

Photochemical bromination of polyolefin surfaces

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Abstract

The gas phase bromination of polyethylene (PE), polypropylene (PP) and polystyrene (PS) film surfaces by free radical photochemical pathway occurs with high regioselectivity. The surface bromination was accompanied by simultaneous dehydrobromination resulting in the formation of long sequences of conjugated double bonds. Thus, the brominated polyolefin surface contains bromide (Br) moieties in different chemical environments. The formation of Br moieties on the brominated polyolefin film surfaces was shown by XPS and ATR-FTIR analysis and long sequences of double bonds by UV-Vis spectroscopy. For comparison, gas phase free radical photochemical chlorination of polyolefin films was also examined. The results show that, chlorination proceeds in a relatively random way and it is also accompanied by simultaneous dehydrochlorination. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Surface modification; Polyolefins; Bromination

1. Introduction

Surface modification of polymers is an important field both in applied [1–4] as well as in basic research [5,6]. This technique is widely used to modify the surface properties of a wide range of polymers [1]. A number of surface modification techniques such as plasma, corona discharge, chemical treatments have been used to modify polymer surfaces, of which, chemical methods are of particular interest, because it can lead to the introduction of specific functional moieties on the polymer surface. Other methods such as plasma, corona discharge, ion-beam modification and flame treatment lead to the introduction of different functional groups in different extent and the resulting surface is chemically and structurally heterogeneous. Further, most of these methods are system dependent [1]. Even in the case of chemical treatment, often the modified surface is chemically heterogeneous [5–7]. Because, most of the reactions used are often accompanied with some side reactions to different extents and it is not possible to remove these side products from the surface. Further, it is known that, the mechanism of the surface reaction may be different from the analogous solution reaction [8]. Thus, in order to extend the known organic chemistry to polymer surfaces it is important to

characterize the modified surface with respect to the nature of functional groups introduced on the surface, chemical environment of the functional groups and occurrence of any side reactions. This information greatly increases our understanding of the reactions occurring at the interface especially about the reactivity of surface functional groups, which in turn is useful to design surface reactions.

This paper describes a detailed study of surface bromination of a low-density polyethylene (LDPE) film by free radical gas phase photochemical reaction. The main emphasis in this paper is on probable mechanism of bromination, nature of the bromide (Br) moieties and the occurrence of any side reactions. We also studied the bromination of polypropylene (PP) and polystyrene (PS) films to examine the effect of polymer structures on the mechanism of bromination. Further, to compare the mechanism of bromination with chlorination, we also studied the chlorination of LDPE, PP and PS surfaces.

Polyolefins contain only C–H and C–C bonds and are non-polar. The first step to modify its surface is to introduce a hetero atom/group. Reactions possible on a polyolefin surface are free radical reactions, oxidation and C–H and C–C bond insertion reactions. Out of these three pathways, oxidation reaction does not introduce specific functional groups, further it introduces only oxygen containing functionalities [8,9]. Whereas C–H and C–C bond insertion reactions, using reactive intermediates such as carbenes and nitrenes, are not understood clearly and the resulting

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surface is known to be chemically complex [10–12]. Free radical reactions such as sulfonation and halogenation of polyethylene (PE) surface are known reactions. Sulfonation of a PE surface results in the introduction of different functional groups [7], whereas it is reported that, halogenation of a PE surface results in the introduction of only halide moieties [13,14].

Thus, towards our effort to modify polyolefin surfaces to improve its wettability, metallization ability [15], lacquer adhesion [16], cell adhesion [16] and permeability [17] and to understand the effect of surface functional groups on these properties, we selected bromination of LDPE, PP and PS surfaces as a first step towards the functionalization of these polyolefin surfaces. The introduction of Br moieties on the polyolefin surface open up a synthetic pathway to introduce a wide range of specific functional groups on the surface under mild conditions via nucleophilic substitution of Br moieties by different nucleophiles [18]. Brominated polyolefin surface is a preferred substrate for nucleophilic substitution reactions compared to fluorinated and chlorinated surfaces due to the better leaving group ability of Br compared to fluoride (F) and chloride (Cl) moieties [18, p. 310–6].

2. Experimental section

2.1. Materials

LDPE films were prepared by compression molding of LDPE pellets (density = 0.916 g/cm³, MFI = 40 g min⁻¹, obtained from IPCL, Baroda, India) at 120°C for 2 min in a laboratory Carver press. The films of 6 × 1.5 cm size were cleaned by soxhlet extraction with dichloromethane followed by iso-propanol, each for 15 h, to remove additives. The films were then dried in vacuum oven for 25 h at 50°C. Similarly PP and PS films were prepared by the compression molding of PP pellets and PS pellets at 180 and at 120°C, respectively. These films were then cut to the required size. PP films were cleaned by soxhlet extraction with dichloromethane followed by iso-propanol and the PS films were soxhlet extracted only with iso-propanol.

Bromine was obtained from Merck, India and used without further purification.

2.2. Characterization

X-ray photoelectron spectroscopy (XPS) analyses were carried out using a V.G. Scientific ESCA-3-MK-II electron spectrometer fitted with Mg-K α radiation (1253.6 eV) X-ray source (non-monochromatic). The anode was operated at 100 W (10 kV, 10 mA) and the analyzer was operated at a constant pass energy of 50 eV. All the spectra were recorded under identical conditions with 4-mm slit and vacuum better than 10⁻⁸ Torr. The binding energy (BE) calibration of the spectrometer was done as reported earlier [7]. The resolution in terms of full width at half maximum (fwhm) of the

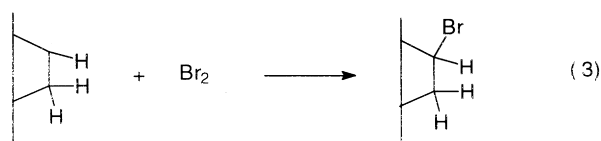
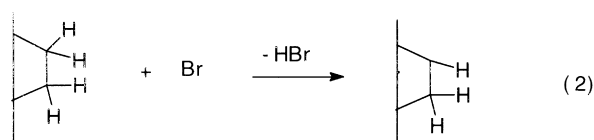
Au 4f_{7/2} level is 1.6 eV. The take off angle (the angle between the sample and the analyzer) was kept constant at 60°. The films were mounted on a stainless steel holder with double-sided adhesive tape. The peak shift due to surface charging was corrected using the C 1s level at 285 eV as an internal standard. Elemental concentrations were calculated using the XPS peak areas and the corresponding photoelectron cross-sections [19].

