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Monte Carlo Simulations of Polymer Degradations. 1. Degradations without Volatilization

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Received July 10, 1989; Revised Manuscript Received September 8, 1989

ABSTRACT: Polymer degradations, involving chain scissions without evolution of volatile products, have been simulated by Monte Carlo procedures in order to establish which parameters are useful to follow the degradation processes. Changes of the dispersity index (X_w/X_n), the ratio of weight- to number-average degrees of polymerization, give important information about randomness of the chain scissions, provided degradation is performed on polymer samples of different initial average degrees of polymerization or of different initial dispersity index. When scissions are completely random the dispersity index approaches the value of 2, independently of the fact that fragments formed in chain scissions might couple with each other. Changes of the value of X_n as the degradation proceeds and the formation of molecules larger than those present in the undegraded sample are also important features of the process.

Introduction

In our previous papers[1–4] we reported that a deeper insight into the mechanisms of thermal degradation of some polymeric materials could be achieved by simulating the degradation processes with Monte Carlo procedures. It has been possible to obtain some interesting information about depolymerization length of the two different chain radicals formed in random chain scissions, as well as about the reliability of the random chain scissions themselves, which occur either as homolytic bond scissions or as a consequence of intermolecular radical transfer.

In the present paper the simulation methods are applied to several hypothetical degradation processes of polymeric substances that take place without significant evolution of volatile products, in order to show their capabilities and limits in giving evidence to important features of polymer degradation. At the same time, these methods can be of value in providing useful suggestions about the choice of experiments to be conducted and of parameters to be measured. The simulation of degradation processes involving extensive volatilization will be a subject of our subsequent publication.

The Monte Carlo program (BASIC language, executable on a MS-DOS compatible PC) used in this study is practically the same as the one already described,[1,2] with minor changes to improve the flexibility in selecting degradation mechanisms and to allow treatment of macromolecules with a degree of polymerization (DP) up to 30 000. The simulation of a degradation process involving more than 10 scissions per original macromolecule or conversions to volatile products higher than 90% requires a few minutes.

The Monte Carlo procedure bears some resemblance with the one described several years ago by Malác[5] but is more exact, in the sense that macromolecules differing in one monomeric unit are separately treated, instead of treating macromolecules differing by less than 50 structural units together. This allows chemical changes (scissions, depolymerizations, coupling of radicals, intermolecular transfers, etc.) to be performed on individual chemical species and any averaging operation to be postponed until the right moment. Furthermore, the present procedure is not limited to closed systems but makes possible the investigation of the changes of parameters related with DP as a function of conversion to volatile products.

Polymer Degradation without Volatilization

In the simulations of polymer degradations it is assumed that fragments from different macromolecules interact with each other or with unbroken macromolecules. A possibility that branched molecules or cross-linked networks are formed is not taken into account. Therefore, when the formation of volatile products does not take place, the degradation is essentially a chain scission process. In the Monte Carlo calculations, however, it has been assumed that molecules with DP up to 5 have sufficient volatility and escape from the degrading sample. This implies a weight loss of less than 0.05% when each original macromolecule with DP higher than 1000 has been subjected, on the average, to ten scissions.

In a polymer degradation process involving almost exclusively chain scissions, the scissions can be either random or nonrandom. In the first case, each bond of a polymer chain has the same probability of cleavage, independent of the length of the chain: for instance, hydrolysis of ester groups in a polyester chain. There is a situation where

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bonds located in different positions in the polymer chains have a different probability of cleavage, and in these cases the scission process becomes nonrandom. It is particularly well-known[6] that in some mechanically induced degradations bonds near the center of a chain break more easily than those near the chain ends. On the other hand, one might expect that when homolytic scissions occur in a molten polymer, the radical fragments must diffuse apart in order to make the chain rupture effective. This might be more difficult when fragments are very long and therefore bonds near the center of long chains are significantly more stable than those near the chain ends and those of shorter chains.

In the virtual absence of volatilization, the most significant parameters to describe the polymer degradation process are related to the changes of DP occurring as degradation proceeds. In the following the discussion will be limited to the number-average DP (X_n), the weight-average DP (X_w), the dispersity index as expressed by the ratio X_w/X_n, and in some cases, the differential distribution curves of DP. Higher moments of the distribution, such as X_z and X_{z+1}, will not be considered here inasmuch as they are, in general, experimentally less accurate than X_n and X_w.

