A DETERMINATION OF RATES RATIO OF SIMULTANEOUS CROSSLINKING AND SCISSION FROM MWD SHAPE

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Abstract—A Monte Carlo model yields a molecular weight distribution (MWD) of a degraded polymer. The simulated MWD is consistent with an experimental MWD with selection of densities of macromolecules scission and crosslinking. When the simulated MWD compares most closely with the real MWD, then the selected values coincide fairly well with real densities of scission and crosslinking.

INTRODUCTION

When polymers are aged, main chain scissions are accompanied frequently by crosslinking of macromolecules. Then, from data from number-average molecular weight measurements, only the apparent number of scissions may be evaluated.

$$N_a = N_s - N_x$$

where N_s and N_x are the numbers of scissions and crosslinkings respectively. Therefore, in the case of simultaneous scission and crosslinking for the separate determination of their rates, it is necessary to include measurements data of high order molecular weights: weight-average M_w and z-average M_z.

Equations correlating the average molecular weights M_n, M_w and M_z with densities of scission and crosslinking have been derived [1, 2] and they were applied by many researchers [3–7]. Treatments of experimental data [3, 5] were carried out using M_n and M_w. In a previous paper [6] the changes of polydispersities both M_w/M_n and M_z/M_w vs the average number of scission were used for the determination of a ratio of rates of chain scission and crosslinking. An original procedure for the determination of scission and crosslinking yields has been developed [7], which employs the combination of the ordinate intercepts of plots of $([M_w(O)/M_w(D)] - 1)/D$ and $([M_z(O)/M_z(D) - 1)/D$ vs dose D. Various ways may be used to obtain the molecular weight averages: gel-permeation chromatography [5], sedimentation equilibrium [7] and light scattering methods [4, 6]. On the other hand, the calculations which use the mathematical construction [1, 2], are confined to the initial Schulz–Zimm distribution [8]. In the present paper a more general approach has been proposed which may be applied to any MWD. It consists of comparing an experimental MWD with one simulated by computer. The ratio of scission and crosslinking rates is changed in the computer model until the simulated MWD graph compares very closely with the experimental distri-

bution. Such a method has already been applied to determine the frequency of the distribution of breakages along a macromolecule [9] and to estimate Degradation Index values from GPC data under ozonolysis and ultrasonic degradation [10]. This method has been applied here to the determination of the ratio of the rates of scission and crosslinking. Oxidative degradation of Low Molecular Weight Polyethylene (LMWPE) has been used as an example.

EXPERIMENTAL PROCEDURES

The initial LMWPE had $M_n = 3.5$ kg/mol and polydispersity 1.46. The LMWPE was oxidized with molecular oxygen at temperature 393 K. A blend of K, Mn and Cr stearates was used as a catalyst (2×10^{-3}, 2×10^{-3}, 5×10^{-4} mol/kg respectively). Acid numbers were measured by alkalimetric titration with isopropanol as solvent. The molecular weight distributions of oxidized samples were determined by a gel-permeation chromatograph (WATERS GPC 200) with styragel columns (100 and 500 Å) in toluene at a flow rate of 9 ml/min. A calibration was performed with nine polystyrene standards having molecular weight in the range from 12,500 to 580 and styrene. Number-average molecular weights were measured with an ebulliometer EP-68 with benzene as solvent. The simulation of MWD changes was performed with a Monte Carlo model. An algorithm of the model is shown in Fig. 1. A subroutine for macromolecules crosslinking was added to the computer program simulating the chain scission, which had been described in an earlier paper [11]. Under a simulation performance the subroutines of scission and crosslinking are executed in turn with repeat numbers NS and NC. The parameters NS and NC are small integers from 0 to 300. They define the ratio rates of scission and crosslinking. The repeat number NG defines a final degree of degradation. This parameter is a large integer and is proportional to a general number of macromolecules in the model system (about 10^6–10^9). So the processes of scission and crosslinking occur quasi-simultaneously because the corresponding subroutines are executed in turn with small degrees of conversion. Therefore, the computer model corresponds more to reality than the mathematical models [5, 6], which assume that crosslinkings occur after all scissions have taken place.
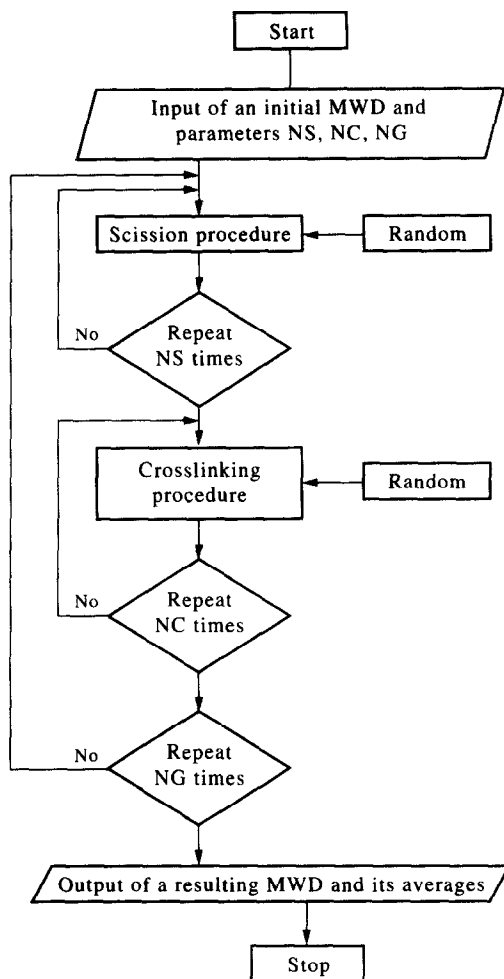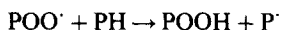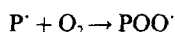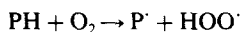
Fig. 1. Algorithm of simulation.

