

Analysis of Chain-Scission and Crosslinking Rates in the Photo-oxidation of Polystyrene

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ABSTRACT: A study of the chain-scission and crosslinking rates in polystyrene photo-degraded in the laboratory with fluorescent tubes (UVA-340) was made using GPC molecular weight distributions. The analysis was based on the assumption that scission and crosslinking occur randomly and employed a Monte Carlo procedure to compute the changes in molecular weight distribution for chosen values of scission and crosslinking rates and compared the computed profiles with measurements made on the photodegraded samples. Results were obtained for three different exposures and at various depths within 3.2-mm-thick bars. The scission/crosslinking ratio, λ , was between 3 and 8 for all samples measured in this study. The lowest values of λ were found near the exposed surface and the highest near the bar center. Both scission and crosslinking rates were much lower in the interior, presumably the result of oxygen starvation. Some bars were exposed while loaded to 10 MNm^{-2} in uniaxial tension. The stress appeared to increase the reaction rates somewhat near the surface and to depress the rates in the interior correspondingly. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3015–3023, 2000

Key words: chain scission rate; crosslinking rate; molecular weight distribution; photo-oxidation; polystyrene

INTRODUCTION

The chemical reactions that occur during photo-degradation of polymers under natural weathering conditions or laboratory conditions chosen to simulate weathering have been presented in many reviews.^{1–6} The products of reaction include radicals that produce more degradation, but from the point of view of the properties of the polymer article, the most important molecular events are chain scission and crosslinking. Therefore, in the study of polymer photodegradation,

molecular weight measurement is an important tool. Most methods for measuring molecular weight provide an average;⁷ this is often satisfactory if the type of molecular change occurring is of one type only (scission or crosslinking) but it cannot give an accurate picture of what is happening if both scission and crosslinking take place simultaneously. In this case, gel permeation chromatography (GPC) is a valuable technique because it measures the molecular weight distribution. It enables calculation of molecular weight averages if required, but it also provides further detailed information, and that was exploited in the study described here.

Commodity polymers are always polydisperse with quite wide molecular weight ranges and it is

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essential to begin any study of molecular weight degradation with a measurement of the starting distribution. If chain scission occurs, the molecular weight distribution drifts toward smaller values and the progressive changes in molecular weight distribution can be modeled if it can be assumed that scission occurs at random.^{8,9} If crosslinking occurs, the molecular weight distribution drifts in the opposite direction. If both scission and crosslinking occur, then the shape of the molecular weight distribution changes considerably.

In earlier studies of the photooxidation of polystyrene, it was observed that there was a general shift of the distribution curve to lower molecular size but that a high molecular weight tail developed under some conditions, showing that some molecules had grown to a size larger than in the initial undegraded specimen. In this case, an average molecular weight does not indicate the full extent of chemical degradation. Although crosslinking may repair some of the damage done by chain scission, which releases entanglements and ultimately destroys the molecular network, the crosslinks do not behave in exactly the same way as do the entanglements. Deterioration of mechanical properties is likely to be greater for a particular reduction in average molecular weight if both scission and crosslinking occur than if it is caused by (a smaller amount of) scission only. Therefore, it would be useful to have a measure of the ratio of crosslinking-to-scission events in order to augment the data on the average molecular weight reduction occurring during a degradation process.

One approach to the determination of the ratio of crosslinking to scission is to model the progress of degradation using a Monte Carlo method¹⁰ and to compare the measured molecular weight distributions with the equivalent computed profiles. This method was used in a study of the oxidation of low molecular weight polyethylene at 393 K.¹⁰ The computed profiles did not match the measured distributions exactly, but the fit was sufficiently good to estimate that the ratio of crosslinking to scission was 0.24 ± 0.04 .

In the work presented here, this procedure has been further refined and applied to samples taken at different depths from the surface of bars photodegraded using ultraviolet radiation (UV) in the laboratory at intensities comparable to solar levels near the equator. The average molecular weight reduction was found to vary steeply with depth.¹¹⁻¹³ This is attributed to an oxygen diffu-

sion-limited reaction and oxygen starvation in the interior.¹⁴ Under the conditions used, the reaction near the surface of the samples is so great that the oxygen is almost completely consumed before it can penetrate very far and reaction occurs mainly within 1.0 mm from the surface, often within 0.5 mm of the surface. The exact limit to the degradation zone depends on the polymer and on the conditions (UV intensity, temperature, etc.) and there is a steep degradation profile within the degraded zone. It is therefore expected that those reactions which do not require oxygen will become progressively more favored as the depth from the surface increases. Of particular relevance here is the reaction between polymer radicals, which is the source of crosslinking. There will be less competition from other reactions in parts of the sample in which the oxygen level is very low. Thus, the purpose of this study was to examine whether the crosslink-to-scission ratio showed any change with the depth from the surface.

