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Photodegradation of chain halogenated polystyrene: Poly (*c*-chloro and *c*-bromostyrene)s

A. Rincón G.

Grupo de Polímeros, Departamento de Química, Facultad de Ciencias,
Universidad de Los Andes, Mérida 5101, Venezuela

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Summary

The photodegradation of films of poly chain-chlorostyrene (PCCS) and poly chain-bromostyrene (PCBS) achieved by exposure to 254-nm radiation under dynamic vacuum was studied. The minor gaseous products obtained were hydrogen halides and monomer. The polymers were investigated by ir, gel permeation chromatography, and microanalysis. Both polymers undergo main chain scission. The ir spectra of the degraded polymers indicate the presence of unsaturated species. An initial α-carbon-halogen bond fission is required to account for the present reaction products. Possible mechanism of the various photoreactions are discussed.

Introduction

It has been reported (1) that halogenated (Cl, Br) polystyrene shows self-extinguishing properties with potential for application as non-inflammable expanded polymer. In particular, brominated polystyrenes may be used as flame retardants when blended with polyesters and polyamides(2). However, little attention have been focused on the photodegradation of chain-halogenated polystyrenes as compared to ring-halogenated PS. In earlier work (3), it has been established that photolysis of ring-substituted (Cl, Br) polystyrene involves simultaneous chain scission and crosslinking reactions when irradiated with UV 254-nm under vacuum. The degradation behavior of these polymers may be qualitatively related to the withdrawing characteristic of the substituents. It has been reported (4) that chain halogenated (Cl,Br)PS(4) undergo slight decoloration and crosslinking when irradiated with 254 and 365 nm UV under vacuum. In the present work the photodegradation of poly c-clorostyrene (PCCS) and poly c-bromostyrene (PCBS) in the form of films were investigated using 254-nm UV light under dynamic vacuum (10^{-5}mm Hg) at room temperature. The polymers degraded at different irradiation times, 1 to 4 hours, were analysed by ir, gel permeation chromatography and microanalysis. The degradation behavior of these polymers is studied.

Experimental

Preparation of chain-halogenated PS samples were made by functionalization reaction of PS (M_w = 325.000) using a vacuum line technique. Solution of PS in AR grade CCl_4 were previously degassed and a known quantity of the halogen was transferred to the PS solution cooled at -196°C. The reaction vessel was then sealed off under vacuum. The chlorination reaction was allowed to proceed at room temperature until the chlorine disappeared. In the case of PS bromination, benzoyl peroxide (0.12 initiator/styrene units) was added to the PS solution as free radical initiator. The sealed tube was placed in a bath at 60°C for 24 hours. After reaction, the polymer solutions were filtered and reprecipitated several times with methanol. The material was dried under vacuum at 30°C, powdered and stored in vacuum. PCCS samples obtained were a white powder with a chlorine content of 35.38% by weight (molar ratio of 1.38/1 Cl/styrene). The PCBS after several reprecipitations remained yellowish-brown and the extent of bromination was 34.89% by weight (molar ratio 0.80/1 Br/styrene). Molecular weight of the original and degraded samples was determined by gel permeation chromatography using THF as solvent. The original weight-average molecular weights of PCCS and PCBS were: PCCS $\bar{M}w=3.1x10^5$ and PCBS $\bar{M}w=5x10^4$ g/mol, respectively. It is observed that some main chain scission occurred during halogenation, and was more important in the bromination reaction due to the free radical initiator used. The polymers were cast into films by the evaporation of dichloromethane solutions on stainless steel plates. Polymer samples with 30 ± 2 mg weight were used. The photochemical technique and optical equipment were similar to those described elsewhere (3).

