induce a preferential hydration of the polypeptide in helical conformation.

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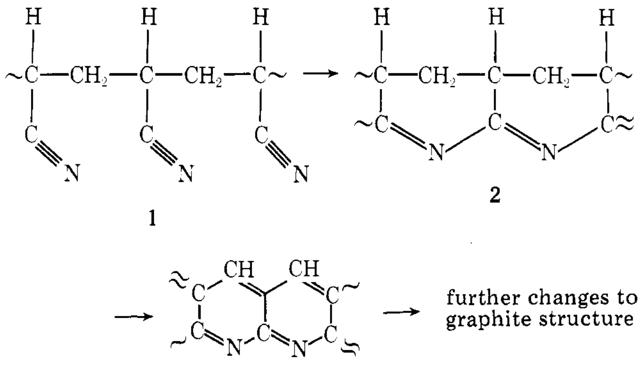
Communications to the Editor

ESCA Studies of Structural Changes of Poly(acrylonitrile) and Poly(chloroacrylonitrile). High-Temperature-, Electron-Impact-, and Ultraviolet-Light-Induced Changes

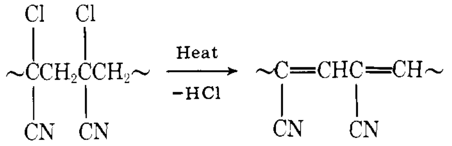
Poly(acrylonitrile) is well known to undergo structural changes in the presence of oxygen at high temperatures as shown in the following,[1]



1 2 3

Coloration, an increased electrical conductivity, and gas evolutions have been taken as evidence for the above structural changes, together with reduced intensity of the cyano group infrared band after heat treatment.[2]

Thermal degradation of poly(α-chloroacrylonitrile) has been studied up to 200 °C.[3] The result showed a facile elimination of hydrogen chloride, far easier than in poly(vinyl chloride), as shown below:



$$\sim\underset{CN}{\overset{Cl}{C}}H_2\underset{CN}{\overset{Cl}{C}}H_2\sim \xrightarrow[-HCl]{Heat} \sim\underset{CN}{C}=CH\underset{CN}{C}=CH\sim$$

4 5

With no other observable gaseous products except hydrogen chloride, the black coloration, the disappearance of the "quenching effect" of chlorine on the infrared absorption intensity of the cyano group, and the appearance of the ethylenic infrared bands are taken as the evidences for structure **5**.[3] A pyrolysis of poly(cyanoacetylene), prepared in a catalytic polymerization of cyanoacetylene, was reported to yield an infrared spectrum similar to the poly(acrylonitrile) baked at high temperature.[4] The changes of the infrared bands alone, however, cannot be taken as evidence for the ladder-type structure, because hydrogen cyanide and other cyano compounds were reported as products in the pyrolysis of poly(acrylonitrile) at high temperature.[5]

We wish to report here our ESCA studies of structural changes of poly(acrylonitrile) and poly(α-chloroacrylonitrile) induced by high temperature, electron impact, and UV-light exposure.

Poly(acrylonitrile) used was obtained from Polysciences Inc., and its thin films were cast from a dimethylformamide solution on substrates such as aluminum, silicon, or gold by spin-coating. Poly(α-chloroacrylonitrile) was prepared from its monomer obtained from Polysciences in a similar way as described in the literature.[2] Its thin films were cast from a dimethylformamide solution in the same way as for poly(acrylonitrile). Surface photopolymerization from gaseous 2-chloroacrylonitrile on proper substrates was also carried out with low-pressure mercury lamps; our technique has already been reported with methacrylic anhydride.[6]

Heating of the polymer films was carried out in a sealed tube under vacuum. Electron beam exposures were performed with an Auger electron gun made by Varian in a dosage of 10^{-4} to 10^{-3} C/cm^2 at 3 keV. The UV light exposure was made under vacuum with low-pressure mercury lamps for 6 h. ESCA measurements were conducted at room temperature under a vacuum better than 2×10^{-9} Torr with a Hewlett-Packard Model 5650A ESCA spectrometer, which had resolution better than 1 eV. The samples were flooded with thermal electrons during the data collections to neutralize the charge effect. The reported binding energies were referred to $Au_{4f_{7/2}}$ transition at 83.9 eV.

