Polymer Bulletin 40, 35–42 (1998)

Polymer Bulletin

Polymerization by phase transfer catalysis

23. Synthesis of poly(amide-ester)s derived from diphenols with the amide group in the side chain

L. H. Tagle*, F. R. Diaz, G. Cerda, M. Oyarzo, G. Peñafiel

Organic Chemistry Department, Faculty of Chemistry, Catholic University of Chile,
P.O. Box 306, Santiago, Chile

Received: 18 August 1997/Revised version: 13 November 1997/Accepted: 21 November 1997

SUMMARY

The synthesis of poly(amide-ester)s derived from the diphenol-amides N-(2,6-dichloro-4-nitrophenyl)-2,2-bis(4-hydroxyphenyl)-propanamide, N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl)-butanamide, and N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide and terephthaloyl chloride, isophthaloyl chloride and adipoyl chloride, is described under phase transfer conditions, using several quaternary ammonium salts as phase transfer catalysts. The behaviour of the catalysts was evaluated through the yields and inherent viscosity measurements and compared with those obtained without a catalyst. In general, the phase-transfer process was effective, and the best catalyst was benzyltriethylammonium chloride, which has hydrophilic characteristics and is suitable for transporting lypophilic dianions such as those used in this synthesis. Other catalysts also showed a good behaviour. All poly(amide-ester)s were insoluble in the reaction media, which limited their growth and the molecular wieght.

INTRODUCTION

Phase-transfer catalysis (PTC) has been widely used in the synthesis of several kinds of polymers, such as polyesters [1], polycarbonates [2], polythiocarbonates [3-4], and others [5]. The catalyst in this tecnique, normally quaternary ammonium or phosphonium salts, has the function of transfering the diphenolate in the form of an ion pair, from the aqueous phase to the organic one, in which the reaction with the diacid chloride takes place. Experimentally, only mild conditions are required and the use of anhydrous or aprotic solvents are avoided [6].

For polymer synthesis, the principal limitation of this technique is the solubility of the growing polymer chain, because this will have a great influence on the molecular weight. A precipitation of the polymer in the reaction media will negatively affect the molecular weight.

In recent years we have focussed our attention on the synthesis of polymers containing two functional groups in the repeating unit, describing

---

* Corresponding author

the synthesis of poly(ester-carbonate)s and poly(ester-thiocarbonate)s, containing the ester group in both in the main chain [7-8] and in the side chain [9]. We have also described the synthesis of poly(amide-carbonate)s and poly(amide-thiocarbonate)s containing the amide group in the main chain [10]. In these papers the influence of the nature of the catalyst was studied, showing that the yields and inherent viscosity values are increased when some catalysts are used, compared to the tests without it, in which an interphasial polycondensation process takes place. One of these catalysts was benzyltriethylammonium chloride (BTEAC), described as hydrophilic and suitable for transporting lypophilic dianions [11].

As a continuation of our work in the synthesis of polymers containing two functional groups in the repeating unit, we describe in this paper the synthesis of poly(amide-ester)s derived from the diphenol-amides N-(2,6-dichloro-4-nitrophenyl)-2,2-bis(4-hydroxyphenyl)-propanamide (**I**), N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl)-butanamide (**II**), and N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**III**), with three diacid chlorides under phase transfer conditions and using several quaternary ammonium salts as phase transfer catalysts. The behaviour of the catalysts was evaluated by the yields and inherent viscosity values compared to those obtained without them.

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 ™), 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 the solvent and TMS as an internal standard. Viscosimetric measurements were made in a Desreux - Bischof [12] type dilution viscosimeter at 25ºC.

Monomers

The diphenol-acids 2,2-bis(4-hydroxyphenyl)-propanoic and 3,3-bis(4-hydroxyphenyl)-butanoic were synthesized according to a procedure described previously [9], and the acid 4,4-bis(4-hydroxyphenyl)-pentanoic was a commercial product.

The diphenols-amides N-(2,6-dichloro-4-nitrophenyl)-2,2-bis(4-hydroxyphenyl)-propanamide (I), N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl)-butanamide (II), and N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (III), were synthesized according to the following general procedure: 0.244 mol of the diphenol acid were mixed with 30 mL of $SOC1_2$ and the mixture refluxed for two hours. After this time, 6 g (0.29 mol) of 2,6-dichloro-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 and washed with a $NaHCO_3$ solution several times. The solid was then dissolved in a NaOH solution to remove the unreacted aniline and precipited by HCl addition. This procedure was repeated again, obtaining a light brown solid corresponding to the diphenol-amide. The three diphenol-amides decomposed before melting.

