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Spontaneous copolymerization of *N*-(2-hydroxyethyl)ethyleneimine with isatoic anhydride

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SUMMARY

The polymerization of isatoic anhydride (electrophilic monomer) with N-(2-hydroxyethyl)ethyleneimine (nucleophilic monomer) was studied in the absence of added initiator at different feed monomer concentrations, temperature, and time of copolymerization. The copolymers were characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy, and TGA. Based on spectroscopic data and copolymer composition, a copolymer structure was suggested.

INTRODUCTION

A polymerization reaction usually requires an initiator, catalyst or high energy radiation. However, by spontaneous zwitterion polymerization it is also possible to get alternating and statistical copolymers by interaction of an electrophilic monomer (M_E) and a nucleophilic monomer (M_N) (1-22). This interaction produces an ionic intermediate ${}^{+}M_NM_E^{-}$, which is responsible for both initiation and propagation.

$$M_N + M_E \longrightarrow \underset{\textbf{1}}{{}^{+}M_NM_E^{-}}$$

$$\textbf{1} + x\textbf{1} \longrightarrow {}^{+}M_N(M_EM_N)_x\, M_E^{-}$$

In general:

$${}^{+}M_N(M_EM_N)_m\, M_E^{-} + n\,{}^{+}M_NM_E^{-} \longrightarrow {}^{+}M_N(M_EM_N)_{m+n+1}\, M_E^{-} \quad (m>>1)$$

A dipole-ion reaction is also possible, e.g.

$$M_N + {}^{+}M_N(M_EM_N)_x\, M_E^{-} \longrightarrow {}^{+}\underline{M_NM_N}\,(M_EM_N)_xM_E^{-}$$

This type of polymerization has been extensively studied by our group (6-22). In this paper, the spontaneous copolymerization of N-(2-hydroxyethyl)ethyleneimine (M_N) with isatoic anhydride (M_E) under different experimental conditions was studied.

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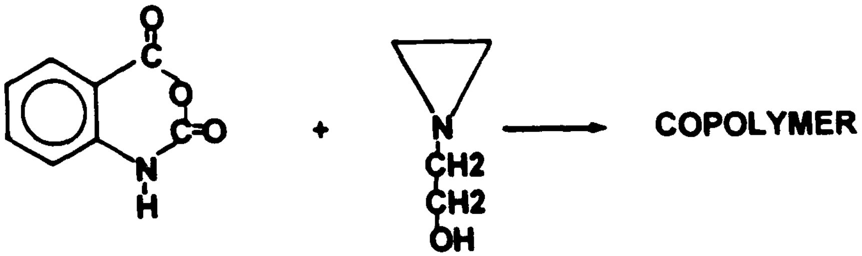


Isatoic anhydride N-(2-hydroxyethyl)ethyleneimine

EXPERIMENTAL PART

Reagents

N-(2-hydroxyethyl)ethyleneimine (HEEI) (Fluka) was purified by distillation. The solvents were dried according to published methods (23).

Copolymerization

General procedure: A mixture containing HEEI and isatoic anhydride (ISA) was polymerized under nitrogen by varying the feed monomer ratio, temperature and time. The total number of moles was 0.04 in 10 mL of DMF. The copolymer mixture was precipitated in diethyl ether and was purified by reprecipitation in DMSO/diethylether and dried under vacuum up to constant weight.

Measurements

FT-IR spectra were recorded on a Magna Nicolet 550 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in a Bruker AC-250P spectrometer at 29°C with TMS as internal standard. Thermal analysis was carried out by a Polym Lab. STA 625 system under N_2 at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

A set of 9 copolymerizations varying the feed monomer ratio, time and temperature of copolymerization was carried out (see Table 1). The copolymers are hygroscopic amber solids.

Table 1 shows the effect of the feed monomer ratio on copolymer composition; copolymer **4** is the richest in HEEI units. As the polymerization time increases, the incorporation of HEEI increases, yielding finally copolymers with homodiads of HEEI. The opening of the aziridine ring is promoted at the highest temperature.

Table 1. Copolymerizations and composition of the poly(hydroxyethyl)ethyleneimine-*co*-isatoic anhydride)s[a].

Copolymer	Feed monomer ratio HEEI/ISA	Temperature (°C)	Time (days)	Copolymer comp.[b] HEEI/ISA
1	1.00 : 2.00	30°	14	0.55 : 1.00
2	1.00 : 1.00	30°	14	0.76 : 1.00
3	1.00 : 0.67	30°	14	0.98 : 1.00
4	1.00 : 0.33	30°	14	1.70 : 1.00
5	1.00 : 1.00	30°	7	0.64 : 1.00
6	1.00 : 1.00	30°	14	0.77 : 1.00
7	1.00 : 1.00	30°	21	0.82 : 1.00
8	1.00 : 1.00	40°	7	0.75 : 1.00
9	1.00 : 1.00	50°	7	1.00 : 1.00

a) The copolymerization yield ranged between 40 and 55%.

b) It was determined by ^{1}H-NMR spectroscopy.

