Monte Carlo Simulations of Polymer Degradations. 2. Degradations Involving Random Chain Scissions and Volatilization of Low Molecular Weight Products

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Received June 25, 1990; Revised Manuscript Received September 25, 1990

ABSTRACT: Polymer degradations involving chain scissions and evolution of low molecular weight products (monomer and oligomers) have been simulated by Monte Carlo procedures to find the most useful parameters to be followed at increasing volatilization and the most significant experiments needed to characterize degradation processes. It has been found that the ratios X_n/X_{n0} and X_w/X_{w0} between number- and weight-average degrees of polymerizations of the polymer samples at any stage of the degradation, and the corresponding values for the undegraded samples, together with the ratio R_m between the number of molecules in the degraded and undegraded samples, give useful information on the degradation mechanisms. In cases when chain scissions are not completely random, such as when they preferentially occur near particular positions in the polymer chains, it is also convenient to follow the dispersity ratio X_w/X_n and changes in the shape of the distribution curves of the degrees of polymerization.

Introduction

Monte Carlo procedures have been successfully employed[1] to simulate polymer degradation occurring without evolution of low molecular weight products and provide information about its mechanism (e.g., completely or partially random chain scissions and interactions between the resulting fragments). They also indicate the most useful parameters and the most meaningful experiments for characterization of the entire process. In this paper they are applied to degradations involving both scissions of the polymer chains and depolymerization of the fragments, yielding either pure monomer, as in the case of poly(methyl methacrylate),[2] or monomer and oligomers, as in the case of polystyrene.[3]

The basic difference between this type of degradation and that involving only changes in the degree of polymerization (X) is obviously the weight loss of the sample with increasing degradation. This is expressed through the conversion c to volatile products:

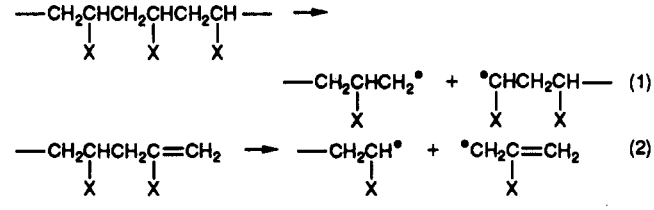
$$c = 1 - u/u_0$$

where u_0 and u are the number of structural units in (or the weight of) the undegraded and partially degraded sample, respectively, and can easily be followed thermogravimetrically. The possible relation of parameters based on X (e.g., different average Xs and/or their ratios) with c seems a reasonable approach to clarification of the degradation mechanism. The classic approach is the kinetic one first attempted by Simha[4] and then developed by Boyd,[5] who regarded degradation involving volatilization of low molecular weight products as a chain reaction characterized by initiation, propagation, and termination. This approach, however, has two inherent drawbacks: (i) the behavior of the two fragments (often two free radicals) formed in chain scissions is taken as identical, despite the fact that they are frequently different and thus endowed with a different reactivity; (ii) the resulting rate equations are extremely complicated, and their application must be confined to particular and sometimes experimentally difficult situations. Monte Carlo simulation of polymer degradation provides an alternative approach, since these drawbacks can be readily circumvented. As will be seen in the next section, this is naturally offset by a less detailed description of the degradation mechanism.

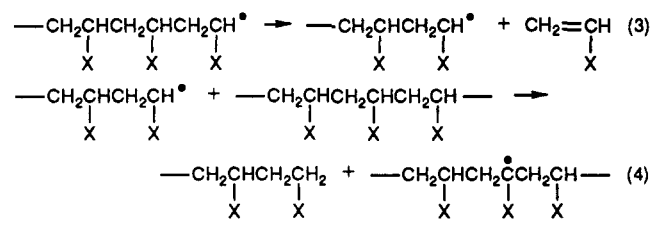
Simulations of Polymer Degradations

Monte Carlo simulation of polymer degradations involving depolymerization does not explicitly take their chain reaction nature into account. It is as well to point out the differences between the kinetic and the Monte Carlo approaches.

