species of macromolecules: (i) IT; (ii) IA_mT; (iii) IB_nT; (iv) I$(A_xB_y)_z$T where only the last sequence is a true copolymer macromolecule.

The frequency f_1 of the species (i) is x_T because x_T represents the fraction of units, T, in the second urn. The frequencies f_2 and f_3 of the species (ii) and (iii) are given by the composite probability:

$$f_2 = \sum_{m=1}^{\infty} x_A^m x_T = \frac{x_T x_A}{1-x_A} = x_A x_T \bar{k}_A$$

similarly, $f_3 = x_B x_T \bar{k}_B$. For species (ii) and (iii) the average lengths of the A and B blocks are $\bar{k}_A$ and $\bar{k}_B$; for the species (ii):

$$\frac{\sum_{m=1}^{\infty} m x_A^m x_T}{\sum_{m=1}^{\infty} x_A^m x_T} = \frac{1}{1-x_A} = \bar{k}_A$$

similarly for the species (iii). The frequency, f_4, for species (iv) is:

$$f_4 = 1 - f_1 - f_2 - f_3$$

i.e.

$$f_4 = 1 - x_T(1 - x_A\bar{k}_A - x_B\bar{k}_B)$$

The weight-average molecular weights, M_i, of the four species are:

$$M_1 = M_I + M_T$$

$$M_2 = M_1 + \bar{k}_A M_A$$

$$M_3 = M_1 + \bar{k}_B M_B$$

$$M_4 = M_1 + \bar{n}(\bar{k}_A M_A + \bar{k}_B M_B)$$

where M_I and M_T are the average molecular weights of the initial and terminal units and M_A and M_B are the molecular weights of the A and B units.

The numerical molecular weight M_n is:

$$M_n = x_T M_1 + x_T x_A \bar{k}_A M_2 + x_T x_B \bar{k}_B M_3 + [1 - x_T(1 + x_A\bar{k}_A + x_B\bar{k}_B)] M_4 \tag{6}$$

In equation (6) there are two terms, $\bar{n}$ and x_T, which must be determined. In order that the equation (6) be solved, it is necessary to find a relation between x_T and $\bar{n}$, linearly independent of equation (6). This can be obtained from the balance of monomers T with respect to the number of monomers A + B + T. Hence we obtain:

$$x_T = \frac{1}{1 + f_2\bar{k}_A + f_3\bar{k}_B + f_4(\bar{k}_A + \bar{k}_B)\bar{n}}$$

and finally the required equation:

$$\bar{n} = \frac{(1/x_T) - 1 - x_T(x_A\bar{k}_A^2 + x_B\bar{k}_B^2)}{(\bar{k}_A + \bar{k}_B)[1 - x_T(1 + x_A\bar{k}_A + x_B\bar{k}_B)]} \tag{7}$$

Knowing X_A and X_B and using the equations (4), (5), (6) and (7) x_T and $\bar{n}$ are completely determined and consequently so are P_{AA} and P_{BB}.

From a practical point of view it is useful to know the following: (a) the probability, $P_A(k)$, that the length of a block of units A is k; (b) the mole fraction, $\chi_A(k)$, of units A (with respect to the total amount of units A) included in blocks of length k; (c) the integral curve of $\chi_A(k)$; (d) the weight fraction $W_A(k)$ of units A (in relation to the total number of the units present in the polymer) included in blocks of length k; (e) the integral curve of $W_A(k)$.

These are given by:

$$\text{(a)} \quad P_A = (1 - x_A)x_A^{k-1}$$

$$\text{(b)} \quad \chi_A(k) = \frac{kP_A(k)}{\sum_{k=1}^{\infty} kP_A(k)} = kx_A^{k-1}(1-x_A)^2$$

$$\text{(c)} \quad \sum_{k}^{\infty} \chi_A(k) = k(1-x_A)x_A^{k-1} + x_A^k \tag{8}$$

$$\text{(d)} \quad W_A(k) = \frac{x_A M_A \chi_A(k)}{x_A M_A + x_B M_B + x_T(M_I + M_T)}$$

$$\text{(e)} \quad \sum_{k}^{\infty} W_A(k) = \frac{x_A M_A[k(1-x_A)x_A^{k-1} + x_A^k]}{x_A M_A + x_B M_B + x_T(M_I + M_T)}$$

Similar expressions are obtained for B units.

