PHOTODEGRADATION OF St-MMA COPOLYMERS: CORRELATION OF DEGRADATION, STYRENE CONTENT, AND PHOTOPHYSICS

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ABSTRACT

A series of styrene(St)-methyl methacrylate(MMA) copolymers with compositions ranging from 0 to 100% St were synthesized and exposed to UV light for various periods of time. The changes in yellowing (yellowness index—YI) and absorbance of exposed films were evaluated as a function of photolysis time and St content. Both the changes in YI and absorbance at 400 nm were found to increase dramatically for polymer films with styrene (St) content greater than about 50%. A direct correlation between increases in the YI and absorbance at 400 nm with mean styrene sequence length was found with a maximum change being obtained for copolymers with mean sequence length of approximately 5 St units or greater. A small absorbance shoulder at 270–290 nm was observed for copolymers with St content less than 30% after relatively short irradiation times (e. g. 2 hours). Excimer formation of copolymers in dilute solution was found to increase with an increase in St content and St sequence length; in films, a plateau in the relative excimer emission was attained with a St content of 60%, corresponding to a mean St sequence length of 2.

Key Words: Excimer; Fluorescence; Styrene-methyl methacrylate copolymer; Photolysis.

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INTRODUCTION

Copolymers comprised of styrene (St) and methyl methacrylate (MMA) monomer units incorporated into the polymer backbone have potential as lower cost (as opposed to pure methacrylate) latexes for a variety of applications. Since styrene has similar reactivity to methyl methacrylate, and their homopolymers (PS and PMMA) have similar thermal transitions and mechanical properties, copolymers between the two monomers readily form and have properties similar to their homopolymer counterparts.

In contrast to the pure polymethylmethacrylate homopolymer, the polystyrene homopolymer leads to severe discoloration and yellowing upon exposure to ultraviolet (UV) light, whereas polymethylmethacrylate discolors little in sunlight. When exposed to UV light in the presence of oxygen, pure PMMA readily undergoes a chain scission process [1], while photolysis of PS not only results in chain scission and crosslinking [2], but also produces new chromophores such as conjugated polyenes, carbonyls, acetophenone, conjugated dialdehydes, and benzalacetophenone [2–9]. The yellowing of pure polystyrene is primarily due to buildup in the concentration of conjugated polyene structures, although other chromophores may make minor contributions.

Torikai and colleagues [10, 11] investigated the viscosity and molecular weight changes upon photolysis of a series of St-MMA copolymers ranging in St content from 0 to 100%. They reported that changes in molecular weight and the total concentration of radical intermediates decreased with St content. Conversely, Berko *et al.* [3] measured the mechanical property changes of a series of St-acrylonitrile copolymers with St content ranging from 40 to 100% and found that tensile modulus, tensile strength, and elongation to fracture were highly dependent upon the St content. They also reported that changes in the ultraviolet absorption spectra upon photolysis of St-acrylonitrile increased with St content (their results were for samples ranging in St content from 40 to 100% St repeat units). They attributed the yellowing to polyene formation and indicated that it increased with St content, although no quantitative correlation of the St sequence length and the discoloration process was made. Fox and Price [4] also observed the formation of trienes in the UV degradation of St-MMA alternating copolymers and regarded it as the main reason causing photoyellowing of the copolymer. The color produced upon photolysis was attributed to ene sequence formation involving both St and MMA repeat units. Polyene formation was faster for photolysis of the homopolymer of polystyrene than for the St-MMA alternating copolymer for photolysis in a nitrogen atmosphere. They reported that the alternating copolymer underwent photoinduced yellowing more rapidly in vacuum than in air and suggested that oxidation of trienes in air reduces the discoloration rate. In no case to date that we are aware of has a correlation of St content to photoyellowing been reported. Such a detailed correlation of discoloration with St content would allow assessment of the role of St sequence length in the determination of the onset of yellowing with respect to St content. This information is critical in the design of stable St-MMA copolymers with enhanced light stability. Furthermore, by evaluation of samples

with lower St content (< 40%) it may be possible to detect the absorption of the primary photoproduct produced upon initial photolysis since it is expected that the primary photoproduct would rapidly react upon exposure to additional radiation to build up the concentration of ene sequences of higher length. This would be particularly interesting since no report to date gave any evidence to show the presence of the monoene during UV irradiation.