Fig. 2. Carboxyls (1) and scissions (2) concentration in LMWPE vs time of oxidation.

RESULTS

An intensive carboxyl group formation occurs during the oxidation of LMWPE—see Fig. 2. Consequently, the scission of polymer chains takes place. Initial products of the oxidation are free radicals and hydroperoxides, whose formation and mutual conversion occur according to the well-known scheme [12, 13]

$$PH + O_2 \rightarrow P^{\cdot} + HOO^{\cdot}$$

$$P^{\cdot} + O_2 \rightarrow POO^{\cdot}$$

$$POO^{\cdot} + PH \rightarrow POOH + P^{\cdot}$$

$$POOH \rightarrow PO^{\cdot} + {}^{\cdot}OH \text{ etc.}$$

where $P^{\cdot}$ is a long alkyl radical. Among hydroperoxides. secondary ones are formed predominantly because the numbers of —CH_3 and —CH groups in polyethylene are much less as compared

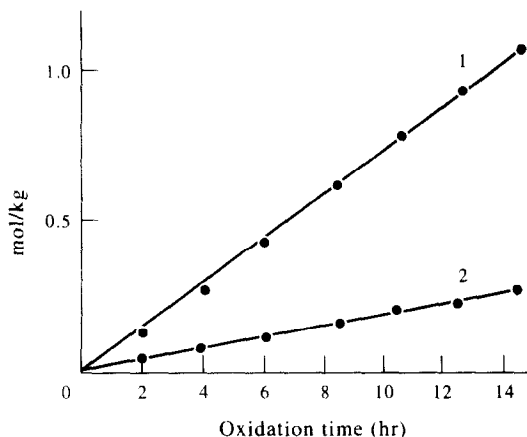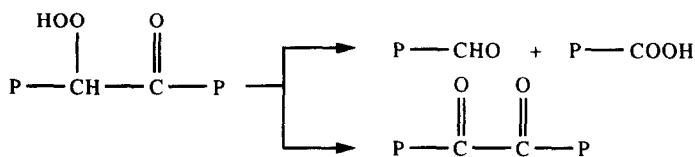with the number of —CH_2— groups. A conversion of the secondary hydroperoxides in a medium saturated by oxygen has been well investigated in the oxidation of long-chain paraffins. There are two main ways of sec-hydroperoxides decay: (see Schemes 1 and 2) [14–16].
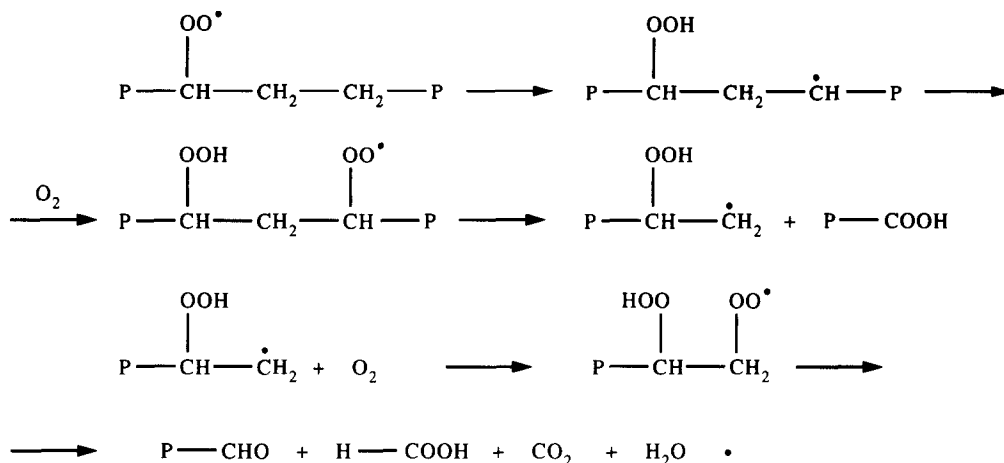
At conditions of high temperature and oxygen saturation the formed aldehydes are oxidized quickly into organic acids, and formic acid is oxidized into carbon dioxide or is carried away by the oxygen flow. The crosslinkings occur under recombination of alkyl-alkoxyl- and hydroperoxy-macroradicals. In such cases the following structures are formed [17] (see Scheme 3).

