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Photodegradation of ring halogenated polystyrenes: poly(*p*-chlorostyrene) and poly(*p*-bromostyrene)

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Summary

Photodegradation of poly(p-chlorostyrene) (PPCS) and poly(p-bromostyrene) (PPBS) films was studied using 254nm UV under dynamic vacuum at room temperature. The polymers were examined by IR, and NMR spectroscopy, gel permeation chromatography, and microanalysis. Solubility data confirms that both polymers undergo chain scission and crosslinking simultaneously. Evidence of scission of the C-Ph bonds in the chain backbone has been found. Possible mechanisms of the various reactions are discussed.

Introduction

A number of photolysis studies on ring substituted polystyrene (PS) (1-3) suggested that the degradation behavior of these polymers may be qualitatively related to the electron-donating or withdrawing characteristic of the substituents. It has been reported that p-halogenated polystyrenes (4) undergo main-chain scission and crosslinking when irradiated with 254nm UV under high vacuum. Photophysical investigations on halogenated PS (5) indicated that halogen substituents produce an internal quenching, reflected in the low values of fluorescence quantum yield, and hinders also the formation of excimers. In PPCS (6) formation of dimers in the ground state has been reported. However, in this case the chlorine atoms interfere with the energy migration, a mechanism that converts dimers into excimers. This effect has been explained in terms of a greater polarity of the chromophore group and the steric interactions of Cl atoms that increase the torsional barrier giving a less flexible polymeric structure. Radiolysis work on p-halogenated PS (7) using γ radiation *in vacuo* showed that the hydrogen production diminished as compared to PS. This is interpreted in terms of the destabilizing effect of the substituent on the macroradicals formed in the primary photochemical process. Strong tendency to crosslinking was also noted in these polymers. It is suggested that fission of C-Ph bond may occur in PS (8). In the present work the photodegradation of PPCS and PPBS films was investigated using 254 nm UV under dynamic vacuum (10^{-5} mm Hg) at 20±1°C. The degradation products, namely the volatile condensables and solid fractions were analysed by IR, NMR spectroscopy, and gel permeation chromatography. A comparative study of the degradation behavior of these polymers is made. Experimental evidence of C-Ph bond fission is found.

Experimental

The monomers (Aldrich) previously purified were polymerized in bulk at 70°C under vacuum. In both polymerizations the initiator used was azobisisobutironitrile (0.01%w/v) and the polymerization time was 24 h. The reaction product was diluted with dichloromethane and the polymers isolated by pouring in methanol as non-solvent. The filtered material was dried under vacuum at 30°C, powdered and stored under vacuum. The molecular weight of the polymers was determined by gel permeation chromatography using tetrahydrofuran (THF) as solvent. The weight-average molecular weights of the samples used were: PPCS, $\bar{M}w=1.9 \times 10^6$ and PPBS, $\bar{M}w=8x10^5$. Microanalysis for PPCS gave C 69.0%, H 5.2%, Cl 25.8% and for PPBS C 52.7%, H 3.7%, Cl 43.6% in good correspondence with the theoretical values for the structural units C_8H_7Cl and C_8H_7Br, respectively. The polymers were dissolved in dichloromethane (40mg/ml) and the films were prepared by deposition on a stainless steel tray (diameter=3,8 cm^2). The solvent was evaporated first at atmospheric pressure and then under vacuum.

Irradiation experiments were run using a photolysis cell (9) coupled to a 4-line TVA system (10^{-5} mm Hg) (10). A medium pressure mercury lamp (Universal UV lamp CAMAG, model TYP-TL-900) was used as the source. Lamp output at 15 cms distance from the sample was $8.6x10^{12}$ photons/seg.cm^2. Samples (20±1mg) were irradiated at 20±1°C for up to 6 hours. The condensable volatile fraction formed was collected with a trap cooled at -196°C. After irradiation, the trap was warmed up in a controlled manner and the volatile products collected in an IR gas cell and examined by IR spectroscopy. The irradiated films were treated with THF giving soluble and insoluble fractions that were separated by filtration. The former was isolated by evaporation of the solvent and the latter was washed with THF. The two fractions were dried under vacuum at 30°C and then weighed.