In this paper, we thus report on the photochemistry and photophysics of a series of St-MMA copolymers with St content ranging from 0 to 100%. The effect of St sequence structure on the photoinduced discoloration was followed by both yellowness index measurements and absorption spectroscopy, and a direct relationship between discoloration and excimer formation in copolymers was established. This correlation provides for the first time a quantitative description and spectroscopic method for defining and identifying the critical St concentration for generating color upon exposure to light.

EXPERIMENTAL

Materials

Styrene, methyl methacrylate, AIBN, methylene chloride, methanol, hexane were obtained from Aldrich Chemical Company. Both styrene and MMA were purified before polymerization.

Synthesis of St-MMA Copolymers

A series of St-MMA copolymers of varying composition was synthesized according to reference [12] by free radical polymerization at 60°C under N_2. AIBN (0.02%) was employed as initiator. The degree of conversion was limited to < 10% (polymerization time 30 minutes or less) in order to minimize chain transfer. Under these polymerization conditions, random St-MMA copolymers are formed [12]. The composition of the products was determined by ^{1}H-NMR and confirmed by UV spectroscopy. GPC determination showed that the number average molecular weight of products was ~10^5 Dalton.

Sample Preparation

The synthesized polymer solution was precipitated in hexane and washed with methanol, and then dissolved in methylene chloride and precipitated in methnol. This procedure was performed three times to remove unreacted monomer and initiator. The obtained product was dried in vacuum oven at room temperature for 24 hours. This sample can be used for composition and molecular weight determinations. UV irradiation samples were films (0.06—0.08mm thickness) cast from their methylene chloride solutions.

Instrumentation

UV irradiation was performed by a series of low-pressure mercury lamps (300 nm peak emission) with total light intensity of 0.6–0.7 mW/cm^2 in a Rayonet photochemical reactor. Yellowness Index was determined according to ASTM Method D 1925–70 using a CS-5 Chrome-sensor from Applied Color Systems Inc. Fluorescence spectra were obtained on a Spex 1680 Fluorometer by exciting with a wavelength of 255 nm and scanning from 265 to 400 nm. I_{360}/I_{285} was used to characterize the excimer formation. UV spectra were measured on a PE Lambda 6 UV/VIS Spectrophotometer. Polymer composition was determined by ^{1}H-NMR using a Bruker AC 200 NMR Spectrometer and a standard analytic technique for analysis of St-MMA copolymers [12].

Calculation of Sequence Distribution and Mean Sequence Length of St in St-MMA Copolymers

The sequence distribution of monomer M_i in a copolymer can be easily calculated [13] by Equation 1.

$$P(n, M_i) = P_{ii}^{(n-1)} P_{ij} \tag{1}$$

where $P(n, M_i)$ is probability of finding a sequence of n units of monomer M_i in a chain. Pij is the propagating step probability for addition of monomer j to a growing chain radical ending in monomer i. P_{ij} is given by:

$$P_{ij} = k_{ij} [M_j]/(k_{ii} [M_i]+k_{ij} [M_j]) \tag{2}$$

where k_{ij} is the rate constant for addition of monomer j to a growing radical ending in M_i and $[M_i]$ and $[M_j]$ are the molar concentrations of monomers i and j, respectively. The reactivity ratio $r_{ij} = k_{ii}/k_{ij}$ can be used to replace k_{ii}/k_{ij}, which is obtained by manipulating Eqn.(2). The statistic mean sequence length L_i of monomer M_i in copolymer chain can be calculated from the sequence distribution by Equation 3.

$$L_i = \sum np(n, M_i) \tag{3}$$

The sequence distributions and mean sequence lengths of St in different St-MMA copolymers were calculated by using Equations1–3. Reactivity ratios of 0.46 and 0.52 for MMA and St, respectively, were used [14].

RESULTS AND DISCUSSION

Data will be presented for the photodegradation of a continuous series of copolymers comprised of styrene (St) and methylmethacrylate (MMA). Herein, we will confine our results to consideration of photoinduced changes in film yellow index (YI), which is a non-wavelength specific evaluation of polymer absorp-

tion changes at wavelengths greater than 400 nm, and electronic absorption spectral changes, which define specific changes in absorption as a function of wavelength. Particular attention will be afforded to determination of the dependence of yellowing and color formation on St content. The results will be interpreted in light of the excimer forming properties of the series of St-MMA copolymers in solution. In this way the microstructure of the polymer will be related semi-quantitatively to the tendency of St-MMA copolymers to discolor upon exposure to light.

