

STUDIES OF UV-PHOTOLYSIS OF VINYLIDENE CHLORIDE-METHYL ACRYLATE COPOLYMER BY USING X-RAY PHOTOELECTRON SPECTROSCOPY*

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ABSTRACT

The UV-photolysis of vinylidene chloride-methyl acrylate copolymer (VDC-MA) has been studied by X-ray photoelectron spectroscopy (ESCA) under atmospheric and inert environment. From the results of ESCA study with different irradiation time, several possible photochemical reactions, such as cleavage of C—Cl bond and photo-oxidation, have been proposed and discussed.

INTRODUCTION

The application of ESCA to the study of polymer surfaces such as the composition and structure of surface regions^[1, 2], reactions on polymer surface^[3, 4] and morphology and topography of multicomponent copolymer film^[5, 6], has attracted a lot of interest.

Only a few investigations on the photolysis of vinylidene chloride-methyl acrylate copolymer (VDC-MA) have been reported^[7]. In this paper, the study of the UV-photolysis of VDC-MA with ESCA was conducted under atmospheric conditions and in argon. From the changes in the characteristics of the relative intensities of C_{1s} , O_{1s} and Cl_{2p} levels and chemical shifts of C_{1s} peaks observed from the ESCA spectra, several possible photochemical reactions have been proposed and discussed. Our experiments showed that the cleavage of C—Cl bond in VDC-MA is faster than in polyvinylidene chloride (PVDC). In addition, the effect of different degrees of substitution of chlorine atoms for carbon atoms upon photochemical reactions was determined by comparing the ESCA spectra of polyvinyl chloride (PVC) with PVDC after UV-irradiation under atmospheric conditions. However, all of the above structure changes have not been observed by using multiple-attenuated total reflectance spectroscopy (MATR) and elementary analysis.

EXPERIMENTAL

1. Preparation of samples

(1) Synthesis of the materials Copolymer (VDC-MA): Copolymerization of an equi-

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molar mixture of vinylidene chloride (VDC, $n_D^{20} = 1.4248$) with methyl acrylate (MA, $n_D^{20} = 1.4028$) in toluene solution was initiated by 0.1% of AIBN related to the monomers at $60 \pm 0.2^\circ\text{C}$ under N_2 atmospheric conditions. The product was reprecipitated twice from toluene solution by using methanol as the non-solvent. The molar ratio of VDC and MA units (VDC:MA = 1:1) was determined by chemical analysis. The chlorine content in the copolymer was 40%.

Polymethyl acrylate (PMA): PMA was prepared and purified in the same manner.

Polyvinylidene chloride (PVDC): Autopolymerization of VDC was carried out under N_2 at room temperature. The product was washed with ethyl alcohol and dried in a vacuum.

(2) Preparation of samples for ESCA. PMA and VDC-MA were studied as thin films prepared by dip-coating from 1% toluene solutions (spectroscopically pure) onto a flat Ag substratum. The samples were dried in a vacuum at ambient temperature for two days. Thin PVDC film (thickness 0.1 mm) was formed from its powder under 100 kg/cm^2 pressure.

2. UV-irradiation

The samples, which were placed in a quartz container filled with argon or air, were irradiated with a 10W low-pressure mercury lamp ($\lambda_{\text{max}} = 253.7 \text{ nm}$) at ambient temperature. The irradiation times chosen were 5 (t_1), 15 (t_2), 30 (t_3) and 60 (t_4) minutes, respectively.