Results and discussion

The infrared spectra of PPCS and PPBS are shown in Figs. 1 (a) and (b). Both polymers have similar absorption bands, namely the C-H stretch at 3020-3060 cm^{-1}, the aliphatic C-H stretch absorption at 2850 and 2920 cm^{-1}. Other bands observed are at 1895cm^{-1}, which is characteristic of p-disubstitution, the strong C-H in-plane deformation of the p- disubstituted ring at 1010 and 1075cm^{-1} and the out-of-plane deformation band of the p-disubstituted phenyl ring at 825 cm^{-1}. The region below 800cm^{-1} show several absorption peaks that may be attributed to C-halogen bands.

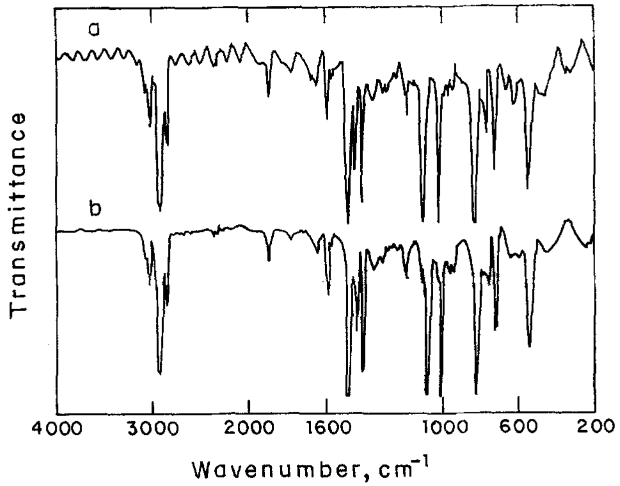


Fig.1 Infrared spectra of (a) poly(p-chlorostyrene) (b) poly(p-bromostyrene). Films were obtained by evaporation on salt plate from a dichloromethane solution.

The condensable volatile fraction collected after degradation was very small and consisted of monomer and hydrogen halides (HCl, HBr). The monomer obtained may be due to a small quantity that remained in the original polymer after purification, or is formed during degradation.

The ^{1}NMR spectra of the original polymers and the soluble products obtained after degradation for 6 h are shown in Figs. 2 and 3 (a), and (b). There are three groups of peaks in the spectra of the polymers. PPCS (Fig. 2a) shows signals at 7.06-6.40 ppm attributed to aromatic ring protons, at 2.16-1.92 ppm assigned to methine protons in $-CH_2CH(ArCl)$ and 1.54-1.32 ppm to methylene protons in chain backbone environment. The PPBS spectrum (Fig.2b) also shows similar peaks at 7.18-6.39 pmm, 2.16ppm and 1.53-1.24 pmm. The soluble fraction of PPCS (Fig.3a) also gives additional peaks at 5.8-5.3 ppm assigned to olefinic protons in -CH=CH-, at 3.6 ppm attributed to $-C(ClAr)=CH_2$ end groups and around 0.82-0.91 assigned to methyl end groups in $-CH(ArCl)CH_2CH_2CH_3$. The soluble part of PPBS (Fig.3b) has similar peaks at 3.65 and 0.90 ppm. These results indicate that the PPCS soluble product consisted of short chain fractions containing: (i) olefinic bonds in main chain, (ii) methylene end group formed by diproportionation and (iii) methyl end group that results from C-phenyl bonds fission, H-abstractions and further chain scission. The soluble part of PPBS also contains methylene and methyl end groups, but does not show the presence of olefinic bonds in the backbone.

