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Poly[*N*-(hydroxyethyl)ethyleneimine-*co*-phenyl succinic anhydride]

Synthesis and structure

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Summary

Five copolymers from N-(hydroxyethyl)ethyleneimine as nucleophilic monomer and phenylsuccinic anhydride (PhSAn) as electrophilic monomer, were synthesized according to the spontaneous copolymerization concept. These copolymers were characterized by elemental analysis, FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The copolymer composition determined from the ^{1}H-NMR spectra showed that the copolymers are not alternating. According to all the data, it was suggested a copolymer structure which includes ester and anhydride bonds. The molecular weights determined by vapor pressure osmometry ranged between 5.100 and 6.100 g/mol.

Introduction

Usually, polymerizations require an initiator, catalyst, or high radiation energy. However, it has been informed by several authors (1-11) of the spontaneous copolymerization, which occurs through zwitterion intermediates. It is based on the organic chemistry reactions of nucleophilic and electrophilic reagents. In this copolymerization an electrophilic monomer (ME) reacts spontaneously with other nucleophilic monomer (MN) to yield alternating or statistical copolymers. The interaction between these two monomers produces an intermediate species $^+$MNME- called "genetic zwitterion" which is the key in both initiation and propagation reactions.

$$\mathbf{MN} + \mathbf{ME} \rightarrow {}^{+}\mathbf{MNME}^{-} \quad (1)$$

$$\mathbf{1} + \mathbf{1} \rightarrow {}^{+}\mathbf{MNMEMNME}^{-}$$

In general:

$$^{+}\mathbf{MN(MEMN)}_{m}\mathbf{ME}^{-} + \mathbf{n}\,^{+}\mathbf{MNME}^{-} \rightarrow {}^{+}\mathbf{MN(MEMN)}_{m+n+1}\,\mathbf{ME}^{-} \qquad (\mathbf{m} > \mathbf{1})$$

According to this copolymerization concept, we have previously reported the synthesis of copolymers from nucleophilic monomers (oxazolines, aziridines) and electrophilic monomers (anhydrides, lactones, acrylic acid, acrylic acid derivatives) (3-11). The aim of this paper is the synthesis of new functional copolymer under different experimental conditions from N-(hydroxyethyl)ethyleneimine (MN) and phenylsuccinic anhydride (ME). These copolymers contain different groups such as amino, hydroxyl, and carboxylic.

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Experimental Part

Reagents: N-(hydroxyethyl)ethyleneimine, HEEI (Fluka) was purified by distillation. Phenylsuccinic anhydride, PhSAn (Merck, 98%) was used without further purification. The solvents were purified according to the published methods (12).

Copolymerization: General procedure: In a polymerization glass, a mixture of comonomers with different mol ratios was prepared keeping constant the total mol number (0.04). 10 mL of acetonitrile were added under N_2. The copolymerization reaction was kept for the time and temperature desired. After that, it was precipitated in diethyl ether, the copolymers separated by centrifugation and purified by reprecipitation in DMSO/diethyl ether. They were dried to constant weight.

Measurements: The FT-IR spectra were recorded on a Magna Nicolet 550 spectrophotometer. The ^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker AC-250 P spectrometer at 29°C using TMS as internal standard. The molecular weights were determined in DMSO at 85°C by a Knauer pressure osmometer.

Results and Discussion

Five copolymerizations among HEEI and PhSAn varying the feed mole ratio but keeping constant the total mol number, were carried out. The copolymerization is lightly exothermic. The copolymers are yellowish hygroscopic solids. The conditions and some results are summarized in Table 1.

Table 1. Conditions and results of the copolymerization between HEEI and PhSAn at 30°C for 48h.

Copolymer N°	Monomer ratio in the feed HEEI/ PhSAn	Copolymer composition HEEI/ PhSAn[a]	Yield (%)	Molecular Weight $\overline{Mn} \times 10^{-3}$ [b]
1	3.0 : 1.0	1.77 : 1.0	43	5.1
2	1.5 : 1.0	1,21 : 1.0	49	5.2
3	1.0 : 1.0	0.50 : 1.0	51	5.5
4	0.67 : 1.0	048 : 1.0	33	5.8
5	0.33 : 1.0	0.32 : 1.0	2.6	6.1

[a] Obtained from ^{1}H-NMR spectra

[b] Determined by vapor pressure osmometry at 85°C in DMSO.