Results and discussion

In Fig. 1, ir spectra of c-chloro PS (PCCS) and c-bromo PS (PCBS) are shown. Both polymers have strong bands between 3100 to 3020 cm^{-1} corresponding to the aromatic C-H stretch absorption. The weak band at 2850 may be assigned to the methine bond stretch absorption. In the region 2000-1700 cm^{-1}, several bands are observed which are characteristic of aromatic monosubstitution. PCCS shows highly superimposed bands between 1400-1050 cm^{-1}. The absorption band at 1235 cm^{-1} is attributed to the substituted α -carbon $C(Cl)-CH_2$ bending. PCBS shows a weak band at about 1400 cm^{-1}, which may be due to $C(Br)-CH_2$ bending. Two bands in the region 1100 to 1000 cm^{-1} and at 825 cm^{-1} are indicative of the presence of some p-halogen susbtitution. However, they are weak. The region below 800 cm^{-1} show several absorption bands. The C-Cl and C-Br absorption bands, expected to appear at about 735 and 685 cm^{-1}, respectively are not clearly observed because of the presence of strong out- of- plane bending aromatic band at 700 cm^{-1}.

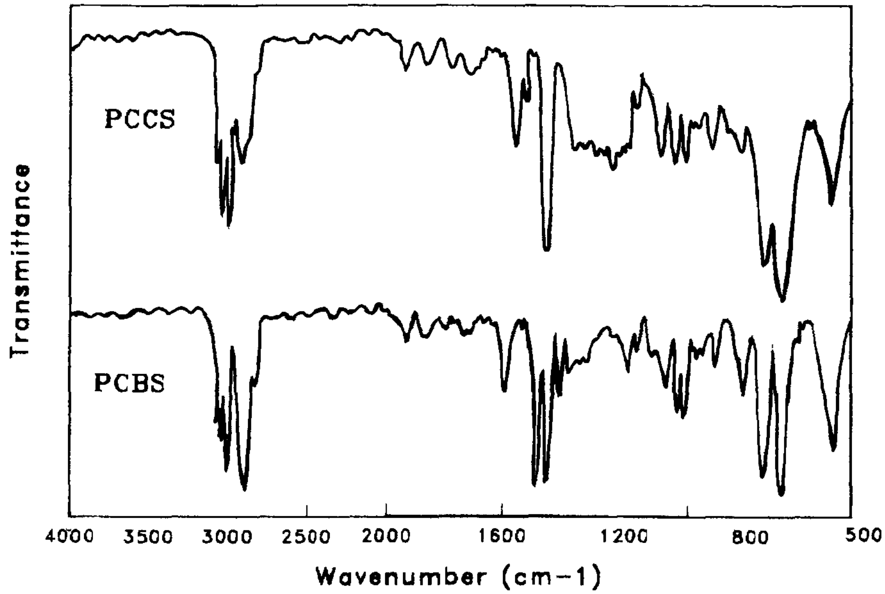


Fig. 1. Infrared spectra of films obtained by evaporation from dichloromethylene solution: poly c-chlorostyrene (PCCS); poly c-bromostyrene (PCBS).

The nmr spectra of chain halogenated (Cl, Br) PS, recorded with a 60 MHz Varian spectrometer, show two groups of poorly resolved broad peaks. These are assigned as follows: PCCS, δ 7.1-6.8 ppm and PCBS δ 7.06-6.9 ppm due to aromatic ring protons and PCCS, δ 2.0-1.3 ppm and PCBS δ 2.0 - 1.0 ppm corresponding to methylene and methine protons.

The photolysis of PCCS and PCBS yielded minor amounts of gaseous products collected as condensable volatile fractions which consisted of hydrogen halides (HCl, HBr) and monomer. When PCCS and PCBS are photodegraded at different time intervals with 254-nm UV light, the remaining partially degraded polymers are soluble in chloroform, benzene and dichloromethane. The films become yellowish on irradiation.

The infrared spectra of the degraded PCCS and PCBS showed the appearance of new bands at 1585 and 940 cm^{-1} which can be attributed to main chain unsaturations $(\text{—RHC=CHR—})_n$.

The molecular weight distribution curves for the original and the photodegraded PCCS and PCBS, obtained after 4 hours of irradiation, are compared in Fig. 2. After exposure to 254-nm UV light the average molecular weight of both PCCS and PCBS shift to lower values. This indicates main-chain scission.

