

Effect of Molecular Weight on Changes Produced in the Surface Layer of Polystyrene Film in a Nitrogen Atmosphere by Ultraviolet Irradiation

KOICHIRO KATO, *Second Technical Division,
Industrial Arts Institute, Tokyo, Japan*

Synopsis

The effect of molecular weight on the changes in the surface layer of polystyrene films on near-ultraviolet irradiation has been studied in a nitrogen atmosphere at 25°C. Changes produced by irradiation were followed by determining the amount of solvent-insoluble portions, the molecular weight changes, and the intrinsic viscosity changes. Most crosslinking took place in the range of the transmissible depth of 2537 Å light. Low molecular weight samples formed a small amount of solvent-insoluble material. High molecular weight samples formed a large amount of solvent-insoluble material. In the range above a certain molecular weight, the amount of solvent-insoluble material approached an asymptotic value with increasing molecular weight, because of the limited penetration of 2537 Å light. Since most crosslinking took place in the range of the transmissible depth of 2537 Å light, the average number of crosslinks in the solvent-soluble portions was influenced by the amount of solvent-insoluble material. Low molecular weight samples produced many crosslinks. High molecular weight samples produced a few crosslinks. In the range above a certain molecular weight, the average number of crosslinks in the solvent soluble portions approached an asymptote with increasing molecular weight. Chain scission seems to have occurred in every sample.

There have been several reports^{1,2} of the photolysis of polystyrene films. However, the effect of molecular weight on the changes produced in the surface layer when polystyrene films were irradiated in a nitrogen atmosphere by near ultraviolet light has received relatively little attention. This paper describes the effect of molecular weight on the changes in the surface layer in a nitrogen atmosphere on irradiation.

EXPERIMENTAL

Materials

Styrene monomer was polymerized in bulk under an oxygen-free atmosphere without use of catalyst. The polymer was fractionated by a fractional dissolution method. The highest molecular weight fraction, A, the lowest molecular weight fraction, E, and the three intermediate fractions, B, C, and D were selected as samples. The weight-average molecular

weights, \bar{M}_w , the heterogeneity ratios, \bar{M}_w/\bar{M}_n , and the intrinsic viscosities, $[\eta]$, are given in Table I.

TABLE I
Weight-Average Molecular Weights, Heterogeneity Ratios, and Intrinsic Viscosities of Benzene-Soluble Portions in Unirradiated and Irradiated Samples

Sample	Weight-average molecular weight $\times 10^{-4}$	Heterogeneity ratio ^a	Intrinsic viscosity, dl/g
Unirradiated	A	15	0.60
	B	33	1.07
	C	80	2.10
	D	150	3.20
	E	340	5.10
Irradiated	A	26	0.58
	B	42	0.97
	C	98	1.76
	D	160	—
	E	300	—

^a Number-average molecular weights were calculated³ from the intersection of the asymptote on the ordinate in the Zimm plots.

Preparation of Films

Films were prepared by dissolving in benzene the weight of polymer necessary to give the film thickness required, pouring the solution on glass plate, and allowing it to evaporate slowly at room temperature for 24 hr. In order to remove the last traces of benzene, the films were placed in a high-vacuum system until the benzene absorption at 670 cm.^{-1} in the infrared spectrum had disappeared. Removing the benzene from the film could be much accelerated by pressurizing the system with nitrogen at 300–600 mm, evacuating at intervals, and warming to 60°C . Film thicknesses were measured by weighing a section of known area.

Ultraviolet Irradiation

Irradiation Source. A high-pressure mercury lamp, Toshiba mercury lamp, H-400 P, was used in this work. The intensities of the various wavelengths for the lamp (according to the manufacturer's data)⁴ are presented in Figure 1. The intensities (wavelength width = $10 \text{ m}\mu$) of the various wavelengths were determined by a photometer which was mounted 1 m from the lamp. A glass color filter, Toshiba filter UV-D 25, was used in this work. The intensities of the various wavelengths at the film are shown by the shaded sections.