Photolysis of Copolymers—Yellowness Index (YI) Changes

Figure 1 shows changes in the YI upon photolysis (6, 18, 36 and 66 hours in a Rayonet Reactor with 300 nm lamps) of the series of St-MMA copolymer films. As might be expected, the YI is proportional to both St content and irradiation time. After six hours the YI did not change for any of the samples except for a small change in the pure polystyrene film. However, after exposure to the Rayonet Lamps for 18 hours, there were distinct measurable changes in YI with especially large changes for the samples with greater than ~ 80% St content. For longer irradiation times (36 and 66 hours), the point at which the YI values began to experience a steep increase with St composition shifted to progressively smaller St content, i.e., 70% St for 36 hours and 50–60% for 66 hours photolysis. There are a considerable number of reports in the literature [3–5, 7, 9] that correlate the yellowing of polystyrene with the formation of ene sequences absorbing at wavelengths greater than 400 nm. Although other products that form color may form upon photolysis of polymers with St derived repeat units, they do not appear to be the primary reason for color formation; in the case of other types of products,
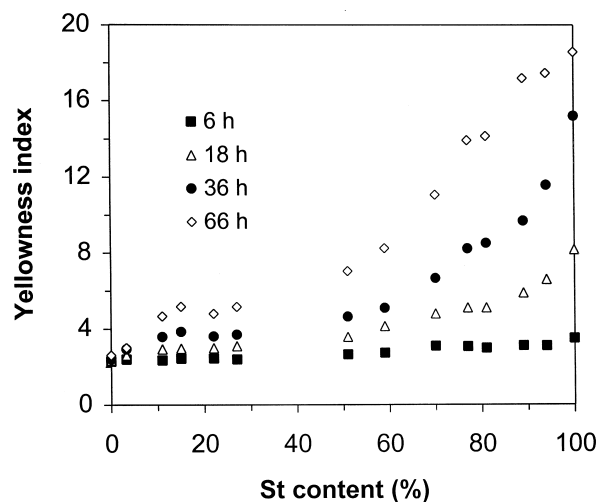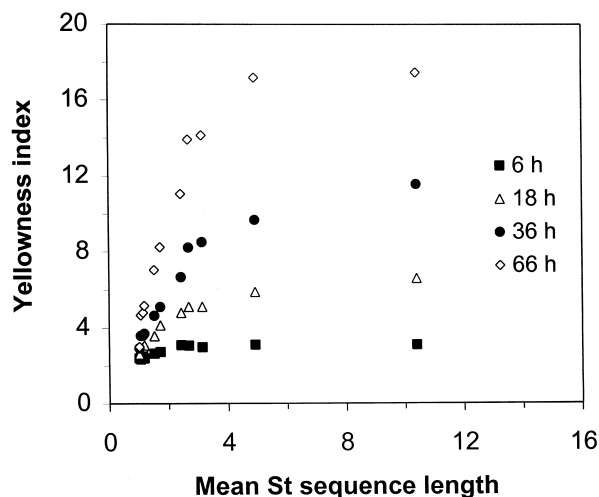

Figure 1. Dependence of yellowness index (YI) of St-MMA copolymers on St content.

Figure 2. Variation of yellowness index (YI) with mean St sequence length.

color formation should be a linear function of the fraction of St in the polymer, and as shown in Figure 1, this is not so. Since the ene sequence is expected to contribute to discoloration (i.e. absorption at wavelengths of greater than 400 nm) when a critical sequence length is achieved, a distinct dependence of YI on St mean sequence length certainly might be expected. Figure 2 shows a plot of YI versus mean St sequence length for 6, 18, 36, and 66 hours photolysis. First consider the results in Figure 2 for the photolysis at 66 hours. A plateau value in the YI is attained for samples with a St mean sequence of ~5 or greater. This is consistent with a limitation and ultimate plateau in the absorbance with the ene sequence length. For the samples photolyzed 18 or 36 hours, a plateau in the YI values was never achieved regardless of the St mean sequence length. Apparently, at 18 and 36 hour photolysis times, ene formation is incomplete (for a given sample) and the samples with longer St sequences do result correspondingly in longer ene sequences (and concomitant coloration due to higher absorbances at visible wavelengths) being formed.