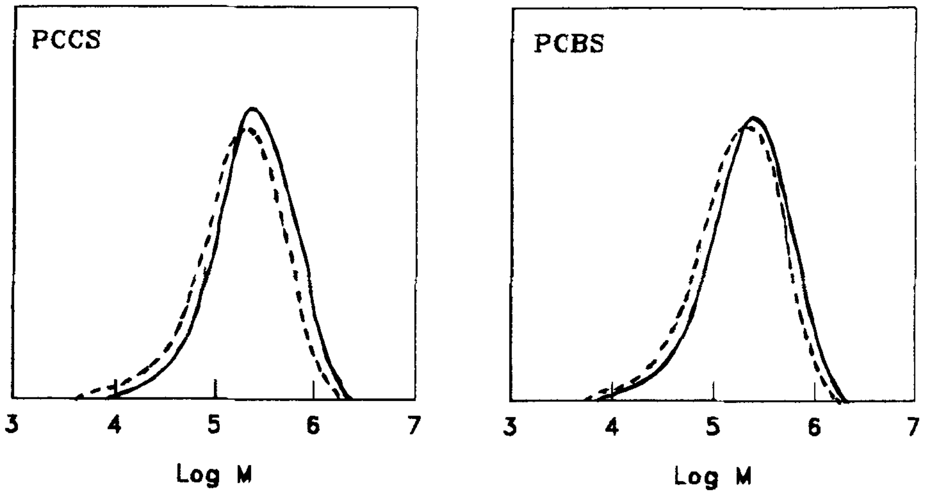
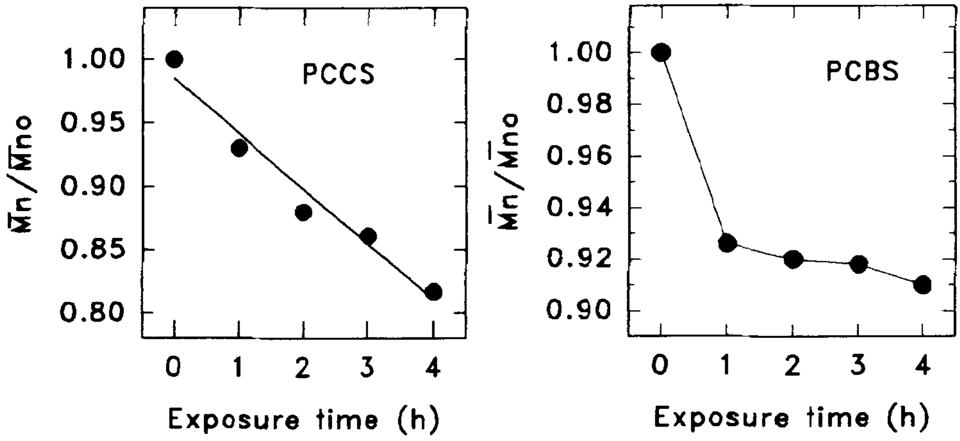


Fig. 2. Molecular weight distribution of PCCS and PCBS(——) and the degraded polymer (---). Polymer films were irradiated for up to 4 h.

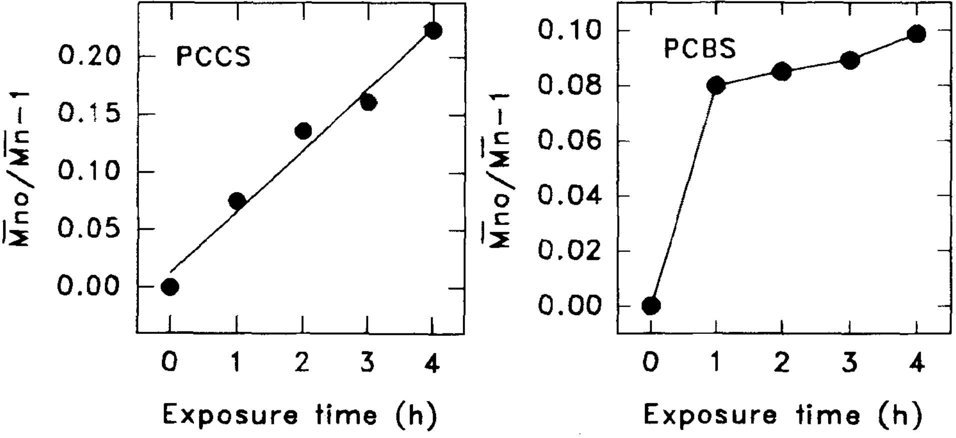
Figs.3 and 4 show the number-average molecular weight changes ($\bar{M}n/\bar{M}no$) of PCCS and PCBS of the remaining partially degraded polymer after degradation (λ=254-nm) as a function of time of irradiation for up to 4 h.



