Surface Oxidation of Polyethylene, Polystyrene, and PEEK: The Synthon Approach

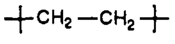
A. G. Shard and J. P. S. Badyal*

Department of Chemistry, Science Laboratories, University of Durham, Durham DH1 3LE, U.K.

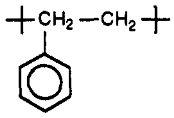
Received May 24, 1991
Revised Manuscript Received September 11, 1991

Introduction

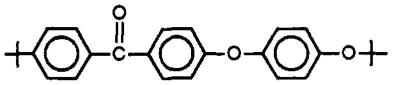
Cold plasmas are of great chemical interest, since they provide a medium in which thermodynamically unfavorable processes can occur. Surface modification of a polymer by a glow discharge comprises degradation and reaction of the substrate with ions, free radicals, excited species, electrons, and electromagnetic irradiation.[1] This has important technological implications for increasing the surface energy of polymers and improving their adhesive properties. A variety of surface species are known to be generated during UV and plasma oxidation of polymers.[2-5] However, the precise mechanistic details are a matter of much debate. In this paper we model the role of vacuum-ultraviolet radiation during plasma oxidation of polyethylene, polystyrene, and poly(ether ether ketone) (PEEK). Also, the relationship between chemical structure of the starting polymer surface and its reactivity toward an oxidizing environment is examined.



polyethylene



polystyrene



PEEK

Experimental Section

A 13.56-MHz radio frequency generator was inductively coupled to a cylindrical glass reactor via an externally wound copper coil; this was used for the plasma treatments. The glow discharge was initiated at a pressure of 0.3 Torr of O_2, at a constant flow rate of 1.1 cm^3 min^{-1}, and run at a power of 10 W for 3 min. This was found to be sufficient, since longer periods resulted in no further changes at the polymer surface (as determined by XPS).

An additional glass chamber was attached to the aforementioned plasma reactor for the photooxidation experiments (Figure 1); the two vessels were connected via a lithium fluoride window. Both sides were evacuated by two-stage rotary pumps to a pressure better than 2×10^{-2} Torr. A nitrogen glow discharge (50 W, 1.1 cm^3 min^{-1}) was used to generate vacuum-UV radiation. The lithium fluoride window was transparent to the strongest lines at 174 and 149 nm. A strip of polymer was irradiated under 25 Torr of O_2 gas. One-hour exposures were found to be sufficient for yielding limiting XPS features.

Research grade quality oxygen (BOC) was used. Low-density polyethylene, polystyrene, and PEEK films were carefully washed with isopropyl alcohol and subsequently dried in air.

X-ray photoelectron spectra were acquired on a Kratos ES300 surface analysis instrument. Mg Kα radiation (1253.6 eV) was used as the excitation source with electron detection in the fixed retarding ratio (FRR) analyzer mode. XPS measurements were taken with an electron takeoff angle of 30° from the surface normal. Data accumulation and component peak analysis were performed on an IBM PC computer. All binding energies are referenced to the hydrocarbon component ($\underline{C}_xH_y$) at 285.0 eV.[6] For these experiments, the instrumentally determined sensitivity factors are such that for unit stoichiometry the C(1s):O(1s) intensity ratio is ~0.55. Detailed chemical information about the modified polymer surfaces was obtained by fitting the C(1s) XPS spectra to a range of carbon functionalities (with the exception of π–π^*, all components were assigned a Gaussian peak shape with fixed fwhm; Figure 2): carbon adjacent to a carboxylate group $\underline{C}CO_2$ ~ 285.7 eV); carbon singly bonded to one oxygen atom $\underline{C}$—O ~ 286.6 eV); carbon singly bonded to two oxygen atoms or carbon doubly bonded to one oxygen atom O—$\underline{C}$—O or $\underline{C}$=O ~ 287.9 eV); carboxylate groups O—$\underline{C}$=O ~ 289.0 eV); and carbonate carbons O—$\underline{C}$O—O ~ 290.4 eV).[7] Loss of aromaticity was monitored by the decrease in intensity of the $\pi \rightarrow \pi^*$ shake-up satellite. All of the values reported correspond to limiting O(1s):C(1s) ratios.

