Photooxidative Degradation of Styrenic Polymers: ^{13}C-NMR and Morphological Changes upon Irradiation*

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ABSTRACT: Thin films of high impact polystyrene (HIPS 8350) and styrene–butadiene–styrene triblock copolymers (SBS) were exposed to polychromatic light for different time intervals in SEPAP 12/24 at 55°C in atmospheric air. The photooxidized samples were analyzed by ^{13}C-NMR spectroscopy in the liquid state. Epoxides and alcohols were photoproducts in the SBS. Epoxides were not observed in the HIPS. The morphological changes of the solution cast HIPS and SBS films caused by irradiation were studied by scanning electron microscopy. The property deterioration was explained in terms of scission reactions in the HIPS and SBS matrix. The micrographs indicate that both materials are of a two phasic system. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 637–645, 1998

Key words: high impact polystyrene; styrene–butadiene–styrene; photooxidation; ^{13}C-NMR; scanning electron microscopy

INTRODUCTION

In recent years there has been a lot of interest in the area of thermoplastic elastomers.[1,2] High impact polystyrene (HIPS) consists of a continuous glassy PS matrix and an elastomeric dispersed polybutadiene (PB) phase.[3,4] The dispersed PB phase is compatibilized with the glassy PS phase by the presence of PS grafts during the synthesis. The PB portion is generally in the range of 5–10%.[5] In styrene–butadiene–styrene (SBS) triblock copolymer, the central domain is PB and the end domains are PS. These two phases behave as two distinct phases, where the PS block acts as a crosslink, as well as a filler, in the network system.[6]

In both of these polymers the PB phase is more susceptible to photooxidation.[7] The photooxidized polymer loses its weight and mechanical proper-

ties and shows discoloration and surface embrittlement. The photooxidation of HIPS and SBS has been studied by the IR technique,[8,9] but less attention has been paid to the mechanism of photooxidation by ^{13}C-NMR and morphological changes upon photoirradiation in HIPS and SBS. The ^{13}C-NMR spectroscopy provides a very useful and sensitive method for detection of photoproducts in contrast with IR spectroscopy. Scanning electron microscopy (SEM) is a powerful tool for morphology characterization. In the present investigation we studied ^{13}C-NMR and morphological changes upon photooxidation of HIPS and SBS.

EXPERIMENTAL

Materials

The HIPS (HIPS 8350) sample was obtained from M/s. Elf-Atochem, and the SBS triblock copolymer was received through the courtesy of the M/s. Shell Company.
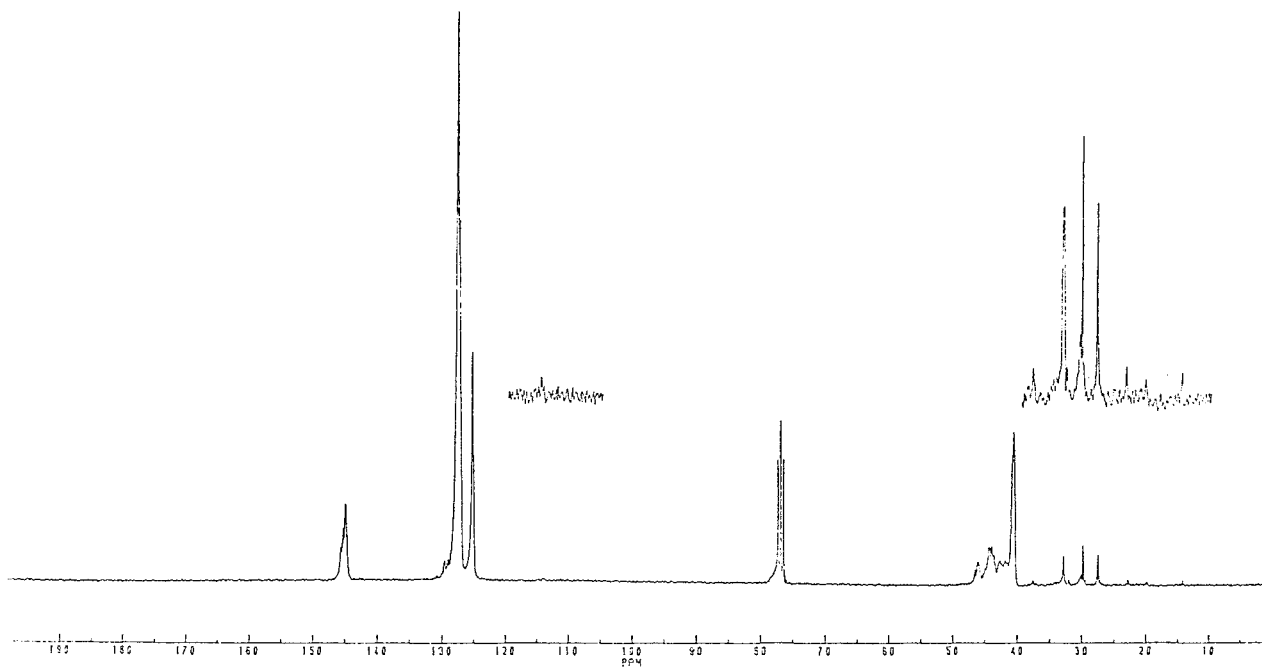
Figure 1 ^{13}C-NMR spectrum of HIPS 8350 neat in CDCl$_3$ solution.