EXPERIMENTAL

Preparation of Test Pieces

The experiments were conducted on injection-molded bars made for the earlier studies¹¹⁻¹³ from polystyrene (BP HH101) containing no UV stabilizer, according to the manufacturer. Samples were made in the form of injection-molded bars measuring approximately $190 \times 12.7 \times 3.2$ mm using a tool with an end-gated cavity. The molecular weight distribution for an as-molded sample was found to be almost indistinguishable from that for the virgin material.¹²

Exposure Conditions

The bars were exposed to UV on open racks or in a creep rig under constant stress or in a bending jig under constant strain in a room in which the temperature was maintained at $30 \pm 1^\circ\text{C}$. Fluorescent tubes type UVA-340 (Q-Panel Co.) were used as the UV radiation source. The tubes used were chosen because their output in the UV matches the spectrum of solar radiation at the Earth's surface fairly closely.¹¹ Measurements made using a Bentham Instruments photoradiometer showed that the illumination falling onto a flat test piece with its axis perpendicular to the tube axes is fairly uniform over the gauge length.

The separation between the test-piece surface and the plane containing the tube axes gave an intensity of up to 4 Wm^{-2} in the wavelength range 295–320 nm, that is, the total radiation below the 320 nm wavelength. This level of UV illumination corresponds to midsummer conditions in Jeddah, Saudi Arabia, which has one of the most severe climates in which polymer weathering trials have been conducted.^{15–18} Continuous exposure meant that there was no opportunity for oxygen recovery during dark periods as can happen at night in outdoor exposure. The illumination level diminishes as the UV penetrates deeper into the bar and the absorption coefficient was measured to permit calculation of the intensity at all levels in the bar during exposure.¹¹ Most of the analyses reported here were conducted on bars exposed for 4 or 6 weeks plus some additional ones on bars exposed for 2 weeks.

Molecular Weight Measurement

Samples for molecular weight analysis were prepared by milling material from the bars using a single-point cutter with a fly-cutting action. The machine swarf or chips were collected for GPC analysis. It was established that this procedure did not produce any detectable damage additional to that caused by photodegradation.¹¹ Approximately 0.2–0.3 mm were removed from the bar surface each time; the material used for molecular weight measurement was taken from the central 70 mm of the gauge length. This provided a sample from each depth of about 0.2 g, sufficient to make two GPC runs. Comparison with results obtained with virgin material showed that very little degradation took place during injection molding.¹²

The molecular weight analysis of the samples was carried out by GPC at Rapra Technology Ltd. using the standard systems and procedures of the Polymer Supply and Characterisation Centre. The columns used were Polymer Laboratories PL gel $2 \times$ mixed gel-B, with a column length of 300 mm and a particle size of 10 microns. The solvent was tetrahydrofuran and the solution concentration was 2.0 kg m^{-3} . The injection volume was 200 mm^3 (0.2 mL), and the flow rate, $10^3 \text{ mm}^3 \text{ min}^{-1}$ (1.0 mL min^{-1}); the temperature was $<30^\circ\text{C}$. The system was calibrated with narrow molecular weight distribution polystyrene calibrants (Polymer Laboratories Ltd) and the data were processed using “GPC-PRO” software (Viscotek Corp.) using procedures described previously.¹²

The results were presented as the number-average molecular weight, M_n , weight-average molecular weight, M_w , and as continuous size-distribution plots versus molecular weight. It is the latter on which the focus of the current article was placed. A reference sample cut from a virgin pellet of the polymer under examination was run at the beginning of each batch of GPC runs.

The effect of molecular shape is ignored in this work. It is accepted that a crosslinked molecule will pass through the column at a slightly different rate to a linear molecule of the same mass, but in the absence of an independent measure of the concentration of crosslinked molecules, this is an inevitable limitation.

