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Synthesis of condensation polymers derived from halogenated diphenol-amides with the amide group in the side chain

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SUMMARY

Poly(amide-ester)s, poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from the diphenols-amides N-(2,6-dibromo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**I**) and N-(2,6-diiodo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**II**) and terephthaloyl chloride (**a**), isophthaloyl chloride (**b**), and adipoyl chloride (**c**), and phosgene (**d**) and thiophosgene (**e**) respectively, 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 to the hydrophilicity of this catalyst. Poly(amido-ester)s derived from **II** and aromatic diacids were insoluble in all the organic solvents, and the effectivity of the process was evaluated by the increase of the yields with respect to the essays without catalysts.

INTRODUCTION

Phase transfer catalysis has been a widely used tool in polymers synthesis, because it offers important tecnical advantages compared to other polymeric synthetic methods, such as solution or interphase polymerization [1].

In this technique, the catalyst has the function of transfering one of the reagents from the aqueous phase to the organic one in which the polymerization takes place. One of the most important limitations of this technique is the solubility of the polymer chain in the organic phase, because this factor has a great influence on the molecular weight.

Recently we have focussed our attention on the synthesis of condensation polymers obtained under phase transfer conditions and containing two functional groups in the repeat unit. In previous works [2-3] we have described the synthesis of polycarbonates, polythiocarbonates and polyesters also containing the amide in the side chain, and derived from the diphenol N-(2,6-dichloro-4-nitrophenyl)-4,4-his (4-hydroxyphenyl)-pentanamide. In general, for these polymers the catalyst benzyltriethylammonium chloride (BTEAC) was the most effective due to its hydrophilic character, which makes it useful for

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tranporting very lypophilic dianions. All the polymers were insoluble in the reaction media, which was an important limitant for obtaining high molecular weights.

In this work we describe the synthesis of the same condensation polymers derived from an analogous diphenol-amide, but containing bromine or iodine atoms instead of the chlorine atoms. The behaviour of the catalyst was evaluated by the yields and inherent viscosty measurements.

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), methyltrioctylammonium chloride (ALIQUAT 336^{TM}), benzyltriethylammonium chloride (BTEAC), and hexadecyltrimethylammonium bromide (HDTMAB).

The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^{1}H and ^{13}C NMR on a 200 MHz instrument (Bruker AC-200), using DMSO-d_6 as a solvent and TMS as an internal standard. Viscosimetric measurements were made on a Desreux - Bischof [4] type dilution viscosimeter at 25°C.

Monomers

The diphenol-acid 4,4-his(4-hydroxyphenyl)-pentanoic, and the amines 2,6-dibromo-4-nitroaniline or 2,6-diiodo-4-nitroaniline were commercial products.

The diphenols-amides N-(2,6-dibromo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**I**) and N-(2,6-diiodo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide, (**II**), were synthesized according to the following general procedure [2-3]: 0.244 mol of the diphenol-acid were mixed with 30 mL of $SOCl_2$ and the mixture was refluxed for two hours. After this time 0.29 mol of 2,6-dibromo-4-nitroaniline or 2,6-diiodo-4-nitroaniline were added to the homogeneous mixture and the heating was continued for six hours. Then the $SOCl_2$ was distilled, and a saturated $NaHCO_3$ solution was added to the brown oil. The solid was filtered, washed with a $NaHCO_3$ solution several times, dissolved in a NaOH solution to remove the unreacted aniline, and precipited by HCl addition. This procedure was repeated, obtaining a light brown solid corresponding to the diphenol-amide. The two diphenol-amides decomposed before melting.

N-(2,6-dibromo-4-nitrophenyl)-4,4-his(4-hydroxyphenyl)-pentanamide (**I**). IR (cm^{-1}) (KBr): 3300 (OH); 3020 (C-H); 1670 (C=O); 1660, 1550 (C=C); 1540, 1250 (NH). ^{1}H NMR (d) (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}C NMR (d) (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).