1. Simple Scission Processes. A first series of polymer degradations without volatilization will be taken into account in which chain fragments either are stable molecules (which can undergo further scissions) or transform themselves into stable molecules without changing their DP. An example of the first case might be hydrolysis of a polyester already mentioned, whereas the second case might be formation, by homolytic scissions, of chain radicals that interact with each other by disproportionation or transform themselves into stable molecules by random abstraction from other molecules (which are, in turn, transformed into radicals that can randomly break). Such polymer degradations will be termed in the following *simple scission processes*. In these cases, independently of the randomness of the scission process, the simple relationship

$$S = \frac{X_{n0}}{X_n} - 1 \qquad (1)$$

holds between the number of scissions per initial molecule (S), the initial number-average DP (X_{n0}), and the number-average DP (X_n) after S scissions took place. Therefore, the simple measurement of X_n at different stages of the degradation allows calculation of S but gives no information about the randomness of the chain scissions. On the other hand, such information can be obtained by plotting X_w or X_w/X_n as a function of S, as can be seen in Figures 1–3. In Figure 1 are represented the results of the simulations of simple chain scissions of a polymer having an initial dispersity index equal to 2. Such a dispersity index is maintained constant if scissions are completely random, whereas it increases to quite high values if the internal chain scissions are disfavored and decreases to values lower than 2 if scissions near the center of the chains are more likely than those near the chain ends.

Similar results are shown in Figures 2 and 3, which refer to simulations of simple chain scission processes on polymers with initial dispersity indexes equal to 1.10 and 2.57, respectively. In both cases X_w/X_n approaches a value of 2 when scissions are random whereas it tends to deviate from 2 when scissions near the center of the polymer chains are favored or disfavored.

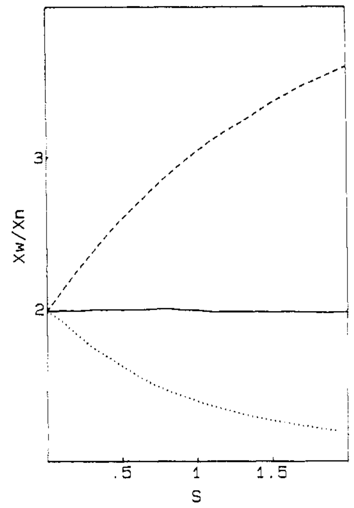

Figure 1. Dispersity indexes versus the number of scissions per original molecule with $X_{w0}/X_{n0} = 2$ in simulation of simple scission processes. (—) random scissions; (- - -) scissions near the center of the largest molecules are disfavored; (···) scissions near the center of the largest molecules are favored.

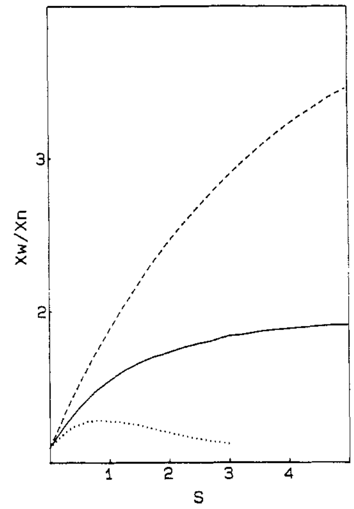

Figure 2. Dispersity indexes versus the number of scissions per original molecule with $X_{w0}/X_{n0} = 1.10$ in simulation of simple scission processes. Line symbols as in Figure 1.

Figures 1–3 show that the plots of the dispersity index as a function of S can give information on the randomness of a simple scission process and also allow one to distinguish between different nonrandom mechanisms (e.g., diffusion controlled or mechanically induced degradations), provided a sufficient number of scissions can be achieved. However, taking into account some details of the simulation procedures, further comments can be made. The simulation procedures are essentially based on the random selection, from a population of several millions of structural units, of one structural unit belonging to a unique macromolecule that is broken into two fragments. In the case of a completely random processes, these fragments are supposed to be transformed into stable molecules, which are possibly involved in subsequent scissions. On the other hand, in the case of nonrandom processes the length of these fragments is compared with a predetermined value, and only after this comparison has been done it is decided that the fragments are either transformed into stable molecules or recombined to reform the original molecule. When the bonds near the center of the macromolecule break more easily than those near the ends, recombination takes place (and the scission is not effective) when at least one of