Attenuated total reflectance-FTIR (ATR-FTIR) spectra were recorded using a Perkin-Elmer 16PC Fourier transform Infrared spectrometer (20 cumulative scans) using an ATR attachment with a KRS-5 crystal at 45°. UV-Vis spectra were recorded on Hewlett Packard 8452A diode array spectrophotometer. Scanning electron micrographs were obtained from Leico SEM Stereoscan-440, Cambridge, UK. The polymer samples were coated with \approx 100 μ m of gold and analyzed at an accelerating voltage of 10 kV.

2.3. Experimental

2.3.1. Procedure for the bromination of polyolefin (LDPE, PP, PS) film surface

The polymer film was suspended inside a Schlank glass tube fitted with an inlet and outlet tube having stopcock for gas and a side arm with a septum. The glass tube was purged with nitrogen gas for 10 min to replace the air inside the tube. Then \sim 0.1 ml of bromine was introduced into the tube via a syringe through the septum. After 5 min, when the bromine got vaporized and filled the tube, the tube was placed in front of a 400 W, high-pressure mercury vapor (HPMV) lamp, at a distance of 7 cm. The film was then irradiated for a specified time. The glass tube was cooled by a small fan throughout the irradiation time and the temperature, when the lamp is on, was 35 \pm 2°C. The vapor pressure of bromine at this temperature is 328 mm Hg [20]. After the specific time of irradiation, the tube was purged with nitrogen for 15 min and then the film was kept in a vacuum oven, at room temperature, for 25 h. Vacuum dried film was then stored in a plastic storage tube for analysis. All the experiments involving handling of bromine was carried out inside a fume



Scheme 1.

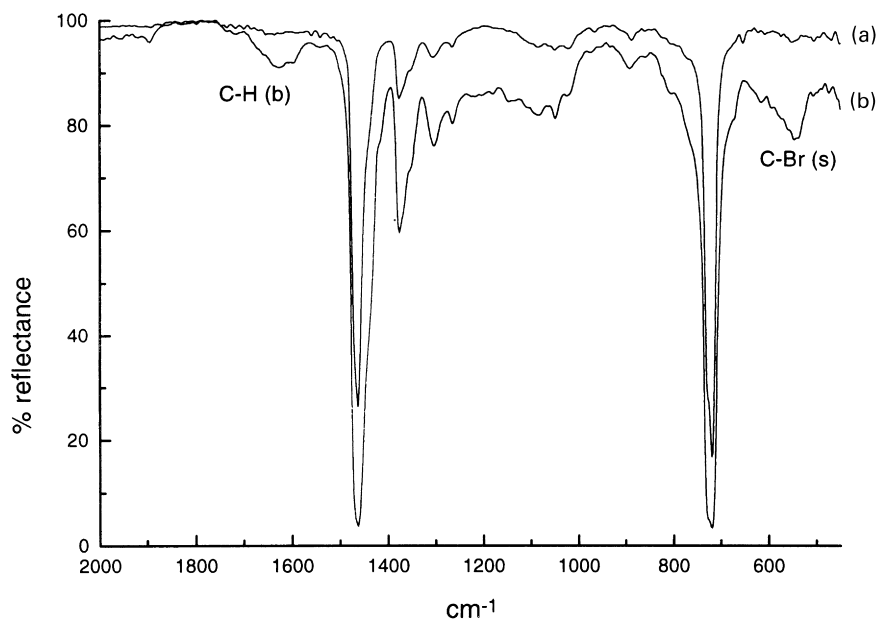


Fig. 1. ATR-FTIR spectra of: (a) LDPE film and (b) 1 h brominated LDPE film.

cupboard. Chlorination of polyolefin films were carried out according to a reported procedure [14].

3. Results and discussion

3.1. Surface bromination of low density polyethylene

LDPE films were brominated via gas phase free radical photochemical pathway as described in Section 2. The first step in this reaction is the homolytic bond cleavage of bromine molecule into two bromine radicals upon exposure to radiation [21]. In the second step, the bromine radical abstracts a hydrogen atom from the methylene unit of LDPE, which results in the formation of a radical center on the LDPE chain. This radical center further reacts with bromine molecule to form C–Br moiety and bromine radical. This bromine radical then reacts with another –CH₂– unit and this chain reaction continues (Scheme 1, the free radical mechanism of bromination of PE film surface) resulting in bromination of PE surface.

The presence of C–Br moieties on the PE–Br surface is shown by ATR-FTIR and XPS analysis. Thus, the ATR-FTIR spectrum (Fig. 1) of 1 h brominated LDPE (PE–Br-1 h) film shows three bands at 550, 568 and 620 cm⁻¹ assigned to C–Br stretching bands [22]. The wide scan XPS of 1 h brominated LDPE film (Fig. 2) shows the presence of Br 3d, Br 3p_{3/2}, Br 3p_{1/2} and Br 3s levels along with C1s peak. The BE values of these peaks determined from the high resolution XPS spectrum is 70.2, 183.12, 189.72 and 257.04 eV, respectively. These values are in good agreement with the reported values for the C–Br moieties [23–25]. Most of the surface Br moieties are

present as secondary bromides and some of the Br moieties may be present as dibromides [13]. The percentage of these two bromides can be obtained by curve fitting the high resolution C1s spectrum of PE–Br as shown by McCarthy and his coworkers in the case of chlorinated LDPE film

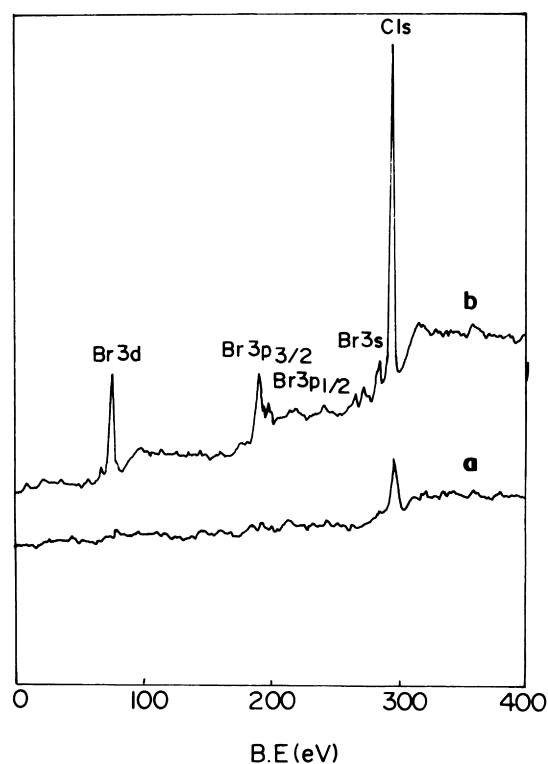


Fig. 2. Wide scan X-ray photoelectron spectrum of: (a) LDPE film and (b) 1 h brominated LDPE film.

surface [13]. But, the virgin PE as well as the brominated PE surface contain some oxygen moieties as seen from O1s peak in XPS. The atom percentage varies from film to film. Thus, the curve fitting of C1s spectrum is complex and not very useful [26].

