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Polymerization by phase transfer catalysis

21. Synthesis of poly(amido-carbonate)s and poly(amido-thiocarbonate)s

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SUMMARY

Poly(amido-carbonate)s and poly(amido-thiocarbonate)s derived from 1,6-bis(4-hydroxyphenyl-carbamoyl)-hexamethylene **I** and 1,4-bis(4-hydroxyphenyl-carbamoyl)-phenylene **II**, and phosgene or thiophosgene, have been synthesized by a phase transfer catalysis process, which was ineffective for polymers derived from monomer **I** because the best results were obtained without catalyst, but was effective for those derived from monomer **II** obtaining higher yields when the catalysts were used. The ineffectivity was attributed to a hydrolytic process of the polymeric chains in the reaction media.

INTRODUCTION

Phase transfer catalysis has been widely used in polymer synthesis, producing a great number of polymers such as polyethers [1], polyesters [2], polycarbonates [3], polythiocarbonates [4], and others [5].

However, there are no works in which phase transfer catalysis was applied to polymer synthesis containing two functional groups, except those that describe the synthesis of poly(ester-carbonate)s and poly(ester-thiocarbonate)s derived from diphenols containing the ester group in the main chain [6-7], and in the side chain [8]. The synthesis of a poly(amido-carbonate) from a diphenol formed by isophthalic acid dichloride and m-phenylene diamine has been described [9]. However, in this synthesis phase transfer conditions, were not used.

In this work, as a continuation of our work of polymer syntheses using phase transfer catalysis [8], we describe the synthesis of poly(amido-carbonates) and poly(amido-thiocarbonates) derived from diphenols, containing the amide group in the main chain, using several phase transfer catalysts and evaluating the efficiency of the process through yields and inherent viscosities.

EXPERIMENTAL PART

Reagents and solvents (from Aldrich or Riedel de Haen) were used without purification. The following catalysts (from Fluka) were used: tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), methyltrioctylammonium chloride (ALIQUAT 336™),

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hexadecyltributylphosphonium bromide, and benzyltriphenylphosphonium chloride (BTPPC).

The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^{1}H NMR on a 200 MHz instrument (Bruker AC-200), using DMSO-d_6 as solvent and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischoff [10] type dilution viscosimeter at 25°C.

Monomers, 1,6-bis(4-hydroxyphenyl-carbamoyl)-hexamethylene **I** and 1,4-bis(4-hydroxyphenyl-carbamoyl)-phenylene **II**, were synthesized according to the following procedure: 8.3 g of 4-acetyl-benzoic acid were mixed with 38 ml of thionyl chloride and three drops of N,N-dimethyl-formamide, and refluxed for 1.5 hours. Then the excess of thionyl chloride was distilled and the solid recrystallized from n-hexane, obtaining 4-acetyl-benzoyl chloride (yield 66%, m.p. 29°C).

1,6-Hexamethylene-diamine or 1,4-phenylene-diamine (2.5 mmol) were dissolved in 20 ml of THF at 0°C and then 50 mmol of 4-acetyl-benzoyl chloride were added in 10 ml of THF. At the same time, 5 mmol of triethylamine in 2 ml of THF were added drop by drop, and then 2.5 ml of pyridine. The solid diamide derived from 1,6-hexamethylene-diamine was recrystallized from ethanol, and that derived from 1,4-phenylene-diamine was used without purification.

One mmol of the diamide obtained previously was dissolved in 2.5 ml of NaOH 1N and the mixture refluxed for 45 minutes. After this time, the mixture was neutralized with acetic acid. The solid, monomers **I** and **II**, were filtered, washed with water, recrystallized from an ethanol/water mixture, and characterized by IR and ^{1}H and ^{13}C NMR spectroscopy.

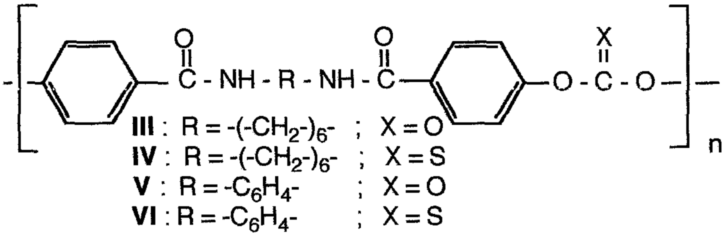
1,6-bis(4-hydroxyphenyl-carbamoyl)-hexamethylene **I**. M.p. 109-111 °C. IR (cm^{-1}) (KBr): 3400 (OH); 3300 (NH); 2930, 2850 (CH_2); 1620 (C=O); 1600, 1500 (C=C); 840 (p-subst.). ^{1}H NMR (δ) (ppm) (DMSO-d_6): 1.2 (m,4H,CH_2); 1.6 (m,4H,CH_2); 3.0 (m,4H,CH_2); 6.8 (d,4H,arom); 7.8 (d,4H,arom); 8.2 (t,2H,NH); 10.0 (s,2H,OH). ^{13}C NMR (δ) (ppm) (DMSO-d_6): 30 (CH_2-CH_2-$\underline{C}H_2$), 33 (CH_2-$\underline{C}H_2$-CH_2), 43 (CH_2-NH), 118 (C arom), 129 (C=O), 132 (C arom), 164 ($\underline{C}$ arom - C=O), 170 (C arom - OH).