Poly(acrylonitrile). The C_{1s} and N_{1s} core level spectra of poly(acrylonitrile) before and after thermal treatment at 500 °C are shown in Figure 1. The maximum peak of the C_{1s} core level signal shifts by the thermal treatment from 285.2 to 284 eV in the binding energy with a pronounced shoulder at 286 eV. The shift of the carbon signal by heat is caused by the structural changes from **1** to **2** and **3**. It is known that the conjugated carbon has a lower binding energy than those in a saturated structure; the carbon core level of a $-C{\equiv}N$ is also known to have a higher binding energy than those of a $>C{=}N-$ group.[7] A partial conversion of the $-C{\equiv}N$ group to the $>C{=}N-$ group of **3** is also shown in the change of the N_{1s} core level signal. After the heat treatment, a symmetrical Gaussian-type N_{1s} core level signal with the maximum peak at 399.0 eV becomes broad and asymmetrical with a newly formed shoulder peak at 400.5 eV in the binding energy; the shoulder peak belongs to the nitrogen of the $>C{=}N-$ group of **3**. A positive shift of 1.5 eV of the N_{1s} from **1** to **3** is consistent with a loss of a negative charge in the nitrogen of the $>C{=}N-$ group from the $-C{\equiv}N$ group.[7] A partial conversion from **1** to **2** and **3** is in agreement with the infrared absorption spectra which reveals that the $-C{\equiv}N$ group is still observable at 2220 cm^{-1} after heating at 500 °C for 15 min, although the cyano group completely converts to the $>C{=}N-$ group in a prolonged heating at this temperature.

Poly(α-chloroacrylonitrile). The C_{1s}, N_{1s}, and Cl_{2p} core level spectra of poly(α-chloroacrylonitrile) films which were cast from a dimethylformamide solution of the polymer prepared in an emulsion polymerization of 2-chloroacrylonitrile

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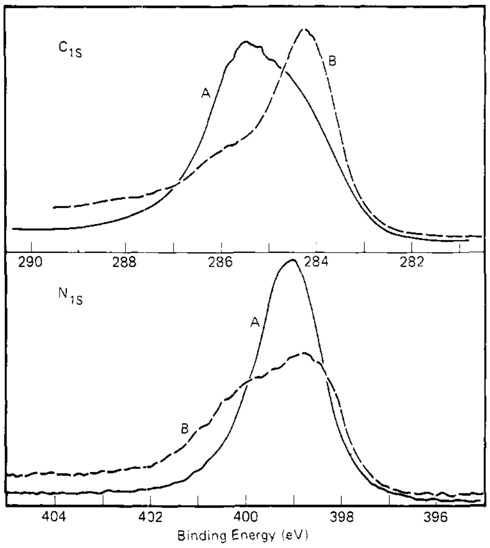

Figure 1. ESCA spectra of poly(acrylonitrile): (A) poly(acrylonitrile) prior to heat treatment; (B) after heating for 1 h at 500 °C.

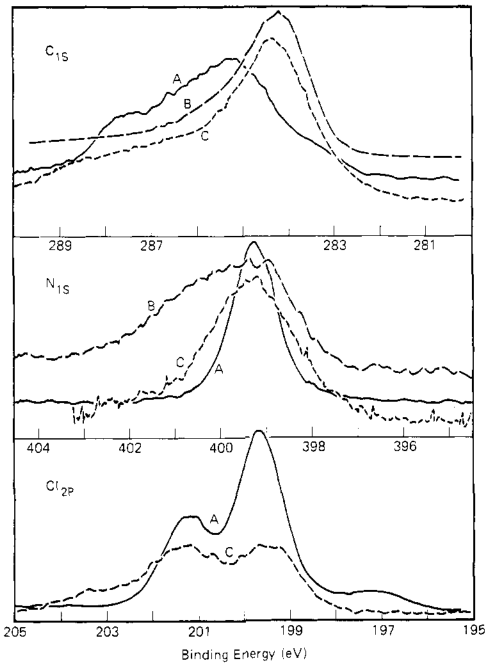

Figure 2. ESCA spectra of poly(α-chloroacrylonitrile): (A) poly(α-chloroacrylonitrile) prior to any treatment; (B) after heat treatment for 1 h at 500 °C; (C) after 6 h of UV light exposure.

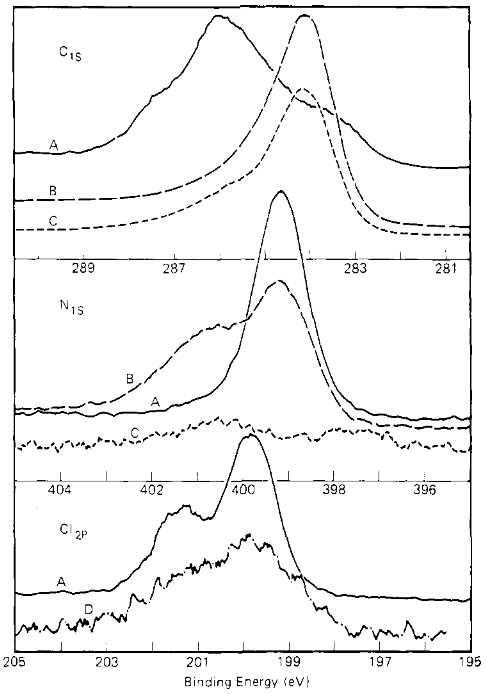

Figure 3. ESCA spectra of the photopolymer of 2-chloroacrylonitrile: (A) the photopolymer prior to any treatment; (B) after heating for 1 h at 500 °C; (C) after heating for 1 h at 1000 °C; (D) after 3-keV electron beam exposure in a dosage of 10^{-4} C/cm^2.