In the kinetic approach, chain initiation, propagation, and termination reactions must be individually postulated: Boyd's scheme[5] embraces two initiation reactions—random chain scissions (with formation of two chain radicals), and end-group initiation (with formation of one chain radical and one monomer radical):



Two propagation reactions are also considered—depolymerization of chain radicals and intermolecular transfer:



as well as two termination reactions—second-order disproportionation and second-order recombination of pairs of chain radicals:

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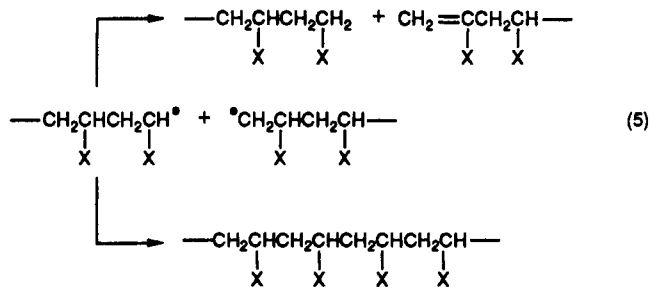
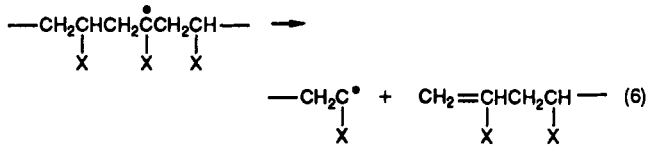


(5)

Even if other possible reactions (such as first-order termination, in which the radicals of reaction 5 disappear without interacting) are disregarded and a stationary state for the reactive intermediates is assumed, the result is formidable relations with a plurality of complex rate constants and kinetic parameters. Some of these can be evaluated from experimental data if various simplifying assumptions are made.

In the Monte Carlo approach, description of the degradation process is far more naïve. Starting from the obvious consideration that if monomer is evolved during degradation some depolymerization of the polymer molecules or their parts must take place, the simulation assumes a scission into two fragments according to either reaction 1 or reaction



(6)

which follows intermolecular transfer 4. Assuming that the unsaturated chain end of one reaction 6 fragment is highly unstable (in degradation conditions) and evolves quickly according to reaction 2, it can be concluded that both homolytic scissions 1 and the sequence of reactions 4, 6, and 2 yield pairs of readily depolymerizable fragments: in the first case, however, the two fragments are different and presumably have different reactivity, whereas in the second case they are identical.

The scissions in reactions 1 and 6 can be (a) completely random along the polymer chains or (b) partially random, i.e., occurring preferentially around some specific positions. Case a is probably the more frequent. However, sometimes a scission might be either easier, for example, near the chain center (as in shear-induced degradations) or more difficult (if the fragments are too large to diffuse quickly apart, thus preventing recombination): these scissions are partially random.

If they do not follow scissions of on-chain radicals according to reaction 6, chain scissions according to reaction 2 occur at a specific position in the chain and are therefore nonrandom. Degradations involving initiation of the chain reactions according to eq 2 will be the object of a subsequent paper.

The fragments formed in homolytic scissions 1 and in the (4), (6), and (2) sequence can undergo depolymerization. In the Monte Carlo simulations, these fragments are shortened by a predetermined number of structural units, called the depolymerization length DL. The DLs of a pair of fragments may or may not be the same (depending on the equal or different reactivity of the active ends). In addition, one or both may be zero (both DLs = 0 is the simulation of polymer degradations without volatilization[1]).

In real depolymerization processes, e.g., in the thermal degradation of polystyrene, oligomers (dimers, trimers, etc.) formed by intramolecular transfer involving a few structural units near the active end of the depolymerizing fragment may be evolved together with the monomer. The Monte Carlo simulations make no provision for this possibility: DL is the average number of structural units evolved from one fragment, as both monomer and oligomers.

