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Radiation Chemical Reactions of Poly-*p*-Chlorphenylmethacrylate by ESCA

M. Wäsche[1], T. Gross[1], and I. von Lampe[2]

[1] Akademie der Wissenschaften der DDR, Zentralinstitut für physikalische Chemie,
DDR-1199 Berlin, German Democratic Republic

[2] Akademie der Wissenschaften der DDR, Zentralinstitut für organische Chemie,
DDR-1199 Berlin, German Democratic Republic

SUMMARY

ESCA is used to characterize ion beam irradiated P(p-ClPhMA)-samples. The results show a chlorine abstraction. The experimental findings are in accordance with a recently proposed model for a crosslinking mechanism of halogenated aromatic polymers.

INTRODUCTION

The ESCA technique is a valuable tool in the compositional and structural analysis of polymeric thin-film materials (CLARK, 1977). The special advantage of ESCA is that, in addition to detecting elements, it provides reliable information on their binding states by means of chemical shifts, line-splitting and shake-up satellites.

We report here ESCA data on poly-p-chlorphenylmethacrylate. In polyphenylmethacrylate the degradation reaction is predominant (RAGHUNATH, 1983), while in poly-p-chlorphenylmethacrylate crosslinking is observed after electron or ion beam irradiation. It is assumed that the crosslinking reaction takes place through abstraction of chlorine under exposure with ionizing radiation. In this paper we wish to report ESCA measurements supporting chlorine abstraction under argon ion beam exposure, which may give rise to crosslinking of polymer chains.

EXPERIMENTAL

Methacrylate monomers were synthesized by reaction of methacryloylchlorid and p-chlorphenol. Poly-p-chlorphenylmethacrylate was prepared by dibenzoylperoxid initiated radical polymerization of monomer in benzene at 80 °C for 20 h. The polymers were isolated by pouring the reaction solution into methanol and purified by reprecipitation. Polymers were dissolved in monochlorbenzene and spincoated on a silicon substrate and baked at 160 °C for 1 h.

The argon beam exposure were carried out with an ion beam gun at 1 keV energy, and ion doses between 10^{13} cm^{-2} and 10^{16} cm^{-2} were used for the experiments.

The ESCA investigations were made with an ÆI-KRATOS ES 200 B electron spectrometer. The analyzer was used in the constant $\Delta E/E$ mode. The photoelectrons were excited with AlK_{α} -radiation. The pressure in the measuring chamber was in the 10^{-7} Pa range.

RESULTS AND DISCUSSION

An ESCA spectrum of P(p-ClPhMA) is shown in Figure 1. Using the C1s, O1s and Cl2p core level intensities, we investigated the influence of ion beam exposure on the polymer samples.

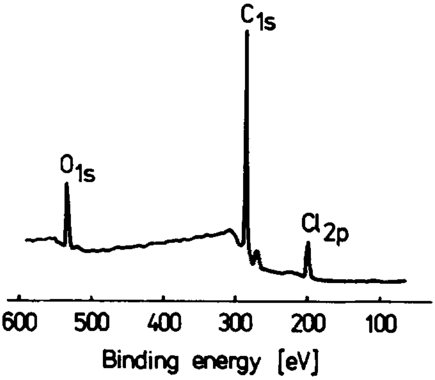


Fig. 1
Wide-scan spectrum of P(p-ClPhMA)

We determined the C1s/Cl2p intensity ratios using the C1s and Cl2p core line integrated intensities. The precision of the relative core line intensities is about 10%. Theoretical atomic photoionization cross sections relative to carbon were used in calculation the atomic ratios (SCOFIELD, 1976). The energy dependences of the escape depth and of the spectrometer transmission were taken into account (RICHTER, 1981). The results are summarized in Table 1.

We used very low ion energies (E = 1 keV), because ESCA is a surface-sensitive method. The overall layer thickness is given by the escape depth of the photoelectrons. The range is from a few monolayers to 100 Å.

TABLE 1

substance	ion dose cm^{-2}	atomic ratios						chlorine removal rate %
		C : Cl		C : O		O : Cl		
		cal.	exp.	cal.	exp.	cal.	exp.	
P(p-ClPhMA)	-	10:1	9,9:1	5:1	5,2:1	2:1	2,1:1	
	$1x10^{13}$		12,8:1		6,1:1		2,3:1	22,6
	$3x10^{13}$		16,8:1		7,2:1		2,6:1	41,1
	$3x10^{16}$		19,4:1		44 :1		0,5:1	48,9

The chlorine removal rate decreases with increasing ion energy, because the energy deposition takes place deeper inside the polymer sample. Argon ions of 1 keV energy deposited their energy only on the top surface. We also used argon ions with energies of 40 keV and larger. In this case we could only detect a very low chlorine removal rate.