3. ESCA measurement

ESCA spectra were recorded with a Shimadzu ESCA-650B X-ray photoelectron spectrometer by using $\text{MgK}_{\alpha,1,2}$ ($E_x = 1253.6 \text{ eV}$) exciting radiation. The samples were attached to the spectrometer probe by double-sided adhesive tape. Typical operating conditions were: X-ray gun, 7KV $\times$ 36 mA; pressure in the source chamber ca. 10^{-8} torr. Gold was deposited on the sample for calibration of the binding energy. The gold $4f_{7/2}$ peak, which has a full-width at half maximum (FWHM) of 1.2 eV and a binding energy (BE) of 84.0 eV, was used for calibration. The time of measurement was the same for each sample and the procedure was repeated 2—4 times. Overlapping peaks were resolved into their individual components by use of an ESCA PAC-660 curve resolver (an analog computer) on the assumption that the distribution curve of each component is approximately Gaussian. The BE were determined with an error of $\pm 0.2 \text{ eV}$.

RESULTS AND DISCUSSION

1. Photolysis of the homopolymer

Fig. 1 shows C_{1s} and O_{1s} core level spectra of PMA before irradiation, and the dotted line shows its resolved spectra.

The C_{1s} spectrum of PMA is composed of a strong peak at 284.8 eV, a shoulder at 286.1 eV and a small peak at 288.6 eV, corresponding to the C_{1s}^a, b ($\text{C}_{1s}^a \rightleftharpoons \text{C}_{1s}^b$), C_{1s}^d and C_{1s}^c of the

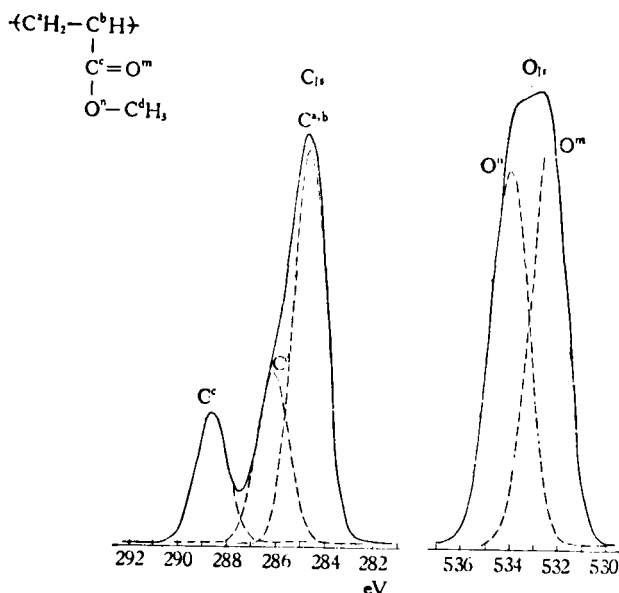
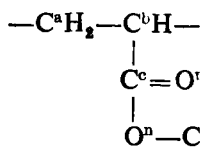


Fig. 1 C_{1s} and O_{1s} core level spectra for PMA homopolymer (the dotted line shows its resolved spectra)



respectively. Its intensity ratios are $C_{1s}^{a,b} : C_{1s}^c : C_{1s}^d = 2:0.9:0.8$

and the intervals between $C_{1s}^{a,b}$ and C_{1s}^d , C_{1s}^c and C_{1s}^d are 1.3 and 2.5 eV, respectively. The O_{1s} spectrum of PMA shows two partially resolved peaks at 532.4 and 533.9 eV of equal peak intensity. The higher binding energy component corresponds to C—O (the single) oxygen while the lower binding energy component to the C=O oxygen (double bonded) of the $\begin{array}{c} \text{—C—O—} \\ || \\ \text{O} \end{array}$. These values are in good agreement with Clark's^[8] and Yamamoto's^[4] results.

After PMA was irradiated for 5 to 60 min under atmospheric conditions and in argon, the C_{1s} and O_{1s} spectra of PMA show no significant changes. This means that some changes of the surface structure and component were not observed in the above mentioned experiments.