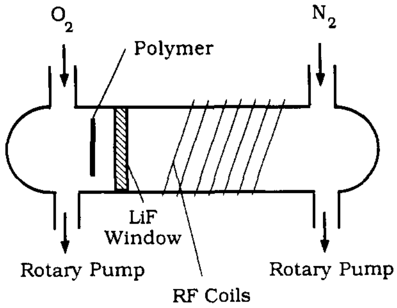


Figure 1. Schematic of apparatus used for vacuum-ultraviolet irradiation.

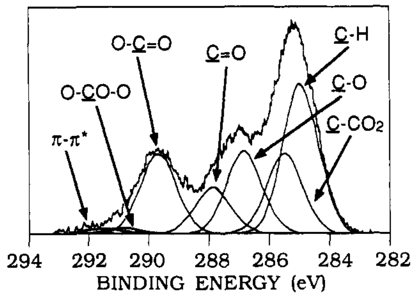


Figure 2. Peak fit of C(1s) XPS spectra for O_2/UV modification of PEEK.

Results

Only one XPS peak is seen for untreated polyethylene at 285.0 eV; this can be associated with the $\underline{C}H_2$ groups. First, in contrast to polystyrene and PEEK, polyethylene undergoes relatively little oxidation (Table I) (N.B. $\underline{C}H_2$ represents all carbon atoms not directly bound to oxygen and $\underline{C}$=O includes O—$\underline{C}$—O). Photooxidation generates a more highly oxidized surface than that found following plasma modification. However, both treatments exhibit a high selectivity toward $\underline{C}$—O functionalities.

In addition to a hydrocarbon component at 285.0 eV, the XPS spectrum of clean polystyrene displays a distinctive satellite structure at ~291.6 eV; this arises from low-energy $\pi \rightarrow \pi^*$ shake-up transitions which accompany core ionization.[8] The results described in Table II again show that both plasma-induced and photoinduced oxidation yield surfaces of similar character, with the latter treatment being slightly more severe. Attenuation of the π–π^* feature is a measure of the extent of attack on the aromatic centers. The dominant oxygenated species present are $\underline{C}$—O, $\underline{C}$=O, and O—$\underline{C}$=O.

The C(1s) spectrum of clean PEEK comprises $\underline{C}$—H, $\underline{C}$—O, $\underline{C}$=O, O—$\underline{C}$=O, and π–π^* components; the relative amounts are consistent with the theoretical values expected from its structure (Table III). Surprisingly, following

* To whom correspondence should be addressed.

0024-9297/92/2225-2053$03.00/0

Table I
Summary of Oxidation Treatments with Polyethylene

treatment	$\underline{C}$—H	$\underline{C}$—O—	$\underline{C}$=O	O—$\underline{C}$=O	O—$\underline{C}$O—O	O:C
clean	100	0	0	0	0	0.01
O_2 plasma	92	5	1	2	0	0.10
O_2 UV	81	8	6	5	0	0.17

Table II
Summary of Oxidation Treatments with Polystyrene

treatment	$\underline{C}$—H	$\underline{C}$—O—	$\underline{C}$=O	O—$\underline{C}$=O	O—$\underline{C}$—O	π–π^*	O:C
clean	94	0	0	0	0	6	0.03
O_2 plasma	62	13	10	9	3	3	0.30
O_2 UV	65	11	9	12	2	1	0.38

Table III
Summary of Oxidation Treatments with PEEK

treatment	$\underline{C}$—H	$\underline{C}$—O—	$\underline{C}$=O	O—$\underline{C}$=O	O—$\underline{C}$O—O	π–π^*	O:C
clean	73	19	4	0	0	4	0.15
O_2 plasma	61	17	9	10	1	2	0.37
O_2 UV	51	18	10	18	2	1	0.52

oxidation, a slight loss in $\underline{C}$—O from the polymer surface is found, with a considerable rise in $\underline{C}$=O and O—$\underline{C}$=O groups. A significant loss of π–π^* intensity is also seen. Of all of these experiments, photooxidized PEEK has the greatest O:C ratio.