The copolymerization yields were low, the highest yield was 51%, being similar to those obtained for the copolymers from HEEI and succinic anhydride (7). The molecular weights ranged between 5100 and 6100 increasing as the incorporation of PhSAn moieties was increased. The copolymer composition depended on the feed monomer ratio.

The FT-IR spectra showed, among other absorption bands, typical absorptions for ν(OH) at approx. 3400 cm^{-1}, ν(C-H) aromatic at approx. 3021 cm^{-1}, and the stretching absorption band of carbonyl ester at 1732 cm^{-1} (see Figure 1). This figure shows that the intensity of the broad absorption ranging between 3600 and 3200 cm^{-1} decreases as the content of PhSAn moiety increases, while the intensity of the absorption band at 1732 cm^{-1} is increased. This evidence allows us to postulate a partial esterification of the hydroxyl groups coming from HEEI by increasing the content of PhSAn in the copolymer.

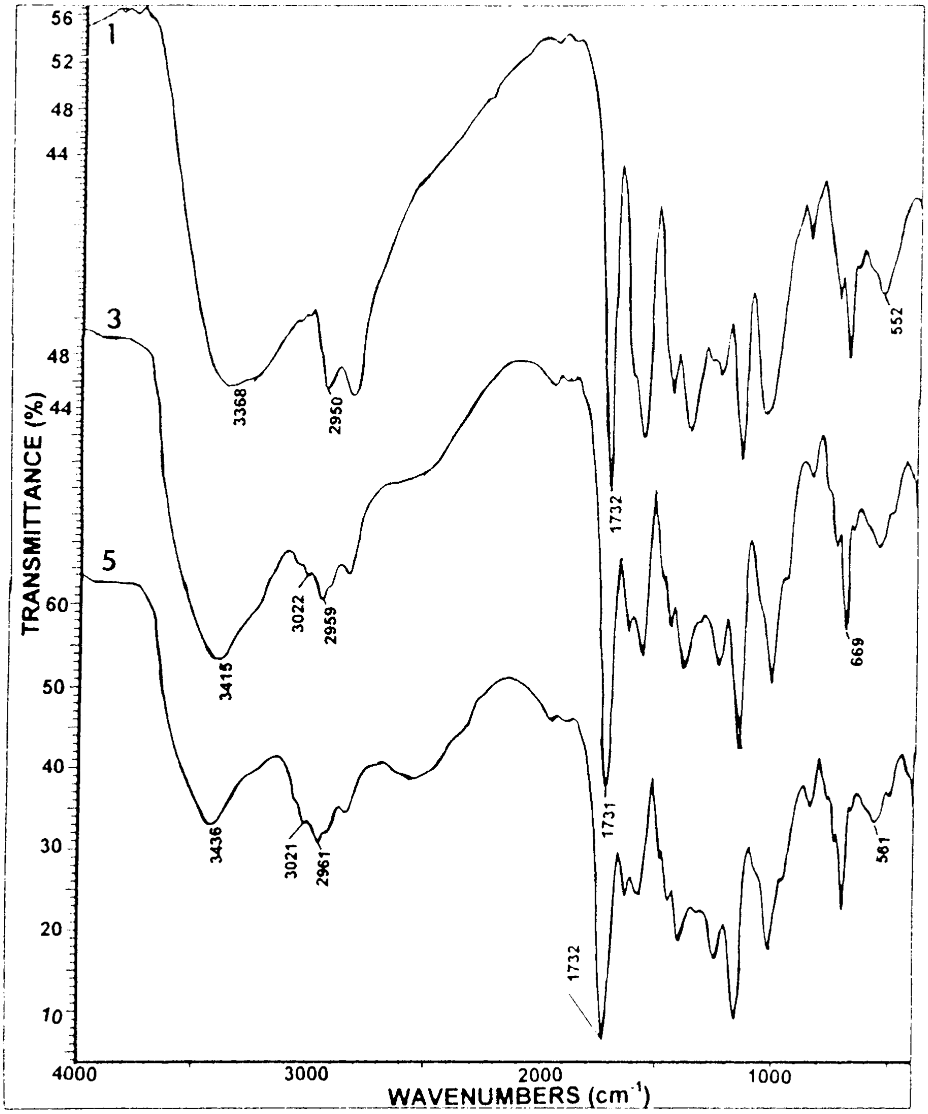


Figure 1. FT-IR spectra of copolymers HEEI/PhSAn samples **1, 3** and **5.**

The ^{1}H-NMR spectra allow to determine the copolymer composition by using as reference the signal corresponding to the aromatic protons (7.3 ppm) (see Table 1 and Figure 2A). The experimental areas of the diasterotopic protons are informed in Table 2.