Photolysis of Copolymers—UV Absorption (400 nm) Changes

As discussed above, and in view of literature reports [3–5, 7, 9], the discoloration of polystyrene and styrene-containing copolymers is attributed primarily to the production of ene sequences during UV irradiation. This production of color was found to be related to the extent of St unit sequences in the polymer chain as described by the mean sequence length. Figure 3 shows the results for the increase in the absorbance of the series of St-MMA copolymers at a single representative wavelength of 400 nm, essentially the onset of the visible region of the electronic absorption spectrum. The absorbance changes at 400 nm indicate that at
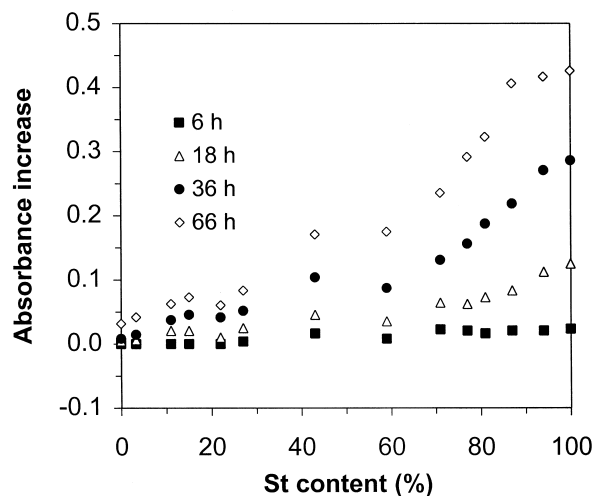
Figure 3. Increase of UV absorbance at 400 nm as a function of St content after different irradiation times.

longer photolysis times there is a distinct non-linear increase in the absorption which begins at a critical St concentration, and as in the case for the YI results, this critical concentration shifts to lower St content at longer photolysis times. As in the case of the YI results, the non-linear increase in absorbance at 400 nm with St fraction is consistent with ene sequence formation being responsible (primarily) for the absorbance increase at this wavelength. Figure 4 shows the corresponding plots of absorbance increase at 400 nm (the difference between the
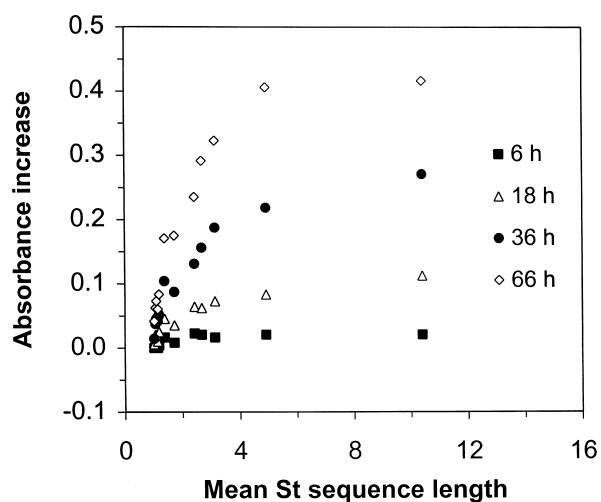
Figure 4. Relationship between the increase of UV absorbance at 400 nm and mean St sequence length.

absorbance before and after photolysis) versus St mean sequence length. Again as with the YI values, at the longest photolysis time (66 hours), the absorbance change reaches a plateau for samples with a mean St sequence length of ~5 and greater. As already discussed, there is apparently an optimum initial St sequence length which must be achieved in order to attain the maximum degree of absorbance at wavelengths of 400 nm or greater.

