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Polymerization by phase transfer catalysis

22. Synthesis of poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from diphenols with the amide group in the side chain

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SUMMARY

Poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from the diphenol-amides N-(2,6-dichloro-4-nitrophenyl)-2,2-bis(hydroxyphenyl)-propylamide (**I**), N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(hydroxyphenyl)-butylamide (**II**), and N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(hydroxyphenyl)-pentylamide (**III**), and phosgene or thiophosgene, have been synthesized under phase transfer conditions using several quaternary ammonium salts as phase transfer catalysts. Benzyltriethylammonium chloride (BTEAC) was effective in practically all cases due the hydrophilicity of this catalysts.

INTRODUCTION

Polycarbonates and polythiocarbonates are widely known types of polymers, the polycarbonate being derived from bisphenol A, a commercial product [1-2]. However, there are only few works in which the carbonate or thiocarbonate function is combined with other functional groups in the repeating unit without forming a copolymer. An example is the synthesis of poly(amide-carbonate)s with both groups in the repeat unit, which results in termostable polymers [3].

We have focussed our attention to the synthesis of polymers containing two functional groups in the repeat unit, and have described the synthesis of poly(ester-carbonate)s and poly(ester-thiocarbonate)s containing the ester group in the main chain [4-5] or in the side chain [6]. Also we have described the synthesis of poly(amide-carbonate)s and poly(amide-thiocarbonate)s in which the amide group is in the main chain [7].

In these works we have used phase transfer catalysis (PTC) by using several quaternary ammonium salts. This technique is a suitable method for the synthesis of these polymers, especially for those in which the ester group is in the side chain [6]. For polymers in wich the ester or amide group is in the main chain, the process is less effective, due principally to the insolubility of the polymer in the reaction media [4-5, 7].

Continuing our works in the aplication of phase transfer catalysis in particular to the synthesis of polymers that contain two functional groups in the repeat

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unit, in this work we describe the synthesis of poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from diphenols containg the amide group in the side chain. The effect of several phase transfer catalysts on the yields and inherent viscosities of the obtained polymers is also analyzed.

EXPERIMENTAL PART

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

IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^{1}H and ^{13}C NMR spectra 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- Bischof [8] type dilution viscosimeter at 25°C.

Monomers

The diphenol-acids 2,2-bis(4-hydroxyphenyl)-propanoic, 3,3-bis(4-hydroxyphenyl)-butanoic were synthesized according to a procedure described previously [6]. 4,4-bis(4-hydroxyphenyl)-pentanoic acid was a commercial product.

The diphenol-amides **I**, **II**, and **III**, were synthesized according to the following general procedure: 0.244 mol of the diphenol acid was mixed with 30 mL of $SOCl_2$ and the mixture refluxed for two hours. After this time, to the homogeneous mixture, 6 g (0.29 mol) of 2,2-dichloro-4-nitroaniline were added, and heating was continued for six hours. After this time, the $SOCl_2$ was distilled, and to the brown oil, a saturated $NaHCO_3$ solution was added. The solid was filtered and washed with $NaHCO_3$ solution. Then, the solid was dissolved in a NaOH solution by removing the unreacted aniline, and then precipited by HCl addition. This procedure was repeated, obtaining a light brown solid corresponding to the diphenol-amide. The three diphenol-amides decompose before melting.

I: IR (cm^{-1}) (KBr): 3300 (OH); 3020 (C-H); 1670 (C=O); 1660, 1550 (C=C); 1540, 1250 (NH). ^{1}H NMR (δ) (ppm) (DMSO-d_6): 2.0 (s,3H,CH_3); 6.8 (d,4H,arom.); 7.2 (d,4H,arom.); 8.4 (s,2H,arom.). ^{13}H NMR (δ) (ppm) (DMSO-d_6): 27.4 (CH_3); 55.2 (C quat.); 114, 115, 123, 129, 130, 133, 135, 155 (C arom.); 173.9 (C=O).