The XPS data (Table 1) shows that, ~ 9 atomic percentage (at.%) of Br moieties were introduced on the LDPE surface after 1 h of bromination, i.e. $\sim 18\%$ of the repeat unit were brominated after 1 h of bromination. Elman et al. reported that in ambient light it takes ~ 150 h to introduce ~ 9 at.% of Br moieties on the LDPE surface [14]. Chew et al. reported that bromination of LDPE film surface in the presence of saturated bromine vapors irradiated from the distance of 40 cm by tungsten lamp introduced ~ 5 at.% of Br moieties on LDPE surface [27]. Our results show that, upon irradiation with the HPMV lamp, the rate of bromination of LDPE surface increases significantly, as expected.

We studied the bromination of LDPE film as a function of bromination time by XPS and ATR-FTIR. Table 1 shows the Br 3d/C 1s ratio of brominated PE film, as measured by XPS and the $\gamma_{C-Br}/\gamma_{C-H}$ band ratio as measured by ATR-FTIR¹ as a function of bromination time. It shows that the extent of bromination as measured by XPS, which analyzes the film to a depth of $\sim 36 \text{ \AA}$ [28]² increases with the time of bromination from 10 min to 1 h. Thereafter, it decreases marginally for 2 and 3 h reaction time and again increases for 5 h of bromination. The loss of Br moieties after 1 h is probably due to some side reactions [26]. But, the extent of bromination as measured by ATR-FTIR, which analyzes a film to a depth of $\sim 6 \text{ \mu m}$ [29], increases continuously with time. Thus ATR-FTIR and XPS data shows that, bromination takes place in the depth, indicating significant diffusion of bromine into the bulk of the film upon long reaction time.

The loss in surface Br moieties after 1 h of bromination, as shown by XPS, may be due to dehydrobromination, which can be a predominant side reaction under the influence of UV light [30] and/or due to UV oxidation, which may result in C–C bond cleavage [26]. Recently, Ulman and his coworkers reported the gas phase bromination of LDPE film surface. They brominated PE surfaces in a number of cycles, with the time period of 30 s/cycle, in the presence of saturated bromine vapors using short wave length UV-lamp at a distance of 2 cm. They reported that, 5.6 at % of Br

moieties are introduced on the surface after irradiation of 30 s (1-cycle). But, after the first cycle, the surface density of Br moieties decreases. Further, there is large variation in bromine concentration. They suggested that, this may be due to UV-oxidation which may result in C–C bond cleavage and even loss of material [26]. Since, the PE film was kept very close to the lamp the rate of bromination increases but it also leads to surface damage. In our experiment, the bromine concentration increases continuously from 10 min to 1 h and only after that, it decreases slightly. Further, the analysis of different PE films brominated for 1 h shows that the variation in bromine concentration is less (9.2 ± 0.4 at.%). Thus, our experimental conditions lead to the PE–Br film containing consistent concentration of Br moieties at the surface, which is important when PE–Br surface is used as a substrate for further reactions.

If the loss of Br moieties is due to dehydrobromination, then it should result in the formation of carbon–carbon double bonds. The ATR-FTIR spectrum of PE–Br-1 h film (Fig. 1) shows a weak peak at 1625 cm^{-1} , which can be attributed to the C=C stretching band [22]. To confirm further, the LDPE films brominated for different period were analyzed by UV–Vis spectroscopy (Fig. 3). The UV–Vis spectra of virgin LDPE film show a small peak at 198 nm, which may be due to some additives present in the bulk of the film. The UV–Vis spectrum of 10 min brominated film shows an additional peak at 212 nm, which is assigned to a conjugated diene structure [22]. This indicates that, dehydrobromination occurs even in 10 min brominated LDPE film. The spectrum also shows that, as the time of bromination increases the absorption band becomes broader towards the higher wavelength side. This band contains a number of peaks separated by a λ_{max} of ~ 30 nm, which correspond to an increase in length of conjugation by one unit [22]. This shows that, as the time of bromination increases the length of conjugation also increases. We noted that, the UV spectra of PE–Br films brominated for longer times

Table 1
The Br3d/C1s ratio (as determined by XPS) and the γ_{C-Br}/ρ_{C-H} ratio (as determined by ATR-FTIR) OF LDPE films brominated for different time periods

Time of bromination (min)	Br3d/C1s	γ_{C-Br}/ρ_{C-H}
10	3.85	– ^a
20	5.83	– ^a
30	6.73	– ^a
60	8.21	0.0405
120	7.85	0.1138
180	7.68	0.1250
300	10.20	0.1486

^a The intensity of the C–Br stretching band is too small and thus the γ_{C-Br}/ρ_{C-H} ratio cannot be determined precisely.

¹ The ratio was obtained by dividing the area of the C–Br stretching band by C–H stretching band at 720 cm^{-1} . This peak was selected, because, the depth of analysis in ATR-IR, is dependent on the wave number of the IR radiation [29]. In order to obtain the ratio of C–Br(s) and C–H (s) from the same depth of the sample, we chose this C–H vibrational band. The area of the peak was obtained using the instrument software, by using the baseline of the peak as described in the instrument manual. Users manual IR data manager, PERKIN–ELMER, USA, 1990, p. 3:10–3:15.

² It was shown that, $\sim 95\%$ of the measured photoelectrons originate from the regions of $3\lambda \sin \theta$, where λ is the inelastic mean free path and θ the angle between the plane of the sample and the detector. The reported values were calculated using the above expression assuming that the value of λ is 14 \AA . This was measured for C1s photoelectrons in poly (p-xylylene).

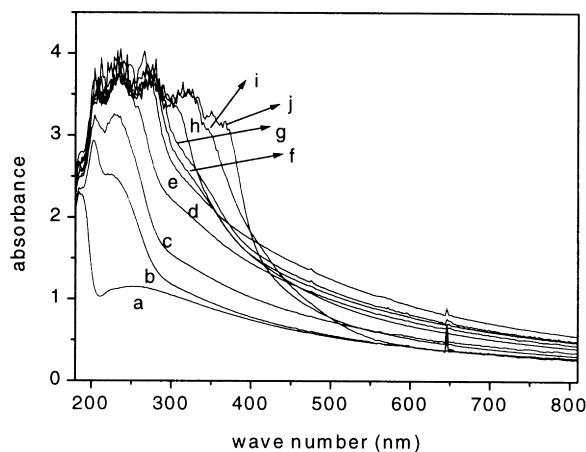
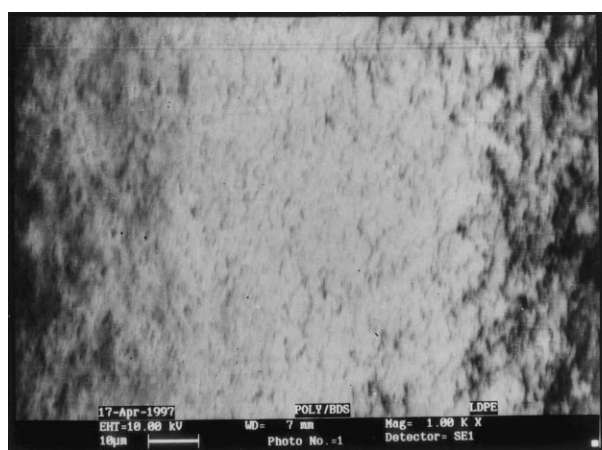