SPECTROSCOPIC DATA

FT-IR spectroscopy. The FT-IR spectra of the HEEI/ISA copolymers show two bands between 3200 and 3600 cm^{-1} attributed to N-H (primary aromatic amine) but the secondary aromatic amine does not completely disappear. The O-H stretching band in the copolymers richest in ISA was not observed. The signal at 1689 cm^{-1} is assigned to the aromatic ester group. These spectra are similar to the methyl ester of o-aminobenzoic acid (antranilic acid) (see Figure 1).

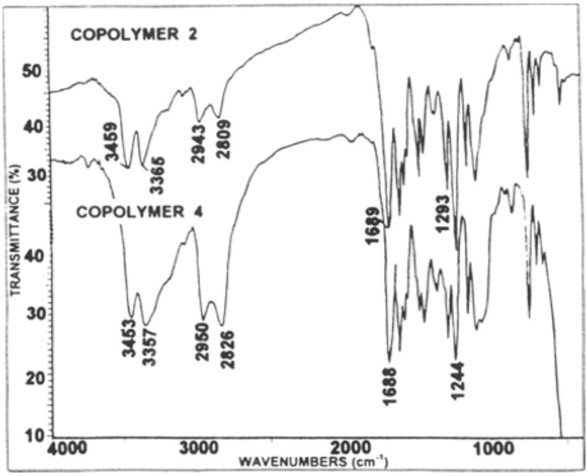


Fig. 1. FT-IR spectra of the copolymers **2** and **4**.

^{13}C-NMR spectroscopy. The ^{13}C-NMR spectra of the copolymers are very simple (see Figure 2). The only carbonyl signal from the copolymer appears at $\delta = 167$ ppm. The signal at $\delta = 162.2$ ppm is attributed to the carbonyl carbon from DMF (solvent).

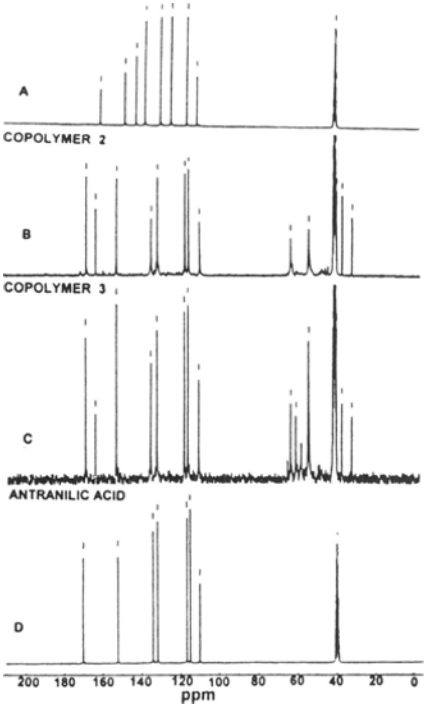


Fig. 2. Comparative ^{13}C-NMR spectra of (A) electrophilic monomer, (B) HEEI/ISA copolymer, sample 2, (C) HEEI/ISA copolymer, sample 3, and (D) antranilic acid.

In the aromatic region, the following signals are observed (in ppm): the quaternary carbons C-NH$_2$ and $\underline{C}$-CO (109.050 and 151.289), 4 signals of the Csp^2 aromatics linked to hydrogen at δ = 133.731 (133.817); 130.559 (131.295) 116.415 (116.439), and 114.557 (114.710). In brackets are included the chemical shifts of the antranilic acid. In the aliphatic region, for copolymers richest in ISA units (see Fig. 2, spectrum B), only two singlets of broad base appear (δ = 62.086 ppm and 52.788 ppm) but do not show the three signals present in the poly(HEEI) (δ = 65.02 ppm; 57.66 ppm and 53.17 ppm), indicating the absence of homodiad of HEEI.

For copolymer **4**, the signal numbers of aliphatic carbons (in ppm) increase in the copolymer richest in HEEI units (δ = 62.133; 53.411, 56.607 and 52.838). The assignment was done according to the chemical shifts of homopolymers, low molecular weight compounds (24), and DEPT-135 spectra.

^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra show at downfield (δ = 8.2 ppm - 6.2 ppm) aromatic proton signals very similar to those observed for antranilic acid (see Figure 3).