While it is possible to gain valuable qualitative information about the degradation of St-MMA copolymers by measuring the changes in YI and absorbance at a single wavelength, it is more informative to consider changes in the actual UV-vis absorption spectra for each of the copolymer films upon photolysis as a function of time. The complete absorption spectra provide a means of observing the evolution of the long wavelength absorbing ene sequences as a function of photolysis time. Figures 5–10 show absorption spectra of photolyzed films of copolymer samples ranging in St content from 0 to 100%. In general, it is readily observed that the absorbance at wavelengths greater than 400 nm increases as the styrene content increases: this is expected from the YI and absorbance changes at 400 nm (Figures 1–4). A particularly interesting, and we believe important, result is seen in Figures 6 and 7 at short photolysis times for the two samples with lower St content (3.3% and 27%). While the sample in Figure 5 with no St present (100 % MMA polymer) and those in Figures 8–10 with high St content exhibit no distinct absorption peaks from 280–300 nm, the copolymer films with 3.3% and 27% St in Figures 6 and 7 exhibit a distinct absorption band with well defined vibrational structure in this region. The absorption bands closely resemble those of the parent monomer styrene and may well be single unsaturated phenyl substituted ene units. The loss of structured absorbance between 280–300 nm upon continued photoly-
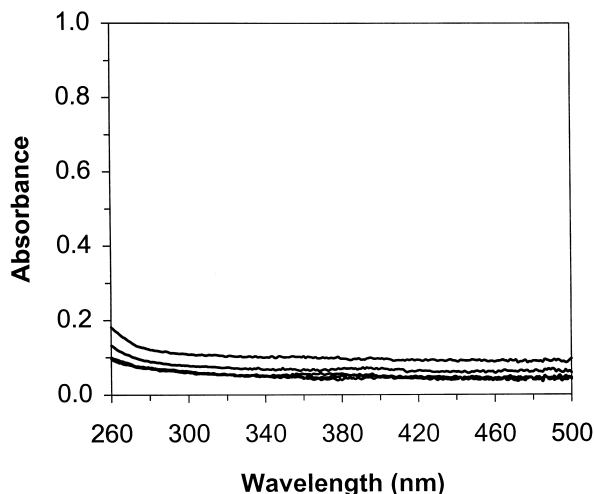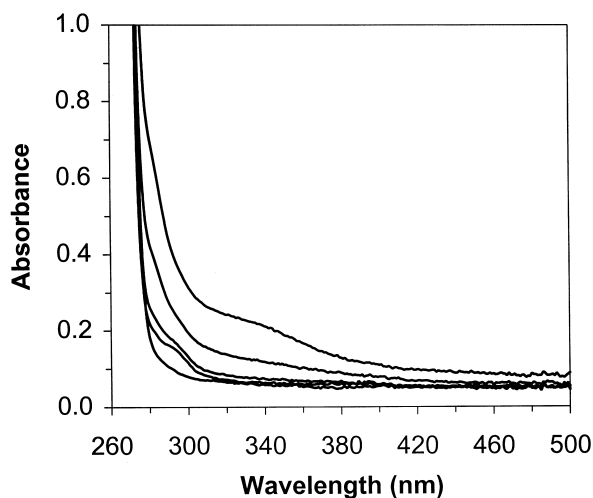

Figure 5. UV spectra of pure PMMA before and after UV irradiation. Curves from bottom to top (at 290 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.
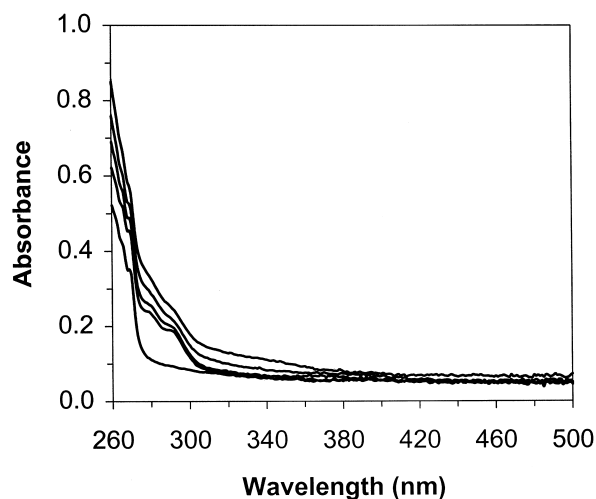
Figure 6. UV spectra of St-PMMA copolymer (St content 3.3%) before and after UV irradiation. Curves from bottom to top (at 290 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.

sis at times greater than 2 hours reflects a slow photo-bleaching process and loss of the chromophore responsible for the structured absorbance. Although we are not able to conclusively determine the species responsible for the new absorption between 280–300 nm, it is certain that some St must be incorporated into the polymer chain since pure PMMA in Figure 5 shows no appreciable absorbance between 280–300 nm upon photolysis for short times. We tried to identify the
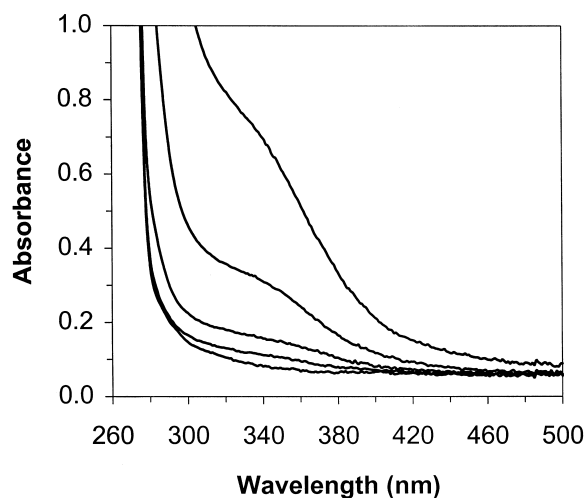