1,4-bis(4-hydroxyphenyl-carbamoyl)-phenylene **II**. M.p. >260 °C. IR (cm^{-1}) (KBr): 3380 (OH); 3300 (NH); 1640 (C=O); 1600, 1500 (C=C); 840 (p-subst.). ^{1}H NMR (δ) (ppm) (DMSO-d_6): 7.0 (d,4H,arom); 7.8 (s,4H,arom); 8.0 (d,4H,arom); 10.0 (s,2H,OH); 10.2 (s,2H,NH). ^{13}C NMR (δ) (ppm) (DMSO-d_6): 120 (C arom), 125 (C arom), 130 (C arom), 134 (C=O), 140 ($\underline{C}$ arom - C=O), 165 ($\underline{C}$ arom - NH), 170 (C arom - OH).

Polymers were synthesized according to the following general procedure: 5 mmol of the monomer and 0.125 mmol of the catalyst were dissolved in 10 ml of NaOH 1N and 10 ml of water; then 20 ml of CH_2Cl_2 were added. Then 5 mmol of phosgene (from a toluene solution) or thiophosgene were added in 15 ml of CH_2Cl_2 and the mixture stirred for 60 minutes. After this time the mixture was poured into methanol and the polymer was filtered, washed with methanol, dried until constant weight, and characterized by IR spectroscopy.

RESULTS AND DISCUSSION

Poly(amido-carbonate)s and poly(amido-thiocarbonate)s with the following structures:



III : R = -(-CH_2-)$_6$- ; X = O
IV : R = -(-CH_2-)$_6$- ; X = S
V : R = -C_6H_4- ; X = O
VI : R = -C_6H_4- ; X = S

were synthesized from the diphenols **I** and **II** and phosgene or thiophosgene under phase transfer conditions in CH_2Cl_2 as solvent at 20°C, and characterized by IR spectroscopy. The structures were in accord with those proposed. In all polymers it was possible to see the hide of the OH band. Poly(amido-carbonate)s showed an absorption band at 1750 cm^{-1} corresponding to the C=O of the carbonate group, and poly(amido-thiocarbonate)s at 1200 cm^{-1}corresponding to the C=S group; also, it was possible to see at 3240 cm^{-1} the band corresponding to the NH group, and at 1640 cm^{-1} that corresponding to the C=O of the amide group. Due to the low solubility of the polymers, it was not possible to obtain NMR spectra. The reaction time was 60 minutes which was determined by the stability of the monomers in the reaction media; after this time both monomers were recovered quantitatively when the reaction was carried out without catalyst and with phosgene or thiophosgene

In the syntheses only the nature of the catalyst was considered; reaction time, catalyst, base concentration, and temperature remained constant.

Table I shows the results obtained for poly(amido-carbonate) **III** and poly(amido-thiocarbonate) **IV** derived from monomer **I**. The results obtained for the synthesis of the poly(amido-carbonate) **III** showed that phase transfer was ineffective because the yields and η_{inh}'s obtained with catalysts were lower than those obtained without catalyst. Probably a hydrolytic process occurs which affects the amido group, which is strongly influenced by the catalysts, and not by the reaction medium because the monomer was stable in the medium. Poly(amido-thiocarbonate) **IV** was insoluble and the η_{inh} could not be determined. However, the yields are similar, they decrease when catalysts are used.

Table I.- Yields and inherent viscosities of poly(amido-carbonate) **III** and poly(amido-thiocarbonate) **IV**

	Poly(amido-carbonate) **III**		Poly(amido-thiocarbonate) **IV**
Catalyst	Yield. (%)	η^*	Yield (%)
-----	90	0.31	94
TBAB	31	0.18	54
HDTMAB	88	0.19	6
ALIQUAT	50	0.08	19
HDTBPB	36	0.12	52
BTPPC	54	0.16	18

* inherent viscosities, in phenol/1,1,2,2-tetrachloroethane 3/2, at 25°C, c = 0.5 g/dl.

Table II shows the results obtained for poly(amido-carbonate) **V** and poly(amido-thiocarbonate) **VI**. Both polymers were insoluble and phase transfer could be evaluated only by the yields. For the poly(amido-carbonate) **V** the yields were higher than those obtained without catalyst, and for the poly(amido-thiocarbonate) **VI** with three catalysts the yields were almost quantitative. It can be observed that the polymers are obtained principally by interphase polycondensation; in spite of this, it is possible to observe that phase transfer was more efficient for polymers **III** and **IV**. The insolubility of the polymers did not allow us to obtain further results.

Table II.- Yields of poly(amido-carbonate) **V** and poly(amido-thiocarbonate) **VI**.

	poly(amido-carbonate) **V**	poly(amido-thiocarbonate) **VI**
Catalyst	Yield (%)	Yield (%)
------	52	81
TBAB	72	66
HDTMAB	57	98
ALIQUAT	83	98
HDTBPB	53	54
BTPPC	78	98

Finally we can conclude that these poly(amido-carbonate)s and poly(amido-thiocarbonate)s are obtained principally by an interphase polycondensation process and the use of phase transfer catalysts does not seem to have a great influence on the increase of the yields and η_{inh}. On the other hand, there is probably also a hydrolytic process which affects both the monomer and even more the polymeric chains, being more reactive those polymers derived from monomer **I**, which arise from an aliphatic diamine.

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