Figs.3 and 4. The number-average molecular weight changes ($\bar{M}n/\bar{M}no$) of PCCS and PCBS films after irradiation (λ=254nm) for up to 4 h under vacuum.

It is observed from Figs. 3 and 4 that the number-average-molecular weights of PCCS and PCBS rapidly decrease during the initial stage of irradiation. This behavior may be due to main-chain scission.

Figs. 5 and 6 show the variation of average number of chain scission ($\bar{M}no/\bar{M}n-1$) for PCCS and PCBS as a function of exposure time (h).

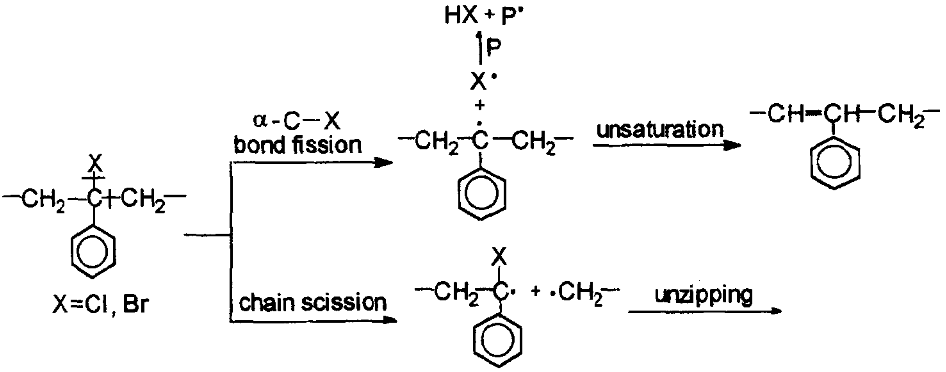


Figs.5 and 6. The variation of average number of chain scission ($\bar{M}no/\bar{M}n-1$) for PCCS and PCBS with exposure time up to 4 h under vacuum.

It can be observed that PCCS undergoes chain scission very nearly linearly with increasing exposure time, whereas in the case of PCBS chain scission first increases sharply and much slower later.

Conclusions

Poly chain-chlorostyrene and poly chain-bromostyrene irradiated under vacuum with 254nm UV light produce minor gaseous products: hydrogen halides and monomer. The main degradation products obtained from both polymers are short chain fragments. The number-average molecular weight changes ($\bar{M}n/\bar{M}no$) of the degraded samples after different periods of irradiation indicate main-chain scission for both polymers. The following scheme summarizes a possible reaction mechanism.



Hydrogen halide may be produced by initial α-carbon-halogen bond fission, that leads to halogen atoms. The latters can participate in H-abstraction. The primary macroradical $-CH_2-\dot{C}Ar-CH_2-$ may undergo disproportionation that leads to main chain unsaturation. This accounts for the olefinic link observed in the PCXS chain fragments.

Initial scission of the C_1-C_2 bond would lead to a radical whose structure is similar to that of the propagating radical that is expected to depropagate. For PCBS the decrease of chain scission with time may be explained by some bromine ring substitution $-CH_2-CH(PhBr)-$ which shows a high susceptibility to crosslinking (3).

Aknowledgement

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