Irradiation Cell. The irradiation cell is shown in Figure 2. A polymer film, D, was placed between two quartz plates, F and G. A black plate, E, was placed under a quartz plate, G. The various wavelengths of

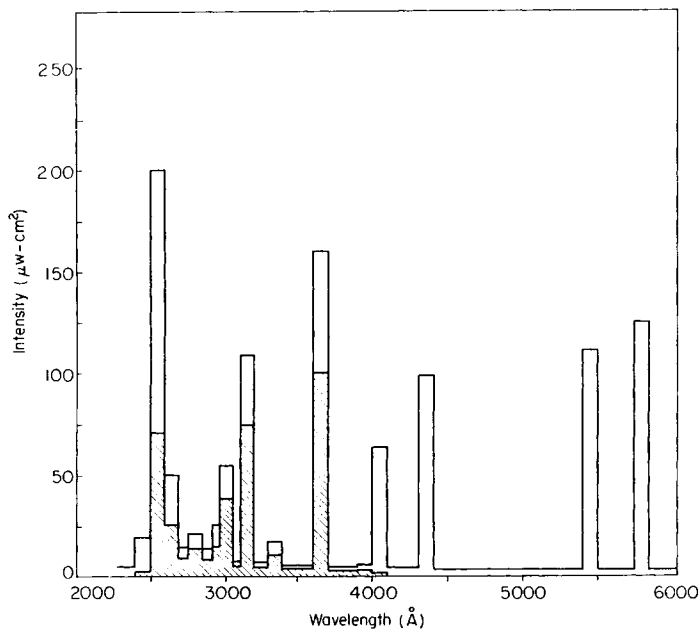


Fig. 1. Intensities of the various wavelengths emitted from a H-400 P lamp. The shaded portions represent the intensities of the various wavelengths from the lamp at the film.

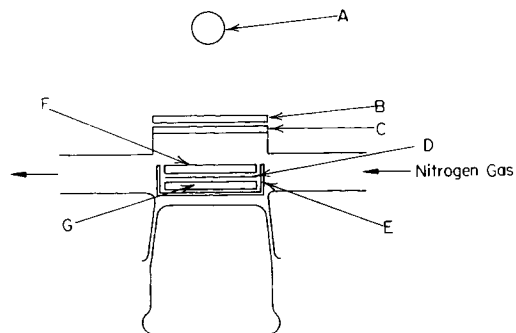


Fig. 2. Irradiation cell.

ultraviolet light transmitted through a film are absorbed on the black plate. The film was placed between two quartz plates and was surrounded by a black plate in order to inhibit the nitrogen flow on the film surface. A glass color filter, B, was placed on a quartz window, C. The transmissions of B, C, and F were measured previously. An irradiation source, A, was mounted 40 mm from the film surface.

Irradiation Procedure. The film was placed as in Figure 2. The cell was evacuated to 10^{-3} mm Hg and flushed with nitrogen gas. This operation was repeated eight times. Then, the cell was exposed to near-

ultraviolet light. Every sample was exposed to the near-ultraviolet light for 6½ hr. During the irradiation, a flow of nitrogen gas was maintained at a rate of about 0.3 cm³/minute in order to inhibit the temperature rise in the film. The temperature in the cell was maintained at about 25°C.

Measurements

Solvent-Insoluble Material. The irradiated films were dissolved in benzene. The insoluble portions were then washed with benzene, dried and weighed.

Molecular Weights. The weight-average molecular weights of the samples were measured with the use of a Shimadzu light-scattering photometer. The instrument was calibrated with polystyrene, Standard Sample 705 of the National Bureau of Standards, Washington. (The weight-average molecular weight of Standard Sample 705 is 189,800 with a standard deviation of 580.) All solutions were clarified with Millipore filters, prior to measurements. The data obtained were interpreted through the use of Zimm plots.³

Viscosities. The viscosities were measured at four rates of shear by using the rate of shear viscometer. The reduced viscosities at each concentration were extrapolated to zero average shear gradient.⁵ The values obtained were extrapolated to zero concentration. Consequently, the intrinsic viscosities were determined at zero average shear gradient.

Absorption Spectra. Spectra of the samples were measured with a Hitachi Spectracord Model EPS-3 recording ultraviolet spectrometer and a Perkin-Elmer Model 13 infrared spectrophotometer.

RESULTS AND DISCUSSION

Absorption Spectra

The ultraviolet spectra of irradiated films showed that the absorptions increase in the region of 2300–2500 Å and in the 3000 Å. Infrared spectra of irradiated films showed that the absorption increases in the 820–830 cm⁻¹ region. Changes in the ultraviolet spectra and the infrared spectra caused by irradiation are compatible with the formation of double bonds^{2,6} along the main chain. An effect of \bar{M}_w on changes in the ultraviolet spectra of polystyrene films was not found.