II: IR (cm^{-1}) (KBr): 3370 (OH); 3020 (C-H); 2970 (CH_2, CH_3); 1660 (C=O); 1600, 1500 (C=C); 1540 (NH). ^{1}H NMR (δ) (ppm) (DMSO-d_6): 1.9 (s,3H,CH_3); 3.2 (s,2H,CH_2); 6.7 (d,4H,arom.); 7.1 (d,4H,arom.); 8.3 (s,2H,arom.). ^{13}H NMR (δ) (ppm) (DMSO-d_6): 28.2 (CH_3); 43.8 (C quat.); 46.8 (CH_2); 114, 123, 127, 133, 139, 141, 144, 154 (C arom.); 167 (C=O).

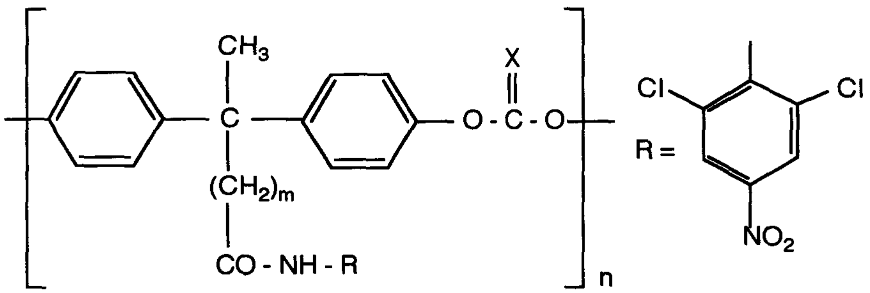
III: IR (cm^{-1}) (KBr): 3353 (OH); 3020 (C-H); 2860 (CH_3, CH_2); 1673 (C=O); 1600, 1500 (C=C). ^1H NMR (δ) (ppm) (DMSO-d_6): 1.62 (s,3H,CH_3); 2.4 (t,2H,CH_2); 2.6 (t,2H,CH_2); 6.8 (d,4H,arom.); 7.2 (d,4H,arom.); 8.3 (s,2H,arom.). ^{13}H NMR (δ) (ppm) (DMSO-d_6): 28.7 (CH_3); 33.2 (C-$\underline{C}H_2$-CH_2), 38.5 (CH_2-$\underline{C}H_2$-C=O); 45.6 (C quat.); 116, 124, 129, 135, 140, 141, 147, 156 (C arom.); 173.4 (C=O).

Polymer synthesis

Poly(amide-carbonate)s and poly(amide-thiocarbonate)s were synthesized according to the following general procedure: in a 250 mL flask 1 g of the diphenol-amide and the catalyst (5% mol) were dissolved in 20 mL of 0.25 M NaOH at 20°C. Then, 20 mL of CH_2Cl_2 and the phosgene (**a**) or thiophosgene (**b**) were added, and the mixture stirred for one hour. After this time the mixture was poured into 500 mL of methanol. The polymer was filtered, washed with methanol and dried until constant weight, and characterized.

RESULTS AND DISCUSSION

Poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from the diphenol-amides **I**, **II**, and **III**, and phosgene (a) or thiophosgene (b), with the following structure:



m = 0 (**I**), 1 (**II**), 2 (**III**) X = O (**a**); S (**b**)

were synthesized under phase transfer conditions in CH_2Cl_2 as solvent at 20°C, and characterized by IR spectroscopy and elemental analysis. The structures were in accord with those proposed. In all poly(amide-carbonate)s and poly(amide-thiocarbonate)s it was possible to see the disappearance of the OH band. Poly(amide-carbonate)s showed a new band at 1770-1775 cm^{-1} corresponding to the C=O of the carbonate group, and poly(amide-thiocarbonate)s showed an increase of the intensity of the band 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 1660-1670 cm^{-1} that corresponding to the C=O of the amide group. Due the low solubility of the poly(amide-carbonate)s and poly(amide-thiocarbonate)s, it was not possible to obtain the NMR spectra. The reaction time was 60 minutes, determined by evaluating the stability of the monomers in the reaction media by dissolving them in 0.5 N NaOH, mixed with CH_2Cl_2 and the catalyst. At this time monomers were recovered quantitatively.