Procedure

HIPS 8350 films were prepared by solution casting. The material was dissolved in toluene (2.00 wt %) and cast over a mercury surface. The solvent was evaporated at room temperature and then dried in a vacuum oven for 24 h at 50°C. SBS films were also
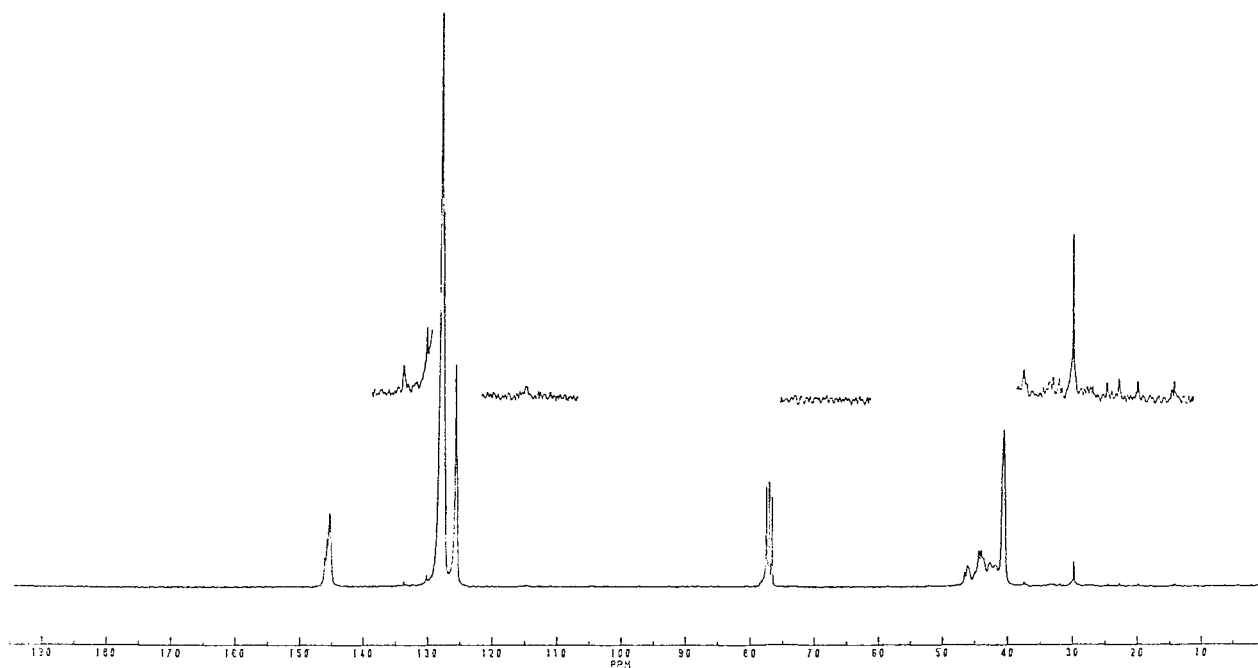

Figure 2 ^{13}C-NMR spectrum of HIPS 8350 after 200-h UV exposure in CDCl$_3$ solution.
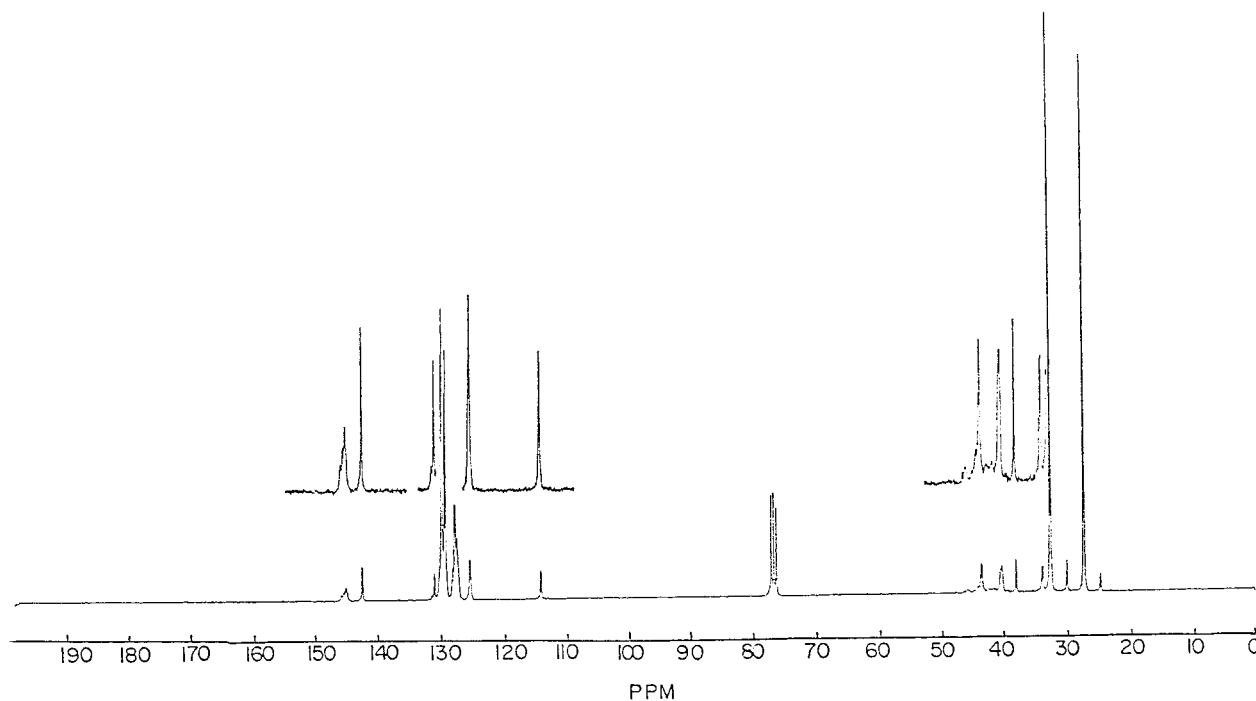
Figure 3 ^{13}C-NMR spectrum of SBS neat in CDCl$_3$ solution.