Depth Crosslinked by Irradiation

When the irradiated films were dissolved in benzene, the insoluble portions of the films precipitated. The insoluble portions still remained in film form even after they were immersed in benzene for 24 hr. Therefore, it is possible that insoluble portions in film form are formed by irradiation. On the assumption that a benzene-insoluble film portion is formed by irradiation and the density is approximately equal to the density of polystyrene, the thicknesses of the benzene-insoluble portions

in irradiated samples were calculated from the weights of the benzene-insoluble portions. In the case of the lowest molecular weight sample, the thickness of the benzene-insoluble portion corresponded to 0.003 mm. In the case of the highest molecular weight sample, the thickness of the benzene-insoluble portion corresponded to 0.025 mm.

According to calculations from the relationship between the film thickness and the transmittance of 0.005 mm film, the 2537 Å light could scarcely transmit when the film was more thick than 0.020 mm thick. Moreover, the energy of the light at various wavelengths absorbed in the film was calculated. The percentage of the energy of 2537 Å light absorbed in the range of 0.025 mm depth from the film surface relative to the total energy from the irradiation source absorbed in the range is about 60%. Similarly, the percentage of the energy of 2650 Å light absorbed in the same range relative to the total energy from the irradiation source absorbed in the range is about 20%. Therefore, the 2537 and 2650 Å energies constitute a large percentage of the total energies absorbed.

The energies associated with 2537 Å quanta (112 kcal/mole) and 2650 Å quanta (108 kcal/mole) are sufficient to break tertiary C-H bonds (dissociation energy = 112 kcal/mole).

Therefore, in the range of 0.025 mm depth from the film surface, it is considered that most tertiary C-H scissions are produced by light of 2537 and 2650 Å wavelengths.

In order to test these hypotheses, two layers of 0.030 mm thick film ($\bar{M}_w = 8 \times 10^5$) were stacked between two quartz plates and irradiated in the nitrogen atmosphere. In the upper film, the solvent-insoluble portion formed (weight percentage of the solvent-insoluble portion = 73%), and crosslinking took place (average number of branch units per molecule = 2.0) in the solvent-soluble portion. In the lower film, however, the solvent-insoluble portion was not formed and crosslinks in the solvent-soluble portion were not found. These results support the hypothesis mentioned above.

The percentage absorption of 2650 Å light exceeds that of 2537 Å light, so that transmissible depth of 2650 Å light is shallower than that of 2537 Å light. Accordingly, it seems most likely that most crosslinking takes place in the range of the transmissible depth of 2537 Å light.

Amount of Solvent-Insoluble Portions

When random scission and crosslinking occur simultaneously on irradiation, the specimen first starts to become insoluble when there is an average of one crosslinked unit per weight-average molecule.⁷ Therefore, at the same dose, high molecular weight samples start to form solvent-insoluble portions earlier than low molecular weight samples.

The amount of benzene-insoluble portions increased with the increase of \bar{M}_w at molecular weights below about 10^5 , as shown in Figure 3. The amount of benzene-insoluble portions approached an asymptote with the

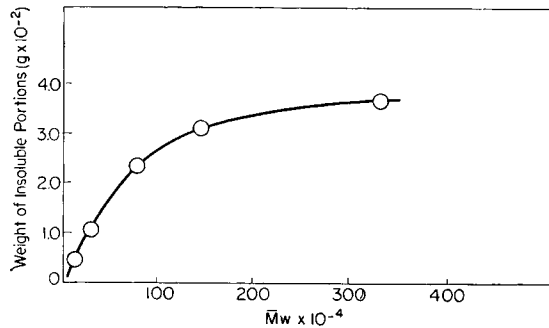


Fig. 3. Effect of \bar{M}_w on the amount of solvent-insoluble portions.

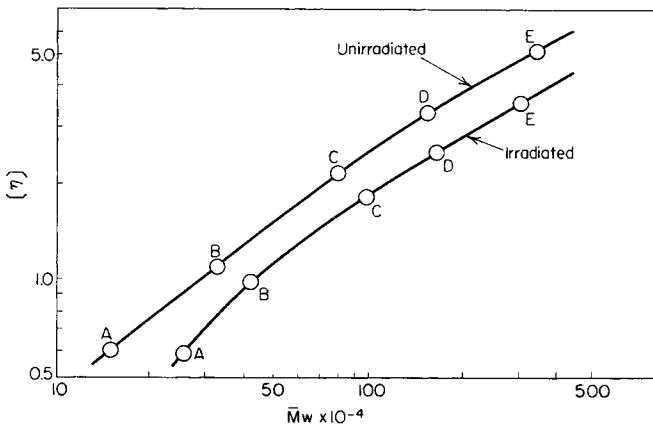


Fig. 4. Intrinsic viscosities for unirradiated and irradiated samples in benzene at 30°C plotted against the weight-average molecular weights on a log-log scale.

increase of \bar{M}_w for molecular weights above 10^5 (Figure 3), probably, because of the limited penetration of 2537 and 2650 Å radiation.