Fig. 3. UV–Vis spectra of LDPE film brominated for different time periods: (a) LDPE film; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 60 min; (g) 90 min; (h) 120 min; (i) 180 min; and (j) 620 min brominated LDPE film.

are similar to that of poly (vinyl chloride) (PVC) film dehydrochlorinated by chemical treatment [31], poly (vinylidenechloride) film dehydrochlorinated by laser irradiation [32] as well as that of conjugated polymers [33].

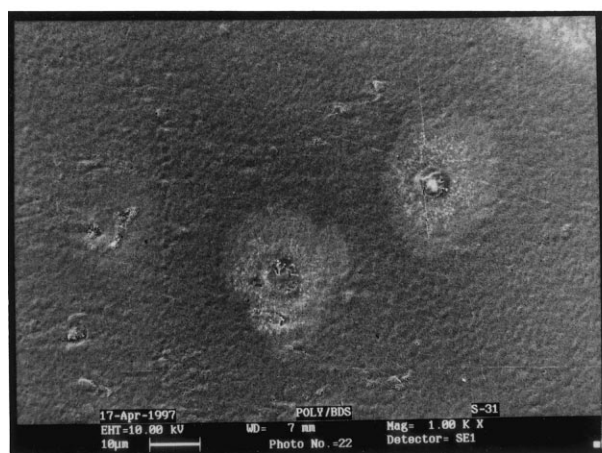
Fig. 4 shows the SEM pictures of the LDPE film brominated for different time periods. The SEM of 10-min brominated film surface (Fig. 5b) shows formation of bubbles on the surface, which is due to the evolution of the gaseous product [30] probably HBr. These bubbles burst at a longer reaction time and form blisters and holes, which is predominant in the 1 h brominated film (Fig. 5c). The SEM of 2 h reacted film (Fig. 5d) shows that the surface starts fragmenting. This explain the decreased surface density of Br moieties in the case of 2 h reacted film. These results suggest that, initially the predominant reaction is the bromination of the PE surface accompanied by simultaneous dehydrobromination and UV oxidation takes place at longer periods.



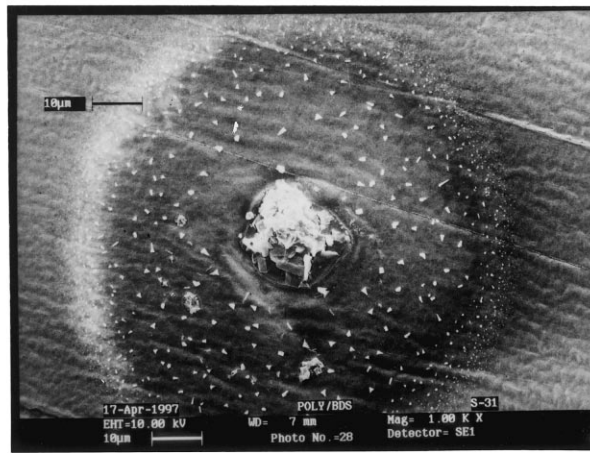
(a)



(b)



(c)



(d)

Fig. 4. SEM of: (a) PE; (b) 10 min PE–Br film; (c) 1 h PE–Br film; and (d) 2 h PE–Br film surface.

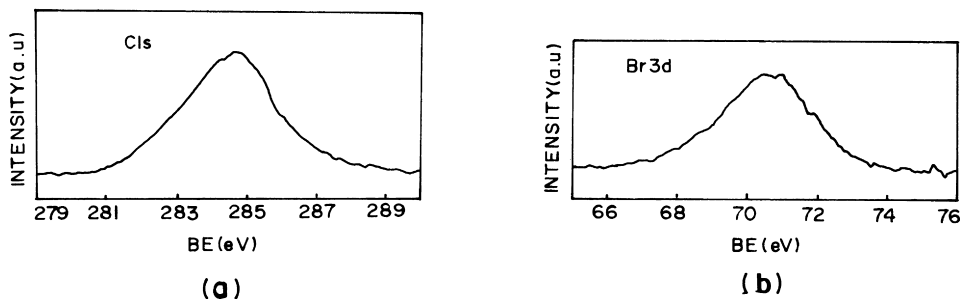
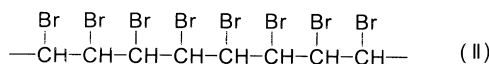
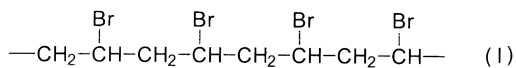


Fig. 5. X-ray photoelectron spectrum of 2 h brominated PP film: (a) C1s level and (b) Br3d level.

3.2. Mechanism of bromination of LDPE film surface

The formation of conjugated polyene structure via dehydrobromination of the brominated PE is possible only if the Br moieties are present on alternate (I) or adjacent carbon atoms (II). The structure (I) is similar to the structure of PVC and structure (II) is similar to chlorinated-PVC



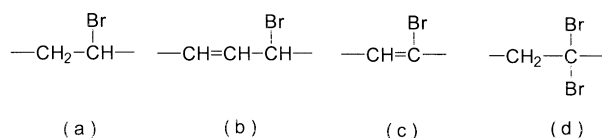
Photolytic halogenation of hydrocarbon normally leads to a mixture of many products [18, p. 620]. However, it was observed that, the gas phase bromination of hydrocarbon occurs with high regioselectivity [34]. It was reported that, bromination of alkyl Br gives 84–94% substitution at the carbon atom adjacent to the carbon atom containing bromine [34]. This unusual regioselectivity is explained by the mechanism known as *neighboring group mechanism* [18, p. 612] in which the abstraction of a hydrogen by a bromine radical is assisted by a neighboring bromine atom [35]. The results of the bromination of LDPE film suggest that, probably this heterogeneous reaction also occurs, to some extent, via a similar regio selective mechanism (Scheme 2, the reaction pathway of free radical gas phase bromination of alkane via neighboring group mechanism).