Table 2. Experimental proton areas obtained from ^{1}H-NMR of HEEI/PhSAn copolymers at different chemical shifts.

Copolymer N°	Signal at 7.3 ppm C-H aromatic	Signal at 4.2 ppm $COOCH_2$ + C_6H_5-CH-COO	Signal at 3.4 ppm CH_2-N-CO + N-CH_2	Signal at 2.9 - 3.3 ppm CH_2COO + N-CH_2
1	7.0	2.80	5.1	16.20
2	10.2	6.2	3.41	16.35
3	18.95	7.9	0.9	17.80
4	17.65	8.12	0.7	15.35
5	18.95	7.7	0.4	13.25

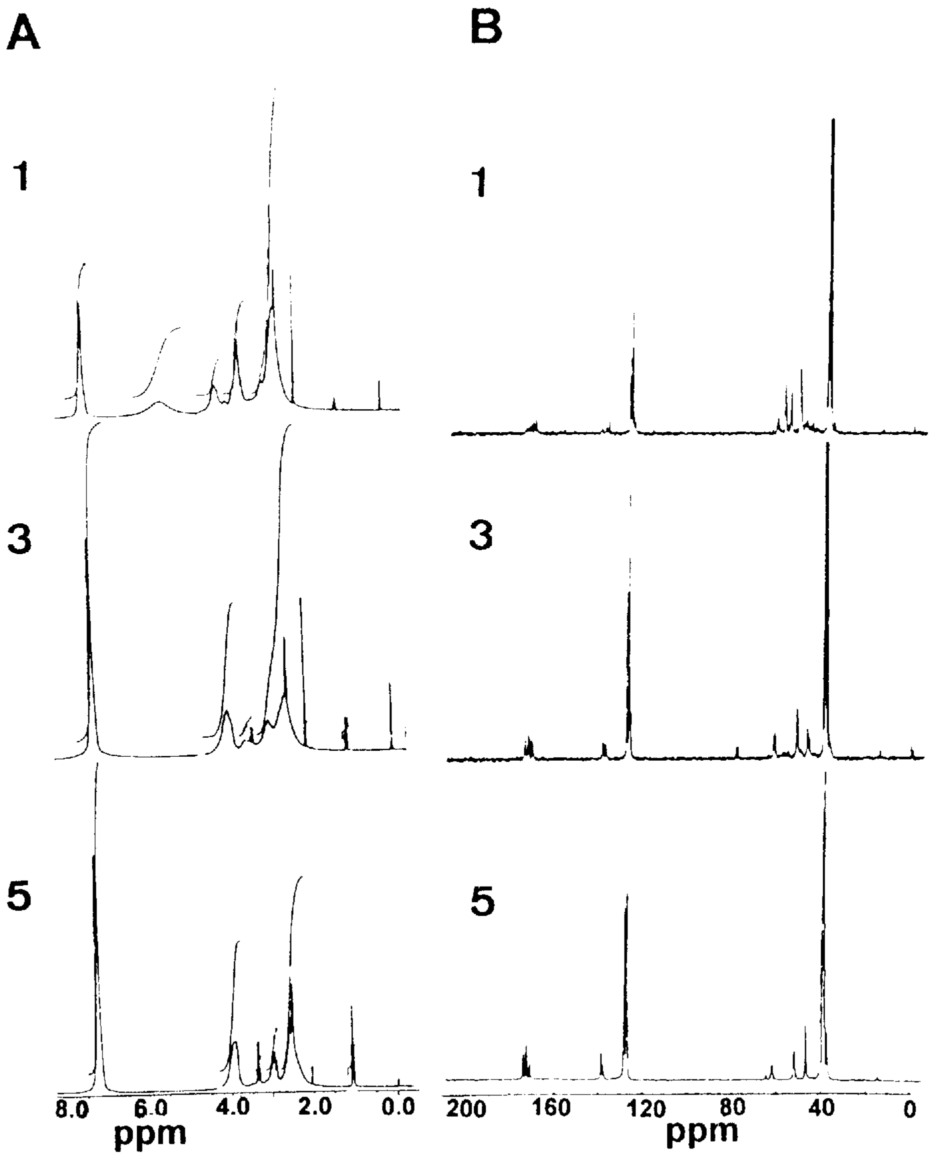
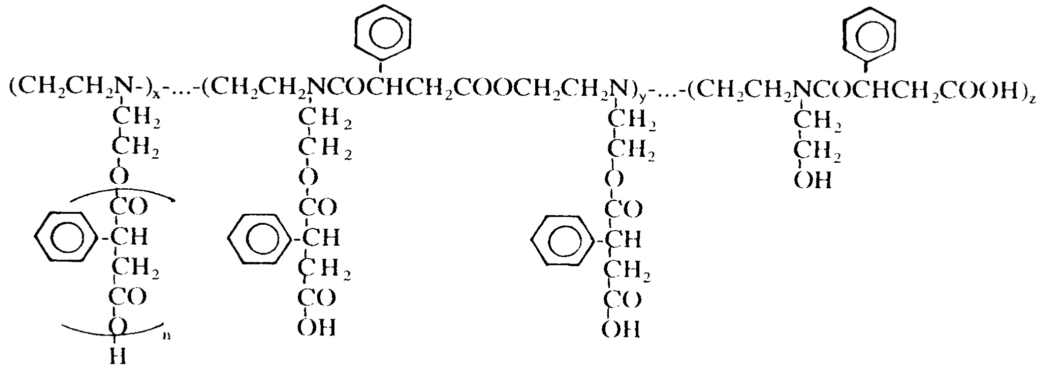