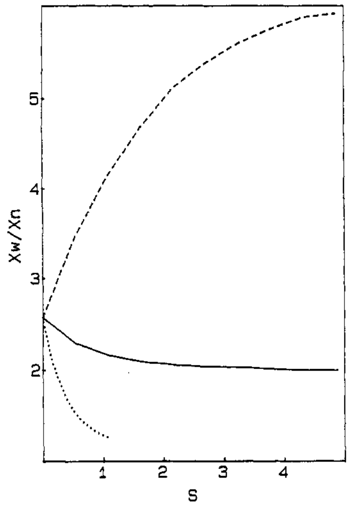

Figure 3. Dispersity indexes versus the number of scissions per original molecule with $X_{w0}/X_{n0} = 2.57$ in simulation of simple scission processes. Line symbols as in Figure 1.

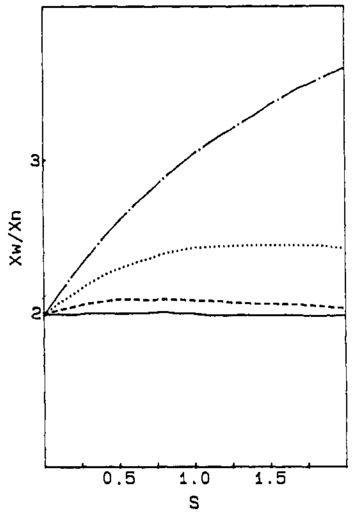

Figure 4. Effect of the parameter X^* on the simulations of scission processes in which scissions near the center of the largest molecules are disfavored ($X_{n0} = 2000$; $X_{w0}/X_{n0} = 2$). (—) $X^* = \infty$ (random scissions); (- - -) $X^* = 4000$; (· · ·) $X^* = 2000$; (- · -) $X^* = 1000$.

the fragments is shorter than a value $X_{\rm rnd}$, which is a random number around a predetermined value X^*. On the other hand, when the internal bonds are more stable than those near the chain ends, recombination takes place when both fragments are longer than a value $X_{\rm rnd}$.

It is clear that the selection of X^* in the simulations is critical in order to give evidence for the nonrandomness of the process, since X^* determines how many molecules in a polymer sample, with a given average degree of polymerization and a given dispersity index, can meet the requirements for immediate recombination after fragmentation. In the case where scissions are more difficult near the center of the largest molecules, X^* can be either too low, thus preventing the scission process from proceeding, or too high, thus making the nonrandom scission process indistinguishable from a random one. In Figure 4 are shown the results of four simulations of diffusion-controlled chain scission processes, with X^* ranging from 1000 to 4000, for a polymer with initial $X_n = 2000$ and $X_w/X_n = 2$, compared with the results of the simulation of the random scission process ($X^* = \infty$). One can see that by increasing X^*, the trend of the dispersity index becomes closer and closer to the trend calculated for the random process. Particularly, when $X^* = 4000$ the dispersity indexes differ from those of the random process by less than the usual experimental error. However, they remain definitely distinct, as a consequence of the presence in the undegraded sample of a significant fraction of molecules with degree of polymerization higher than 4000–5000. This can be better understood by considering the curves in Figure 5 obtained from simulations of degradation processes performed on a polymer sample with initial $X_n = 2000$ and $X_w/X_n = 1.10$ (no molecules have degree of polymerization higher than 5000). The nonrandom curve obtained with $X^* = 2000$ is already superimposable on the random curve and a clear difference between the two processes can be seen only with $X^* = 500$.

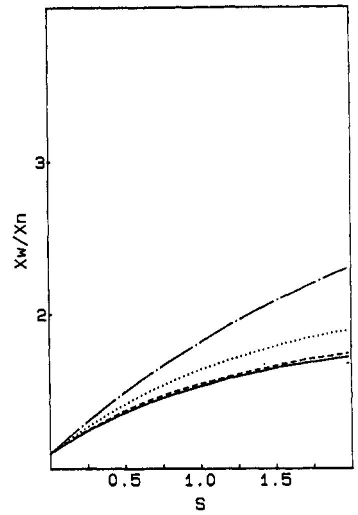

Figure 5. Effect of the parameter X on the simulations of scission processes in which scissions near the center of the largest molecules are disfavored ($X_{n0} = 2000$; $X_{w0}/X_{n0} = 1.10$). (—) $X^* = \infty$ (random scission); (- - -) $X^* = 2000$; (· · ·) $X^* = 1000$; (- · -) $X^* = 500$.