APPLICATIONS AND DISCUSSION

The results obtained so far are of great interest for a deeper understanding of the behaviour of statistical copolymers.

As an example a copolymer made via transesterification according to the reaction:

$$6NT + 6G + PTMEG \rightarrow -A- + -B- + I_A- + I_B- + -T_A + -T_B \tag{9}$$

Where:

$6G \equiv HO(CH_2)_6OH$

$PTMEG \equiv HO[(CH_2)_4O]_nH$ with $MW \sim 1000$

Table 1

Parameter	Theoretical values	Monte Carlo values
M_n	30 000	30 375
f_1	0.038	0.037
f_2	0.015	0.015
f_3	0.078	0.081
f_4	0.869	0.867
$\bar{k}_A$	1.41	1.41
$\bar{k}_B$	3.06	3.07

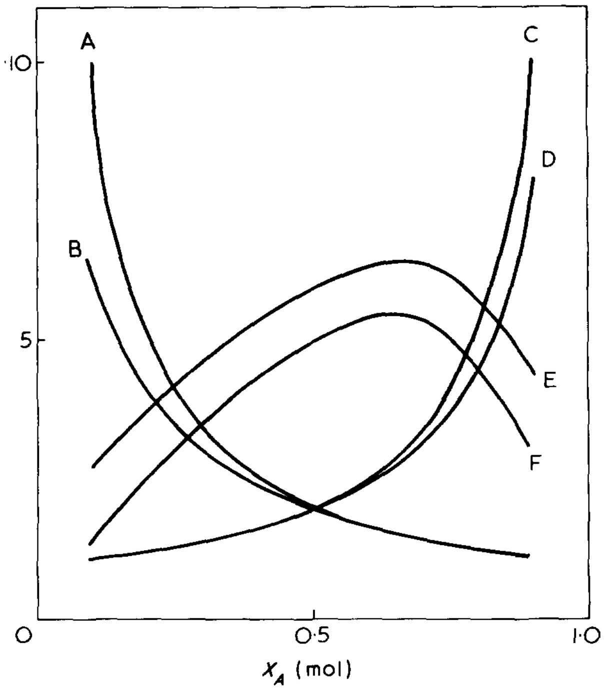
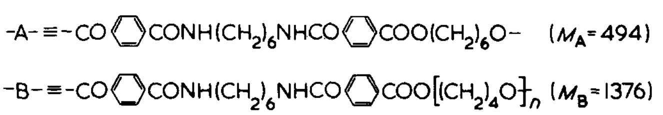


Figure 1 Average lengths of A and B blocks and degree of polymerization for finite (M_n = 20 000) and infinite chain *versus* initial monomer composition A, $\bar{k}_{B\infty}$; B, $\bar{k}_B$, C, $\bar{k}_{A\infty}$; D, $\bar{k}_A$; E, $\bar{n}$; F, $\bar{n}_\infty$



$$I - \begin{cases} I_A - \equiv HO(CH_2)_6O- & (M_{I_A} = 117) \\ I_B - \equiv HO[(CH_2)_4O]_n & (M_{I_B} = 999) \end{cases}$$

$$M_I = X_A M_{I_A} + X_B M_{I_B}$$

$$-T \begin{cases} -T_A \equiv -AH & (M_{T_A} = 495) \\ -T_B \equiv -BH & (M_{T_B} = 1377) \end{cases} \quad M_T = X_A M_{T_A} + X_B M_{T_B}$$

These systems will be examined.

Owing to the polycondensation process, the macromolecules start and end with glycol groups and reaction (9) is always correct.

The use of equations (6), (7) and (8) enables us to calculate the parameters in which we are interested, e.g. $\bar{n}$, $\bar{k}_A$, $\bar{k}_B$, W_A etc., for different M_n and X_A. In order to check the validity of the analysis outlined in the theoretical section, the results were tested numerically by a Monte Carlo method for the copolymers considered. To apply it to the present problem, the computer was used to construct a large number of copolymer molecules (5000 turned out to be an adequate number) in accordance with an appropriate termination probability and a fixed X_A. The simulation gave the $\bar{k}_A$, $\bar{k}_B$, f_i and M_n. In *Table 1* the results obtained by Monte Carlo calculations are compared with the theoretical results for X_A = 0.3 and M_n = 30 000. The agreement is quite satisfactory.