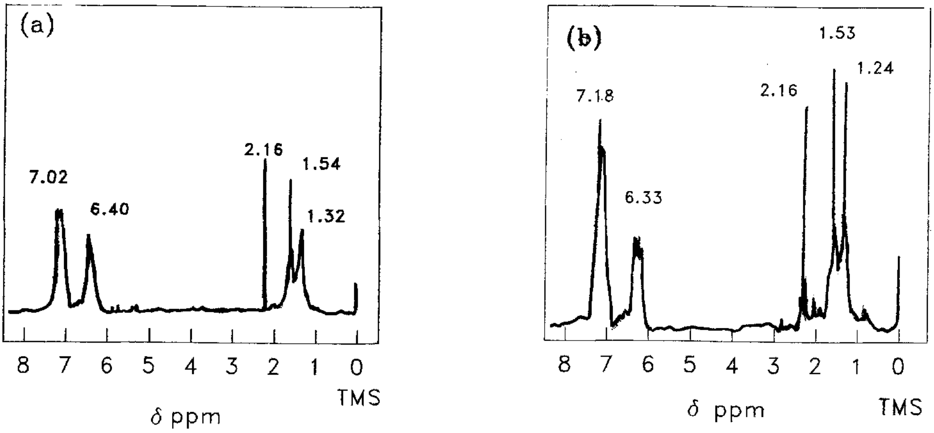


Fig.2 ^{1}NMR spectra of (a) poly (p-chlorostyrene) and (b) poly(p-bromostyrene). Solvent $CDCl_3$

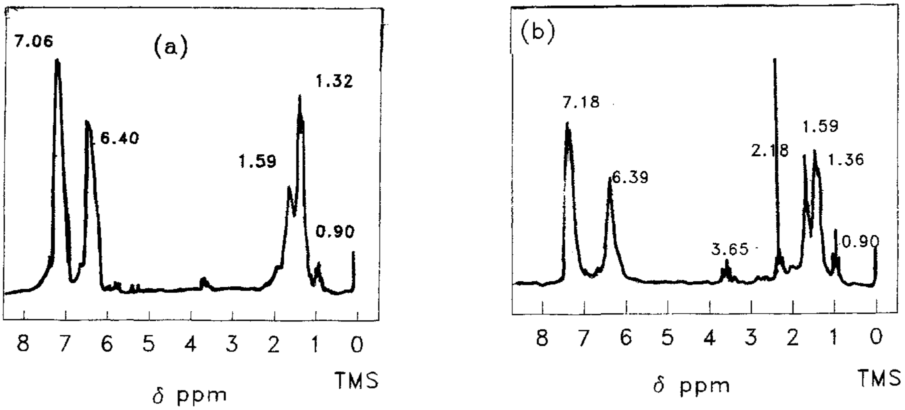


Fig.3 ^{1}NMR spectra of soluble fraction remaning after irradiation for 6h (λ=254nm) of (a) poly(p-chlorostyrene), (b) poly(p-bromostyrene). Solvent $CDCl_3$

The molecular weight distribution curves for the polymers and the soluble fraction obtained after 6 h of irradiation are compared in Figs.4 (a) and (b). After UV exposure the average molecular weight of the soluble fraction of PPCS (Fig. 4a) undergoes a shift to a lower values. This indicates that main-chain scission reactions occurred in the polymer. The GPC curve for the soluble part of PPBS (Fig.4b) shows a shift of the average molecular weight to higher values. This behavior may be due to crosslinking reactions.

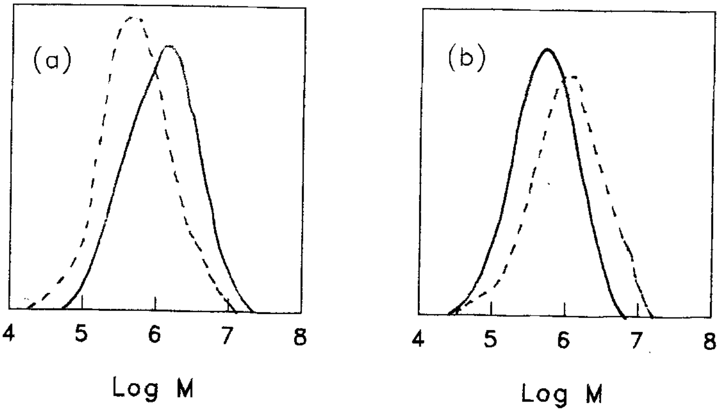


Fig. 4. GPC curves for (a) original PPCS (—) and the soluble fraction (---) (b) original PPBS (—) and the soluble fraction (---). Polymer films were irradiated under vacuum with λ=254nm for 6 h.