Table I
Polymer Samples Employed in the Monte Carlo Simulations

sample	X_{n0}	X_{w0}	X_{w0}/X_{n0}
A1	5009	5511	1.10
A2	5424	9577	1.77
B1	1000	1100	1.10
B2	1016	1943	1.91
C1	501	551	1.10
C2	542	958	1.77
D1	100	110	1.10
D2	105	197	1.88

Depending on the length of the fragment to be shortened and DL, three situations are possible. The fragment can be (1) longer than DL by several structural units, (2) shorter than DL, or (3) longer than DL by a few structural units. In situation 1, the fragment left in the degrading sample is assumed to be transformed by intermolecular transfer (reaction 4) into a stable molecule of equal size or to interact with another fragment according to reactions 5 to yield one or two new molecules. No formation of new molecules occurs in the other two situations. In situation 2, depolymerization unzips the whole fragment formed in the scission, while the short segment left after depolymerization in situation 3 is assumed to evaporate from the degrading sample.

Step by step reckoning of the number of structural units given off and remaining in the degrading sample and their molecular species distribution enables the changes in X at increasing c to be followed. By changing the DLs, the ratio between disproportionation and recombination (reactions 5), and the degree of scission randomness, one can obtain curves of X (or related parameters) vs c and compare them with the experimental ones.

It is clear that the Monte Carlo simulations cannot cater for the fine details of degradation, such as the ratio between the rate constants of the different reactions a given radical can undergo (depolymerization, intermolecular transfer, termination, etc.). They do, however, accurately represent the overall degradation process to a degree that is usually sufficient to clarify the main features of its mechanism.

Results and Discussion

In real degradation situations, several combinations of reactions 1–6, and possibly of other reactions yielding similar products, presumably occur. For a given degradation process, the actual combination should be reflected in the changes of X (or related parameters) with increasing c, which can be experimentally evaluated. Monte Carlo simulations are performed by selecting the DLs, the ratio between disproportionation and recombination in the fragment interactions, and the degree of randomness of the chain scissions and trying to reproduce the experimental X vs c trends. The following results of calculations will show their potentialities and limits.

Monte Carlo simulations were performed on "artificial" polymer samples whose number- and weight-average Xs (Table I) were computed by assuming Schulz–Zimm X distributions.

Figure 1 shows the calculated changes of X_n/X_{n0} and X_w/X_{w0} as a function of c in sample A1 when scissions are completely random, both fragments depolymerize by the

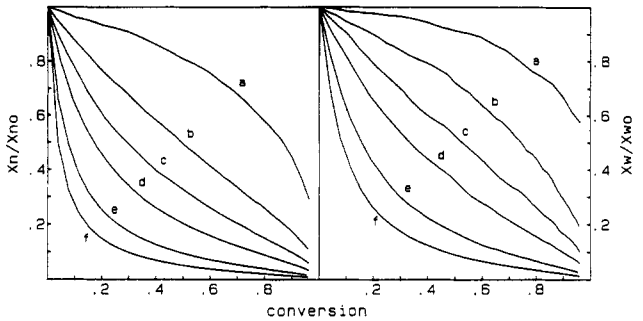


Figure 1. Simulations of degradation of sample A1 by completely random chain scissions and depolymerization of both fragments by the same length: (a) DL = 5000; (b) DL = 2000; (c) DL = 1000; (d) DL = 500; (e) DL = 200; (f) DL = 100.

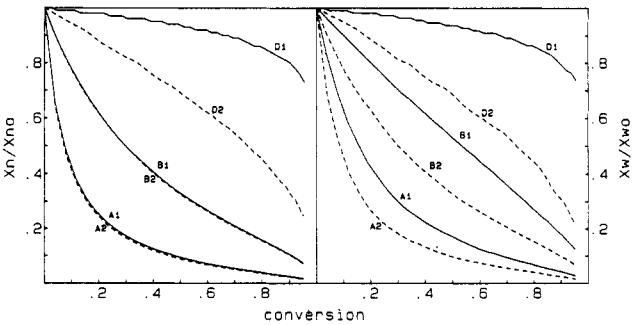


Figure 2. Effect of the initial polymolecularity (see Table I) at the same DL on the decrease of X_n/X_{n0} and X_w/X_{w0} at increasing c.

same DL, recombination of fragments after depolymerization does not take place, and different overall DLs are considered. It results that a series of experimental determinations of X_n and X_w on samples obtained from the degradation of one original polymer up to different values of c should easily provide an initial indication of the overall DL.