The results obtained by ESCA show a chlorine abstraction and support the proposed crosslinking reaction mechanism of halogenated aromatic polymers (IMAMURA, 1984). As can be seen from Table 1, an intense chlorine abstraction is found already for small argon ion doses. For high doses this effect saturates. We compared the chlorine content of a P(p-ClPhMA) sample immediately after irradiation (Ar^+; 1 x 10^{13} cm^{-2}) and after storage for one hour under vacuum conditions. The result was a further loss of chlorine. P(p-ClPhMA) shows a little postirradiation polymerization effect.

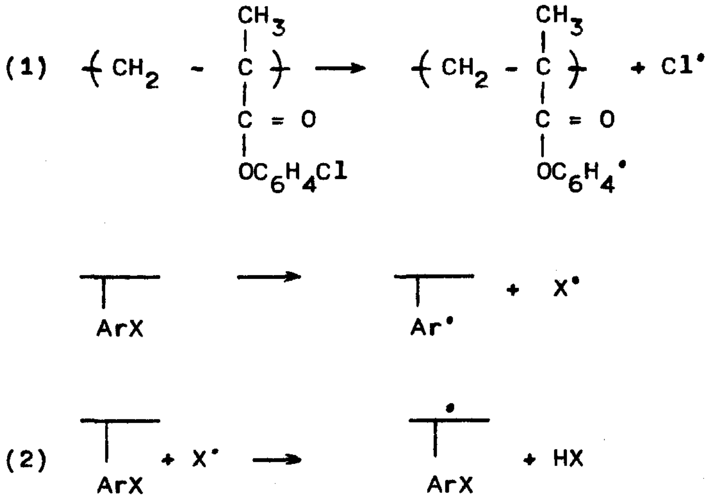
Analysing the C : O, Cl : O atomic ratios (Table 1) and the half width of the O1s core line of the irradiated samples, it can be assumed that in P(p-ClPhMA) simultaneous degradation takes place, with crosslinking being the dominant reaction. Degradation reactions increase with irradiation dose.

Crosslinking reactions in chlorinated aromatic polymers initiated by ionizing radiation start from the dissociation of carbon-chlorine bonds as shown in Figure 2. The second reaction step is the crosslinking between two benzylic radicals. The significant participation of radical species in the crosslinking reaction has been demonstrated by ESR spectroscopy of irradiated halogenated aromatic polymers (IMAMURA, 1984).

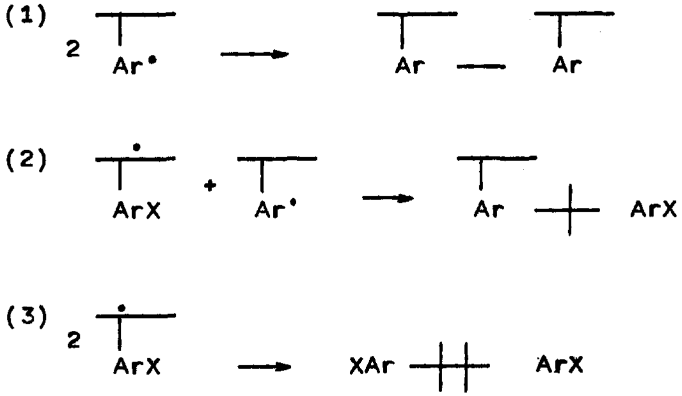
The ion-polymer interaction exhibits additional interesting property changes at higher doses (VENKATESAN, 1983). At argon ion doses of 10^{16} cm^{-2} the ESCA spectra show a relative carbon enrichment of the polymer surface layer. Most of the atoms like H, O and Cl tend to form volatile species, and a large amount of carbon is left.

Fig. 2: Proposed crosslinking reaction mechanism for P(p-ClPhMA)

a) Radical production by ion beam



b) Crosslinking by radical coupling



The carbon core level signal after the high-dose argon ion beam exposure (Figure 3) becomes smaller, and the signal of carbon bonded to oxygen vanishes.

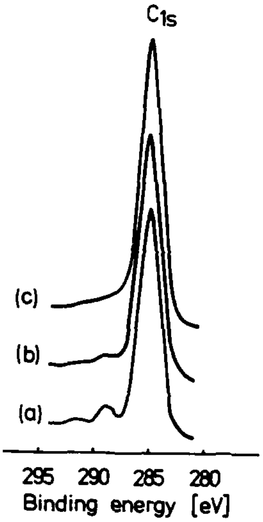


Fig. 3:
C1s core level signal of P(p-ClPhMA)
a) original film
b) and c) 1 keV Ar^+ beam exposed films with doses of
3×10^{13} cm^{-2} respectively
3×10^{16} cm^{-2}

Furthermore, we observe no charging of the polymer film. The electrical conductivity increases with increasing dose. Results of high-dose ion irradiation are the compaction of the polymer and the formation of an amorphous carbon-like surface layer. This carbon enrichment was also observed on PMMA films after ion beam irradiation by Rutherford backscattering spectrometry and Raman spectroscopic investigations (VENKATESAN, 1983).

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