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

Table I.- Yields and inherent viscosities obtained for Poly(amido-carbonate) **I-a** and Poly(amido-thiocarbonate) **I-b**

polymer	**I** - **a** (X = O)		**I** - **b** (X = S)	
catalyst	%	η_{inh}	%	η_{inh}
---	22	0.37	14	0.48
TBAB	50	0.61	30	0.60
ALIQUAT	47	0.64	29	0.60
BTEAC	55	0.67	34	0.68
HDTMAB	49	0.62	32	0.59

η_{inh}: inherent viscosity, in m-cresol at 25°C (c = 0.3 g/dl)

Table I shows the yields and η_{inh} obtained for poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from **I**. Without catalysts low yields and η_{inh} values were obtained, due to interphase polycondensation between the diphenolate dissolved in the aqueous phase and the phosgene or thiophosgene dissolved in the organic one.

When the catalysts were used, an increase of the yields and η_{inh} can be observed, showing the efficiency of the phase transfer process. However, we do not observe important differences in yields and η_{inh}. Moreover, a slow increase of these values can be observed when BTEAC was used. This catalyst is hydrophilic and is suitable for transporting lypophilic or highly organic diphenolates [9-10].

These polymers were insoluble in the reaction media and precipited after the beginning of the reaction, which limited the growth of the chain and reduced the posibility of obtaining high molecular weights. For this reason the catalysts do not show great differences in their effect.

Table II shows the results obtained for the poly(amide-carbonate) and poly(amide-thiocarbonate) derived from **II**. For the poly(amide-carbonate), all the catalysts were efficient but the increase of the yields and η_{inh} were very low. Only with ALIQUAT and HDTMAB was there a small increase in the η_{inh} values in contrast with the other results. On the other hand, HDTMAB due to its long chain and three methyl groups bonded to the N central atom, has been decribed as a micellar agent. Micellization is imposible to rule out [9].

Table III shows the results obtained for the poly(amide-carbonate) and poly(amide-thiocarbonate) derived from **III**. The best results for the poly(amide-carbonate) were obtained with the hydrophilic catalyst BTEAC, useful for transporting lypophilic dianions such as this. TBAB was also effective, probably due to the good separation between the anion and cation in the ion pair which is possible with this symmetrical catalyst. ALIQUAT was ineffective. For the poly(amide-thiocarbonate), the increase of the yield and η_{inh} was very low, and the polymer was obtained principally by interphase polycondensation, only BTEAC being slightly effective.

Table II.- Yields and inherent viscosities obtained for Poly(amido-carbonate) **II-a** and Poly(amido-thiocarbonate) **II-b**

polymer	**II - a** (X = O)		**II - b** (X = S)	
catalyst	%	η_{inh}	%	η_{inh}
---	44	0.48	34	0.22
TBAB	55	0.56	42	0.37
ALIQUAT	42	0.64	35	0.55
BTEAC	46	0.56	37	0.24
HDTMAB	46	0.64	48	0.35

η_{inh}: inherent viscosity, in m-cresol at 25°C (c = 0.3 g/dl)

Table III.- Yields and inherent viscosities obtained for Poly(amido-carbonate) **III-a** and Poly(amido-thiocarbonate) **III-b**

polymer	**III - a** (X = O)		**III - b** (X = S)	
catalyst	%	η_{inh}	%	η_{inh}
---	16	0.63	27	1.02
TBAB	54	1.02	39	1.04
ALIQUAT	83	0.68	47	1.05
BTEAC	48	1.26	32	1.17
HDTMAB	84	0.94	55	1.02

η_{inh}: inherent viscosity, in m-cresol at 25°C (c = 0.3 g/dl)

In general, we obtained low polymers yields, and especially for the poly(amide-thiocarbonate)s, which may be due to a hydrolytic process in both the monomer or the formed polymer. The first case is difficult because the hydrolytic stability of the monomers was studied under similar reaction conditions and they were recovered quatitatively; a hydrolytic process in the polymers is possible, this has been shown in the synthesis of other polythiocarbonates and polycarbonates, influenced by the nature of the catalyst [11-12]. In spite of the low yields, the results obtained for the three monomers were good, and we can observe the efficiency of phase transfer in the synthesis of these kinds of polymers. The principal problem that we observe in this synthesis was the insolubility of the polymers in the reaction media, which limited the yield, η_{inh} and the growth of the chain. However, it is possible to conclude that phase transfer catalysis is a suitable method for the synthesis of these poly(amide-carbonate)s and poly(amide-thiocarbonate)s, and that the process is principally influenced by the nature of the catalyst.

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