N-(2,6-diiodo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**II**). IR (cm^{-1}) (KBr): 3356 (OH); 3020 (C-H); 2969 (CH_2, CH_3); 1667 (C=O); 1611, 1511 (C=C); 1540 (NH); 834 (p-sust.). ^{1}H NMR (δ) (ppm) (acetone-d_6): 1.7 (s,3H,CH_3); 2.3 (d,2H,CH_2); 2.7 (d,2H,CH_2); 6.8 (d,4H,arom.); 7.1 (d,4H,arom.); 8.3 (s,2H,arom.); 8.7 (s,2H,OH). ^{13}C NMR (δ) (ppm) (acetone-d_6): 28 (CH_3); 33 (CH_2); 38 (CH_2); 45 (C quat.); 100, 116,129,135,141, 147, 149, 156 (C-arom.); 172 (C=O).

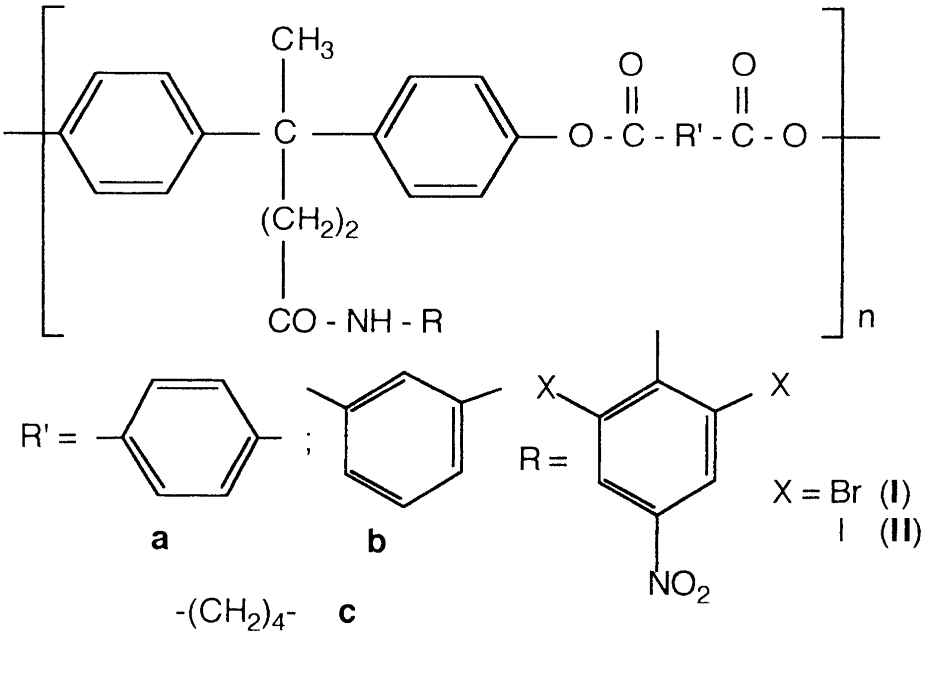
Polymers

Poly(amide-ester)s were synthesized according to the following general procedure: 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 diacid chloride were added. The mixture was stirred for one hour and then poured into 500 mL of methanol. The polymer was filtered, washed with methanol, dried until constant weight and characterized.

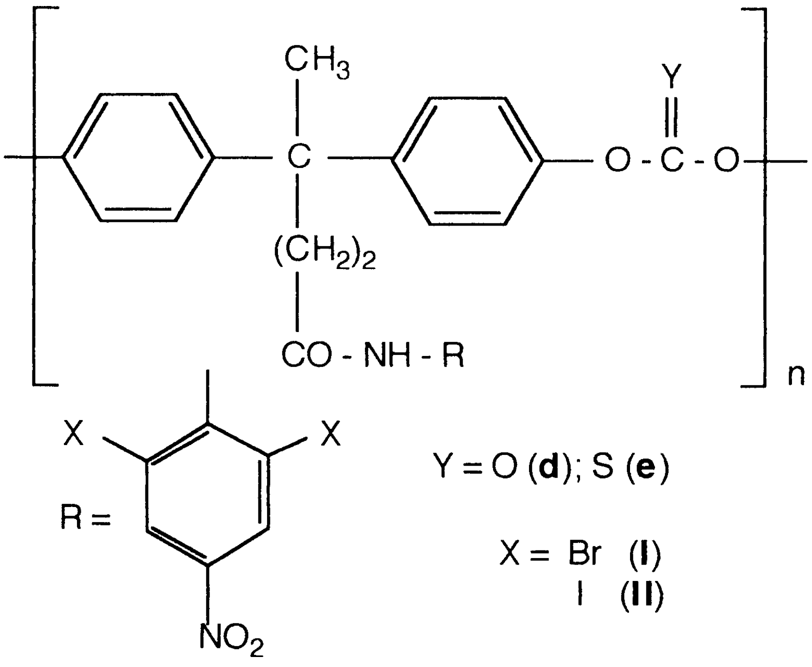
The poly(amide-carbonate) and the poly(amide-thiocarbonate) were synthesized and purified according to the same general procedure.