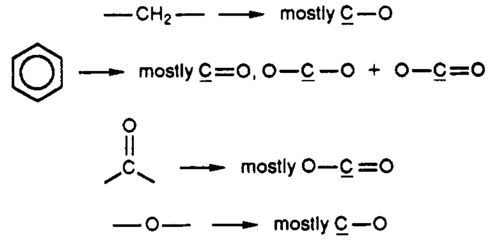
Discussion

Polyethylene is not as susceptible to oxidation as the other polymers; this can be attributed to the absence of any aromatic centers. $\underline{C}$—O is the dominant functionality for this substrate; a slightly greater proportion of carboxyl groups has been reported at longer wavelengths (254 nm).[9]

Photooxidation of polystyrene has been extensively studied.[10] Polystyrene comprises an alkyl chain, to which are attached phenyl rings; these absorb strongly in the UV region. Free-radical sites at the α-carbon atoms along the polymeric backbone are stabilized by the adjacent phenyl rings;[11,12] such centers will be more stable in polystyrene than in polyethylene, and therefore this explains why more $\underline{C}$—O linkages are found in the oxidized surface of the former. Attenuation of the π–π^* peak is consistent with the majority of $\underline{C}$=O and O—$\underline{C}$=O groups originating from photooxidation of the aromatic rings. Much more π–π^* character remains in the plasma-treated polymer due to concurrent etching of the surface, which exposes fresh polystyrene, whereas during just UV irradiation surface species can only escape by volatilization.

Vacuum-UV oxidized PEEK has a very similar surface to that found following photooxidation at longer wavelengths (>290 nm).[13] The benzophenone unit in PEEK is known to be a far stronger chromophore than the ether linkages[14] and would therefore be expected to undergo preferential oxidation. Indeed, not much variation is seen in the $\underline{C}$—O component, and therefore very little ether cleavage must be occurring. However, both $\underline{C}$=O and O—$\underline{C}$=O species increase significantly. Particularly following UV oxidation, there are a large number of O—$\underline{C}$=O moieties present; these must partly originate from photooxidation of the phenyl rings (as seen with polystyrene), but in addition there will be a strong contribution due to the PEEK carbonyl centers undergoing further oxidation. In fact, photooxidized PEEK is the most highly oxidized substrate produced in these experiments. Once more, the greater presence of the π–π^* feature for plasma-oxidized PEEK can be ascribed to the ablative nature of the oxygen glow discharge.

A definite pattern emerges from these experiments, where all parameters have been kept constant to elucidate the chemical reactivity of the different polymers. The following deductions can be made regarding the origins of various oxidized functionalities:



Poly(p-xylylene), –[–CH_2PhCH_2–]–, has the same constituents as polystyrene, i.e., phenyl rings and alkyl groups. Plasma oxidation of this polymer under similar experimental conditions to ours[15] has been reported to result in $\underline{C}$—O > $\underline{C}$=O > O—$\underline{C}$=O > O—$\underline{C}$O—O; this is precisely what is found for polystyrene.

Therefore, if a desired functionality is sought at a polymer surface, it can be generated by careful choice of the substrate prior to oxidation. Alternatively, the reactant gas can be selected for a given polymer.[16] In many ways this is similar to the retrosynthetic approach in organic chemistry,[17] where the target molecule is broken down by a series of disconnections into possible starting materials.

Conclusions

Surface modification of a polymer by an oxygen glow discharge can be modeled by vacuum-UV oxidation. However, during plasma treatment, competing etching/ablation processes also occur, which continuously expose unreacted polymer; this does not happen during UV irradiation, and therefore a greater depth of oxidation is found with the latter. UV/O_2-treated PEEK gives the most highly oxidized surface. A correlation can be made between the oxidized groups generated and the structure of the starting polymer. $\underline{C}$—O linkages originate mostly from the aliphatic component of a polymer, whereas phenyl rings yield predominantly $\underline{C}$=O and O—$\underline{C}$=O species and carbonyls produce mainly O—$\underline{C}$=O groups.

Acknowledgment. A.G.S. thanks Wilkinson Sword for a research studentship.

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