On the average two —COOH groups (or slightly less because of the formation of carbonyl groups) are formed per one fracture of carbon chain. Therefore a quantity of acid groups must be double, or a little less than double, the number of fractures. However, the experimental value of the concentration of carboxyls is more than double the apparent concentration of fractures (Fig. 2). Consequently, in the process studied the crosslinking of macromolecules takes place as well. Also, GPC leads to this inference: it is seen in Fig. 3 that the number fraction of species with most molecular masses increases slightly at low times of oxidation.

The computer simulation was used as well as described above in order to determine the rates of scission and crosslinking. When the only scission procedure takes place under simulation, then the resulting MWD differs very much from the real one [Fig. 3(a)]. In the case when the subroutines both of scission and crosslinking are executed, then the simulated MWD corresponds more to the experimental data [Fig. 3(b,c)]. A performed screening of rates of scission and crosslinking showed that the simulated MWD cannot be compared very closely with

Scheme 1

$$P-\underset{\underset{OO^\bullet}{|}}{CH}-CH_2-CH_2-P \longrightarrow P-\underset{\underset{OOH}{|}}{CH}-CH_2-\overset{\bullet}{CH}-P \longrightarrow$$

$$\overset{O_2}{\longrightarrow} P-\underset{\underset{OOH}{|}}{CH}-CH_2-\underset{\underset{OO^\bullet}{|}}{CH}-P \longrightarrow P-\underset{\underset{OOH}{|}}{CH}-\overset{\bullet}{CH}_2 + P-COOH$$

$$P-\underset{\underset{OOH}{|}}{CH}-\overset{\bullet}{CH}_2 + O_2 \longrightarrow P-\underset{\underset{HOO}{|}}{CH}-\underset{\underset{OO^\bullet}{|}}{CH}_2 \longrightarrow$$

$$\longrightarrow P-CHO + H-COOH + CO_2 + H_2O \bullet$$

Scheme 2

the experimental MWD of oxidized LMWPE—either the left [Fig. 3(b)] or right [Fig. 3(c)] tail of the MWD moves away from the experimental MWD curve. Considering the above data, one can arrive at a conclusion that the real ratio of rates of crosslinking and scission is a value in the range from 5/25 to 8/28. To all appearances the ratio 8/28 corresponds more to reality. In this case the difference between the simulated and experimental MWDs may be explained by the formation of star-branched macromolecules owing to crosslinking. A branched macromolecule has a hydrodynamic volume less than a linear one with the same molecular weight. Therefore, the stars are detected during size-exclusion chromatography at a longer retention time than unbranched macromolecules and, respectively, the gel-chromatograph indicates a lowered content of high-molecular species in which the branched products of crosslinking are concentrated.

In order to verify a reliability of the model, a picture of computed changes of number-average molecular weight has been demonstrated in Fig. 4 together with the experimental data. A basis for comparison is the ebulliometry data, because those are more accurate in the range of low molecular weights in question. It is observed, that the results of GPC measurements differ markedly from the ebulliometric data. This fact may be due to a relative calibration with polystyrene samples, However, an alteration of chemical composition plays an important role as well. This conclusion results from the fact

that at first the M_n data do not differ (Fig. 4) and the discrepancy between GPC and ebulliometry appears progressively with the increase of oxidation extent. Work [18] has inferred convincingly, that polar —OH and —COOH groups effect considerably retention time in GPC because of adsorption. In addition, the formation of star-branched macromolecules also leads to inaccuracy of the GPC data (see above). As to the simulation results, they differ slightly from the ebulliometry data (see Fig. 4). This difference is a result of the inaccuracy of the initial experimental MWD shape. In the mean time, the distortions of molecular weight shape in GPC concern the tails of MWD: polar products of oxidation are concentrated in the low-molecular region and the products of crosslinking distort the high-molecular species. In spite of deviations at the tails, the model holds at the main peak of MWD—see Fig. 3(b,c). That is why the simulated MW data are nearer to ebulliometric results than those of GPC.