Figure 7. UV spectra of St-PMMA copolymer (St content 27%) before and after UV irradiation. Curves from bottom to top (at 290 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.
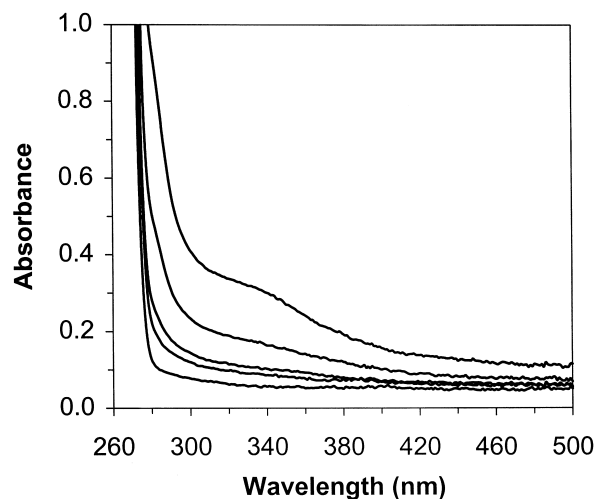
Figure 8. UV spectra of St-PMMA copolymer (St content 43%) before and after UV irradiation. Curves from bottom to top (at 290 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.

species responsible for the absorbance between 280–300 nm in Figures 6 and 7 by excitation of the films at 280 nm. Unfortunately, no fluorescence corresponding to that expected for a single ene repeat unit was found: it is possible that the weak fluorescence expected from such a phenyl substituted ene species is absent due to quenching by other products produced during the photolysis process. Despite the

Figure 9. UV spectra of St-PMMA copolymer (St content 77%) before and after UV irradiation. Curves from bottom to top (at 340 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.
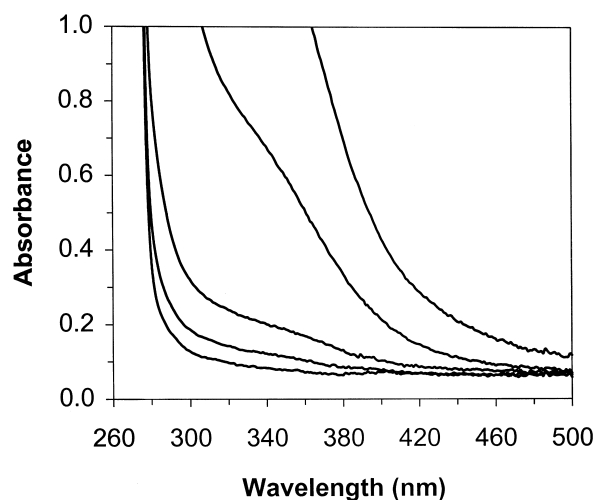
Figure 10. UV spectra of polystyrene before and after UV irradiation. Curves from bottom to top (at 380 nm) are for samples irradiated for 0 hours, 2 hours, 6 hours, 18 hours, and 35 hours, respectively.