SCISSION–CROSSLINK ANALYSIS

The scission-to-crosslink ratio was determined from the GPC molecular weight distribution profiles by comparing the experimental profiles with computer simulations based on an algorithm described in an earlier article.¹⁰ The computation procedure involves the preparation of a numerical table containing molecular weight distribution (MWD) data as the mass fraction versus molecular weight. Simulation software developed by one of the current authors¹⁹ reads a file with the initial MWD and inserts it into the computer memory. The computer then simulates a trial number of macromolecule scissions and crosslinkings, expressed as the scission index (SI) = number of scissions per molecule, and the crosslinking index (CI) = number of crosslinks per molecule. The resulting MWD is compared with the MWD of the degraded polystyrene sample and the sum of the squares of the residuals is calculated for 68 points equally spaced along the log (molecular weight) axis. After considering the match between the experimental MWD and the computer simulation, the operator repeats the simulation using a new pair of input parameters (SI and CI) and this procedure is repeated until the sum of the squares on the residuals is minimized [judged to be reached when a small change in SI or CI ($\sim \pm 0.001$) produces an increase in the sum of the squares]. This simple procedure produces good accuracy in a relatively small number of iterations (e.g., see Fig. 1). The fit between the simulated distribution and the experimental distribution is visually very good when the sum of the squares is about 2×10^{-5} ; some of the simulations gave sums of $\sim 4 \times 10^{-6}$. Even the poorest

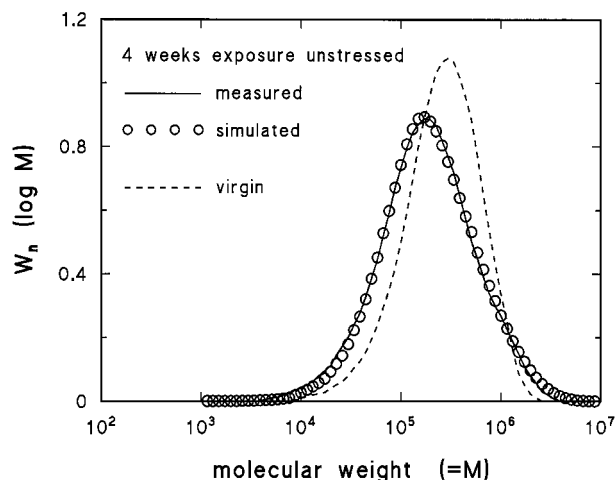


Figure 1 Comparison of the (solid line) GPC experimental MWD and (open circles) computed values for the best fit simulation for a polystyrene sample extracted from near the surface of a bar exposed un-stressed for 4 weeks. The broken line shows the distribution for the virgin polystyrene sample.

fits, with the sum of squares $\sim 10^{-4}$, gave fairly good visual fits and do not indicate a serious departure from the assumed reaction scheme in which random chain scission and crosslinking events dominate over other reactions which might skew the MWDs.

The parameters that can be used to give a quantitative characterization of the degradation extent that can be obtained from this analysis are as follows: scission concentration, C_s , crosslink concentration, C_c (both in mmol kg^{-1}), and their dimensionless ratio, $C_s/C_c (= \lambda)$. The error in the scission and crosslink ratios is estimated to be in the range 2–10%.

RESULTS AND DISCUSSION

Effect of Photodegradation

The MWD for an as-molded sample was found to be almost indistinguishable from the virgin material,¹² and at the current state of development, the modeling procedure introduced here is unable to detect the presence of any crosslinking or scission during molding. The reference samples were extracted from virgin material, removed from granules that had not been subjected to any processing.

Figure 1 shows the molecular weight distribution obtained from GPC analysis of a sample

taken from the surface of a polystyrene bar that had been exposed to UV for 4 weeks, compared with the distribution in the virgin polymer. The profile for the degraded material shows a general shift to the left (smaller molecular size), but it is evident that a high molecular weight tail has developed as well, indicating that although significant scission must have taken place, crosslinking is present as well. In this case, scission has indeed prevailed over crosslinking: The computed profile in Figure 1 represents polystyrene with a scission concentration $C_s = 6.54 \text{ mmol kg}^{-1}$ and a crosslink concentration $C_c = 1.44 \text{ mmol kg}^{-1}$.