prepared by solution casting with various solvents (CCl$_4$, THF, and CHCl$_3$). The material was dissolved in solution (2.00 wt %) and cast over a mer-

cury surface, evaporated at room temperature, and dried in a vacuum oven for 24 h at 50°C. Thin films (~ 0.2 mm thickness) were obtained.
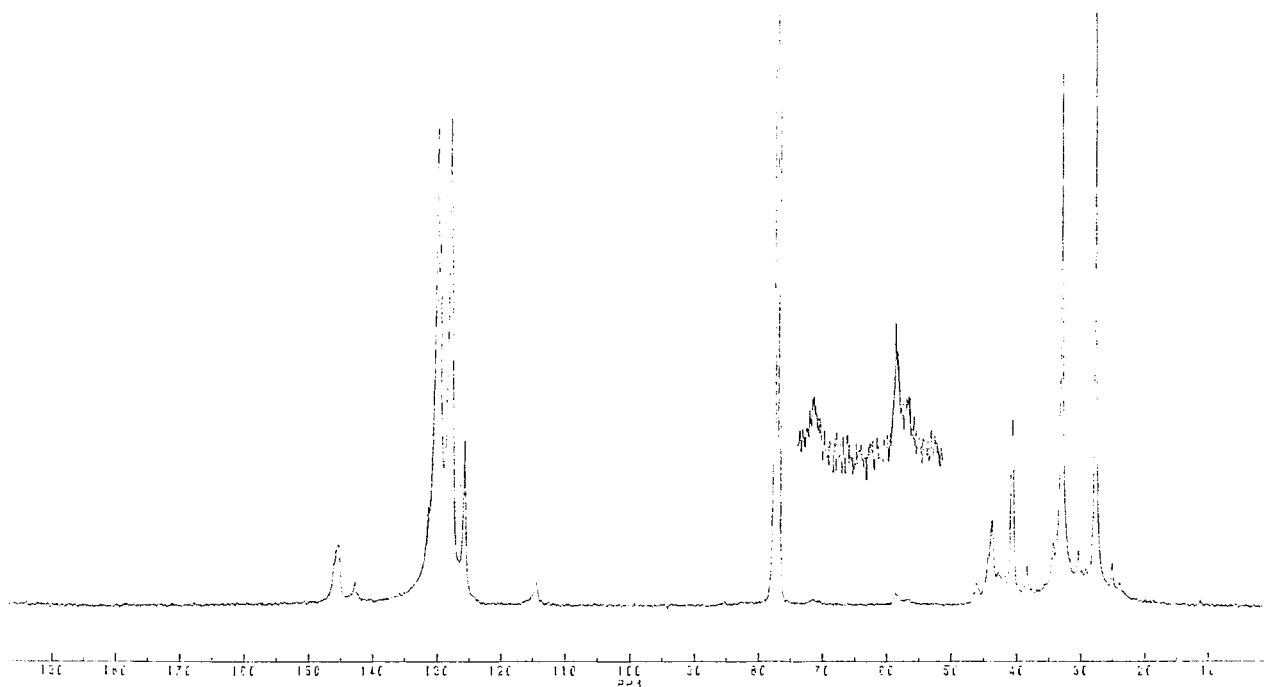

Figure 4 ^{13}C-NMR spectrum of SBS after 100-h UV exposure in CDCl$_3$ solution.