Fig. 2 illustrates the C_{1s} , O_{1s} and Cl_{2p} core level spectra of PVDC before UV-irradiation. The C_{1s} spectrum is composed of two large peaks having equal intensity, corresponding to $\text{—C}^e\text{H}_2\text{—C}^f\text{Cl}_2\text{—}$ peaks, respectively. The binding energies were found to be 286.1 and 288.2 eV and the interval between the peaks was 2.1 eV. The effect of replacing two hydrogen atoms by two chlorine atoms $\text{—C}^a\text{H}_2\text{—C}^b\text{H}_2\text{—} \rightarrow \text{—C}^e\text{H}_2\text{—C}^f\text{Cl}_2\text{—}$ is that the C_{1s}^f peak shifted towards higher binding energy side. Due to the substituent effect of chlorine, evidently C_{1s}^e peak on $\text{—C}^e\text{H}_2\text{—C}^f\text{Cl}_2\text{—}$ unit shifted towards higher binding energy side by comparison with $C_{1s}^{a,b}$ peak of PMA C_{1s} spectrum. The initial sample exhibited a O_{1s} signal at 532.4 eV, corresponding to a carbonyl structural feature, arising from the possible contamination and oxidation of the sample surface.

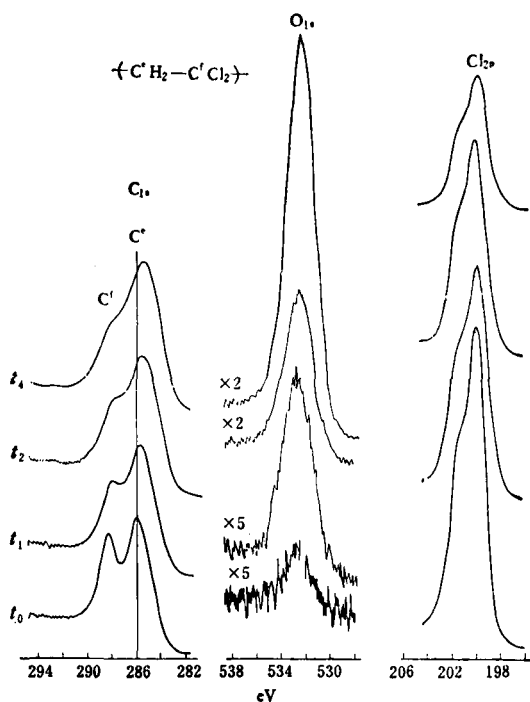


Fig. 2 C_{1s} , O_{1s} and Cl_{2p} core level spectra for PVDC homopolymer
Irradiation time under atmospheric conditions: $t_0 = 0$, $t_1 = 5$, $t_2 = 15$ and $t_4 = 60$ min.

Table 1 Peak intensities ratios and FWHM for PMA and PVDC homopolymers and VDC-MA copolymer before and after irradiation under different ambients

Environment Irradiation time*	Air	Ar	Air	Ar	Air	Ar	Air	Ar	Air	Ar
PMA										
	$C_{1s}^{a,b+d} / C_{1s}^0$	$C_{1s}^{a,b+d} / C_{1s}^0$	$C_{1s}^{a,b+d} / O_{1s}^m$	O_{1s}^m / O_{1s}^n	$C_{1s}^{a,b+d} / FWHM$					
t_0	2.7	2.7	1.1	1.1	1.0	1.0	2.3	2.3		
t_1	2.5	2.7	1.1	1.1	1.0	1.0	2.2	2.3		
t_2	2.6		1.0		1.0		2.4			
t_4	2.5	2.7	0.9	1.0	1.0	1.0	2.4	2.3		
PVDC										
	C_{1s}^e / C_{1s}^f	C_{1s}^e / Cl_{2p}	C_{1s}^e / O_{1s}							
t_0	1.2	1.2	0.4	0.4	9.0	6.0				
t_1	1.5	1.2	0.5	0.4	3.3	4.9				
t_2	1.6	1.3	0.6	0.4	1.6	3.5				
t_4	1.8	2.6	1.1	1.2	0.7					
VDC-MA										
	C'_{1s} / C''_{2s}	C'_{1s} / Cl_{2p}	C'_{1s} / O_{1s}	$C'_{1s} FWHM$	$O_{1s} FWHM$					
t_0	1.9	2.4	0.9	0.9	1.5	1.5	2.8	2.8	2.9	2.6
t_1	2.1	3.2	1.0	1.0	1.3	1.6	2.8	2.7	2.8	2.5
t_2	2.3		1.2		0.9		2.8		2.8	
t_3	3.2		4.1		0.8		2.7		2.8	
t_4	4.0	16	8.3	10	1.0	2.7	2.1	2.5	2.6	1.9