Crosslinking in Solvent-Soluble Portions

Changes in the log-log plot of intrinsic viscosity against weight-average molecular weight of the samples caused by irradiation are shown in Figure 4. The molecular weights showed a tendency to increase, with the exception of the highest molecular weight sample. Therefore, crosslinks seem to have been produced by irradiation.

Since most crosslinks seem to take place in the range of the transmissible depth of 2537 Å light, it is considered that the average number of crosslinks in the solvent-soluble portions was influenced by the amount of solvent-insoluble portions. In the low molecular weight samples, much crosslinking will be taking place in the solvent-soluble portions due to the influence of the small amount of solvent-insoluble material formed. In the high

molecular weight samples, few crosslinks will form in the solvent-soluble portions due to the large amount of solvent-insoluble material formed.

Similarly, in the range above a certain molecular weight, the average number of crosslinks per molecule in the solvent-soluble portions will approach an asymptotic value with increasing molecular weight.

Zimm and Kilb⁸ have presented theoretical formulas for the intrinsic viscosity of some model branched molecules in dilute solution. Using their theoretical expression, they were able to calculate the ratio, g' , of the intrinsic viscosities of several model branched molecules to that of linear molecules having the same molecular weight. In this work, the intrinsic viscosity-molecular weight equation for linear polystyrene in benzene at 30°C is as follows:⁹

$$[\eta] = 1.04 \times 10^{-4} M^{0.733}$$

The g' factors of the intrinsic viscosities of irradiated samples to those of linear molecules having the same molecular weight were calculated. By using the g' factors obtained, the average numbers, m , of branch units per molecule were computed by the approximate interpolation formulas for the tetrafunctional units.⁸

The ratios, \bar{M}_w'/m , of the weight-average molecular weight \bar{M}_w' of irradiated samples (film thickness 0.10 mm) to the average number of branch units per molecule, m , of the irradiated samples were calculated. Plots of the ratios, \bar{M}_w'/m , against \bar{M}_w of the samples are shown in Figure 5. \bar{M}_w'/m increased with increasing \bar{M}_w for molecular weights below near 10^5 and approached an asymptote with increasing \bar{M}_w at molecular weights above near 10^5 . These data support the hypotheses mentioned above.

Chain Scissions in Solvent-Soluble Portions

When a polymer film is irradiated in a nitrogen atmosphere, the nitrogen phase seems to inhibit the diffusion of hydrogen atoms from the polymer.² The hydrogen atoms produced may combine with the radicals formed by C-C bond scissions in the main chains, so that it is possible that radical

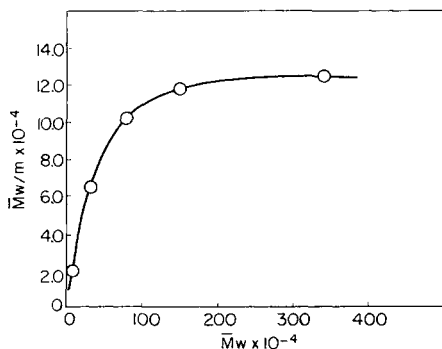


Fig. 5. Effect of \bar{M}_w on \bar{M}_w'/m for irradiated samples.

recombinations are inhibited by the hydrogen atoms. Accordingly, it is possible that ultraviolet irradiation in a nitrogen atmosphere produces a higher scission-to-crosslink ratio than ultraviolet irradiation in a vacuum.

Moreover, it is possible that the polymer bonds oxygen atoms in the main chain. Such bonding may take place during polymerization or may occur during storage of the polymer in air. Therefore, it is possible that the scissions are due to the scissions of a few weak bonds situated at random in the polymer chains.

The energy absorbed in a molecule increases with the increase of the molecular weight, because the energy of the light absorbed per monomer is constant. Therefore, it is possible that many chain scissions per average molecule occur in high molecular weight samples.

In Figure 4, the molecular weight of the highest molecular weight sample (E), showed a tendency to decrease on irradiation. In samples, B, C and D, the intrinsic viscosities showed a tendency to decrease, whereas the molecular weights increased on irradiation. These results indicate that chain scissions have occurred in every sample. Molecular weight distributions changed from a narrow distribution to a wide distribution in every fraction on irradiation (Table I).

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