The effects of the initial polymolecularity of the degraded sample are shown in Figure 2, which gives the curves calculated for degradation by random chain scission, DL = 200 for both scission fragments, and no depolymerized fragment recombination, of samples A1, B1, and D1 (solid lines) and A2, B2, and D2 (dashed lines). The dependences of X_w/X_{w0} on c for samples with the same X_{n0} and a different polymolecularity index X_{w0}/X_{n0} are well distinct, whereas the dependences of X_n/X_{n0} on c are only different when X_{n0} is small compred with DL. Monte Carlo simulation of the experimentally observed changes of number- and weight-average Xs caused by degradation must take the initial polymolecularity of the polymer samples into account. On the other hand, the experimental evaluation of the degradation behavior of samples with different polymolecularities can be useful to assess the overall DL.

Discrimination between mechanisms in which fragments formed in completely random chain scissions depolymerize by equal or different DLs is illustrated in Figure 3 for samples with initial narrower (A1, B1, C1, and D1) and broader (A2, B2, C2,and D2) X distributions: the full lines have been obtained by assuming DL = 100 for both fragments, and the dotted lines by assuming DL = 200 for one fragment and DL = 0 for the other. When the initial X is much higher than DL, the curves are almost superimposable, or very close to each other, whereas discrimination becomes possible as X is increasingly reduced.

The Monte Carlo simulations have revealed another interesting quantity whose dependence on c gives further

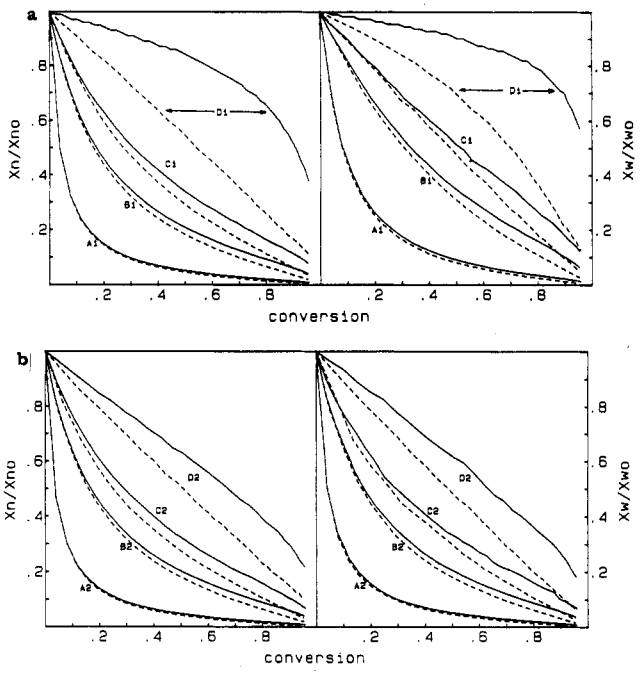


Figure 3. (a) Decrease of X_n/X_{n0} and X_w/X_{w0} at increasing c calculated for degradations involving completely random chain scissions and depolymerization of both scission fragments by DL = 100 (solid lines) and depolymerization of only one scission fragment by DL = 200 (dashed lines). Initially dispersity indexes: 1.10. (b) Decrease of X_n/X_{n0} and X_w/X_{w0} at increasing c calculated for degradations involving completely random chain scissions and depolymerization of both scission fragments by DL = 100 (solid lines) and depolymerization of only one scission fragment by DL = 200 (dashed lines). Initial dispersity indexes between 1.77 and 1.91.