* $t_0 = 0$, $t_1 = 5$, $t_2 = 15$, $t_3 = 30$ and $t_4 = 60$ min.

As seen from Fig. 2 and Table 1, the C_{1s}^f peak intensity reduced slowly with increasing irradiation time, and finally became a shoulder at higher binding energy side. The C_{1s}^e / Cl_{2p} increased from 0.4 at t_0 to 1.1 at t_4 , but the peak intensity at 286.1 eV (t_0) corresponding to $-C^eH_2-$ structural feature, shifted to lower binding energy side at 285.2 eV (t_4). These results indicate that the C—Cl bond on $-CCl_2-$ structure is broken under UV-irradiation, thus the total amount of two chlorine atoms substituted carbon structure is decreased and the substituent effect of chlorine atom on the neighbouring groups is also reduced. Fig. 3 curve 1 shows a plot of the C_{1s}^e / Cl_{2p} ratio increases smoothly with increases of UV-irradiation time, viz. chlorine content at the sample surface is decreased. But C_{1s}^e / O_{1s} ratio associated with the photo-oxidation feature is reduced from 9.0 (t_0) to 0.7 (t_4).

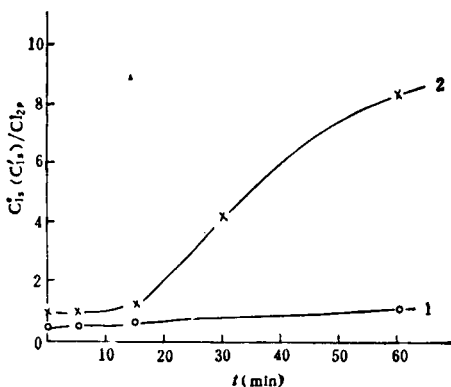


Fig. 3 Relationship between C_{1s}^e (or C_{1s}^f) / Cl_{2p} and irradiation time
1—PVDC, 2—VDC-MA.

2. Photolysis of the copolymer

It was evident from the ESCA spectra of PMA and PVDC that the C_{1s} of VDC-MA should at least be composed of four components, i.e., $C_{1s}^{a,b}$, $C_{1s}^d + C_{1s}^e$, C_{1s}^f , and C_{1s}^g at 284.8, 286.1 (because the morphology of PVDC is different from that of the copolymer, the C_{1s}^e and C_{1s}^f values of the former may be higher), 288.2 and 288.6 eV, respectively.

The core-level spectra of VDC-MA copolymer before being irradiated are shown in Fig. 4 (t_0), where C_{1s} spectrum has only two peaks C_{1s}^f and C_{1s}^g at 285.3 and 288.2 eV, respectively. As the chemical shifts of C_{1s} of these carbon atoms differ relatively little, $C_{1s}^{a,b}$, C_{1s}^d and C_{1s}^e peaks superimpose into C_{1s}^f , and C_{1s}^g peaks superimpose into C_{1s}^g peak.

O_{1s} spectrum of copolymer is composed of overlapping O_{1s}^m and O_{1s}^n peaks. It is obvious that these two components of the O_{1s} level are not of equal intensity. O_{1s}^m signal is stronger while O_{1s}^n signal appear as a shoulder peak, indicating the samples contain excess carbonyl features in the surface regions. It is possible that the surface of the sample was oxidized.