RESULTS AND DISCUSSION

Poly(amide-ester)s derived from the diphenol-amides N-(2,6-dibromo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**I**) and N-(2,6-diiodo-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**II**) and terephthaloyl chloride (**a**), isophthaloyl chlloride (**b**), and adipoyl chloride (**c**), with the following structure:



and poly(amide-carbonate)s and poly(amide-thiocarbonate)s derived from the same diphenols-amides (**I**) and (**II**), and phosgene (**d**) or thiophosgene (**e**) with the following structure:



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 agreed with those proposed. In all poly(amide-ester)s, poly(amide-carbonate)s and poly(amide-thiocarbonate) it was possible to see the disappearance of the OH band. Poly(amide-ester)s showed a new band at 1736-1752 cm^{-1} corresponding to the C=O of the ester group. Poly(amide-carbonate)s showed a new band at 1770 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. For all polymers 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 to the low solubility of these polymers, it was not possible to obtain NMR spectra. The reaction time was 60 minutes and was 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 these polymer synthesis only the nature of the catalyst was considered; reaction time, catalyst and base concentration, and temperature remained constant.

Table I shows the yields and ηinh values for poly(amide-ester)s **I-a**, **I-b** and **I-c**. Without catalysts low yields and ηinh values were obtained, due to an interphase polycondensation process between the diphenolate dissolved in the aqueous phase and the acid chloride dissolved in the organic one.

An important limitation observed in the polymerization process was the insolubility of the poly(amido-ester)s in the reaction media, which limited the growth of the polymeric chain.

Table I.- Yields and inherent viscosities obtained for poly(amide-ester)s **I-a**, **I-b**, and **I-c**

Polymer	**I-a**		**I-b**		**I-c**	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}
---	26	0.13	26	0.10	18	0.07
TBAB	68	0.30	69	0.30	84	0.30
ALIQUAT	53	0.30	77	0.17	92	0.20
BTEAC	54	0.37	54	0.40	91	0.32
HDTMAB	57	0.23	72	0.23	61	0.27

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

When the catalysts were used, an increase of the yields and the ηinh can be observed, showing the efficiency of the phase transfer process. The most effective catalyst for these three poly(amido-ester)s was BTEAC, which has been defined as hydrophilic [5-6] and suitable for transporting dianions of lypophilic character or with a high organic content, such as these used in this work. A similar behaviour has been described for analogous systems [3]. On the other hand, this catalyst has Cl^- as a counterion, which is interchanged more easily than Br^-.

TBAB also was effective as a catalyst for the synthesis of these poly(amido-ester)s, probably due to its symmetrical structure with the four C_4 chain bonded to the N central atom, which confers a good separation between the anion and the cation in the ion pair, and of course a high reactivity in the organic phase. The other catalysts with a higher lypophilic nature due to the longer chains bonded to the central atom, showed a less efective behaviour, although they were effective with respect to the results obtained without a catalyst.

In Table II the yields and ηinh obtained for poly(amide-ester)s **II-a**, **II-b** and **II-c** are shown. Also in this case, the poly(amido-ester)s were insoluble in the reaction media, and precipited during the reacion time. Poly(amido-ester)s derived from aromatic acids (**II-a** and **II-b**) were insoluble in all the organic solvents, and it was not possible to determine any value of ηinh. The effectivity of the transfer process can be seen only by the increase of the yield with respect to that obtained without catalyst. In fact, with all the catalysts, it was possible to see an increase in the yield when the catalysts were used. Nevertheless, the poly(amido-ester) derived from the adipic acid **II-c** was soluble in m-cresol and the ηinh were obtained. It can be seen that the only effect of the catalyst was an increase of the yield. The ηinh were the same with or without catalyst, probably due to the fact that the insolubility of the polymer does not permit the increase of the polymeric chain, and only an increase of the yield can be observed.