Figure 2. A) ^{1}H-NMR spectra of copolymers HEEI/PhSAn samples **1**, **3** and **5** (250 MHz, room temperature, DMSO-d_6, TMS). B) ^{13}C-NMR spectra of copolymers HEEI/PhSAn samples **1, 3** and **5** (room temperature, DMSO-d_6, TMS).

The copolymer structure A is suggested according to the copolymer composition, spectroscopic data, and experimental proton areas :

STRUCTURE A



Considering this general structure, the concentration of the different basic units (**X_o** to **X_4**, **Y**, and **Z**) in the copolymers was determined (see Table 3).

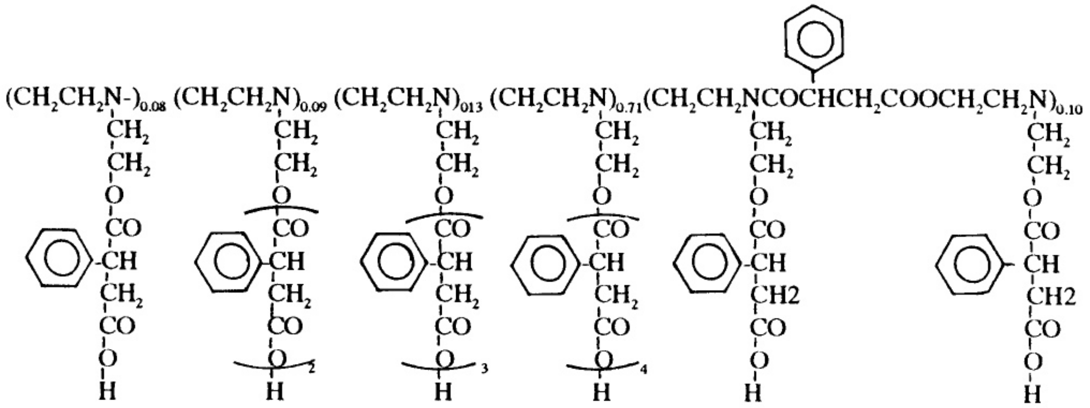
Table 3. Concentration of the basic units in the copolymers.

N°	X_n					Y	Z	Copolymer composition HEEI/PhSAn	
	0	1	2	3	4			Calculated*	Experimental
1	1.08	0.92	0	0	0	0	0.48	1.77 : 1.00	1.77 : 1.00
2	0.87	0.78	0	0	0	0.40	0	1.22 : 1.00	1.21: 1.00
3	0	0.35	0.45	0.0	0	0.25	0	0.50 : 1.00	0.50 : 1.00
4	0	0.28	0.33	0.62	0	0.20	0	0.48 : 1.00	0.48 : 1.00
5	0	0.08	0.09	0.13	0.71	0.10	0	0.32 : 1.00	0.32 : 1.00

*)According to the equation : ($X_o + X_1 + X_2 + X_3 + X_4 + 2Y + Z$)/($X_1 + 2X_2 + 3X_3 + 4X_4 + 3Y + Z$)