The number-average molecular weight changes ($\bar{M}n/\bar{M}no$) of the soluble part remaining after degradation (λ=254nm) as a function of irradiation time up to 6 h are shown in Figs (5) and (6).

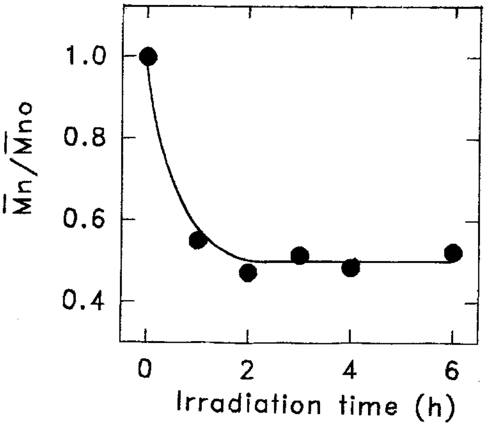


Fig.5 Molecular weight changes ($\bar{M}n/\bar{M}no$) for the soluble fraction of PPCS after irradiation (λ=254nm) under vacuum for up to 6 h. Molecular weights are compared with the initial value for undegraded PPCS.

It can be seen from Fig. 5 that the average-molecular weight changes of the soluble fraction of PPCS at the initial stage of the reaction undergoes a rapid decrease. This indicates a main-chain scission process.

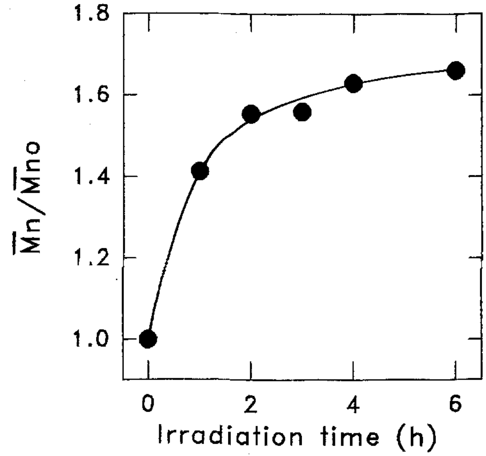


Fig.6 Molecular weight changes ($\overline{Mn}/\overline{Mno}$) for the remaining soluble fraction of PPBS after irradiation (λ=254nm) under vacuum for up to 6 h. Molecular weights are compared with the initial value for undegraded PPBS.

In the case of PPBS (Fig.6) the $\overline{Mn}/\overline{Mno}$ of the degraded soluble fraction shows a continuous increase, that is more rapid at shorter time of irradiation. This behavior suggests, as mentionated earlier, the occurrence of cross-linking reactions. In order to examine the probabilities of chain scission and crosslinking reactions occurring in both polymers, the data of the remaining soluble part of the polymers after irradiation were analyzed using the Charlesby-Pinner equation:

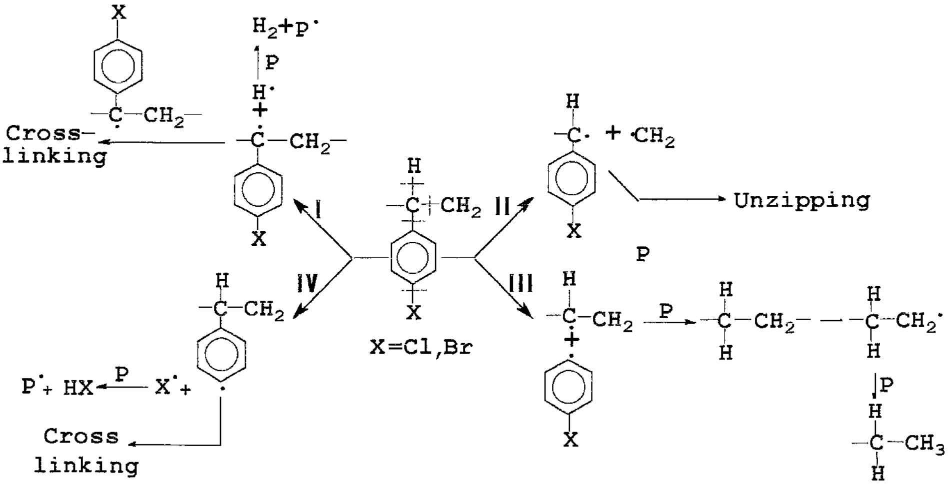
$$s + \sqrt{s} = \frac{\alpha}{\beta} + \frac{1}{X_o \beta t} \tag{1}$$