Depth Dependence of Scission-to-Crosslinking Ratio

Figure 2 shows the MWDs obtained from the GPC measurements made on a series of samples taken from different depths of a polystyrene bar exposed to UV for 4 weeks. There is an overall decrease in molecular weight at each depth; at all depths, there is a general shift to the low molecular weight side. On the other hand, there is no reduction in the mass fraction of the highest molecular weights at any depth. At some depths, a high molecular weight tail developed which lies significantly higher than the virgin polymer line. This is clear indication that crosslinking has occurred. This is confirmed by the detailed analysis (Fig. 3). This shows that crosslinking occurs at all depths but that scission, which has a higher frequency at all depths, is more dominant in the interior, giving a scission-to-crosslink ratio distribution that peaks near the center of the bar (Fig. 4).

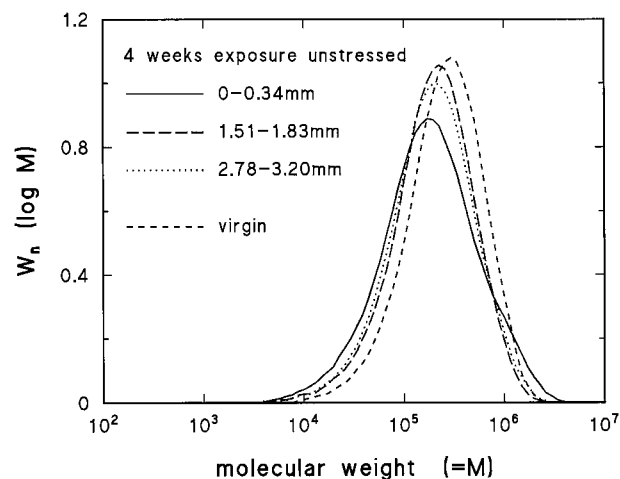


Figure 2 MWDs for samples extracted at different depths from a bar 3.2 mm thick after 4 weeks' exposure un-stressed (GPC data).

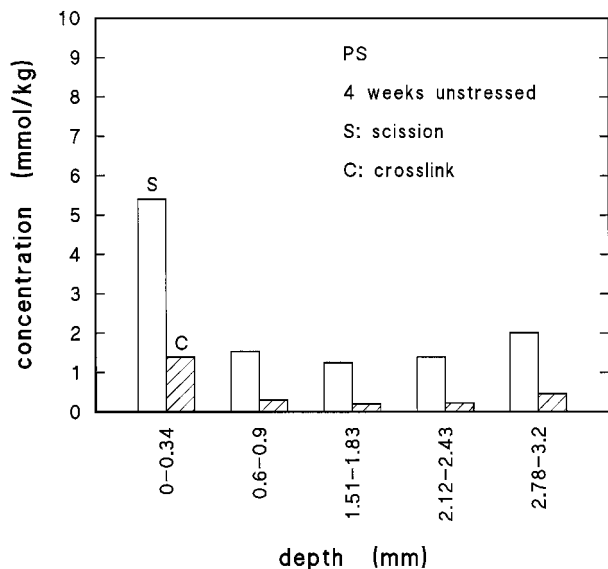


Figure 3 (Light shading) Scission and (dark shading) crosslink concentrations at different depths of a bar exposed for 4 weeks unstressed.

Both scission and crosslinking rates are highest near the exposed face and the second highest rates were recorded near the unexposed face (Fig. 3). This is consistent with an oxygen-diffusion limitation in the interior. (Recall that the UV intensity decreases through the bar and that the UV intensity is lower at the back face than in the interior). The scission-to-crosslink ratio, λ , is greatest in the interior.

Similar results were obtained on a bar exposed for 6 weeks (Figs. 5 and 6). Note that the sample

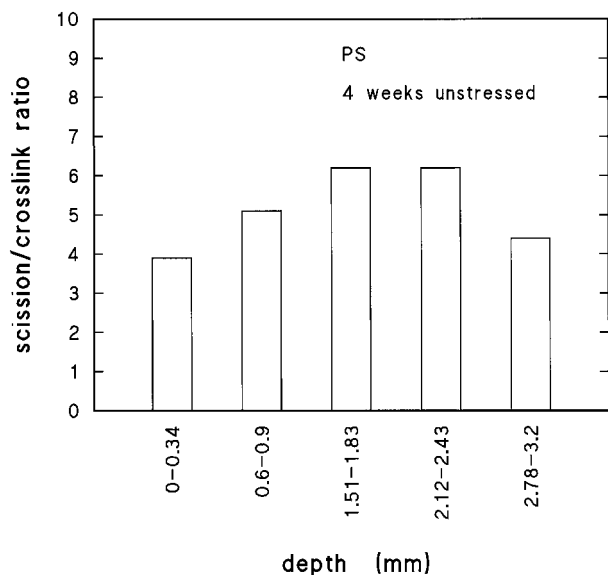


Figure 4 Ratio of scission/crosslink concentrations versus depth for a bar exposed for 4 weeks unstressed.