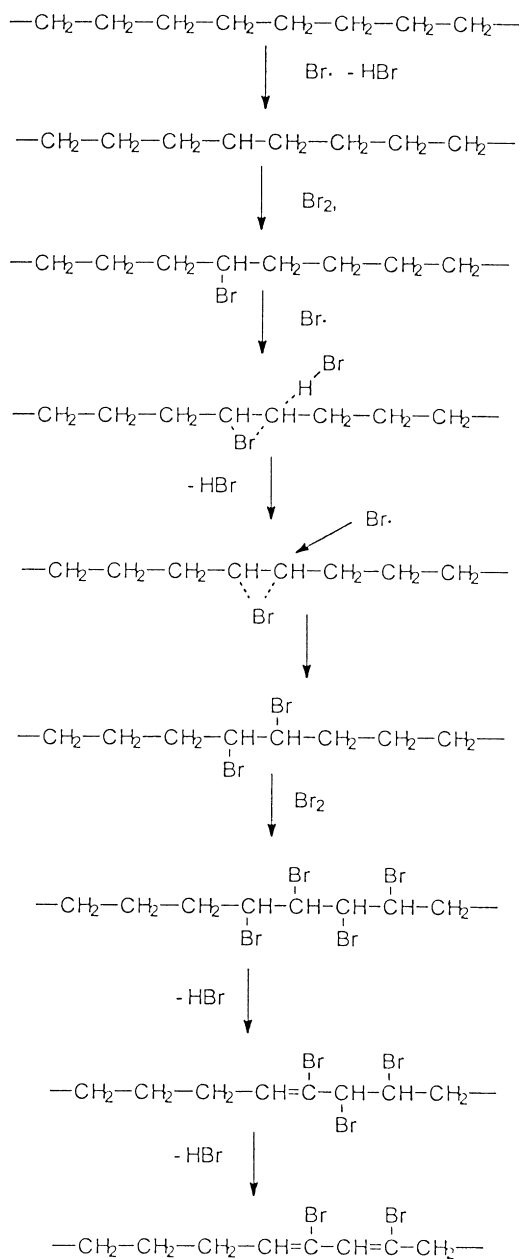
However, if the bromination proceeds by this mechanism then the resulting surface will contain Br moieties at the adjacent carbon atoms (II) and the, dehydrobromination of this surface will lead to the formation of vinyl Br moieties along with secondary bromides and possibly dibromide moieties (Scheme 2). The vinyl Br moieties are unreactive towards further nucleophilic substitution reactions [18, p. 300–1]. It was reported that, the surface secondary Br moieties are also not reactive towards alkyl amines [36]. But, substitution reactions carried out on the PE–Br surface shows that, ~40% of the Br moieties on the 1 h brominated film can be replaced by a number of alkyl amines [37]. This shows that, some of the surface Br moieties are reactive towards nucleophilic substitution reactions, and thus are present in a different chemical environment.

To account for the reactivity of Br moieties towards nucleophilic substitution reactions and the formation of conjugated polyene structure via dehydrobromination, we proposed an alternative mechanism for the bromination of PE surface (Scheme 3, the alternative mechanism proposed for the gas phase bromination of PE film surface). In this mechanism, the initial bromination of PE molecules leads to the formation of secondary Br moieties, which upon dehydrobromination results in the formation of isolated double bonds. The bromine radicals then preferentially attack the carbon atom adjacent to these isolated double bonds, i.e. an allylic carbon atom [18, p. 615] resulting in the formation of allylic Br moieties. These Br moieties upon further dehydrobromination lead to the formation of conjugated diene structure and this sequence continue leading to the formation of highly conjugated polyene structures and allyl Br moieties (Scheme 3). These allyl Br moieties being more reactive towards further substitution reactions compared to secondary Br moieties [18, p. 300–1] undergo substitution reactions with alkyl amines. But it is difficult to determine the exact mechanism, by which the bromination is occurring. Possibly, the bromination may occur via both the mechanisms to a different extent at different bromination times.

Another important reaction during bromination is addition of bromine to C=C bonds resulting in the formation of –CHBr–CHBr– moieties. The presence of C=C bonds in the product film shows that, addition of bromine to C=C bonds as well as elimination of Br via dehydrobromination occurs simultaneously. We suggest that, all the three reactions, substitution, elimination and addition may occur simultaneously resulting in the formation of Br moieties and C=C bonds at any time.

Thus, the Br moieties on the PE surface introduced during bromination may be present in different molecular environments such as secondary Br (a), allyl Br (b) vinyl Br (c) and dibromide (d). However, it is difficult to determine the exact composition of different Br species



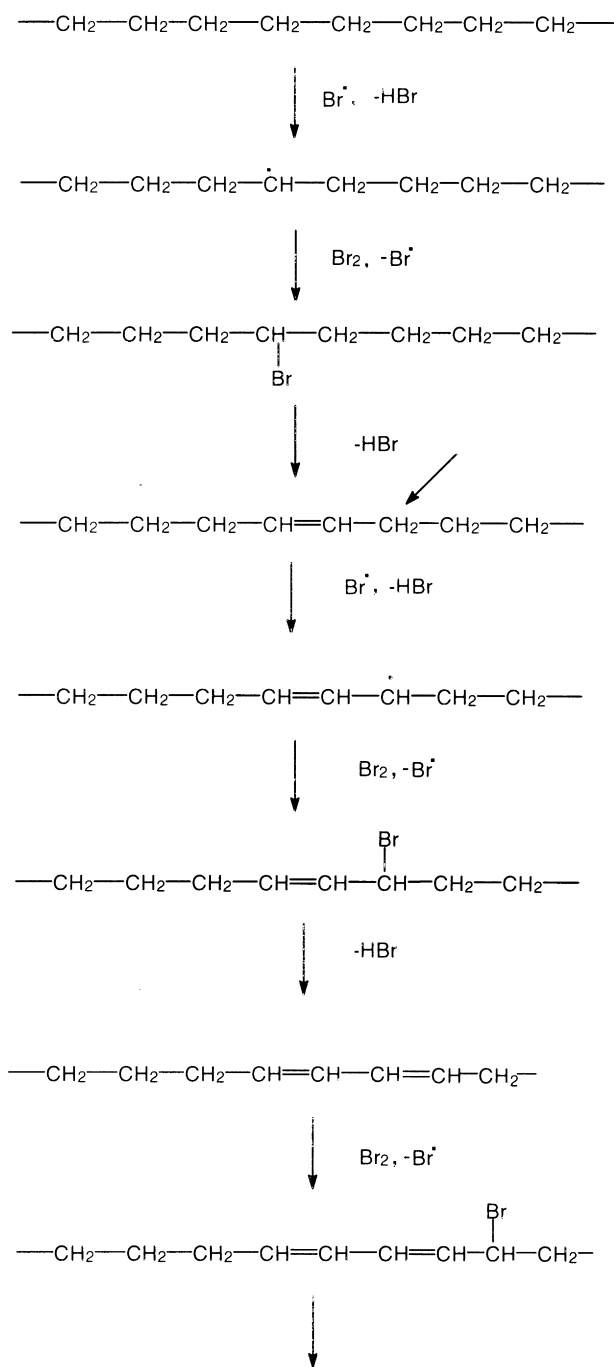


Scheme 2.