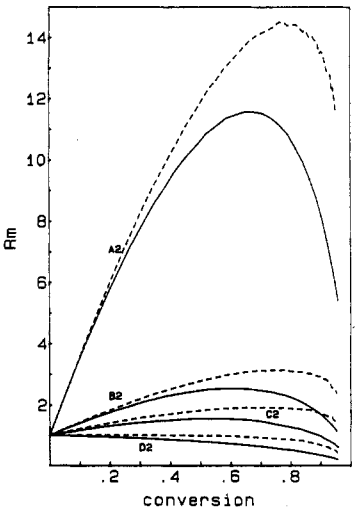


Figure 4. Ratios R_m between the number of molecules in the degrading sample at conversion c and in the undegraded sample. Polymer samples and degradation mechanisms as in Figure 3b.

information on the degradation mechanism, namely, the ratio $R_m = m/m_0$ between the number m of polymer molecules in the degrading sample at conversion c and the number m_0 of molecules in the undegraded sample. This quantity is experimentally accessible since the simple relation holds:

$$R_m = m/m_0 = (1 - c)X_{n0}/X_n$$

Figure 4 shows the trend of R_m vs c for the samples of Figure 3b, degraded according to the same mechanisms. The number of molecules is sensibly different when only one scission fragment or both undergo depolymerization, provided the conversion is high enough, especially in the

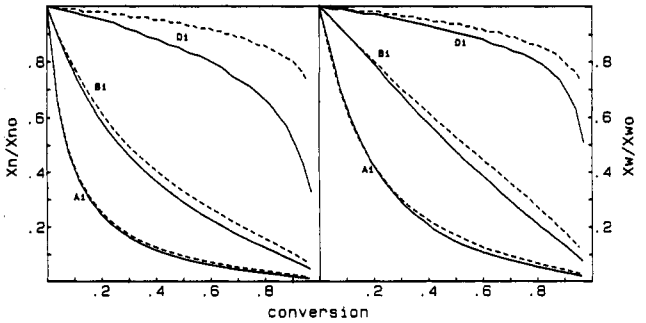


Figure 5. Comparison of X_n/X_{n0} and X_w/X_{w0} vs c curves calculated for degradation mechanisms involving completely random chain scissions and depolymerization of both scission fragments with recombination of either half the depolymerized fragmentss (solid lines) or no fragment recombination (dashed lines).

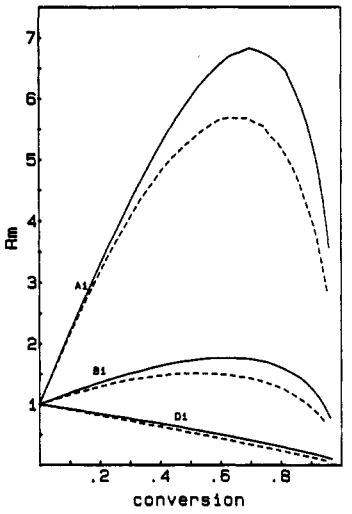


Figure 6. Comparison of R_m vs c curves calculated for degradation mechanims involving completely random chain scissions and depolymerization of both scission fragments with recombination of either half the depolymerized fragments (solid lines) or no fragment recombination (dashed lines).

case of the sample with the highest initial X. Figures 4 and 3b give evidence of the complementary nature of these plots.

Some simulations were also performed by assuming completely random scissions, DL = 100 for both fragments, and recombination of half of the depolymerized fragments. The full lines in Figures 5 and 6 show the X_n/X_{n0}, X_w/X_{w0}, and R_m vs c curves for samples A1, B1, and D1. Their degradations were also simulated according to a mechanism involving completely random chain scission, depolymerization of both fragments by the same DL, and no recombination of the depolymerized fragments. With a DL range of 50–500, it was found that when DL = 200, the X_n/X_{n0} and X_w/X_{w0} vs c curves for the highest initial X sample were very close to those for partial recombination.