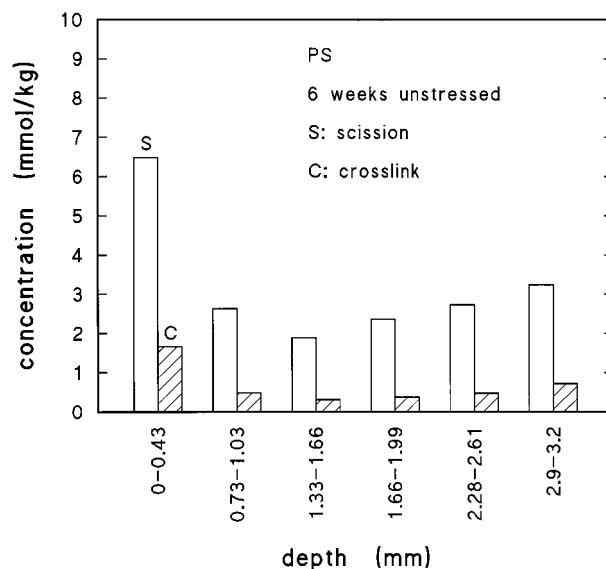


Figure 5 Scission (light shading) and crosslink concentrations (dark shading) at different depths of a bar exposed for 6 weeks unstressed.

taken from near the surface of the 6-week-exposed bar was approximately twice the depth of that taken from the 4-week bar. This makes comparison of results difficult because of the steep degradation profile near the surface. This will cause the scission rate in the surface sample from the bar exposed for the longer period to be, on average, lower than it would have been if the same sample depth had been taken as for the

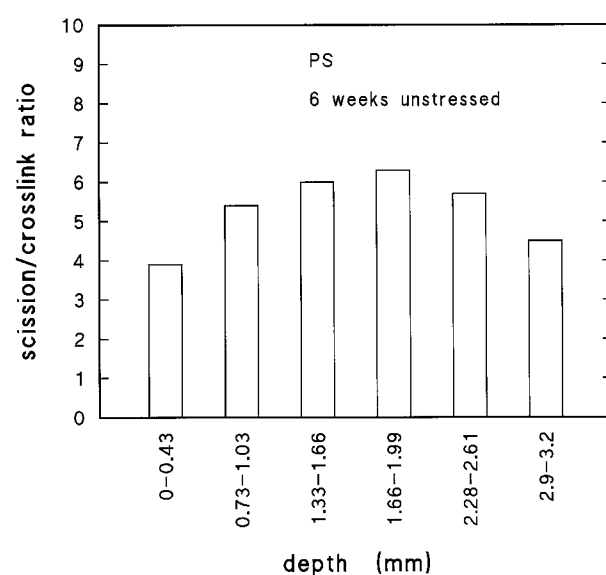


Figure 6 Ratio of scission/crosslink concentrations versus depth for a bar exposed for 6 weeks unstressed.

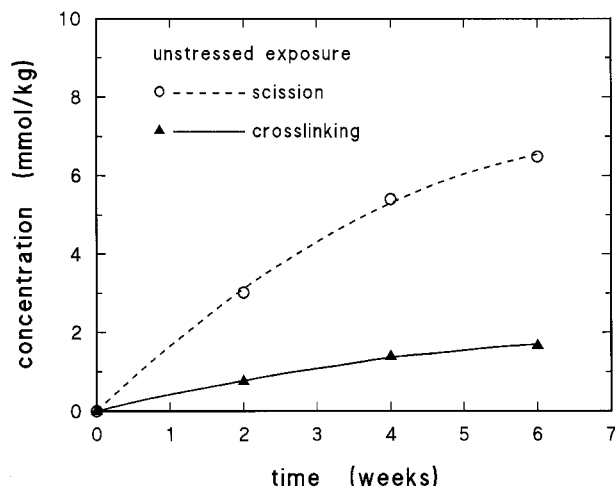


Figure 7 Scission and crosslink concentrations near the exposed surface of bars exposed for various periods unstressed.