Table II.- Yields and inherent viscosities obtained for poly(amide-ester)s **II-a**, **II-b**, and **II-c**

Polymer	**II-a**	**II-b**	**II-c**	
Catalyst	%	%	%	η_{inh}
---	40	65	6	0.73
TBAB	87	99	18	0.64
ALIQUAT	98	98	51	0.73
BTEAC	70	70	35	0.73
HDTMAB	97	98	21	0.59

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

Table III shows the yields and ηinh obtained for the synthesis of the poly(amido-carbonate) **I-d** and the poly(amido-thiocarbonate) **I-e**. Without catalysts, only low yields and ηinh were obtained due to an interfacial polycondensation process. When the catalysts were used, it was possible to see an increase of both the yields and especially the ηinh values.

Table III.- Yields and inherent viscosities obtained for Poly(amido-carbonate) **I-d** and Poly(amido-thiocarbonate) **I-e**

polymer	**I - d**		**I - e**	
catalyst	%	η_{inh}	%	η_{inh}
---	16	0.03	27	0.07
TBAB	48	0.27	41	0.20
ALIQUAT	83	0.37	44	0.27
BTEAC	53	0.10	32	0.37
HDTMAB	78	0.27	54	0.20

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

With BTEAC the yields and ηinh obtained for poly(amido-carbonate) **I-d** were surprisingly low and there is no good explanation about this behaviour, because this catalyst has been very effective in the synthesis of the polymers described in this work and also in those derived from the analogous diphenol-amide but with chlorine atoms [2]. ALIQUAT was the best catalyst for this polymer, although its three long C_8 chains make it a lypophilic catalyst. Probably, if the ionic pair is formed, it will be very reactive because the distance between the anion and the cation will be great and highly reactive. Also this catalyst has Cl^- as a counterion which is interchanged more easily than Br^-. The other catalyst showed less efectivity.

For the poly(amido-thiocarbonate) **I-e** the best yields and ηinh were obtained with BTEAC, which has the hydrophilic characteristics mentioned above, and is suitable for the synthesis of this polymer. With the other catalysts, intermediate values of ηinh were obtained. With this polymer, the yields were low, probably due to a hydrolitic process infuenced by the catalysts as has been described earlier [7-8].

Table IV shows the yields and ηinh obtained for the poly(amido-carbonate) **II-d** and the ply(amido-thiocarbonate) **II-e**. Without catalysts, very low yields but an important value of ηinh were obtained due to an interfacial polycondensation process. For the poly(amide-carbonate) **II-d** only TBAB was effective due to the symmetrical structure of this catalyst which gives the ionic pair an adequate separation. The other catalysts were uneffective, and ALIQUAT and HDTMAB can promote a hydrolitic process due to their lypophilic structure [7].

Table IV.- Yields and inherent viscosities obtained for Poly(amido-carbonate) **II-d** and Poly(amido-thiocarbonate) **II-e**

polymer	**II - d** (X = O)		**II - e** (X = S)	
catalyst	%	η_{inh}	%	η_{inh}
---	4	0.54	1	0.63
TBAB	92	0.79	27	0.46
ALIQUAT	49	0.49	53	0.52
TEBAC	44	0.59	61	0.73
HDTMAB	15	0.46	10	0.79

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

Surprisingly BTEAC was practically uneffective, showing a low increase of the ηinh. For the poly(amide-thiocarbonate) **II-e**, there was an increase in the yields. Only with BTEAC and HDTMAB was it possible to observe a low increase in the ηinh. One important factor that could have influenced these results is the insolublity of the polymers with iodine atoms in the reaction media and it is possible that they were more insoluble. Some of the poly(amido-ester)s were insoluble in all the organic solvents and this fact limited the growth of the polymeric chain. On the other hand, it is also possible that the hydrolytic processes of the polymeric chains will be more important, especially with the lypophilic catalysts.

Finally, we can conclude that the transfer process was effective in the synthesis of these polymers, in spite of their insolubility in the reaction media, which was apparently increased by the bromine or iodine atoms with respect to the analogous with chlorine atoms. In this sense, poly(amide-ester)s derived from the diphenol-amide with iodine atoms and aromatic diphenols were insoluble in all the organic solvents. In practically all cases, BTEAC was the most effective catalyst due to its hydrophilic character which makes it effective for transporting diphenols with high organic content.

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