where s is the soluble fraction remaining after degradation time (t), X_o is the initial degree of polymerization and α and β are the probabilities of chain scission and crosslinking, respectively. This indicates the simultaneous degradation of the polymers through main-chain scission and crosslinking processes. Reasonable linear plots of $s + \sqrt{s}$ versus t^{-1} were obtained. The values obtained through a least squares fit were: PPCS, α=4.8x10^{-4} scission per monomer unit/h and β=3.0x10^{-2} crosslink per monomer unit/h and PPBS, α=1.0x10^{-3} scission per monomer unit/h, and β=8.1x10^{-3} crosslink per monomer unit/h. Since $\alpha_{PPCS} > \alpha_{PPBS}$ and $\beta_{PPCS} < \beta_{PPBS}$, it can be asserted, as suggested earlier, that main-chain scission reactions predominates in PPCS and crosslinking in PPBS.

Conclusions

PPCS and PPBS irradiated under vacuum with 254nm UV produce minor gaseous products such as hydrogen, hydrogen halides, and monomer. The main degradation products obtained from both polymers are short chain fragments and an insoluble material. However, the number-average molecular weight changes ($\overline{M}n/\overline{M}no$) of the soluble part remaining after degradation and the rates values of main-chain scission and crosslinking processes of the polymers indicate that they behave differently on irradiation. A reasonable mechanism that would explain the formation of the degradation products obtained may involve initial cleavage of bonds adjacent to the phenyl group as primary photochemical processes. This is shown in scheme A.

Scheme A



The initial C_1-H bond scission (process I) produces H atom that is expected to abstract a tertiary hydrogen from a PXS unit giving molecular H_2. The scission at C_1-C_2 (process II) would lead to a radical having a structure identical to that of the propagating radical which is expected to depropagate to produce monomer. The short chain fractions formed during degradation show a CH_3 end group at 0.80-0.90 ppm. This is possibly formed by fission at C-Ph bond (process III) that produces a radical type $-CH(ArX)-CH_2-\dot{C}H-CH_2-$. This radical abstracts a hydrogen atom giving a main chain $-CH_2-$ group. This by further scission at C_1-C_2 produces a radical type $-CH(ArX)CH_2CH_2CH_2^{\bullet}$ which could abstract H atom leading to an aliphatic end group.

The loss of halogen atoms (Cl, Br) is indicated by the formation of traces of HX most probably due to scission of Ph-X bond and further H-abstraction from the polymer. An alternative reaction, if it occurs, could be with H atoms. However, this is less likely due to degradation under high vacuum conditions. The olefinic link observed in the PPCS chain fragments may result by disproportionation reaction of macroradical $-CH_2-\dot{C}(ArX)-CH_2-$ formed in process I. The higher rate of chain scission (α) of PPCS can be related probably to a higher inductive effect as compared to bromine. Crosslinking would involve various radicals such as, $-\dot{C}(ArX)CH_2$, $-\dot{C}H(\Phi)CH_2$ and also those produced in the H-abstraction process. The larger extent of crosslinking of PPBS can be explained by the effect of greater steric interaction of bromine that results in an increase of the rotational barrier giving a less flexible polymer than with Cl. The presence of methyl end groups has been established, which is an indication of $C-C_6H_5$ bond scission as has been proposed in an earlier work on the photodegradation of polystyrene (8).

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