In the aliphatic region the signal coming from the incorporated HEEI units was observed. Both ^{1}H and ^{13}C-NMR spectra showed signals corresponding to DMF and DMSO-d$_6$ used as polymerization solvent and lock, respectively.

The copolymer composition was determined from the area of $H_{aromatic}/H_{aliphatic}$.

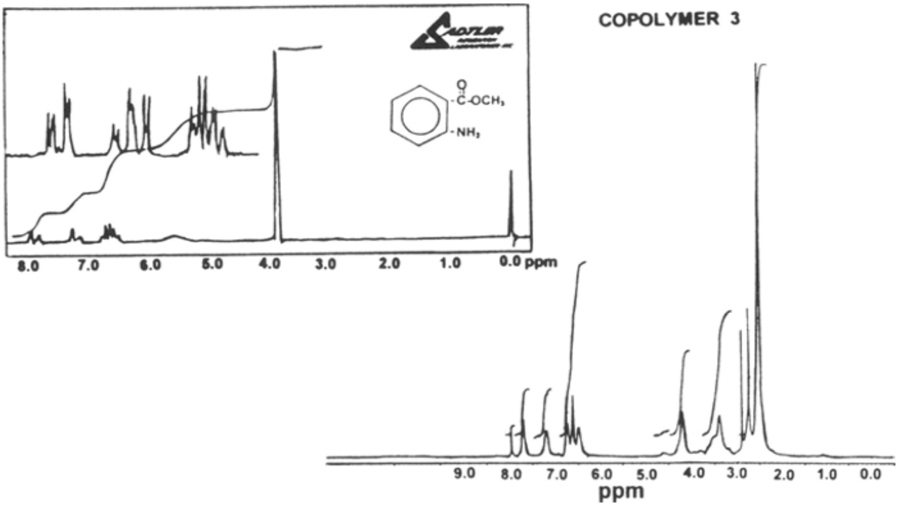
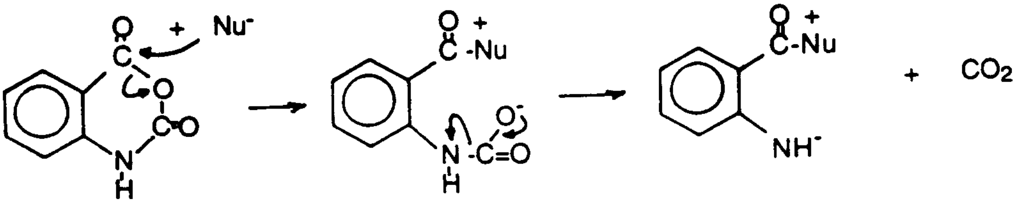


Fig. 3. ^{1}H-NMR spectra of HEEI/ISA copolymer, sample 3 and ortho-methylaminobenzoate or methylantranilate (Sadtler, spectrum Nº 1200 M)

SPECTROSCOPIC AND STRUCTURAL ANALYSIS

FT-IR and ^{1}H-NMR spectra indicate that the isatoic anhydride ring is opened during the copolymerization. From ^{1}H and ^{13}C-NMR spectra it is concluded that the incorporation of ISA units occurs with the $CO_{2(g)}$ evolution. The yielding of the antranilic derivative may be explained as follows: the opening of the isatoic anhydride ring by nucleophilic attack yields a carbamic acid derivative which is decarboxylated to antranilic acid:



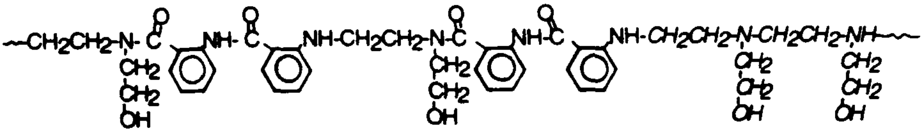
The arylamidide ion is stabilized by conjugation.

The ^{13}C-NMR spectra show only one signal for the carbonyl group. All the possible structures would give two different carbonyl groups (amide and ester).

According to the copolymer composition data (see Table 1) copolymer **1** has incorporated, in average, two ISA units for one HEEI unit. This allows to analyze the following probable copolymer structures.

Structure **A** is basically formed by diads of ISA with HEEI units. Thus, all the ISA units belong to the backbone.