The above discussion on the simulation procedures points out that in order to ascertain the nonrandomness of a simple scission process from an experimental point of view, it is necessary to investigate the degradation behavior of macromolecules of different length: that is, to evaluate the trend of the dispersity index of several polymer samples with either different initial average degree of polymerization or different initial dispersity.

2. Scission-Coupling Processes. In polymer degradations without volatilization, chain fragments formed in chain scissions could interact each other to yield a new macromolecule whose degree of polymerization is the sum of the degrees of polymerization of the fragments. This situation can either occur for all the fragments, an example being transesterification in polyesters, or be in competition with different fragment interactions, as can be imagined for a degradation involving homolytic chain scissions followed by either recombination or disproportionation of the chain radicals. These degradations will be termed *scission–coupling processes*. In these cases eq 1 must be modified to take the form

$$S(1 - C) = \frac{X_{n0}}{X_n} - 1 \qquad (2)$$

where C is the fraction of scission fragments that undergo coupling. The simple determination of the number-average degrees of polymerization is no longer sufficient to evaluate the number of scissions that took place in the polymer sample.

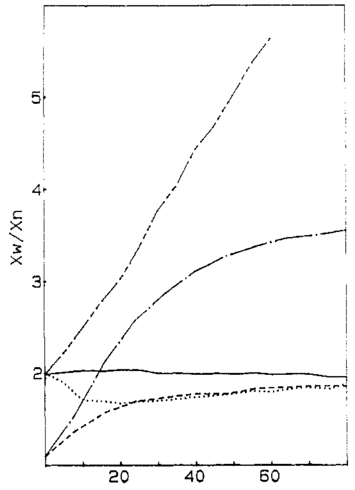

Figure 6. Dispersity indexes versus the number of scissions in simulations of scission–coupling processes with complete coupling. (—) random scissions (undegraded sample with the most probable distribution); (- · · · -) scissions near the center of the largest molecules are disfavored (undegraded sample with the most probable distribution); (· · ·) random scissions (undegraded sample is a mixture of equal weights of two momodispersed polymers); (- - -) random scissions (undegraded sample with narrow distribution); (- · · -) scissions near the center of the largest molecules are disfavored (undegraded sample with narrow distribution).

2.1. Complete Fragment Coupling. In the limiting case where $C = 1$ (all the fragments interact each other and couple), it can be seen from eq 2 that X_n remains constant independently of S. Such a constancy is clear-cut evidence for a degradation mechanism based only on chain scissions and 100% fragment coupling, provided, of course, it can be demonstrated that scissions do occur. This can be done simply by following the changes of X_w/X_n. In Figure 6 are shown the results of simulations of degradations of this type, performed on three polymer samples with initial X_w/X_n of 1.10 and 2, assuming that scissions are either completely random or more difficult in the internal parts of the longest molecules. The changes in X_w/X_n allow one to again distinguish between random (X_w/X_n remains close or tends to 2) and nonrandom (X_w/X_n becomes greater than 2) processes.

The number of scissions can be evaluated very easily in the simulation calculations but not in experimental scission–coupling degradations. Therefore, the curves of Figure 6 must be substituted, in practical experimental cases, with curves of X_w/X_n as a function of time. Under the reasonable hypothesis that some simple relation exists between the number of scissions and the degradation time, the experimental curves should look like those of Figure 6.

Some further considerations must be made concerning the random scission–coupling process in the polymer samples with initial $X_w/X_n = 2$ (Figure 6). These two samples differ in the fact that one is a mixture of 240 fractions of monodispersed polymers with degrees of polymerization ranging from 50 to 12 000, distributed according to the Schulz–Flory distribution and the other one is a mixture of equal weights of two monodispersed polymers with degrees of polymerization 1000 and 5820, respectively. A scission–coupling process on the first sample does not change the initial most probable distribution, which is in fact an equilibrium distribution. On the contrary, the initial $X_w/X_n = 2$ in the second sample is not indicative of a situation of equilibrium, and the scission–coupling process initially induces a decrease of the dispersity index and then a slow increase toward the equilibrium value. From an experimental point of view it should be possible to follow in this last case the changes in X_w/X_n as a function of time, thus making the scission–coupling process evident. On the other hand, in the case of a polymer sample with the most probable distribution from the beginning of the experiment, it would be impossible to detect the occurrence of a scission–coupling process by simply measuring X_w/X_n. It follows that from an experimental point of view, in order to test the reliability of a scission coupling process involving complete fragment coupling, it is useful to treat several polymer samples with different initial distributions of degree of polymerization.