The X_n/X_{n0}, X_w/X_{w0}, and R_m vs c curves calculated for no recombination and DL = 200 for both fragments are shown in Figures 5 and 6 as dashed lines. The full and the dashed lines for the highest initial X sample are almost coincident in Figure 5, whereas those for lower initial X samples are substantially different. On the other hand, the full and dashed curves in Figure 6 are well separated for the highest initial X sample and become increasingly close together with decreasing initial X and practically indistinguishable for the lowest initial X sample. It thus appears that a reasonably accurate picture of a degradation mechanism can be reached if the changes of both X and

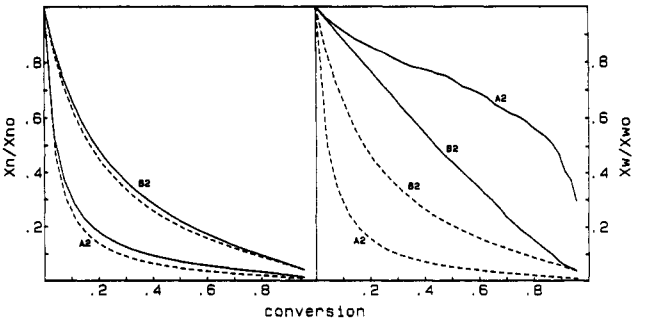


Figure 7. Comparison between X_n/X_{n0} and X_w/X_{w0} vs c curves calculated for a mechanism involving partially random (solid lines) and completely random (dashed lines) chain scissions. In partially random scissions, those near the center of the longest molecules are disfavored.

R_m are followed as a function of c and samples widely differing in initial X are used.

In the polymer degradations considered so far completely random chain scissions were assumed but, as mentioned earlier, scissions near the center of the largest molecule may be either favored (e.g., shear-induced degradations) or disfavored (e.g., diffusion-controlled degradations) and hence partially random. (Scissions at specific points in the chain are nonrandom, and degradations extensively involving them will not be considered in the present paper.)

It seems reasonable to argue that partially random chain scissions might be reflected in the dependences on c of parameters related to X such as X_n/X_{n0}, X_w/X_{w0}, and R_m, and possibly others. The question arises: can the Monte Carlo simulations take a loss of complete randomness into account and suggest the most useful parameters to be evaluated and experiments to be performed?

An answer is given by the curves in Figure 7, which show that the X_n/X_{n0} values for diffusion-controlled degradation (DL = 100 for both fragments and no recombination) of samples A2 and B2 (solid lines) are very close to those for completely random scissions (dashed lines), whereas the X_w/X_{w0} values are completely different. The difference is greater for the highest initial X sample A2, since here the number of molecules that meet the requirements for a more difficult scission near their center is relatively higher. This suggests that X_w/X_{w0} changes as a function of c should be investigated in samples with the highest possible initial X. Similar conclusions can be drawn from the plots of R_m vs c.

The different behavior of X_n/X_{n0} and X_w/X_{w0} for degradations involving partial as opposed to complete chain scission is strongly reflected in the trend of the dispersity index X_w/X_n as a function of c. When chain scissions are completely random, this index approaches 2 as degradation proceeds but greatly exceeds this value when they are partially random (as high as 40 for sample A2, Figure 7). Partially random degradations without evolution of low molecular weight products have provided similar results.[1]

High X_w/X_n values are easily predictable from the trends of the solid lines in Figure 7: they show a strong decrease of X_n at low conversions, compared with a substantially slower decrease of X_w, since in degrading samples the longest molecules are more stable than the shortest. Experimental evidence of this situation should be given by the X distribution curves, provided by size exclusion chromatography. Figures 8 and 9 show the X distribution curves obtained from simulations of the degradation at different conversions of sample A2, assuming either completely or partially random chain