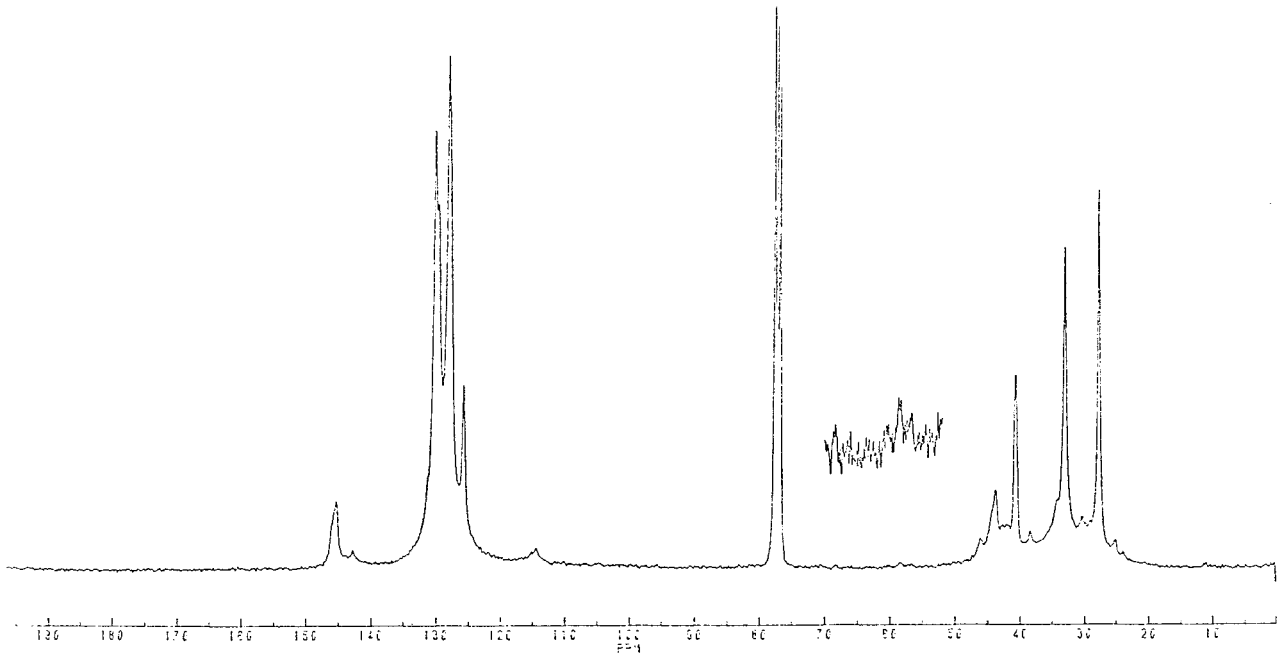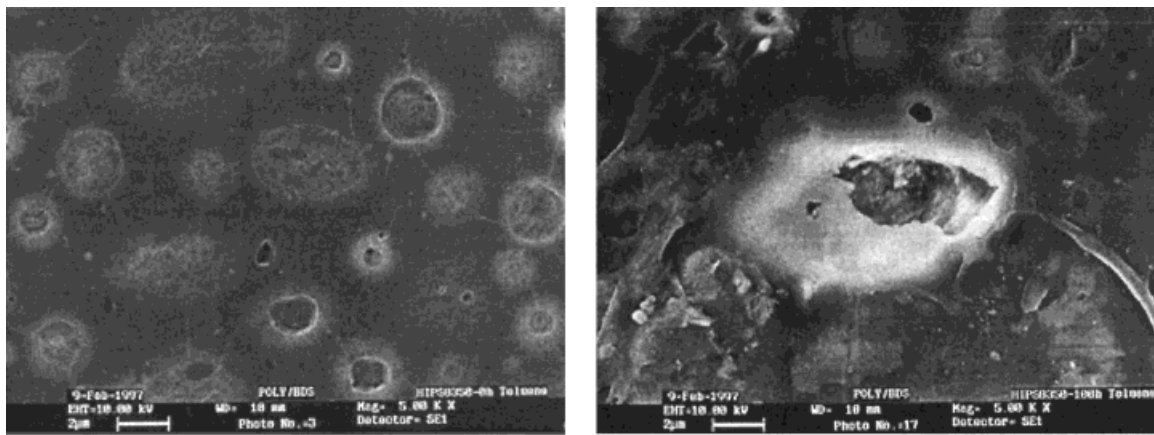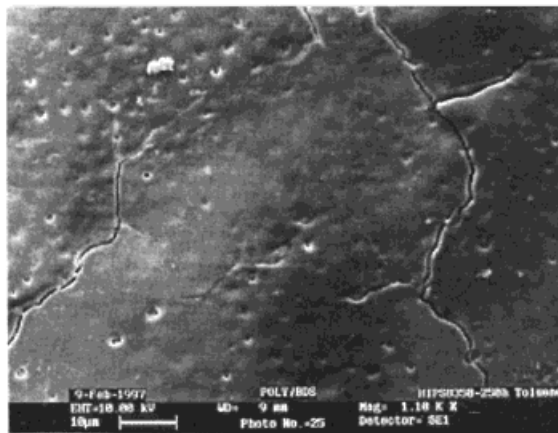**Figure 5** ^{13}C-NMR spectrum of SBS after 300-h UV exposure in CDCl$_3$ solution.