4-week bar. Thus, the progression of degradation with time is greater than what appears to be present at first sight. On increasing the exposure time from 4 to 6 weeks, the scission-to-crosslink ratio did not change markedly at the various locations through the depth. At the surface, the crosslinking index advanced almost linearly with exposure time, whereas the scission index increased less than linearly with exposure (Fig. 7). This may be because the fraction of very low molecular weight material, which falls below the detection limit for the GPC method, increases with exposure, although this effect was not apparent with samples exposed while stressed (see below).

Effect of Stress on Scission and Crosslinking Rates

Measurements made on a bar exposed to UV for 4 weeks while under an applied tensile stress of 10 MNm^{-2} are given in Figures 8–10. On comparing the results in Figure 8 with those given in Figure 3 for an unstressed bar exposed under the same conditions, it appears that the presence of the tensile stress caused an increase in degradation at the exposed surface, whereas the degradation in the interior was less. Regrettably, the sample taken from near the surface of the bar exposed in the unstressed condition was much thicker than that taken from near the surface of the stressed bar. Thus, an alternative explanation for the difference in the unstressed and stressed samples is the steep degradation gradient known to be present near to the surface and it is not possible

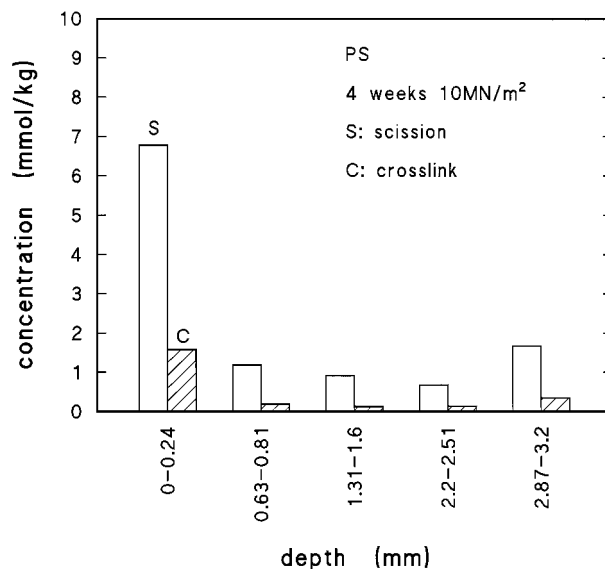


Figure 8 (Light shading) Scission and (dark shading) crosslink concentrations at different depths of a bar exposed for 4 weeks while stressed in uniaxial tension at 10 MNm^{-2} .

to attribute this effect to stress with certainty. A similar problem exists with the results obtained after 6 weeks' exposure (Fig. 11; cf. Fig. 6). Nevertheless, in both the 4-week and the 6-week comparisons, the indicated degradation in the interior is lower in the presence of stress, which is consistent with oxygen starvation caused by (stress-)

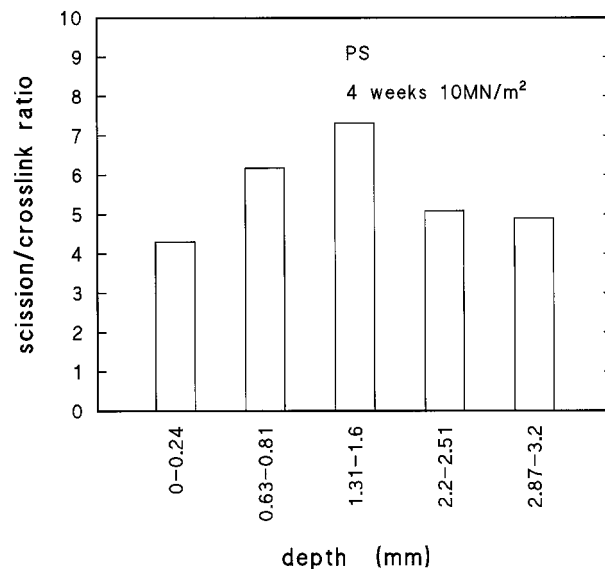


Figure 9 Ratio of scission/crosslink concentrations versus depth for a bar exposed for 4 weeks while stressed in uniaxial tension at 10 MNm^{-2} .