We studied the surface bromination of PP and PS to examine the effect of polymer structure on the extent of bromination and dehydrobromination.

3.3. Bromination of PP films

The XPS and ATR-FTIR analysis of the brominated PP film (PP-Br) confirmed the formation of Br moieties on the PP film surface upon bromination. The XPS of the 2 h brominated PP film (PP-Br-2 h) (Fig. 5) shows the presence of the Br3d peak at 70.2 eV. The ATR-FTIR of the same film shows the C-Br stretching bands at 571, 640 and at 661 cm^{-1} [22], further confirming the presence of Br moieties on the PP surface. It also showed a small peak



Continues.....

Scheme 3.

at $\sim 1600 \text{ cm}^{-1}$ which can be due to C=C stretching vibration (Fig. 6) [22]. The UV-Vis spectra of PP films brominated for different period (Fig. 7) show that, PP-Br films also contain long sequences of conjugated double bonds. This shows that, PP also undergoes dehydrobromination upon bromination. Further, the extent of double bond formation and the length of conjugated polyene structure increase with increasing time of bromination.

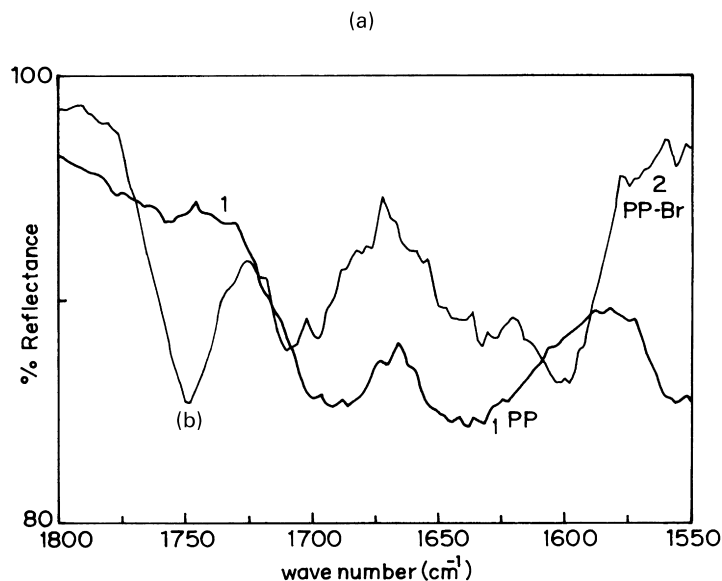


Fig. 6. ATR-FTIR spectra of: (a) PP film and (b) 2 h brominated PP film.

This shows that surface bromination of PP also occurs regioselectively.

The Br3d/C1s ratio of a 2 h brominated PP film is 0.0832. This shows that, approximately 25% of the PP repeat units become brominated, which is a higher value compared to the ~18% bromination of PE repeat units after 2 h of bromination. This can be explained by the difference in the structure of PE and PP. PE contains only secondary carbon atoms (with few branch points) [38]. PP contains primary, secondary and tertiary carbon atoms in the repeat unit. The rate of the free radical reaction at a tertiary carbon atom is greater than the rate at a secondary carbon atom due to the stabilization of free radical by hyper conjugation [18, p. 164]. This will lead to an increased rate of bromination. Further, the comparison of UV-Vis spectra of brominated PP and PE

show that, for the same time of bromination, the extent and the length of conjugation in PP-Br is higher compared to that of PE-Br film. This is because, the C-Br bond energy decreases in the order of $1^\circ > 2^\circ > 3^\circ$. This decrease in bond energy increases the rate of dehydrobromination in PP-Br. Thus, the structural feature of PP enhances both the rates of bromination as well as dehydrobromination compared PE.

3.4. Bromination of polystyrene films

We also studied the bromination of PS films, in order to compare the effect of the structure of the polymer on the mechanism of the bromination. Since 50% of the PS backbone contains benzyl carbon atoms and 50% contain secondary carbon atoms, an increased rate of the bromination compared to that of PE is expected [18, p. 164]. We have used XPS and UV-Vis spectroscopy for the analysis of brominated PS films. ATR-FTIR was not used in this case because PS itself has a number of strong bands in the C-Br stretching band region and hence the identification of C-Br stretching band was difficult.

Surprisingly, XPS spectra of brominated PS films do not show any Br signals (Br3d, Br3p and Br3s) even for films brominated for a long period of 10 h.³ However, the UV-Vis spectra of these films (Fig. 8) show a very broad peak in the wave length region of above 200 nm, indicating the formation of a highly conjugated structure. The formation of highly conjugated double bond sequences in combination with XPS results indicate regioselective bromination of PS followed by immediate dehydrobromination. The formation of carbon-carbon double bond via dehydrobromination is

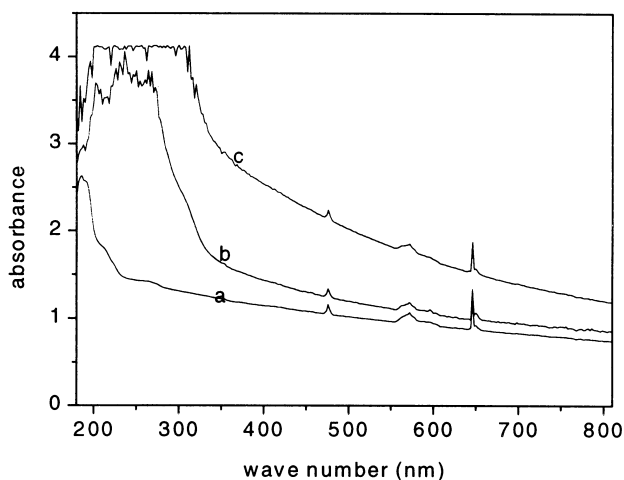


Fig. 7. UV-Vis spectra of PP films brominated for different time periods: (a) virgin PP film; (b) 30 min; and (c) 120 min brominated PP film.

³ We repeated this experiment. In some instances we got a small Br3d signal.