As indicated above, the changes of C_{1s} and O_{1s} level spectra for PMA have not been observed under the above mentioned experiments, but for copolymers UV-irradiation causes dehydrochlorination, photo-oxidation, cross-linking and cyclization reactions as shown in the ESCA spectra.

C_{1s} , O_{1s} and Cl_{2p} level spectra of copolymer after being irradiated for various time are

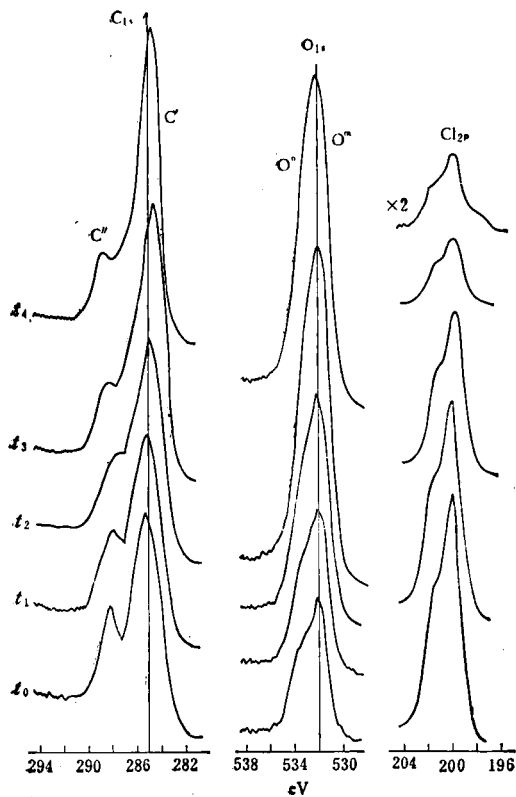
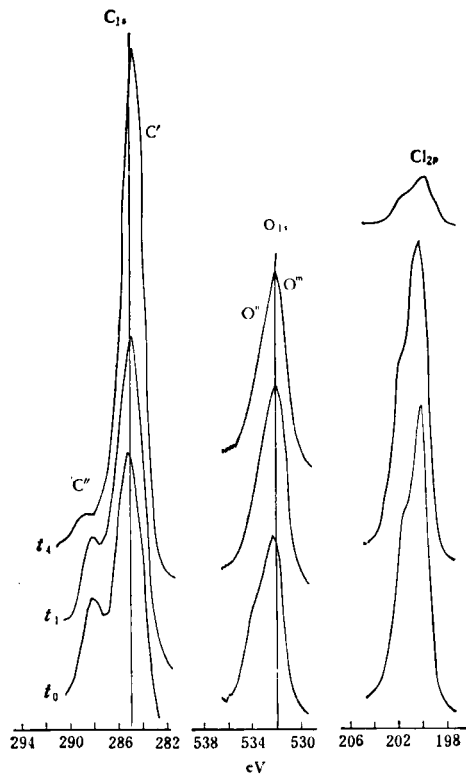


Fig. 4 C_{1s} , O_{1s} and Cl_{2p} core level spectra of VDC-MA copolymer before and after irradiation under atmospheric conditions
 $t_0 = 0$, $t_1 = 5$, $t_2 = 15$,
 $t_3 = 30$ and $t_4 = 60$ min.

Fig. 5 C_{1s} , O_{1s} and Cl_{2p} core level spectra for VDC-MA copolymer before and after irradiation in Argon
 $t_0 = 0$, $t_1 = 5$ and $t_4 = 60$ min.