failure to identify the product responsible for the structured absorbance between 280–300 nm at short photolysis times of low content, it is tempting to assign this absorbance to that of a single phenyl substituted ene, which upon continued photolysis is depleted by a photochemical/photooxidation process to produce oxidation products with concomitant decrease in absorbance between 280–300 nm. Such a phenyl substituted ene group would be the result of primary photochemical step(s) (see References [3–5] with speculation on how an initial ene group in the chain is formed upon photolysis) leading to phenyl substituted ene formation. Finally, the lack of a structured absorbance between 280–300 nm at even relatively short photolysis times for samples of greater styrene content (Figures 8–10) reflects an enhanced lability of the species absorbing between 280–300 nm. This would be reasonable based upon an increase in the relative number of St groups with nearest neighbor St units, which enhances the ability to photooxidize and generate multiple (at least greater than 1) ene sequences with concomitant loss of structured absorbance at 280 nm.
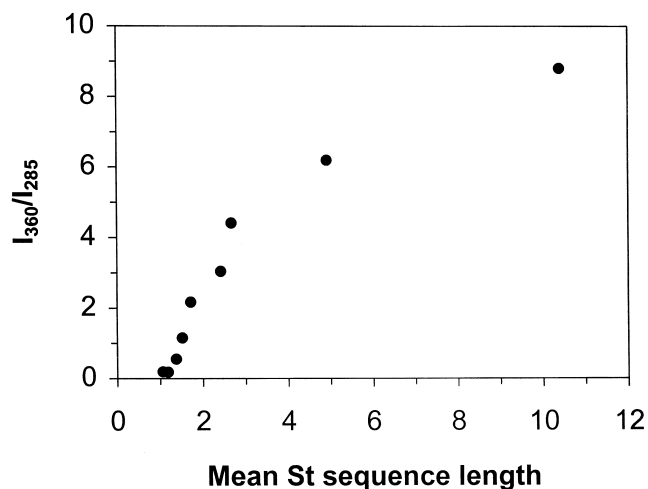
Excimer Formation in St-MMA Copolymers

Excimer formation in PS and St-containing copolymers, studied for more than three decades, results from the interaction of an excited state phenyl group with a nearby ground state phenyl group. The energy from this excited state species is shared by the two phenyl groups and the resultant fluorescence is red-shifted compared to the emission of a single chromophore (termed monomer). Since geometrical requirements dictate that the participating phenyl groups

should be spaced three carbon atoms apart for maximum excimer formation [15–17], it is reasonable to assume that the degree of excimer formation, as indicated by the relative amount of fluorescence, should be an excellent indicator of St-MMA copolymer microstructure and thereby aid in interpreting the photodegradation and discoloration results already presented. The relative extent of excimer formation *(obtained from the fluorescence spectra recorded by exciting at 255 nm)* for the St-MMA copolymers in dilute dichloromethane solution in Figure 11, based upon the ratio of the intensity of excimer (represented by the intensity of emission at 360 nm and designated I_{360}) to monomer emission intensity (represented by the intensity of emission at 285 nm and designated I_{285}), shows a marked increase for copolymers with greater than about 50% St units. (Similar variations were also observed in St-AN and St-MMA copolymers [18, 19]). Accordingly, a plot of I_{360}/I_{285} versus St mean sequence length (Figure 12) increases rapidly with St mean sequence length at low St sequence lengths followed by a more gradual rise as the St content increases. Interestingly, the I_{360}/I_{285} ratio does not attain a plateau and continues to increase with styrene content. This indicates that even for samples with a mean sequence length of St of 2 or greater, where statistically each St repeat unit has a nearest neighbor St unit (which meets the 3 carbon spacer requirement for excimer formation), the extent of excimer formation is not complete, i.e., the amount of excimer emission continues to increase with increasing St content even though each St unit already has a St nearest neighbor. Although the number of St units with excimer forming sites (St-St nearest neighbors) increases modestly with St content, it would seem that this could not account for the substantial increase in excimer emission for samples with higher styrene content. The results in Figure 12 are most consistent with an enhancement in energy migration to excimer forming sights which would increase
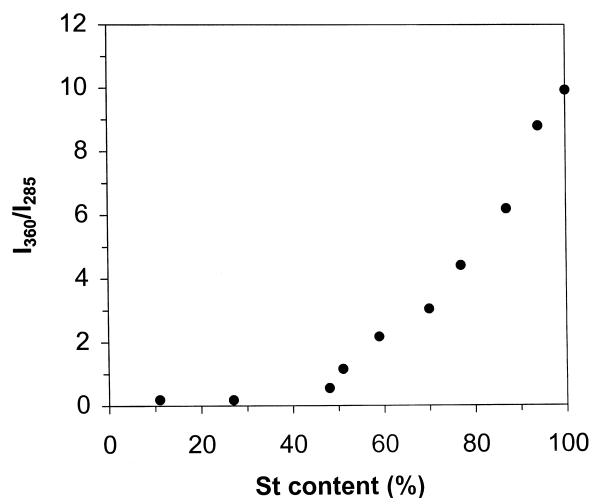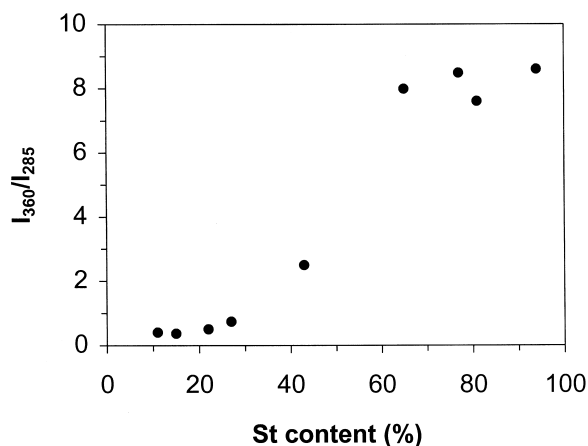