(a)

(b)

(c)

Figure 6 SEM photographs of neat and photooxidized HIPS 8350: (a) neat film, (b) 100-h UV exposure, and (c) 250-h UV exposure.
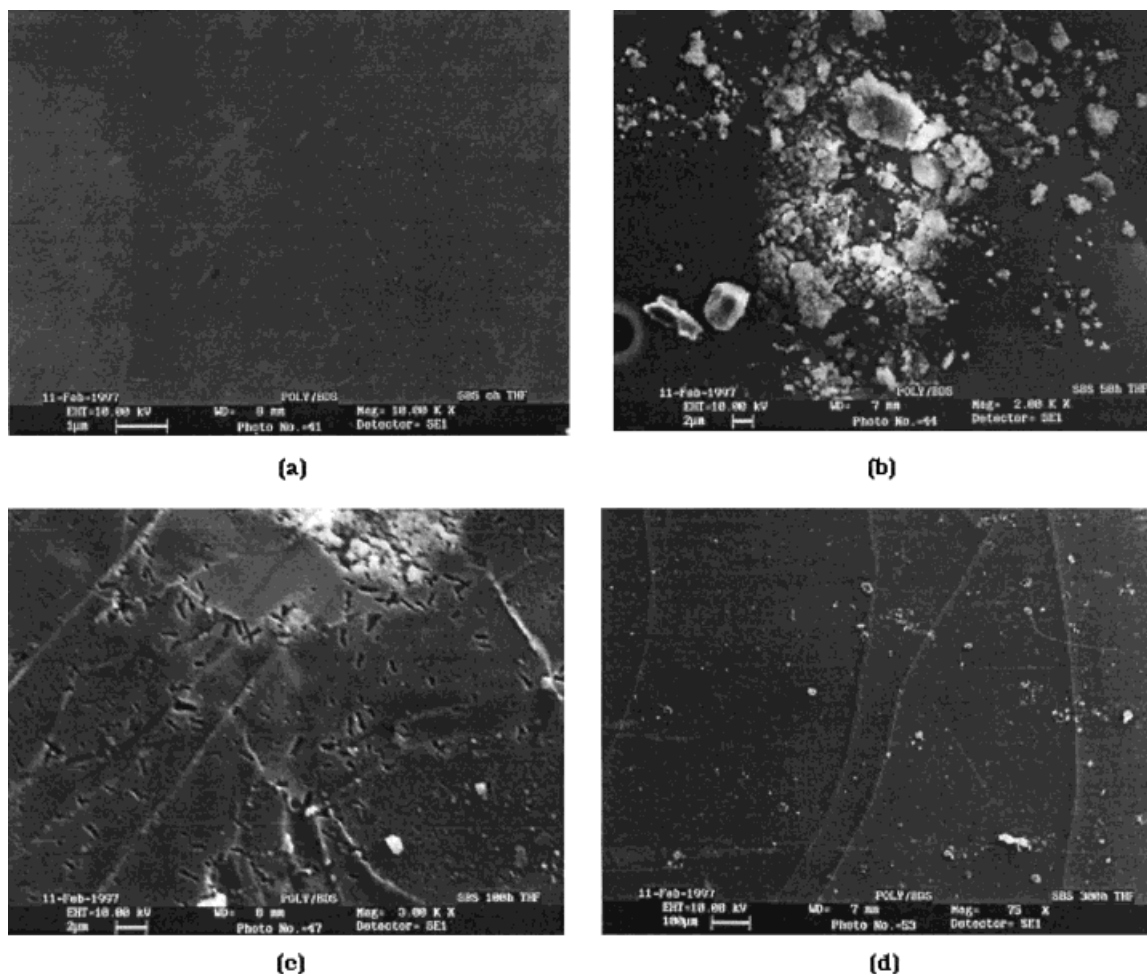
Figure 7 SEM photographs of SBS film cast from THF solvent: (a) neat film, (b) 50-h UV exposure, (c) 100-h UV exposure, and (d) 300-h UV exposure.

Photoirradiation

Films were irradiated in a SEPAP 12/24 (Material Physico Chimique, Neuilly/Marne, France) at 55°C. The unit consists of four 400-W medium pressure mercury sources filtered by a Pyrex envelope supplying radiation of wavelengths longer than 300 nm. The equipment is described elsewhere.[10]

Characterization

Neat and photooxidized films were dissolved and swollen in $CDCl_3$. ^{13}C-NMR spectra were recorded on a Bruker MSL 300 spectrometer in a 10-mm tube at 25°C with TMS as the internal standard. The films were examined by a scanning electron microscope (Leica Cambridge Stereoscan 440 model) for morphological changes. The neat and oxidized films were placed in stoppered bottles containing osmium tetraoxide (2% aqueous) and allowed to stand for 48 h. The films were washed with water and dry ethanol. The stained samples were dried under a vacuum for 24 h at 50°C. The gold coated samples were examined under the electron microscope.