CONCLUSION

The ratio of rates of scission and crosslinking, occurring simultaneously, may be determined by comparing a computer simulated MWD with an experimental one. In the considered case they are equivalent when $N_x/N_s = 0.24 \pm 0.04$. To increase the accuracy of the described method, it is reasonable to use the MWD determination methods which do not distinguish between linear
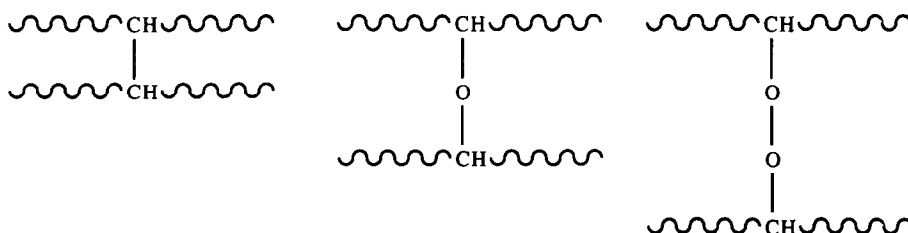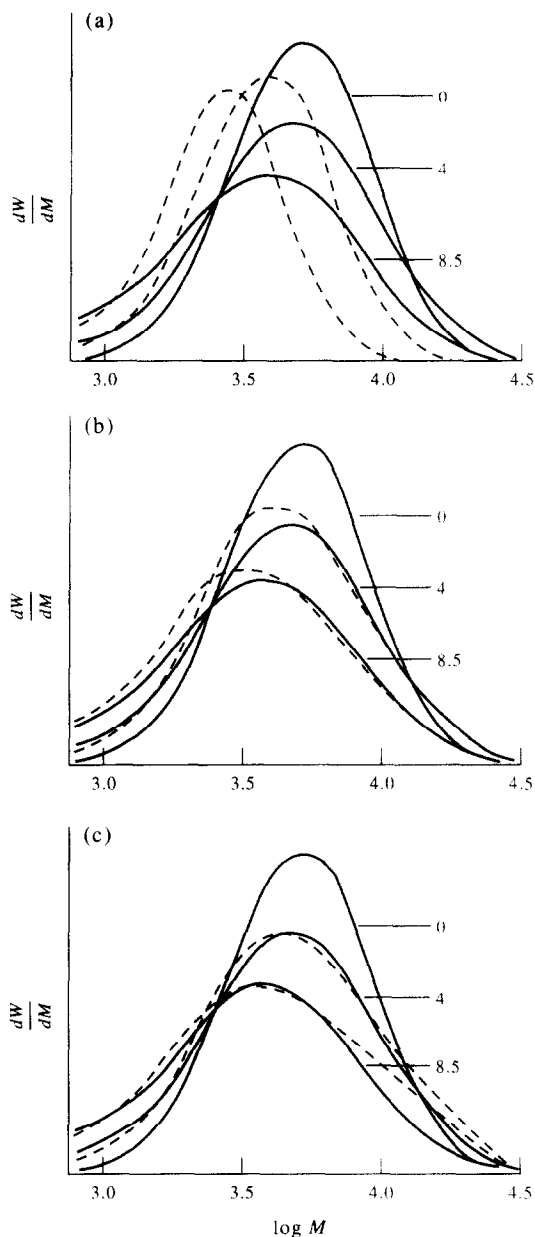
Scheme 3

Fig. 3. Molecular weight distributions of the experimental samples of LMWPE (solid lines). Numbers near the curves mark the reaction time. Broken lines display the computer simulated MWDs at the following ratios of crosslinking and scission rates: (a) 0, (b) 5/25 and (c) 8/28.

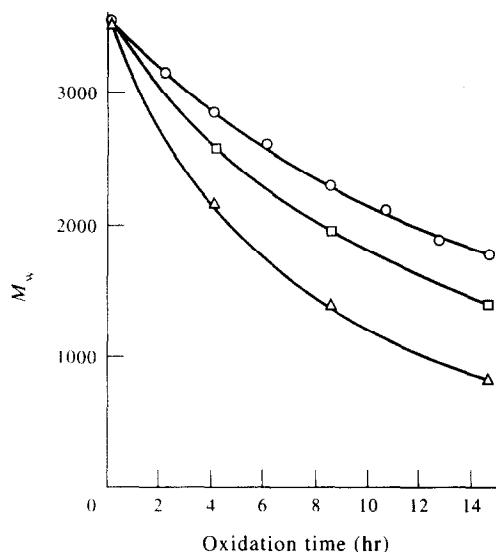and branched macromolecules, e.g. sedimentation equilibrium or low-angle laser light scattering.

Fig. 4. Comparison of number-average molecular weight data: (○) ebulliograph; (□) computer simulation; and (△) gel-permeation chromatograph.

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