are shown in Figure 2. The changes of the core level spectra by the UV light exposure and by the heat treatment are also presented. The C_{1s} core level spectrum of the polymer films before any treatment reveals a distinct shoulder peak at 287.5 eV corresponding to the carbon atom with a chlorine atom attached. The inductive effect of the chlorine, and in a small degree of the cyano group, is responsible to a shift to a higher binding energy of the C_{1s} core level, as also found in poly(α-chloroacrylate).[7] A small shoulder found at 284 eV may be due to a small amount of unsaturated carbons produced by hydrogen chloride elimination from the main polymer chain, as evidenced by a pale brown color of our sample. A central part of the C_{1s} core level spectrum with the maximum peak at 285.2 eV in the binding energy is a composite of the C_{1s} signals of the $-C{\equiv}N$ group and the $-CH_2-$ group.

After heating for 1 h at 500 °C under vacuum, and also after 6 h of UV light irradiation, the C_{1s} core levels change to the signals B and C of Figure 2 which have the maximum peak at 284.2 eV with a tailing in the side of the higher binding energy; the tailing is due to the hidden C_{1s} core level of the cyano group.

As found in poly(acrylonitrile), the N_{1s} core level of poly(α-chloroacrylonitrile) prior to any treatment has a symmetrical Gaussian type distribution as shown in Figure 2A. The UV light exposure makes the N_{1s} core level distribution broad with the maximum peak location unchanged. The heating at 500 °C, however, makes the spectrum not only broad but also unsymmetrical with a shoulder appearing at 400.5 eV in the binding energy. These results indicate that the UV light exposure at room temperature only leads to elimination of hydrogen chloride resulting in the polymer structure **5** still with cyano groups attached to the main chain and that the heat treatment at 500 °C causes not only the hydrogen chloride removal but also the structural change to the doubly conjugated ladder-type structure **3**, as observed for poly(acrylonitrile).

The elimination of hydrogen chloride is also substantiated by the change of the Cl_{2p} core level signals as shown in Figure 2. The original poly(α-chloroacrylonitrile) has the main $Cl_{2p_{3/2}}$ core level signal at 199.7 eV with a side band at 201.3 eV in the binding energy. The major part of the 201.3-eV peak may be due to the trapped hydrogen chloride or chlorine, because the satellite band of $Cl_{2p_{1/2}}$ is usually very weak in comparison to the $Cl_{2p_{3/2}}$ peak, and because the ratio of the main to the satellite peaks varies from 2 to 1. The UV light irradiation reduces markedly the intensity of the main Cl_{2p} core level signal revealing the hydrogen chloride removal. The sideband intensity, however, does not change very much. The heat treatment at 500 °C results in no observable intensity in the energy range of the Cl_{2p} core level, indicating all chlorine atoms are removed in these conditions.

Photopolymer of 2-Chloroacrylonitrile. The surface photopolymer of 2-chloroacrylonitrile has essentially the same

ESCA data as the one reported for poly(α-chloroacrylonitrile) in the previous section. During the UV light exposure for the polymerization, however, a partial elimination of hydrogen chloride takes place resulting in a diminished intensity of the C_{1s} core level signals of the carbon with chlorine attached and the $-CH_2-$ groups; the maximum peak of the main part of the C_{1s} core level thus locates at 286 eV with a small shoulder due to the conjugated carbon atoms at 284.2 eV, as shown in Figure 3A. The heat treatment at 500 and 1000 °C and the electron beam exposure all shift the maximum peak to 284.2 eV with the tailing in the higher binding energy side, as shown in Figures 3B and 3C. The electron beam exposure at 3 keV yields the same results as the UV light irradiation, which has been described in the preceding section in respect to the C_{1s}, N_{1s}, and Cl_{2p} core level spectra. In Figure 3, the effect of the electron exposure is shown only for the Cl_{2p} core level, which clearly substantiates the elimination of hydrogen chloride. The electron exposure alone cannot induce the structural change to the doubly conjugated ladder-type polymer.