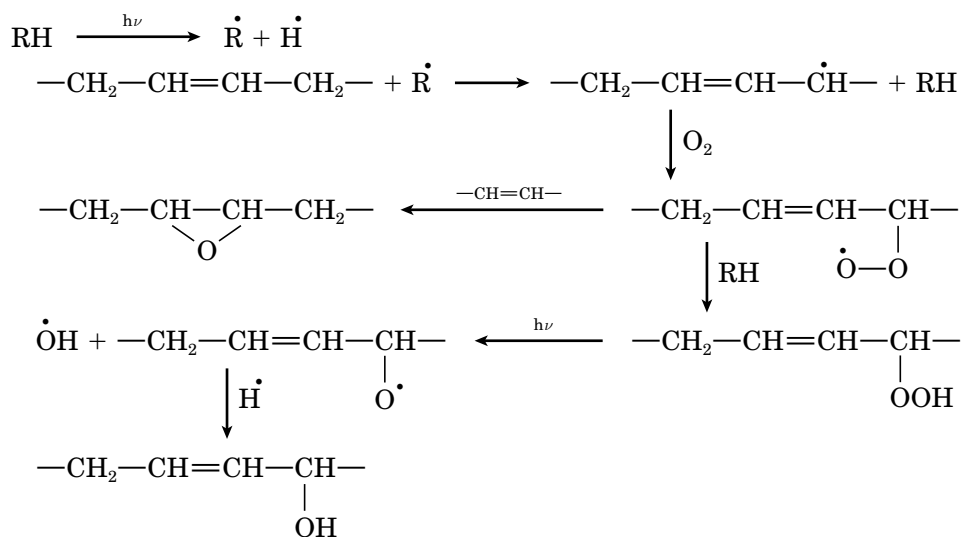## RESULTS AND DISCUSSION

Characterization by High Resolution ^{13}C-NMR in Solution

^{13}C-NMR spectroscopy is known to be more suitable for the determination of cis, trans, and vinyl contents of PB in HIPS.[5] Figure 1 shows the *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 in both the aliphatic (27.3 and 32.6 ppm) and olefinic regions (114.2 ppm). The resonance peaks at δ 27.3, 32.6, and

114.2 ppm are *cis*-1,4, *trans*-1,4, and *vinyl*-1,2, respectively. These units have σ and π orbitals. The lowest energy state in these orbitals is a (π-π^*) nature. The intensity of these peaks decreases with the increasing exposure time (Fig. 2), meaning that the initial photooxidation occurs at the PB phase only. The photooxidized films showed hydroxyl and carbonyl bands at 3450 and 1717 cm^{-1}, respectively. We observed a decrease of unsaturation (997 cm^{-1}) in the PB portion,[7] which is in agreement with our ^{13}C-NMR results. The neat sample dissolved very well in CDCl$_3$, but the photooxidized films were phase separated in CDCl$_3$. We were unable to assign the peaks for epoxides and alcohols due to the low content of PB. The photooxidized films became yellow in color due to the chain scissions that occurred in the PB phase. Scott[11] postulated that the C—H bond of PS is more stable than the C—H bond of the allyl group of PB due to the induction effect, the steric hindrance of the phenyl group, and delocalization of radicals by the allyl group: (CH$_2$=CH—CH$_3$ $\rightleftharpoons$ CH$_2$=CH—$\dot{\text{C}}$H$_2$ + $\dot{\text{H}}$); therefore, oxidation naturally begins in the rubbery phase (allyl group) of PB. The yellowing in HIPS is due to PS, which is well documented.[12,13] Due

to crosslinking, the phase separation was observed in photooxidized films (200 h) in CDCl$_3$ solvent.

In the SBS triblock copolymer the PB block is also susceptible to photooxidation. The *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 PB phases (Fig. 3) were present in the SBS copolymer also. The photooxidized (100-h irradiation) SBS films showed the appearance of *cis*-epoxides (δ 56.4 ppm), *trans*-epoxides (δ 58.3 ppm), and alcohol (δ 71.2 ppm) (Fig. 4), but on longer hours of irradiation there is a decrease in epoxides and alcohol peaks (Fig. 5). This decrease with longer irradiation is due to the decomposition of epoxides and alcohols to carbonyls end products. The generation of these groups and then their decomposition confirms that oxidation primarily initiates in the PB phase of the SBS. Adam et al.[14] also observed a weak resonance in PB. The weak signals are responsible for alcohols (65–77 ppm) and peroxides (78–88 ppm). The peaks at δ 56.4 and 58.3 ppm are identified[14] as a *cis*-epoxide and *trans*-epoxide, respectively. The very weak crosslinking peaks were also observed at δ 29.5, 40.3, 41.6, and 42.4 ppm. The following mechanism is proposed for the epoxide formation:

$$\text{RH} \xrightarrow{h\nu} \dot{\text{R}} + \dot{\text{H}}$$

$$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2- + \dot{\text{R}} \longrightarrow -\text{CH}_2-\text{CH}=\text{CH}-\dot{\text{C}}\text{H}- + \text{RH}$$

$$\downarrow \text{O}_2$$

$$-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2- \xleftarrow{-\text{CH}=\text{CH}-} -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}-$$
$$\diagdown\text{O}\diagup \qquad\qquad \dot{\text{O}}-\text{O}$$

$$\downarrow \text{RH}$$

$$\dot{\text{O}}\text{H} + -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}- \xleftarrow{h\nu} -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}-$$
$$\qquad\qquad\qquad \dot{\text{O}} \qquad\qquad\qquad \text{OOH}$$

$$\downarrow \dot{\text{H}}$$

$$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}-$$
$$\qquad\qquad\qquad \text{OH}$$

The PB peak intensities decrease with increasing exposure time, meaning that photooxidation initiation also occurs in the PB phase in the SBS copolymer.