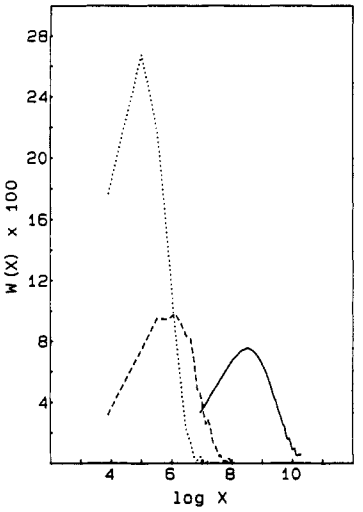


Figure 8. Distributions of degrees of polymerization in sample A2 degraded according to a mechanism involving completely random chain scissions: solid line, undegraded sample; dashed line, after 0.38 conversion; dotted line, after 0.71 conversion.

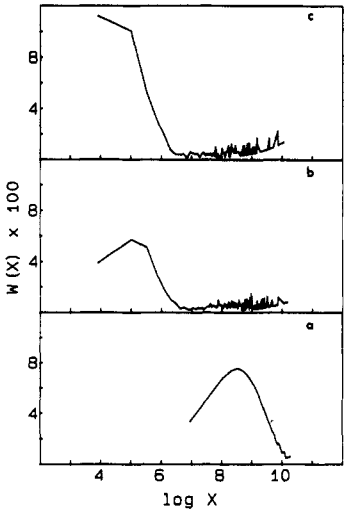


Figure 9. Distributions of degrees of polymerization in sample A2 degraded according to a mechanism involving partially random chain scissions: (a) undegraded sample; (b) after 0.35 conversion; (c) after 0.66 conversion.

scissions: high-X tails in Figure 9 and their absence in Figure 8 are clearly indicated.

Finally, we make a brief comment on shear-induced degradations. Although no experimental evidence is reported that in such degradations an extensive evolution of low molecular weight products takes place, some Monte Carlo simulations have been performed on sample A2. The results showed that X_w/X_n decreases with increasing c to values decidedly lower than 2, as reported for shear-induced degradation without evolution of volatile products.[1] Evaluation of X_w/X_n as the degradation proceeds thus enables these degradation mechanisms to be recognized.

Conclusions

Monte Carlo simulations of polymer degradation involving chain scissions and depolymerization of the fragments show that useful information on the degradation mechanisms can be achieved by plotting as a function of the conversion c to volatile products the ratios X_n/X_{n0} and X_w/X_{w0} between the number- and weight-average degrees of polymerization of the sample degraded up to c and the corresponding initial values and the ratio R_m between the numbers of molecules in the degraded and undegraded sample.

The plots of X_n/X_{n0} and X_w/X_{w0} vs c and of R_m vs c can be considered as complementary in the sense that the former discriminate degradation mechanisms when the initial characteristics of the polymer sample are different from those necessary for the latter (compare Figures 3b and 4 and Figures 5 and 6). They also provide quite accurate indications of the overall depolymerization length (i.e., the number of structural units evolved on the average after each polymer chain scission), the depolymerization lengths of both scission fragments, and the relative importance of the routes (typically, intermolecular transfer and combination) by which the depolymerizing fragments deactivate. For this purpose it is necessary to degrade samples with different initial degree of polymerization, and it may sometimes be useful to treat samples with a different initial dispersity index.

These plots also distinguish mechanisms involving completely as opposed to partially random scissions. However, other signals, as suggested by the Monte Carlo simulations, can also be considered in these cases. When scissions are completely random, the dispersity index X_w/X_n invariably approaches 2 as the degradation proceeds, and the X distribution curves shift toward lower X values without evidence of distortions. By contrast, when scissions around the center of the longest molecules are disfavored, X_w/X_n values become higher than 2, and tails at high X values are observed in the X distribution curves. When scissions around the center of the longest molecules are favored, X_w/X_n becomes lower than 2.

Acknowledgment. This work was carried out with the financial support of the Ministero dell'Università e della Ricerca Scientifica.

References and Notes

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