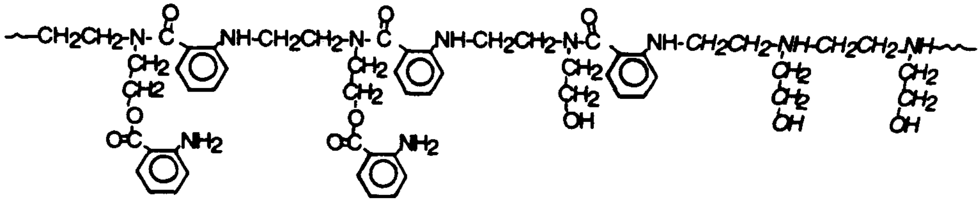
A



For the structure of copolymers **1** and **2** (rich in ISA units) the homodiads of HEEI would not be present, which is in agreement with the absence of the aliphatic carbon signals of HEEI diads in the ^{13}C-NMR spectra. The presence of the HEEI diads in the copolymer **4** is corroborated by ^{13}C-NMR spectroscopy and would explain the richest composition in HEEI units. This structure presents two types of carbonyl groups of different amides: aliphatic-aromatic and aromatic-aromatic. The chemical shift of both carbonyl carbons are by chance the same. But structure **A** is not in agreement with the expected FT-IR spectra. The intensive OH band in the region of 3300 cm^{-1} is absent in the FT-IR spectra of copolymers richer in ISA units. Moreover, structure **A** cannot explain the double signal of amine between 3200 and 3500 cm^{-1} because the amine group is not present in the structure.

Structure **B** corresponds to an almost alternating copolymer with esterified CH_2OH groups at the side chain. The ISA units are in both main and side chains. The esterification of the pendant CH_2OH group of HEEI units for copolymers of different anhydrides has been reported previously (17-22). Structure **B** explains the presence of ester bonds and Ar-NH_2 groups observed in the FT-IR spectra. The previous analysis of structure **A** regarding the presence of homodiads only in copolymers rich in HEEI units, is applicable for structure **B** and **C**. Due to a large excess of HEEI in the feed, the formation of homodiads by homopropagation of aziridine ring is postulated. The C=O groups (amide and aromatic esters) would be by chance equivalent.

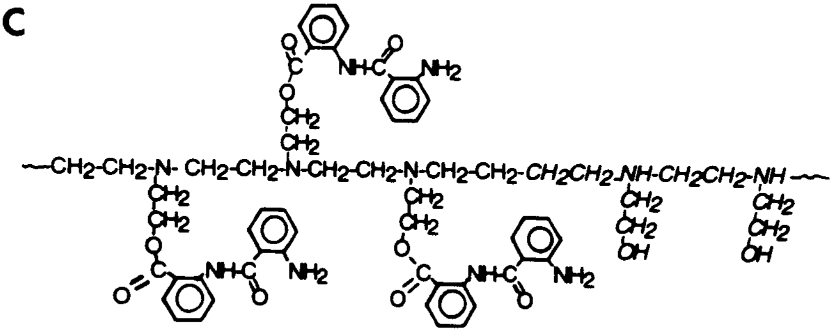
B



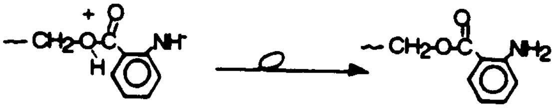
The concentration of HEEI units with free CH_2OH groups in the copolymers **1** and **2** (rich in ISA units) is too small, and increases slowly for the copolymers **3** and **4** which contains the lowest concentration of ISA units (see Table 1). This is correlated for the sharper OH-signal in the FT-IR spectra of copolymers **3** and **4**.

Structure **C** is formed by a main chain with HEEI units and with ISA units placed only in the side chain.

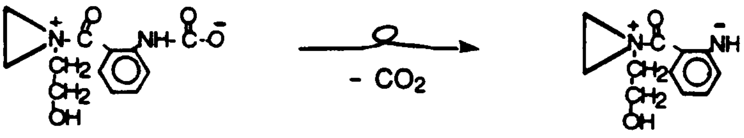
C



This structure shows aromatic ester and diaromatic amide groups whose carbonyl carbons must have the same chemical shift. The structure also shows NH_2 groups but not the OH groups, which is in agreement with the information given by FT-IR spectra. However, it is very difficult for HEEI to homopropagate yielding a backbone of poly(HEEI) in the presence of one ISA. The reaction between HEEI and ISA must produce a "genetic zwitterion" able to propagate. For this reason the incorporation of ISA units is expected on the main chain. Moreover, the attack of an alcohol on ISA would give a zwitterion which would be rearranged to react with a new ISA molecule to produce a diad of ISA units at the side chain:



Other possible structures have been considered but discarded. The "genetic zwitterion" postulated is:



Structure **B** agrees better with the spectroscopic data and the chemical composition.

The thermograms of the HEEI/ISA copolymers are very similar. At 500°C they decompose less than 10%. By increasing the concentration of HEEI units, the thermal stability decreases. The reaction order of thermal decomposition was zero, i.e., the geometry of the sample controls the diffusion of the volatiles at the surface of the sample and their evaporation.

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