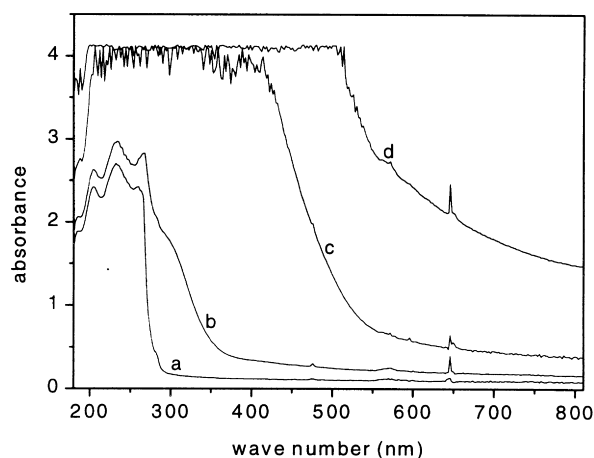


Fig. 8. UV-Vis spectra of PS films brominated for different time periods: (a) virgin PS film; (b) 10 min; (c) 600 min; (d) 1260 min brominated PS film.

more facilitated in PS compared to PE and PP due to the fact that these carbon-carbon double bonds are in conjugation with the benzene ring. This will reduce the energy of activation of dehydrobromination, and thus enhance the formation of carbon-carbon double bonds. These results also indicate that, in the case of PS, the rate of dehydrobromination is greater than the rate of bromination. The formation of the highly conjugated structures in the PS-[Br] film, upon longer time of bromination, may render the PS-[Br] film as a conductive substrate [39]. Further studies in this area are in progress.

3.5. Surface chlorination of polyolefins

In the gas phase halogenation of alkane, bromination occur regioselectively whereas chlorination occurs randomly [18, p. 620]. The results discussed earlier shows that, gas phase bromination of PE surface occurs, to some extent, regioselectively. In order to see, whether the gas

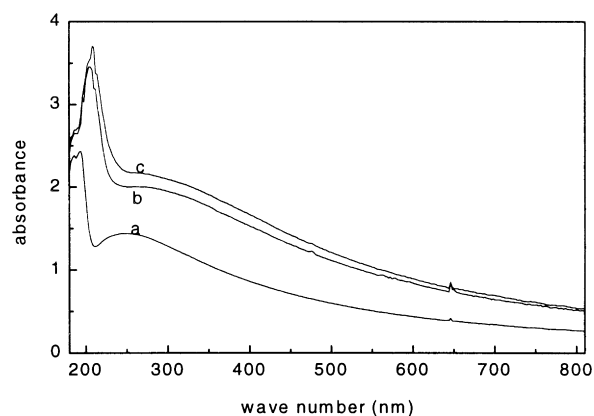


Fig. 9. UV-Vis spectra of LDPE films chlorinated for different time periods in the presence of the HPMV lamp: (a) LDPE film; (b) 30 min; and (c) 120 min chlorinated LDPE film.

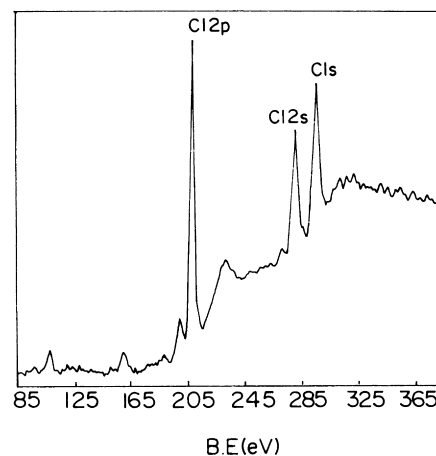


Fig. 10. Wide scan XPS spectrum of LDPE film chlorinated in ambient light for 10 min.

phase chlorination of polyolefins occurs relatively randomly as in the case of gas phase chlorination of alkane, we studied the gas phase free radical photochemical chlorination of LDPE, PP and PS films.

The gas phase chlorination of the LDPE surface has been studied under ambient light [13,14] as well as in the presence of UV radiation [13]. The resultant surface was reported to consist of C-Cl and $-CCl_2-$ moieties [13,14]. However, the formation of carbon-carbon double bonds, i.e. simultaneous dehydrochlorination, during chlorination has not been reported in these studies. We carried out the chlorination of the LDPE film (PE-Cl) for different period of time in the presence of the HPMV lamp to investigate whether dehydrochlorination occurs simultaneously along with chlorination. The ATR-FTIR of the 10 min chlorinated LDPE film showed the C-Cl stretching band at 612 and 666 cm^{-1} and thus confirming the formation of chloride moieties [22]. The UV-Vis spectra of LDPE films chlorinated for different periods are shown in Fig. 9. The PE film chlorinated for 10 min shows one peak at 212 nm corresponding to a diene structure [22] similar to the UV-Vis spectrum of the 10 min brominated LDPE film. However, chlorination for a longer time period (3 h) does not broaden this peak as in the case of bromination, instead, the intensity of the 212 nm peak increases marginally with increase in chlorination time. It indicates the formation of two or three chloride moieties on alternate or adjacent carbon atoms, respectively, which upon dehydrochlorination leads to the formation of only diene structures. These results show that, chlorination in the presence of UV light occurs in a relatively random way.

We also carried out chlorination in ambient light under similar conditions. The ATR-FTIR spectrum of this film showed the presence of C-Cl stretching band at 616 and 666 cm^{-1} [22]. The XPS of the 10 min chlorinated LDPE film shows the presence of Cl 2s and Cl 2p levels at 270.6 and 200.6 eV [13], respectively (Fig. 10). The Cl 2p/C 1s

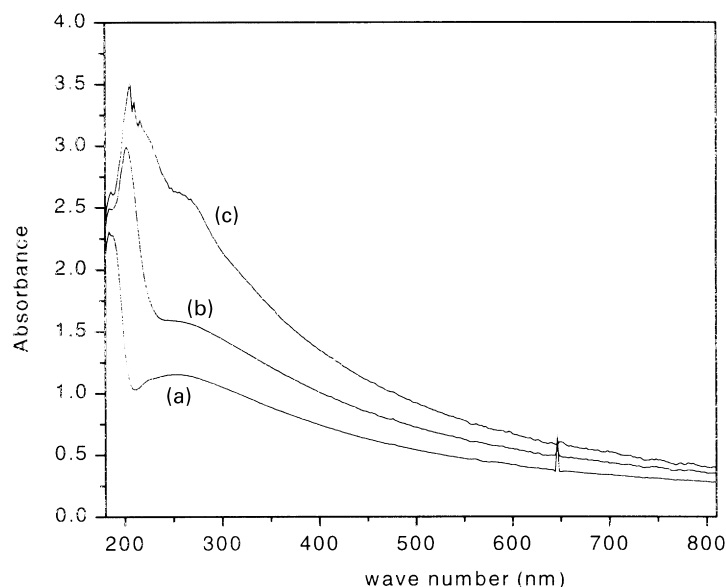


Fig. 11. UV-Vis spectra of: (a) LDPE film; (b) LDPE film chlorinated in ambient light for 10 min; (c) film (b) further irradiated with the HPMV lamp for 1 h.

ratio is $\sim 25\%$. The UV-Vis spectrum of this film (Fig. 11) shows only one additional peak at 212 nm corresponding to a diene structure [22]. It indicates that, chlorination is also accompanied by simultaneous dehydrochlorination even in the absence of UV light. Further, this result also suggests that, chlorination is relatively a random process and the dehydrochlorination of the resultant chlorinated PE surface leads to the formation of a diene structure only. But, it may be possible that, only few Cl moieties have undergone dehydrochlorination in ambient light during short period of 10 min chlorination and other Cl moieties remained intact. In order to effect further dehydrochlorination, to indirectly determine the sequence of Cl moieties along the PE chain, this film was further irradiated with the UV radiation in nitrogen atmosphere [30] for 1 h. The UV-Vis spectrum

of the resulting film (Fig. 11) shows increase in the intensity of the peak at 212 nm without further broadening. This again indicates that, chlorination of PE surface occurs randomly.