For the copolymers under examination the influence of the finite nature of the chain length is particularly significant for $M_n < 30\,000$.

In *Figure 1*, $\bar{k}_A$, $\bar{k}_B$ and $\bar{n}$ for M_n = 20 000 as a function of X_A and those for infinite chain length, indicated $\bar{k}_{A\infty}$, $\bar{k}_{B\infty}$ and $\bar{n}$ are reported. A point of great interest is to discover the fraction (mole or weight fraction) of macromolecules of different species. For instance the weight frequency distribution of true copolymer, W_4 *versus* X_A is plotted in *Figure 2* for different M_n. The true copolymer exhibits a weight fraction ranging from 0.55 to 0.85 of the polymeric mass for M_n = 10 000 and $0.1 \leqslant X_A \leqslant 0.3$.

Similarly, with other copolymers[6], the crystallization is due to the hard units (–A–) belonging to blocks having k or more units; consequently it is useful to know the weight fraction of the –A– units with respect to the polymer weight.

In *Figure 3*

$$\sum_{k}^{\infty} W_A(k)$$

is plotted *versus* k for different X_A content. Our copolymer and similar classes of copolymers[7] are peculiar in the sense that the –A– and –B– units, which build up the hard and soft phases, contain one identical sequence derived from biesters. This implies, at first, that a block of –A– units

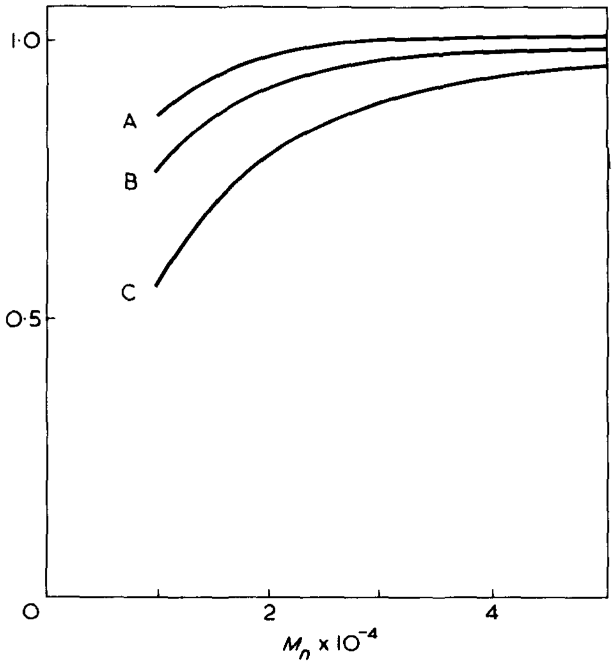


Figure 2 Copolymer weight frequency distribution, w_4 *versus* M_n for different initial monomer compositions A, X_A = 0.3; B, X_A = 0.2; C, X_A = 0.1

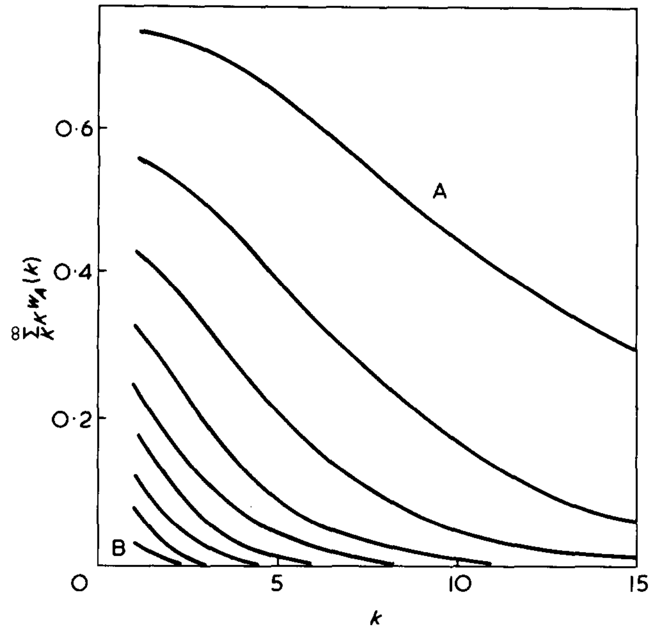


Figure 3 Integral curves of $W_A(k)$ for different monomer compositions *versus* k. A, $X_A = 0.9$; B, $X_A = 0.1$. $M_n = 20\,000$