The heat treatment at 500 °C induces the change to the ladder-type polymer as evidenced by the appearance of the clearly distinguishable shoulder peak at 400.5 eV in the N_{1s} core level spectrum. The heat treatment at 1000 °C, however, loses almost all the nitrogen signal except a trace amount of the N_{1s} signal corresponding to the $>C{=}N-$ group, as revealed in Figure 3C. This indicates that under such a high temperature the carbonization of the polymer proceeds extensively by removal of nitrogen and hydrogen.[8]

The infrared absorption studies of the polymer films support the results obtained by the ESCA data. The cyano group infrared band of poly(α-chloroacrylonitrile) prior to the treatments is barely observable because of the "quenching effect" of the chlorine.[3,9] However, the UV light and electron beam exposures make the infrared absorption at 2250 and 2220 cm^{-1} clearly observable, and the heating at 180 °C makes the band at 2220 cm^{-1} very intense because of the loss of the hydrogen chloride in these treatments. The complete conversion to the structure **3**, however, is a slow process, because even after heating at 400 °C for 30 min the cyano group infrared band is still intense with both poly(acrylonitrile) and poly(α-chloroacrylonitrile) in agreement with the ESCA data presented here.

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Control of Structural Isomerism in Polyamides

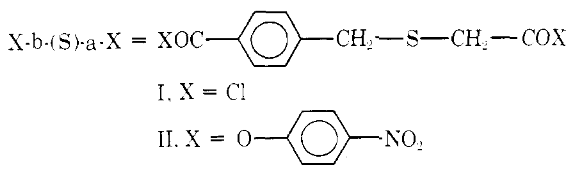
Although the possibility of structural isomerism in condensation polymers, derived from two different monomers of the type X-ab-X and Y-cc-Y, has long been recognized,[1,2] the phenomenon has been little investigated up to now.[3-7] In a few cases[4-6] NMR has been used for the quantitative determination of the sequences -acca-, -bccb-, and -accb-which can be present in the polymers but possible errors connected with the presence of a relatively large concentration of the terminal groups have not been considered. In only one case[5,6] low molecular weight polyesters with different properties have been prepared from identical monomers and on the basis of a NMR analysis their properties were related to structural isomerism. Polyamide hydrazides with different degrees of chemical order have been apparently obtained[7] from the polycondensation of terephthaloyl chloride with p-aminobenzhydrazide; however, no quantitative determination of the different types of sequences present in these terpolymers[8] was carried out.

Table I
Properties of Polyamides Obtained from I or II and Ethylenediamine

Property	Polyamides[a]			
	P-1	P-2	P-3	P-4
$[\eta]^b$ dL/g	0.51	0.60	0.13	0.54
$\overline{M}_n{}^c$				10000
$\overline{M}_w{}^d$	12000			
UV[e] λ_{max}, nm	261	261	261	261
log ϵ	4.13	4.14	4.14	4.23
Mp,[f] °C	228	248	256	229
$\Delta H°_M$,[f] kcal/mol[h]	2.3	3.9	5.1	2.6
Solubility in DMF[g]	s	sl s	v sl s	s

[a] The polymers were obtained at room temperature as follows: P-1, by addition of II (305 mmol/L in Me_2SO) to an equimolar amount of diamine in solution (305 mmol/L in Me_2SO); P-2, by very rapid addition of the equimolar amount of pure diamine to a solution of II (175 mmol/L in Me_2SO); P-3, by slow addition (5 min) of the equimolar amount of diamine in solution (288 mmol/L in Me_2SO) to a solution of II (288 mmol/L in Me_2SO); P-4, by interfacial polycondensation. A solution of I (146 mmol/L in CCl_4) was vigorously mixed with an aqueous solution containing an equimolar amount of the diamine (113 mmol/L) and 2 equiv of NaOH. The yields of purified polymers, calculated with respect to the quantities obtainable for a complete conversion, were 87% (P-2), 88%, (P-3), and 63% (P-4). In the case of P-1, which was not purified, the yield was 94%. [b] In m-cresol at 30 °C. [c] By vapor pressure osmometry in DMF at 100 °C. [d] By sedimentation equilibrium measurements at 30 °C in Me_2SO. [e] In sulfuric acid at 25 °C. [f] From DTA measurements. [g] At room temperature: s, soluble, sl s, slightly soluble; v sl s, very slightly soluble. [h] Per mole of structural unit (M, 250.3).

We report the synthesis of isomeric polyamides containing -acca-, -bccb-, and -accb- sequences the structure of which, determined by quantitative degradation,[9] can be controlled in the range between 47 and 19% of the sequence -accb-. The former figure corresponds closely to a random distribution of the two relative orientations of the -ab- units and the latter corresponds probably to the maximum order achievable in the polycondensation of the monomers used, with the chosen temperature and solvent. These polyamides were obtained from the two monomers of the type X-a-(S)-b-X, I and II, and ethylenediamine (H-cc-H) under different conditions.



For both monomers I and II, no significant change in the reactivity of one functional group upon reaction of the other is expected. Depending on polycondensation conditions, poly-

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