Morphological Changes upon UV Irradiation
HIPS

In toluene solvent the PS matrix is soluble and the rubber particles can swell to such an extent that the

resulting system appears to the naked eye as a true solution, particularly on sufficiently high dilution.[15] The 100-h exposed film (Fig. 6) showed microcavities on the surface. This was because of chain scission that is initially occurred in the PB phase. Singh et al.[16] explained the changes in viscosity, tensile impact strength, and yellowing upon exposure to UV light. These cavities are regular and spherical
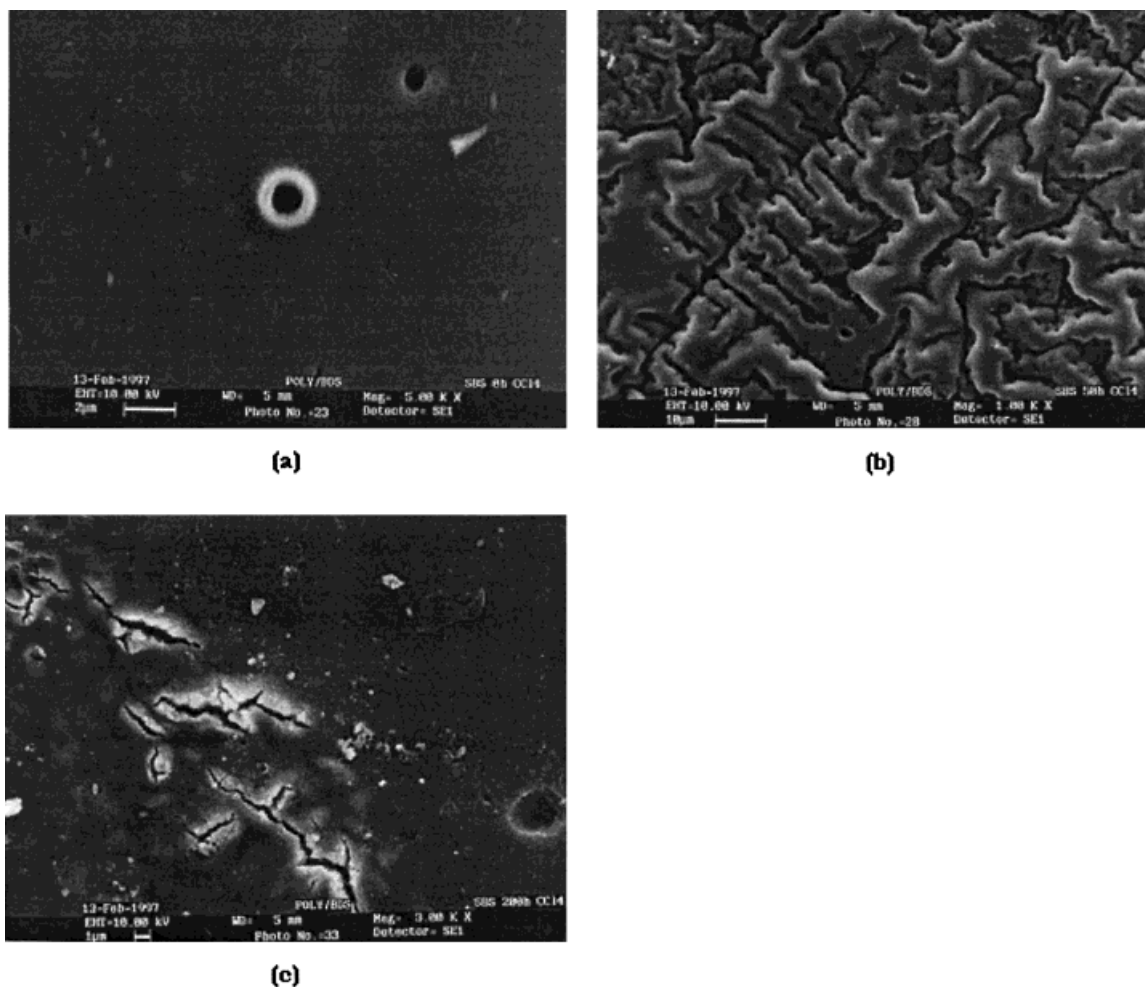
Figure 8   SEM photographs of SBS film cast from CCl$_4$ solvent: (a) neat film, (b) 50-h UV exposure, and (c) 200-h UV exposure.

in nature. The internal surfaces of the cavities are rough in nature. The film irradiated for 250 h showed microcracks on the surface. The cracks propagated through the rubber particles.

SBS Copolymer

The morphology in the SBS triblock copolymer changes with the solvent system. Photooxidized films showed surface embrittlement and yellowness. This was because the chain scission occurred in the PB portion. Photooxidized SBS films showed microcracks and microcavities on the polymer surface. The breaking of polymer bonds under UV irradiation produces fragments that occupy more volume than the original macromolecules, causing strains and stress that can be responsible for the formation of microcracks.[14]

Tetrahydrofuran [THF, solubility parameter 9.1 (cal cm^{-3})$^{1/2}$] is a good solvent for PS compared to PB[18]; therefore, the THF solvent system showed the phase separation very well.[19] The swollen end blocks aggregated into a spherical form (Fig. 7). Photooxidized films showed the aggregation of the PS block very well (50 h). The 100-h exposure film showed the microcavities on the polymer surface. This was due to the initial degradation of the PB portion. The 300-h irradiated film showed microcracks on the surface.