2.2. Partial Fragment Coupling. When C in eq 2 is less than 1, X_n decreases with increasing S as in the case of simple scission processes ($C = 0$). However, since C is generally not known, it is impossible to evaluate S according to eq 2 from measurements of X_n. In practice, it can be assumed as in the case of complete coupling processes that S is simply related to the degradation time and the process can be followed by plotting X_w/X_n as a function of time.

The Monte Carlo simulations of partial fragment coupling processes performed with values of C between 0 and 1 give X_w/X_n versus S plots that are qualitatively similar to those obtained for simple scission processes: X_w/X_n approaches the equilibrium value of 2 when the scissions are completely random along the polymer chains, whereas it takes different values when the probability of cleavage depends on the location of the bonds in the polymer chain. The question to be answered is, is it possible to distinguish between simple scission and partial fragment coupling processes? The Monte Carlo simulations suggest that it is, provided an efficient experimental technique (such as GPC) is available to determine the distributions of the degree of polymerization, that is, to evaluate the weight fraction $W(X)$ of molecules with degree of polymerization X, for every value of X. In fact, in the early stages of fragment coupling processes molecules larger than those in the starting sample can be formed, which can be seen in the distribution curves, as well as in the GPC chromatograms,[4] on the side of higher values of X.

Figures 7 and 8 show the results of simulations of fragment coupling processes performed on polymer samples with initial X_w/X_n of 2 and 1.10, respectively, under the assumption that $C = 0.25$ (i.e., one-fourth of the fragments recombines). The formation of larger molecules ($X > 13\,000$ and $X > 5000$, respectively), which were absent in the original samples, is clearly seen. The possibility of observing such a phenomenon increases obviously with increasing C, but in any case it is confined at the early stages of degradation since the newly formed larger molecules will subsequently undergo fragmentation.

The fact that the Schulz–Flory distribution is the equilibrium one in the random scission–coupling processes requires some comments, since it is often said in the literature that when coupling takes place a narrower distribution should be expected, in analogy with what happens in addition polymerizations with termination by recombination. It has been reported[7,8] that when coupling takes place in a degradation process X_w/X_n should approach 1.5. It must be pointed out that the termination by coupling during a polymerization is a statistical process that is completely different from the coupling of fragments formed after chain scissions. In the former

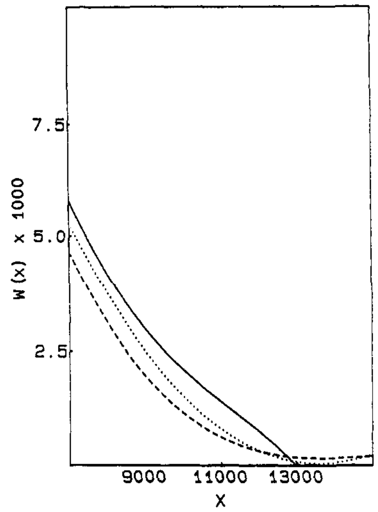

Figure 7. Portions at high degrees of polymerization of the differential distribution curves of a polymer sample with an initial most probable distribution, degraded by a scission-coupling process with partial fragment coupling ($C = 0.25$). (—) undegraded sample; (···) after 0.1 scissions per original molecule; (- - -) after 0.2 scissions per original molecule.

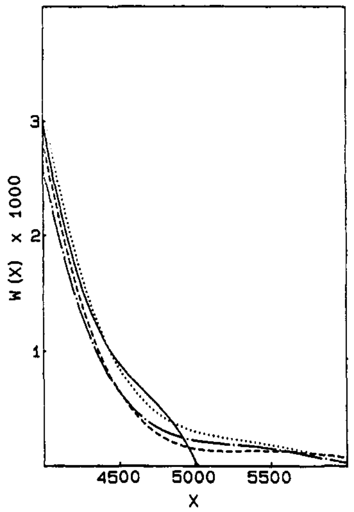

Figure 8. Portions at high degrees of polymerization of the differential distribution curves of a polymer sample with initial narrow distribution, degraded by a scission–coupling process with partial fragment coupling ($C = 0.25$). (—) undegraded sample; (···) after 0.1 scissions per original molecule; (- - -) after 0.2 scissions per original molecule; (-··-) after 0.3 scissions per original molecule.