Thus, chlorination of PE surface in presence or absence of UV light not only leads to the formation of secondary chlorides and dichloride moieties [13] but also leads to the formation of allyl chloride and vinyl chloride moieties. XPS cannot differentiate between secondary, vinyl and allyl chlorides. In order to prove this, we reacted chlorinated PE film and PVC film, which contain only secondary chloride moieties, with methylamine. XPS analysis of the resulting surface shows that, only PE-Cl surface undergoes this substitution reaction to some extent while PVC surface does not undergo this reaction. This result shows that, some of the Cl moieties present on the PE-Cl surface are more reactive than secondary Cl moieties and thus supports our suggestion.

To investigate the effect of polymer structures on the mechanism of chlorination, we studied the chlorination of PP and PS films. The PP film was chlorinated in the presence of the HPMV lamp for 10 min and 3 h. The ATR-FTIR spectrum of 10 min chlorinated PP film showed the presence of the C-Cl stretching band at 574 and 620 cm^{-1} confirming the formation of C-Cl moieties. Fig. 12 shows the UV-Vis spectra of the virgin PP film, PP film chlorinated for 10 min and 3 h. The virgin PP film shows a peak at 210 nm, which is probably due to the residual additives present in the bulk of the film. The spectrum of 10 min chlorinated PP film also shows only one peak at 210 nm, but the intensity of this peak is greater than that of virgin PP film. The spectra of 3 h chlorinated PP film show a marginal increase in the intensity of this peak. It also shows a less intense band in the range of 226–239 nm. These

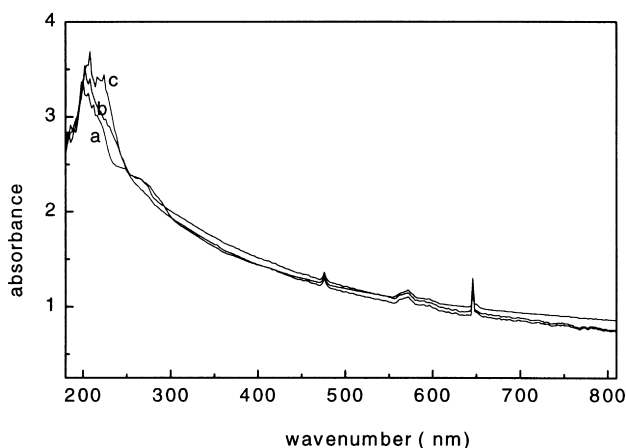


Fig. 12. UV-Vis spectra of PP films chlorinated for different time periods in the presence of the HPMV lamp: (a) PP film; (b) 30 min; and (c) 120 min chlorinated PP film.

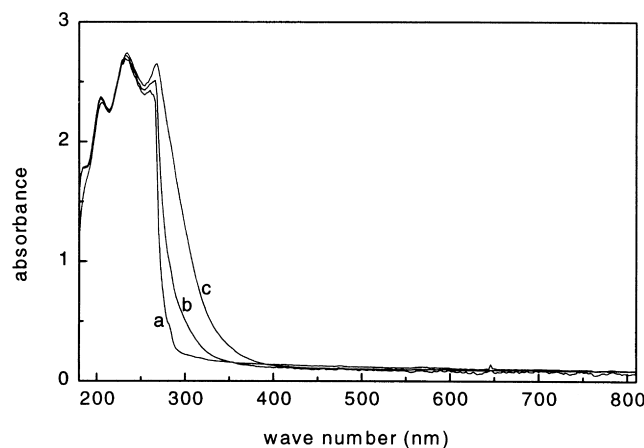


Fig. 13. UV-Vis spectra of PS films chlorinated for different time periods in the presence of the HPMV lamp: (a) PS film; (b) 30 min; and (c) 120 min chlorinated PS film.

results indicate that, chlorination of PP occurs randomly, resulting in the formation of two or three C-Cl moieties on alternative or adjacent carbon atoms, respectively.

Analysis of the chlorinated PS film shows that, chlorination introduces C-Cl moieties on the PS surface. The XPS of the 30 min chlorinated PS film showed the presence of Cl 2s and Cl 2p peaks. The UV-Vis spectrum of the virgin PS film along with PS films chlorinated for 10 min and 3 h is shown in Fig. 13. The UV-Vis spectra of virgin PS show four peaks at 214, 242, 268 and 274 nm originating from $\pi \rightarrow \pi^*$ transition [22]. The UV-Vis spectra of the 10 min and 3 h chlorinated PS films show a peak at 286 nm with marginal increase in the intensity. This indicates that, in case of PS also, chlorination proceeds in a relatively random way.

Although surface chlorination [13,14] and bromination [14,26,27] of polyolefin surfaces was investigated extensively, the occurrence of simultaneous dehydrohalogenation during halogenation has not been reported. The importance of this side reaction is that, it leads to the formation of reactive allyl halide moieties of the polyolefin surface and thus makes halogenated polyolefin surface useful for surface functionalization of polyolefins. Further, it also shows that, bromination of polyolefin surface occurs regioselectively, which on dehydrobromination results in the formation of highly conjugated polyene sequences whereas chlorination of polyolefin surface occurs relatively randomly which on dehydrochlorination results in the formation of only diene sequences.

4. Conclusions

Gas phase free radical photochemical bromination of polyolefin surfaces in the presence of the HPMV lamp is accompanied by simultaneous dehydrobromination. The results also indicate that, bromination occurs regioselectively, which on dehydrobromination leads to the formation

of long polyenes during bromination. Importantly, bromination of the PE surface leads to the formation of allyl Br moieties, which are reactive towards further substitution reactions and thus make the PE-Br a useful substrate for the functionalization of the PE surface. Gas phase free radical photochemical chlorination of polyolefins films is also accompanied by simultaneous dehydrochlorination resulting in the formation of only diene sequences, which shows that, chlorination proceeds in a relatively random way.

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