Figure 11.   Excimer formation as a function of St content in St-MMA copolymer dilute solutions.
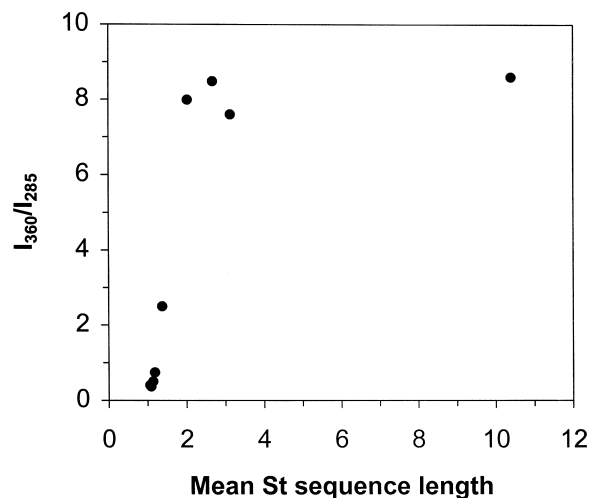
Figure 12. Dependence of excimer formation in St-MMA copolymer dilute solutions on mean St sequence length.

dramatically as the styrene-ene sequence length increases. An increase in the excimer emission would thus be expected even for St sequence lengths greater than 5 since energy migration no doubt increases with St content up until pure St homopolymer is attained. As discussed previously, the increase in YI and absorbance at 400 nm plateau after reaching a mean St sequence length of about 5, an approximate optimum minimum length for color formation.

The variation of excimer emission with St content was also measured for solid St-MMA copolymer films. Compared with the spectra in solution, a plateau in the I_{360}/I_{285} ratio is attained (Figure 13) for St-MMA samples with about 60% or greater St. This corresponds to maximum relative excimer formation being

Figure 13. Excimer formation as a function of St content in St-MMA copolymer films.

Figure 14.   Dependence of excimer formation in St-MMA copolymer films on mean St sequence length.

reached when the St sequence length in the copolymer is 2 or greater (Figure 14). A mean St sequence of 2 means that essentially all St units have a nearest neighbor St unit capable of excimer formation, provided that geometrical considerations are met. Apparently, with a mean St sequence length of 2, it is possible in St-MMA films to funnel almost all of the excited state energy (possibly via energy migration) to all potential excimer forming sites. This would not be expected to occur in dilute polymer solutions since energy migration is strictly intrachain. In comparing the I_{360}/I_{285} ratio variation with St content to the YI and absorbance increases with St content in Figures 2 and 4, it is obvious that the excimer solution results in Figure 12 and not the results in film (Figure 14) most closely correlate with the results attained in Figures 2 and 4. This is reasonable since the solution excimer data is responsive to a continuing increase in the St sequence length, whereas the film excimer formation reaches a plateau at a St sequence of approximately two.

CONCLUSION

The UV exposure induced discoloration of St-MMA copolymers has been characterized by yellowness index (YI) and UV absorption increases. The extent of excimer emission in film reaches a maximum for a St mean sequence length of 2, while in solution the relative excimer to monomer emission ratio increases with St mean sequence length, even for values greater than 5. The extent of change in YI and absorption has been correlated with the excimer to monomer fluorescence ratio measured in solution, which serves as an indication of the extent of St sequence length in the copolymers. The maximum discoloration reached a plateau

for copolymers with mean St sequence length of greater than about 5. Evidence consistent with polyene formation was presented and a small shoulder in the UV absorbance spectrum at about 280nm was observed which may be due to the formation of a monoene for copolymer with St content less than 30%.

ACKNOWLEDGMENT

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