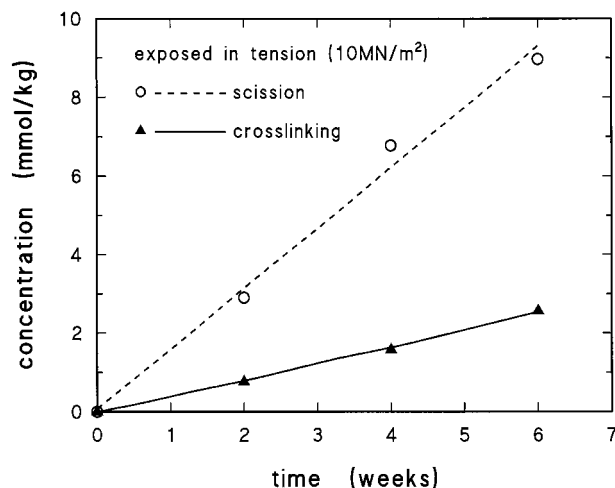


Figure 10 Scission and crosslink concentrations near the exposed surface of bars exposed for various periods in uniaxial tension at 10 MNm^{-2} .

accelerated degradation at the surface. Comparison of Figures 7 and 10 seems to indicate that tensile stress accelerates both scission and crosslinking, but definite conclusions cannot be drawn because of the uncertainty of the effect of sample thickness. The scission/crosslink ratios at different depths in the stressed samples are given in Figure 12.

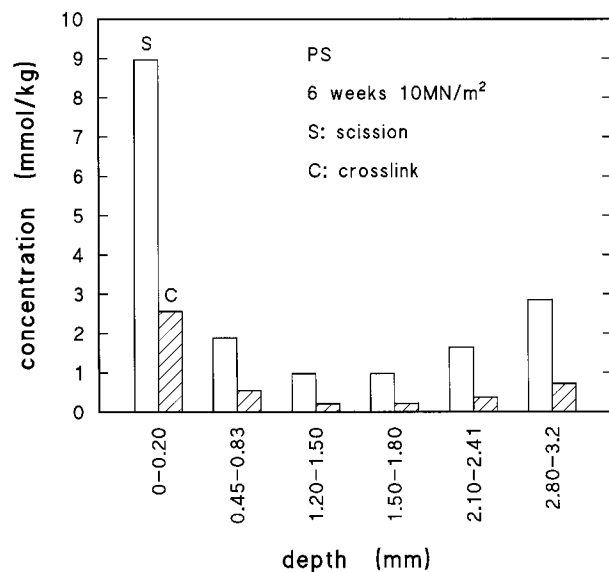


Figure 11 (Light shading) Scission and (dark shading) crosslink concentrations at different depths of a bar exposed for 6 weeks while stressed in uniaxial tension at 10 MNm^{-2} .

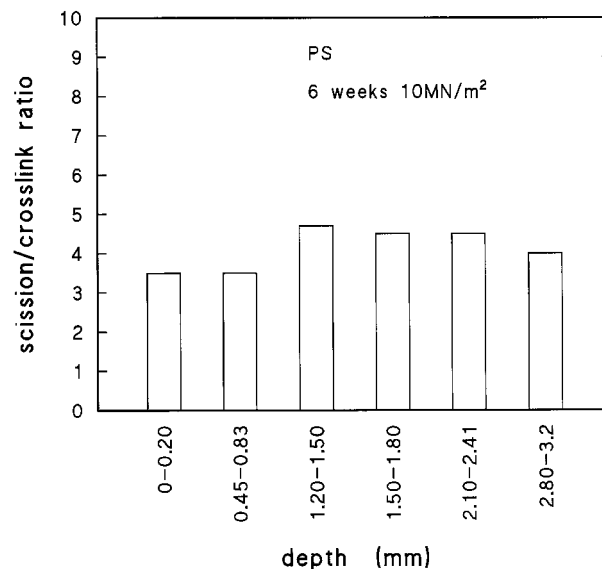


Figure 12 Ratio of scission/crosslink concentrations versus depth for a bar exposed for 6 weeks while stressed in uniaxial tension at 10 MNm^{-2} .

