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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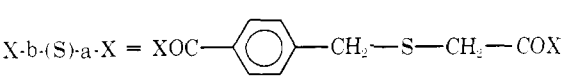
Received December 15, 1977

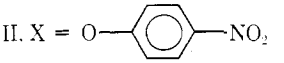
Control of Structural Isomerism in Polyamides

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.

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.



I, X = Cl



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-

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).

0024-9297/78/2211-0624$01.00/0

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

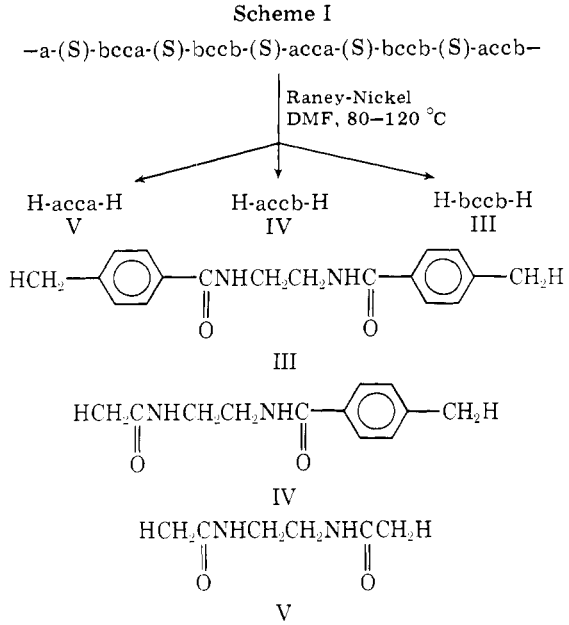
Polymer[a]	Sequences[b] (molar fraction × 100) –bccb– d	–bccb– e	–acca– d	–acca– e	–accb– d	–accb– e	s^c d	s^c e
P-1	26	27	27	28	47	45	0.47	0.45
P-2	38	37	36	37	26	26	0.26	0.26
P-3	41	41	40	43	19	16	0.19	0.16
P-4	30	31 (29)	30	30 (31)	40	39 (40)	0.40	0.39 (0.40)

[a] See Table I. [b] See Scheme I. [c] s = [–accb–]/([–acca–] + [–bccb–] + [–accb–]). [d] From the analysis of the cleavage products (90-MHz NMR in Me_2SO solution at room temperature. The CH_3 resonances at 1.81 ppm (CH_3CO–) and 2.35 ppm (CH_3–C_6H_4–) have been used). [e] From a 90-MHz NMR analysis of the polymer in Me_2SO (Figure 1). The values in parentheses for P-4 concern measurements at 360 MHz.

amides having the properties indicated in Table I were obtained. The structure of these polymers was determined by cleavage with Raney-Nickel[10] in DMF[11] at 80–120 °C. The yields of the three possible cleavage products III, IV, and V, reflecting the three possible structural units present in the polymers (Scheme I), were in all cases higher than 94%. The quantitative analysis of the cleavage products was made by ^1H NMR spectroscopy using the CH_3 resonances, after separating the products into two fractions, the first containing IV and V and the second III and IV. This separation was accomplished by sublimation at 130 °C (0.05 mmHg). The results (Table II) were compared with the values obtained by using ^1H NMR for a direct structure determination[4] of the polymers. The values obtained by using the CH_2 resonances of the diamine residues in the 90-MHz spectra of the polymers (Figure 1) differ only slightly from those derived from the analysis of the cleavage products (Table II). Since peak overlap might affect the results obtained at 90 MHz, we repeated the analysis of P-4 at 360 MHz (Figure 1). The good agreement between the results obtained at 90 and 360 MHz (Table II) further confirms in this case the reliability of the former.

Comparing the data shown in Tables I and II, it appears that the differences in physical properties of the polymers are related to the polymer structure with solubility in DMF decreasing and with melting point and melting enthalpy increasing upon increasing the structural regularity.[12]