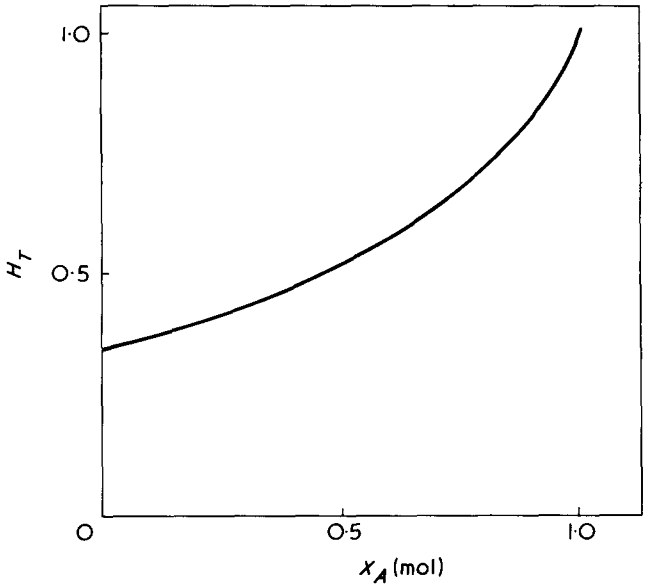
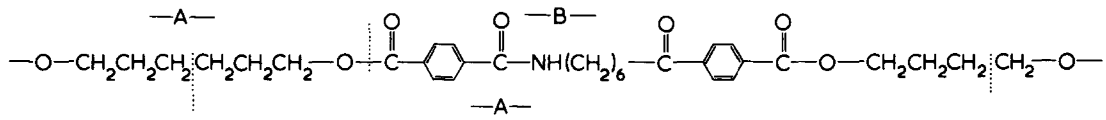


Figure 4 Effective hard phase weight content *versus* initial monomer composition



does not end with the last –A– unit, but continues, incorporating the initial part of a –B– unit according to the scheme scheme shown above.

This is of some importance because the initial part of the –B– block can be crystallized with one preceding –A– block and this is relevant if the number of consecutive –A– units necessary for crystallization is small. In this way the effective hard content is always higher than the theoretical content. We note that isolated –A– units are incorporated in the –B– blocks when the length of the –B– blocks is two or more units. In order to quantify the weight fraction, H_T, of the effective hard phase content, it is sufficient to note that for each molecule of the type (a), (b), (c) and (d), there are 1, $k_A + 1$, $k_B + 1$ and $\bar{n}(\bar{k}_A + \bar{k}_B) + 1$ –A– units. Therefore:

$$H_T = \frac{M_A}{M_n}\{f_1 + f_2(\bar{k}_A + 1) + f_3(\bar{k}_B + 1) + f_4[\bar{n}(\bar{k}_A + \bar{k}_B) + 1]\}$$

The effective hard phase weight content as a function of X_A for $M_n = 20\,000$ is reported in *Figure 4*. Similarly, the effective weight fraction, H_k, of –A– units present in blocks of length k will be:

$$H_k = \frac{kM_A}{M_n}(1 - x_A)^2(k - 1){x_A}^{k-2}[f_2\bar{k}_A + f_4 k\bar{k}_A]$$

with $k \neq 1$

$$H_1 = \frac{M_A}{M_n}\{f_1 + f_3(\bar{k}_B + 1) + f_4[\bar{n}(\bar{k}_B - 1) + 1]\}$$

with $k = 1$ where

$$\sum_{1}^{\infty}{}_k H_k = H_T$$

REFERENCES

1 Harrell Jr, L. L. *Macromolecules* 1969, 2, 607
2 Frensdorff, H. K. *Macromolecules* 1971, 4, 369
3 della Fortuna, G. and Zotteri, L. Italian Pats 25 548 and 23 701
4 Ham, G. E. 'Copolymerization', Interscience, New York, 1964
5 Helfand, E. *Macromolecules* 1972, 5, 301
6 Cella, R. J. *J. Polym. Sci. (Polym. Symp.)* 1973, 42, 727
7 Hoeschele, G. K. and Witsiepe, W. K. *Angew. Makromol. Chem.* 1973, 29/30, 267