DISCUSSION

In previous studies of the photooxidation of polystyrene,^{11,13} the number-average molecular weight, M_n , and, to a lesser extent, the weight-average molecular weight, M_w , were used to follow the molecular degradation. In the present work, based on the same GPC data, a more detailed analysis is attempted. Whereas in previous studies M_n was used to generate a scission rate, S , derived on the assumption that crosslinking was negligible, the present study follows changes in both scission and crosslinking with exposure and at different depths from the molding surface. At the surface, a high molecular weight tail developed, indicating, clearly, that crosslinking must have occurred. The same was observed to a lesser extent at the unexposed face and at some locations within the moldings, and an objective of the work described here was to quantify the amount of crosslinking using an analysis based on the full GPC MWD.

The results confirmed that scission dominated over crosslinking at all depths. Values for the scission/crosslink ratio of between 3 and 8 were measured for exposures of 4 and 6 weeks at tropical UV intensity levels (continuous exposure). The lowest values were always obtained near the exposed surface and the highest values near the bar center. This was an unexpected result because it had been anticipated that the shortage of

oxygen would favor radical–radical combination (creating crosslinking) relative to other reactions involving free radicals. On the other hand, an intense reaction will create large numbers of radicals in near proximity, favoring combination, and the results reported here indicate that this is more important than is the relative competition between reactions. There was an apparent slowing of the scission rate with exposure near the surface; the crosslinking rate here apparently remained constant as degradation proceeded.

Comparison of results obtained with bars exposed unstressed and under a uniaxial tensile stress (of 10 MNm^{-2}) seems to indicate that the presence of the (applied) tensile stress accelerated the reaction near the surface, increasing both scission and crosslinking rates, but this cannot be regarded as certain because of the difference in sample depths taken from bars exposed stressed and unstressed, respectively. In the case of 4 weeks' exposure, this was accompanied by an increase in the scission/crosslinking ratio, λ . Weir and Whiting observed that the scission rate of polystyrene in solution was greater than that in films and attributed this to recombination, which they noted is more likely in film.²⁰ We speculate that tensile stress reduces the likelihood of recombination once scission occurs and it is possible that this accounts for the increase in both the scission index and the crosslinking index. Intuitively, this will have a greater effect on scission and, hence, an increase in λ might be expected. An applied stress will have this effect at all depths, but it must be remembered that injection moldings also contain residual stresses. In the as-molded state, the residual stresses in polystyrene moldings of this kind are tensile in the interior and compressive near the surface.²¹ Although the residual stresses change significantly under photooxidation and eventually become reversed,²¹ for the exposure times investigated here, the stresses in the center of the bar remain tensile throughout. Thus, in the case of the bar exposed without applied stress discussed above, the observation of λ values near the center higher than those near the surface could be due to the tensile residual stresses in the center causing a greater preference for (observed) scission events. Compressive stresses apparently have an opposite effect on photooxidation to that produced by tensile stresses.¹³ The results obtained for 6 weeks' exposure indicated a reduction in λ in the interior when tensile stress was applied, an effect for which we can offer no explanation at the present time.

The scission index is lower in the interior of a tensile-loaded bar than that for a similarly exposed unstressed bar at this location. It is noted that both SI and CI are higher at the surface of the stressed bar, indicating higher reaction rates. Tensile stress is believed to cause acceleration of polymer oxidation rates^{11,22,23} and the consequential increase in oxygen consumption near the surface can be expected to lead to even greater starvation in the interior, reducing all degradation reactions.

CONCLUSIONS

A method developed earlier^{8–10} to determine chain-scission and crosslinking rates in polymer degradation has been refined and applied to the photodegradation of polystyrene. Significant changes in MWDs were found to occur and the analyses showed that both chain scission and crosslinking occurred and that scission dominated. The scission-to-crosslinking ratio was between 3 and 8. The lowest values were recorded near to the exposed face, whereas the highest values occurred near the bar centers, indicating that a high rate of radical production (as at the exposed face) had a (relatively) greater effect on crosslinking than on chain scission. This is a particularly important result because it had been expected that crosslinking reactions would show greater relative prominence when oxygen was in low concentration. Oxygen starvation limited both scission and crosslinking in the interior, with the greatest effect when a tensile stress was applied, presumably because of the consequent enhanced reaction rate at the surface.

The experimental program in which the original data analyzed here were obtained was supported by an SERC research grant. S. R. Holding of Rapra Technology Ltd. made the GPC molecular weight measurements and gave invaluable assistance in refining the method of converting the chromatograms into MWDs. The polystyrene was a generous gift from BP Chemicals, Grangemouth. We are grateful to Diana Stavichna for assisting with some of the computations.

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