Scheme I



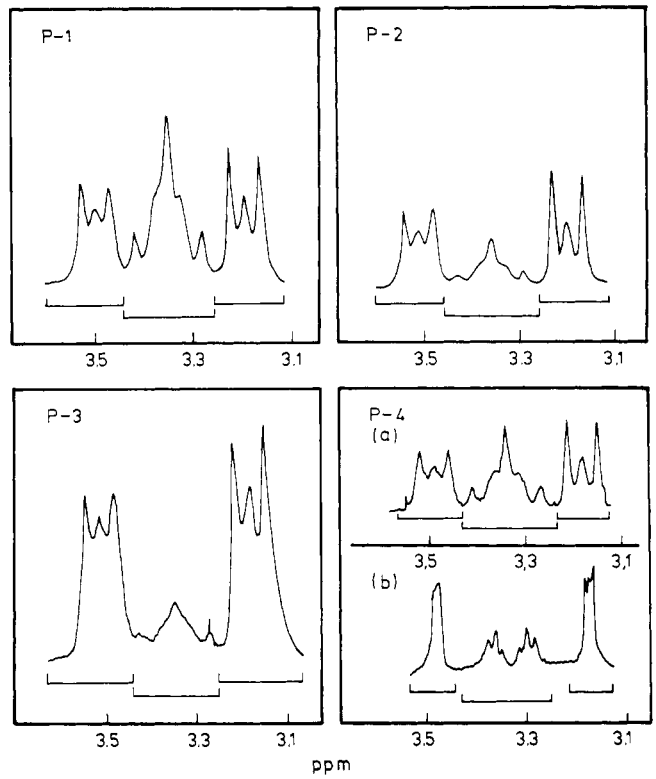


Figure 1. CH_2 resonances of the diamine residues in the NMR spectra of the polymers reported in Table I (solvent Me_2SO). The spectra of P-1, P-2, P-3, and P-4 (a) were measured at 90-MHz and 120 °C and that of P-4 (b) at 360-MHz and 134 °C. The brackets define the regions with the resonances attributed to the three sequences –acca–, –accb–, and –bccb– (from right to left) which have been used for the determination of the polymer structure.

As in the case of polyesters[5,6] and of polyamide hydrazides,[7] control of the structure can be achieved by adding the symmetrical monomer to an excess of the nonsymmetrical one. In our case (P-2 and P-3, Table II), the control is probably connected to the fact that the prevailing intermediate in the first steps of polycondensation is X-b-(S)-acca-(S)-b-X, X-a– being the arbitrarily assumed[13] more reactive ester group of nonsymmetrical monomer II. On the other hand, a composition corresponding to a random orientation of the –ab– units is achieved by adding II to an excess of the diamine (P-1, Table II), the prevailing intermediate in the first steps of polycondensation being in this case H-cca-(S)-bcc-H, which contains two amino groups having approximately the same reactivity.

The structure of the polymer can be described conveniently by the probability s of an –accb– placement:

$$s = [\text{–accb–}]/([\text{–acca–}] + [\text{–bccb–}] + [\text{–accb–}])$$

This probability is lowest (i.e., the regularity of the head-to-head, tail-to-tail type is highest) for an infinitely long polymer chain when H-cc-H is added "infinitely" [14] slowly to X-a-(S)-b-X. In this case, and if conversions of monomers to polymer is substantially complete, the ratio $r = k_b/k_a$ (<1) between the rate constants k_b (for the reaction X-a-(S)-b-X + H-cc-H → X-a-(S)-bcc-Y) and k_a (for the reaction X-a-(S)-b-X + H-cc-H → X-b-(S)-acc-Y) is the parameter essential for controlling structural regularity.[15] If the reactions are of first order with respect to the functional group in X-a– and X-b–, s is related to r according to the equation

$$s = r \int_0^1 (r + x^{(1-r)})^{-1}\, dx$$

where x is the fraction of unreacted X-a- groups. For reactions which are of second order[16] with respect to the same functional groups, s is given by the equation

$$s = \frac{r^{1/2}}{1-r}\left[\arctan\frac{1}{r^{1/2}} - \arctan r^{1/2}\right]$$

For the solution polycondensation investigated it seems very likely that the maximum regularity corresponding to "infinitely" slow addition of the diamine to the diester has already been achieved in the case of P-3 (Table II). Indeed, a polymer with the same structure as P-3 has been obtained in a preliminary experiment under conditions comparable to those used for P-3 (Table I) but by adding the diamine to the diester during 120 min rather than during 5 min.

Further research is needed to explain the results obtained by interfacial polycondensation (Table II, polymer P-4). The small regularity obtained in P-4 is probably connected with the actual relative concentration of I and ethylenediamine in the phase, or at the interfacial layer, where they react. It seems possible to use the determination of structural regularity in condensation polymers as a convenient tool in the investigation of the mechanism of interfacial polycondensation.

Acknowledgment. This investigation has been supported by research grants from the Swiss National Science Foundation (No. 2.054.73 and 2.498.75).

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(11) The following abbreviations are used: DMF, dimethylformamide; Me_2SO, dimethyl sulfoxide.
(12) The melting point of a polymer having a completely regular structure of the head-to-head, tail-to-tail type should not be very different from the melting point (276 °C) of an oligomer synthesized (E. Marti-Baumann, Diplomarbeit 3692, ETH, Zurich, 1974/75) from ethylenediamine and $(-CH_2NHCOC_6H_4CH_2SCH_2COOH)_2$, using the mixed anhydrides method (V. Bruckner, J. Kovács, H. Nagy, and M. Kajtár, *Acta Chim. Acad. Sci. Hung.*, **6**, 219 (1955)).
(13) Aminolysis of *p*-nitrophenyl esters, which has been extensively investigated (see, e.g., D. P. N. Satchell and I. I. Secemski, *J. Chem. Soc. B*, 130 (1969); F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, **94**, 3824 (1972)) does not seem to have been studied using ethylenediamine in Me_2SO. Work is in progress to determine, with the aid of suitable models, which of the ester groups of II is more reactive.
(14) Calculations suggest that the addition of H-cc-H can be considered as practically "infinitely" slow when it is done at such a rate that its concentration in the reaction mixture never exceeds ca. 2% of the initial concentration of X-a-(S)-b-X.
(15) A similar theoretical treatment, addressing the problem of structural regularity in terpolycondensates, has been published by S. I. Kuchanov, *Vysokomol. Soedin., Ser. A*, **16**, 1125 (1974).
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Received November 28, 1977