Carbon tetrachloride [solubility parameter 8.6 (cal cm^{-3})$^{1/2}$] is a good solvent for both the PB and PS.[18] In SBS-CCl$_4$ solution an interface is exists between the PS and PB portions. This was observed with dynamic mechanical testing.[20] At 50-h exposure the PB portion started to degrade
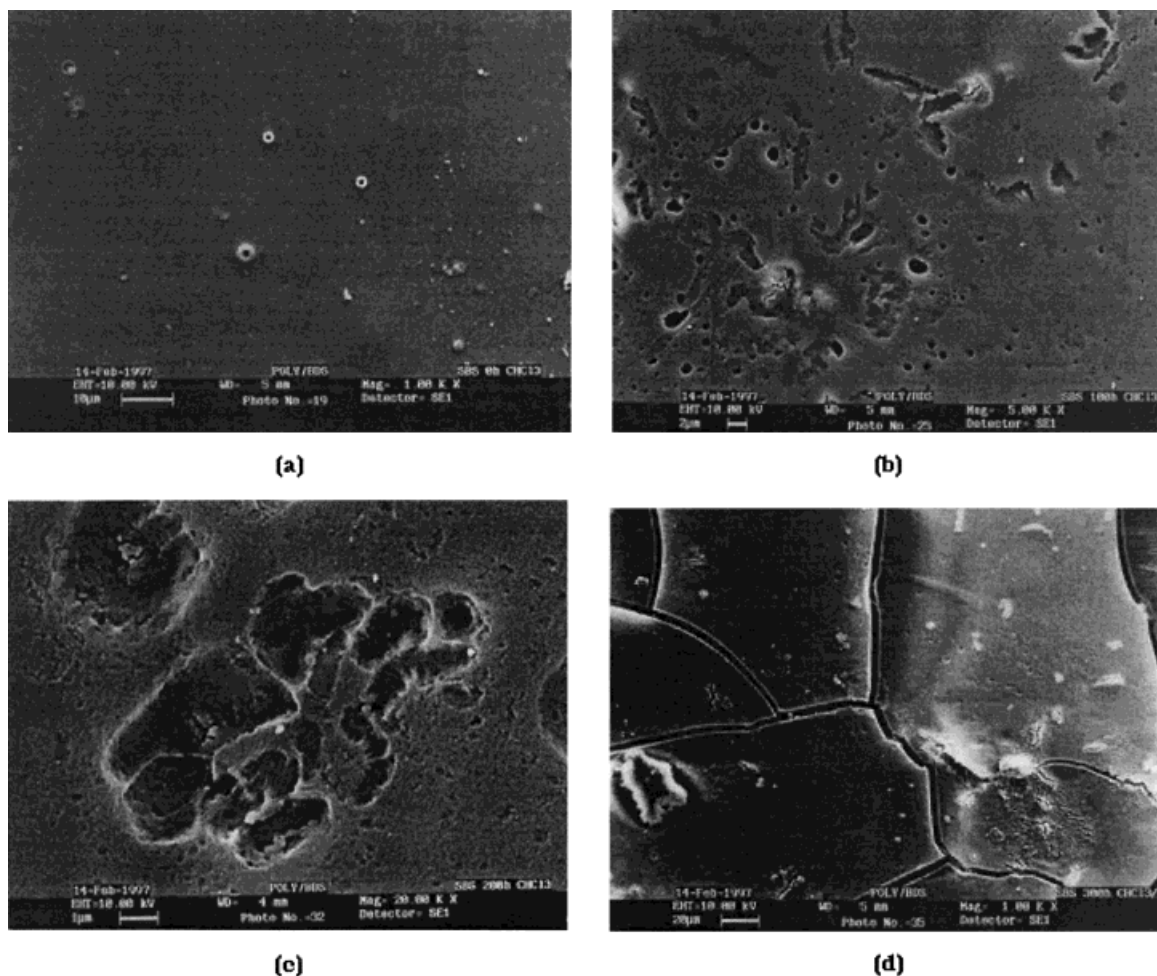
Figure 9 SEM photographs of SBS film cast from CHCl$_3$ solvent: (a) neat film, (b) 100-h UV exposure, (c) 200-h UV exposure, and (d) 300-h UV exposure.

and phase separation is very clearly observed in Figure 8. At longer times (200 h) the PS phase also started to degrade as is evidenced by the cracks on the white portion.

In chloroform [solubility parameter 9.3 (cal cm^{-3})$^{1/2}$] solvent the PS and PB phase separated very well.[21] Figure 9 shows the microcracks observed on the surface upon UV exposure. At 100-h UV exposure the microcavities formed and the PS phase also started degradation. The microcavities are irregular in shape and the internal surfaces of the cavities are rough in nature. At a longer exposure the macrocracks and macrocavities were observed on surface.

CONCLUSION

The characterization and assignment of a particular signal in a glassy insoluble polymer net-work are the major analytical applications of the NMR technique. The best results are expected in solution, but on photoirradiation the samples are slightly crosslinked. The samples of HIPS and SBS subjected to polychromatic irradiations underwent cracks on the surface that led to the serious loss of impact strength in the former and elastomeric properties in the latter. The microcracks were developed due to the formation of photoproducts during irradiation. Both polymers also displayed distinct microphase separation.

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