shown in Fig. 4 (t_0-t_4). The main spectral features are as follows: (1) The Cl_{2p} signal as well as the C'_{1s} signal decrease as the time of UV-irradiation increases. After 60 min exposure, the C'_{1s}/C'_{1s} and C'_{1s}/Cl_{2p} ratios increase from 1.9 to 4.0 and 0.9 to 8.3, respectively. The decrease in chlorine content on the surface regions is revealed by a large decrease in the intensity of the component derived from $-CCl_2-$ structural feature, viz. Cl_{2p} level. These observations are entirely consistent with the dehydrochlorination mechanism, in which $\underline{CH_2}$ and $\underline{CCl_2}$ features are converted into $\underline{CH}$ and $\underline{CCl}$, respectively. Since the effect of CCl_2 structure on the neighbouring groups was decreased as a consequence of decreasing of CCl_2 structure on the $-CH_2-CCl_2-$ unit, the C'_{1s} peak which contained CH_2 (CH) structural features shifted from 285.3 eV to a lower binding energy of 284.8 eV. At the same time, C'_{1s} component tends to become evident and C'_{1s} peak containing C'_{1s} component shifted to a higher binding energy side. After 1 hr irradiation, the C_{1s} spectrum of the copolymer is analogous to that of PMA as shown in Fig. 1, because their corresponding compositions are quite similar. (2) The change of O_{1s} spectra with irradiation time exhibited the same trend. After irradiation for 1 hr, the C'_{1s}/O_{1s} ratio decreased from the initial value of 1.5 to 1.0. The tendency towards change of C_{1s} and Cl_{2p} spectra of copolymer under an inert environment is similar to that of copolymer under atmospheric environment (Fig. 5 and Table 1). But C'_{1s}/O_{1s} ratio is increased from 1.5 to 2.7 in consequence of the absence of oxygen. (3) After 1 hr exposure, C'_{1s} peak becomes narrower and FWHM reduces from 2.8 eV to 2.1 eV. It is probably due to the cyclization occurring between neighbouring groups, so that the content of C^d structure on MA unit is decreased. Finally, comparing Fig. 4- t_4 with 4- t_0 and 5- t_4 with 5- t_0 , the total C'_{1s} intensity for the irradiated sample is larger than that for the initial copolymer. This behaviour is consistent with a "shrinking" of the polymer surface through cross-linking resulting in a higher number density of carbon atoms on the surface regions of the sample. It should be emphasized, however, that by using conventional techniques, such as ATR infrared spectroscopy and elementary analysis, these samples appear perfectly normal and the samples show no evidence of structure changes on the surface regions.

Fig. 3 curve 2 shows the relation between C'_{1s}/Cl_{2p} ratios and irradiation time. It would appear that the cleavage rate of the C-Cl bond in the copolymer is faster than that of the VDC homopolymer. The tendency of photolysis is the same under inert environment. Boyer^[7] proposed that the greater stability of VDC-acrylate copolymers was related to the fact that long VDC sequences were broken up by an "unzipping" reaction. But Burnett and his colleagues^[9-11] studied the kinetics of decomposition of several copolymers of VDC with MMA, acrylonitrile or styrene. Their data show that the copolymers degrade faster than the VDC homopolymer, due to changes in the neighbouring environment of a VDC unit in copolymer (such as neighbouring group interactions, inter-molecular attraction or change in crystallinity, etc.) and change in activation energy resulting in an increase of dehydrochlorination rate. For example, the activation energy of dehydrochlorination may decrease 4-7 kcal/mol in VDC-St or VDC-MMA copolymer. As seen from our results, the photolysis tendency of VDC homopolymer and copolymer is similar to that of the pyrolysis. The comonomers appear to act as an intramolecular "weak link", as postulated from the effect of sequence distribution of copolymer of vinylidene bromide with MA, MMA or St comonomer

on the photolysis^[12].

In addition, we have reported previously that the change of C_{1s}/Cl_{2p} ratio of PVC film in the ESCA spectrum was not apparent, but the change of C_{1s}/O_{1s} ratio was quite distinct after 1 hr irradiation in air indicating that this reaction is mainly a photo-oxidation^[13]. But when a VDC homopolymer or copolymer was irradiated under the same experimental conditions, the change of C_{1s}/Cl_{2p} was quite distinct. This result could be explained by their difference in the degree of chlorine substitution, causing their difference in the C—Cl bond energy.

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