case, starting from a population of reactive species, a new population of stable molecules is formed. The number of stable molecules is one-half the number of reactive species and the number-average degree of polymerization of the reactive species (Y_n) is $X_n/2$. It can be shown (see Appendix) that, independently of the distribution of the reactive species, if their dispersity index is given by Y_w/Y_n, X_w/X_n of the resulting stable molecules takes the form

$$\frac{X_w}{X_n} = \frac{1}{2}\left(1 + \frac{Y_w}{Y_n}\right) \tag{3}$$

Incidentally, eq 3 suggests a route to obtaining polymer samples of very narrow molecular weight distributions, e.g., by anionic living polymerization terminated with a coupling agent. In the scission–coupling processes the number of molecules increases or remains constant, the number-average degree of polymerization decreases or does not change, and any molecule formed by coupling of fragments can undergo further scissions. Independently of the starting distribution, after a sufficient number of scission–coupling events the most probable distribution is attained, for which $X_w/X_n = 2$.

Conclusions

The simulation by Monte Carlo procedures of polymer degradation processes occurring without evolution of volatile products has shown that the randomness of chain breaking can be conveniently tested by following the trend of the dispersity index X_w/X_n as a function of the degradation time. If scissions are random, X_w/X_n invariably approaches the equilibrium value of 2, whereas different values are reached when bonds located in special positions along the polymer chains are preferentially broken. When the degradation is too slow to ascertain with confidence the trend of X_w/X_n, it is useful to treat several polymer samples differing as much as possible in initial dispersity indexes.

The changes of X_n are also indicative of important features of the degradation process. If X_n remains constant (while X_w varies) as the degradation proceeds, clear evidence is given of a process in which all the fragments formed in chain scissions recombine with each other. On the other hand, a decrease of X_n means that fragments can be transformed without significant changes in the degree of polymerization into stable molecules. In order to establish if this is the destiny of all the fragments, or of only a part of them, the others being involved in coupling processes, it is necessary to analyze the distribution curves of the degrees of polymerization determined on the polymer samples at the early stages of degradation. The presence of molecules longer than those in the undegraded samples is certainly a consequence of the fact that some fragment coupling took place.

Appendix

Given a population PY of N polydispersed macromolecules that can randomly recombine with each other to yield a new population PX of $N/2$ polydispersed macromolecules, one can find the relationships between the number- and the weight-average degrees of polymerization of the two populations.

With Y_n as the number-average degree of polymerization of population PY, since the coupling process halves the number of macromolecules without changing the number of structural units, it follows that the number-average degree of polymerization X_n of population PX is simply given by

$$X_n = 2Y_n \tag{A1}$$

The number fraction n_i of molecules of the ith species in population PY is also the probability of finding a molecule of that species in the population. Therefore, the number fraction n_{ij} $(i \neq j)$ in the population PX is given by the probability $n_i n_j$ of finding consecutively in the population PY a molecule of the ith species and a molecule of the jth species, plus the probability $n_j n_i$ of finding consecutively a molecule of the jth species and a molecule of the ith species. Since $n_i n_j = n_j n_i$, one obtains

$$n_{ij} = 2n_i n_j \quad (i \neq j) \tag{A2}$$

The number fraction n_{ii} in the population PX of molecules formed by coupling of identical molecules of the population PY is simply given by

$$n_{ii} = n_i^2 \tag{A3}$$

Taking into account (A1), (A2), and (A3), the weight fractions w_{ij} and w_{ii} are given by

$$w_{ij} = n_{ij}X_{ij}/X_n = n_i n_j(Y_i + Y_j)/Y_n \qquad (A4)$$

$$w_{ii} = n_{ii}X_{ii}/X_n = n_{ii}^2 Y_i/Y_n \qquad (A5)$$

where Y_i and Y_j are the degrees of polymerization of the two molecules of population PY, which couple to give one molecule of population PX with degree of polymerization X_{ij} (or X_{ii} when $i = j$).