N-(2,6-dichloro-4-nitrophenyl)-2,2-bis(4-hydroxyphenyl)-propanamide (**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}C NMR (δ) (ppm) (DMSO-d_6): 27.4 (CH_3); 55.2 (C quat.); 114, 115, 123, 129, 130, 133, 135, 155 (C atom.); 173.9 (C=O).

N-(2,6-dichloro-4-nitrophenyl)-3,3-bis(4-hydroxyphenyl)-butanamide (**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,CH2); 6.7 (d,4H,arom.); 7.1 (d,4H,arom.); 8.3 (s,2H,arom.). ^{13}C NMR (δ) (ppm) (DMSO-d_6):28.2 (CH_3); 43.8 (C quat.); 46.8 (CH2); 114, 123, 127, 133, 139, 141, 144, 154 (C arom.) ; 167 (C=O).

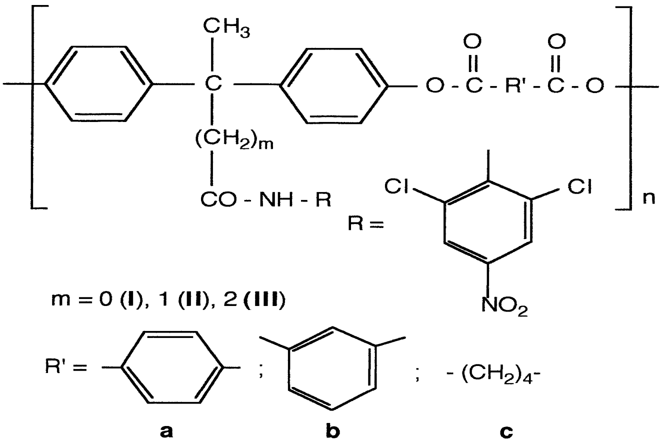
N-(2,6-dichloro-4-nitrophenyl)-4,4-bis(4-hydroxyphenyl)-pentanamide (**III**). IR (cm^{-1}) (KBr): 3353 (OH); 3020 (C-H); 2860 (CH_3, CH_2); 1673 (C=O); 1600, 1500 (C=C). ^{1}H NMR (δ) (ppm) (DMSO-d_6): 1.62 (s,3H,CH_3); 2.4 (t,2H,CH_2); 2.6 (t,2H,CH_2); 6.8 (d,4H,arom.); 7.2 (d,4H,arom.); 8.3 (s,2H,arom.). ^{13}C NMR (δ) (ppm) (DMSO-d_6): 28.7 (CH3); 33.2 ($C\text{-}\underline{C}H_2\text{-}CH_2$), 38.5 ($CH_2\text{-}\underline{C}H_2\text{-}C{=}O$); 45.6 (C quat.); 116, 124, 129, 135, 140, 141, 147, 156 (C arom.); 173.4 (C=O).

Poly(amide-ester)s synthesis

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 20ºC. 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 and dried until constant weight and characterized.

RESULTS AND DISCUSSION

Poly(amide-ester)s derived from diphenol-amides **I**, **II**, **III** and terephthaloyl chloride (**a**), isophthaloyl chloride (**b**) and adipoyl chloride (**c**), with the following structure:



were synthesized under phase transfer conditions in CH_2Cl_2 as a solvent at 20°C, and characterized by IR spectroscopy and elemental analysis. The structures were in accord with those proposed. In all poly(amide-ester)s it was possible to see the disappearance of the OH band, and all of them also showed a new band at 1735-1750 cm^{-1} corresponding to the C=O of the ester group. Due to the low solubility of the poly(amide-ester)s, 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 the poly(amide-ester) synthesis only the nature of the catalyst and its infuence in the yields and inherent viscosity values (ηinh) was considered; reaction time, catalyst and base concentration, and temperature remained constant.

Table I shows the yields and ηinh obtained for the poly(amide-ester)s derived from the diphenol-amide **I**, and the three diacid chlorides. Without a catalyst, low yields and ηinh values were obtained due to interphase polycondensation between the diphenolate dissolved in the aqueous media and the diacid chlorides dissolved in the organic one. When the catalysts were used, an increase of the yields and, more importantly, in the ηinh values, could be observed showing the efficiency of the phase transfer process.

With the three poly(amide-ester)s, the best results were obtained with BTEAC, which has been described as a hydrophilic catalyst and adequate for transporting lypophilic or highly organic dianions [11]. ALIQUAT, which has three octyl chains bonded to the N central atom, has more lypophilic character, and showed lower values of ηinh, especially for the poly(amide-ester) **I-b**. On the other hand, both catalysts have Cl^- as counterion, which is interchanged more easily than Br^-, the counterion of the other catalysts. TBAB also was efficient, due to its symmetrical form, which confers to the ion pair a good separation between the cation and the anion. HDTMAB has one long chain and three methyl groups bonded to the central N atom, which confers the characteristic of a micelar agent [6]. With these last two catalysts good results were also obtained for the three poly(amide-ester)s derived from the diphenol-amide **I**.