The before mentioned equation allows to calculate the composition of each copolymer based on the concentration of the basic units given in Table 3. There is a very good concordance between the experimental and the calculated values. In copolymer **1**, 65% of PhSAn is incorporated to the side chains and the esterifying hydroxyl groups of HEEI. The remaining PhSAn units form part of the backbone. Due to that copolymer **1** is richer in HEEI units, a high concentration of free CH_2OH groups remains (see **X_o** in Table 3). Copolymer **2** shows free CH_2OH and some PhSAn units incorporated to the main chain. Copolymers **3** and **4** were similar without free CH_2OH (see **X_o** in Table 3). This was corroborated by the almost disappearance of the proton signal at 3.4 ppm attributed to CH_2OH and CH_2CON- (see Figure 2A). It was also observed that the basic unit **Y** decreased, due to that PhSAn was preferentially incorporated to the side chain through the anhydride bonds. It was corroborated by FT-IR deconvolution technique (see **X_2** and **X_3** in Table 3). Copolymer **5** (HEEI/PhSAn = 0.32/1.00) was constituted basically by a main chain of HEEI units where all the CH_2OH side groups were esterified, forming short anhydride chains (see structure B). The formation of basic units X_4 was directly related with the decrease of the basic units, **X_1**, **X_2**, and **X_3**. ^{13}C-NMR spectra of these copolymers showed that the copolymer composition depends on the monomer feed ratio. The aliphatic carbons for the copolymers HEEI/PhSAn **1**, **3** and **5** show chemical shifts at low field due to that all the sp^3 carbons were linked to the heteroatoms (see Fig. 2B). In figure 2B a decrease of the number of signals is observed as the copolymers are richer in PhSAn units. This is in agreement with the simplification of the number of methylene carbons in the copolymer structure. Structure B is suggested for copolymer **5:**

STRUCTURE B



In this structure, the presence of the methylene carbons $N\underline{C}H_2\underline{C}H_2OH$ which absorb at 56.38 ppm (NCH_2) and at 58.99 ppm (CH_2OH) respectively, is not observed, being present in the spectrum of copolymer **1** (see Figure 2B). Moreover, this structure shows a high regularity in the methylene carbons of the HEEI units in the first 4 basic units ($\mathbf{X_1}$; $\mathbf{X_2}$**;** $\mathbf{X_3}$ and $\mathbf{X_4}$), observing only two types of methylene carbons: $\underline{C}H_2OCO$ which absorbs at 62.30 ppm and the CH_2N at 52.30 ppm. The tertiary carbons (C_6H_5-$\underline{C}H$) present in this structure absorb at 47.19 ppm (corroborated by DEPT 135) and the methylene carbons $\underline{C}H_2COO$ at 37.78 ppm, corresponding to PhSAn units. The methylene carbons $(\underline{C}H_2)_2NCO$ of the basis unit **Y** absorb at approx. 43 ppm, appearing as a broad signal attributed to the character of double bond of the amide bond. In Figure 2B, an important increase of the intensity of the signal at 47.19 ppm (C_6H_5-$\underline{C}H$) when PhSAn units are increased in the copolymers, was observed.

A simplification of the carbonyl carbon signals and the aromatic carbons was observed in the copolymers HEEI/PhSAn (see Figure 2B, copolymer **5**).

The assignment of the signals was carried out considering the chemical shifts of the poly(HEEI) and the low molecular weight analogue compounds[13)].

To verify the suggested general structure **A**, the areas which would rise the different protons present in the copolymer structure were calculated according to the values given in Table 3. The experimental and calculated area values are summarized in Table 4.

Table 4. Comparison of the calculated and experimental ( ) proton areas of the copolymers HEEI/PhSAn at different chemical shifts.

Copolymer N°	Signal at 7.3 ppm C-H aromatic	Signal at 4.2 ppm $COOCH_2$ + C_6H_5-CH-COO	Signal at 3.4 ppm CH_2-N-CO + N-CH_2	Signal at 2.9 - 3.3 ppm CH_2COO + N-CH_2
1	7.0 (7.0)	2.8 (2.8)	5.1 (5.5.)	16.24 (16.20)
2	10.2 (10.2)	6.1 (6.2)	3.42 (3.41)	16.50 (16.35)
3	18.9 (18.95)	7,85 (7.9)	1.0 (0.9)	17.0 (17.80)
4	17.0 (17.65)	7.1 (8.12)	0.8 (0.7)	14.03 (15.35)
5	18.95 (18.95)	6.41 (7.7)	0.4 (0.4)	14.21 (13.25)

From Table 4 it is concluded that the model of the structure proposed (structure A) describes adequately the structure of the HEEI/PhSAn copolymers.

Acknowledgments

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