If all the possible weight fractions of population PX are written in triangular form as

$$\begin{array}{ccccc} w_{11} & w_{12} & w_{13} & \cdots & w_{1n} \\ & w_{22} & w_{23} & \cdots & w_{2n} \\ & & w_{33} & \cdots & w_{3n} \\ & & & & \cdot \\ & & & & \cdot \\ & & & & \cdot \\ & & & & w_{nn} \end{array}$$

the weight average degree of polymerization can be put in the form

$$X_w = \sum_{i=1}^{n} w_{ii}X_{ii} + \sum_{1\le i<j\le n} w_{ij}X_{ij}$$

and introducing (A4) and (A5)

$$X_w = \frac{1}{Y_n}[2\sum_{i=1}^{n} n_i^2 Y_i^2 + \sum_{1\le i<j\le n} [n_i n_j (Y_i + Y_j)^2] \qquad (A6)$$

Since

$$Y_n^2 = (\sum_{i=1}^{n} n_i Y_i)^2 = \sum_{i=1}^{n} n_i^2 Y_i^2 + 2 \sum_{1\le i<j\le n} n_i n_j Y_i Y_j$$

from (A6) one obtains

$$X_w = \frac{1}{Y_n}[Y_n^2 + \sum_{i=1}^{n} n_i^2 Y_i^2 + \sum_{1\le i<j\le n} n_i n_j Y_i^2 + \sum_{1\le i<j\le n} n_i n_j Y_j^2] \qquad (A7)$$

The three summations in (A7) are developed as

$$\sum_{i=1} n_i^2 Y_i^2 + \sum_{1\le i<j\le n} n_i n_j Y_i^2 + \sum_{1\le i<j\le n} n_i n_j Y_j^2 = n_1 n_1 Y_1^2 + n_1 n_2 Y_1^2 + n_1 n_3 Y_1^2 + \ldots + n_1 n_n Y_1^2 + n_1 n_2 Y_2^2 + n_2 n_2 Y_2^2 + n_2 n_3 Y_2^2 + \ldots + n_2 n_n Y_2^2 + n_1 n_3 Y_3^2 + n_2 n_3 Y_3^2 + n_3 n_3 Y_3^2 + \ldots + n_3 n_n Y_2^2 + \ldots + n_1 n_n Y_n^2 + n_2 n_n Y_n^2 + \ldots + n_{n-1} n_n Y_n^2 + n_n n_n Y_n^2 = \sum_{i=1}^{n} n_i Y_i^2 = Y_n Y_w$$

and from (A7) one obtains

$$X_w = Y_n + Y_w \qquad (A8)$$

By combination of (A8) with (A1), eq 3 of the text is obtained.

It is of interest to observe that no assumption has been made about the distribution of PY, and consequently (A1) and (A8) do not contain any information on the type of the distribution of PX. Therefore, $X_w/X_n = 1.5$ for population PX is not typical of the coupling process from population PY to population PX, but is only one particular result that is obtained when, for population PY, $Y_w/Y_n = 2$ (a value that does not necessarily correspond to the most probable distribution).

Acknowledgment. This work has been carried out with the financial aid of Ministero della Pubblica Istruzione (60%).

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Communications to the Editor

Liquid-Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 8.[†] Morphological Evidence for Microphase Separation in Poly(methylsiloxane-*co*-dimethylsiloxane)s Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups

Recently, by analogy with the behavior of block and graft copolymers, we have suggested that highly or even completely decoupled side-chain liquid-crystalline polymers would be realizable for systems in which the mesogenic side groups and the polymer backbone are microphase separated.[1–8] Such a morphology is particularly favorable for smectic copolymers based on flexible backbones that contain mesogenic and nonmesogenic structural units. Most probable, a microphase-separated morphology like this is induced by the thermodynamic immiscibility between the random-coil polymer backbone and the rodlike mesogenic units, which in the liquid-crystalline phase tend to segregate into isotropic and anisotropic domains. The tendency toward microsegregation is enhanced when the polymer backbone and the side groups are, due to their chemical dissimilarity, immiscible even within their isotropic phase. Such a microphase-separated morphology can be best observed in copolymers containing about similar weight ratios between the polymer backbone and the mesogenic side groups.

In a previous publication[8] we have presented our investigations on poly(methylsiloxane-*co*-dimethylsiloxane)s containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-

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[†] Part 7: ref 8.

0024-9297/90/2223-2092$02.50/0