Table I.- Yields and inherent viscosities obtained for polyesters **I-a**, **I-b**, and **I-c**

Polyester	**I-a**		**I-b**		**I-c**	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}
---	28	0.58	32	0.59	22	0.48
TBAB	52	0.98	48	0.85	46	0.86
ALIQUAT	51	0.93	51	0.66	37	0.86
BTEAC	49	1.02	53	0.89	43	1.00
HDTMAB	49	0.94	56	0.90	41	0.78

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

For poly(amide-ester) **I-a**, all catalysts were efficient, showing a very similar behaviour, observing an increase in both, the yields and ηinh values. But for poly(amide-ester)s **I-b** and **I-c**, although all the catalysts were efficient, there were more differences between their behaviour, which can be due to the different influence of the diacid chlorides on the solubility of the poly(amide-ester)s, although the three polymers were insoluble in the reaction media.

Table II shows the results obtained for poly(amide-ester)s derived from the diphenol-amide **II**, with the same diacid chlorides. In this case, the poly(amide-ester)s were also obtained without a catalyst, showing the presence of interphase polycondensation. BTEAC was clearly the best catalyst for the three poly(amide-ester)s, obtaining the highest values of yield and ηinh, due to its hydrophilic character and the more lypophilic condition of this diphenolate. ALIQUAT was effective only for poly(amide-ester)s **II-b** and **II-c**, but with low yields. For poly(amide-ester) **II-a**, the other three catalysts showed a similar behaviour, only slightly superior to that obtained without catalyst.

For poly(amide-ester)s **II-b** and **II-c** the catalysts were effective in all cases, because an increase of the ηinh values was observed, but the yields were only slightly superior to those obtained without a catalyst, especialy with poly(amide-ester) **II-c**.

Table II.- Yields and inherent viscosities obtained for polyesters **II-a**, **II-b**, and **II-c**

Polyester	**II-a**		**II-b**		**II-c**	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}
---	43	0.38	45	0.14	30	0.04
TBAB	62	0.45	55	0.66	32	0.25
ALIQUAT	35	0.39	21	0.42	38	0.36
BTEAC	66	1.06	67	0.71	40	0.48
HDTMAB	36	0.45	36	0.57	38	0.39

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

Table III shows the results obtained for poly(amide-ester)s derived from diphenol-amide **III** and the diacid chlorides. In general, there was an increase of the yields and the ηinh values in comparision to those obtained without a catalyst. ALIQUAT was inefficient as a catalyst, probably due to its higher lypophilic character compared to the other catalysts, except for polyester **III-b**, which showed a low increase of ηinh. On the other hand, BTEAC showed a very good behaviour for the three poly(amide-ester)s, and was the most hydrophilic catalyst with the greatest lypophilic diphenol-amide. TBAB also showed a very good behaviour with the three poly(amide-ester)s, and HDTMAB with poly(amide-ester)s **III-a** and **III-b**, the former being a symmetrical catalyst showing an adequate separation in the organic pair, and latter a micellar agent, which has shown an exceptional behaviour in the synthesis of other polymers [3, 6].

Table III.- Yields and inherent viscosities obtained for polyesters **III-a**, **III-b**, and **III-c**

Polyester	**III-a**		**III-b**		**III-c**	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}
---	26	1.04	30	0.95	20	0.56
TBAB	60	1.56	69	1.56	85	1.29
ALIQUAT	50	1.04	75	1.23	96	0.57
BTEAC	57	1.53	61	1.52	94	1.88
HDTMAB	57	1.31	79	1.71	66	0.64

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

If we observe the results for all poly(amide-ester)s, it is possible to point out that the phase-transfer process was effective in the mayority of cases. The increase of the yields and ηinh values depended on of the nature of the catalyst, in the sense that when a hydrophilic catalyst as BTEAC is used, it is possible to transfer a more lypophilic dianion.

When the results obtained for the three diphenol-amides are compared, the best values, with few exceptions were obtained with the diphenol-amide III, that has the longest side chain and more organic character, which could make them more soluble in the reaction media, and consequently obtain higher values of ηinh. It is necessary to point out that all poly(amide-ester)s were insoluble in the reaction media, which was the principal limitation of this synthesis, because the growth of the polymeric chain is hindered.

In general in this type of phase-transfer polymerization process, the limiting step is the transfer of the dianion to the organic phase rather than the reaction in that phase, due to the high reactivity of the diacid chloride. In this transfer-process, the nature of the catalyst has a significant influence. The principal limitation in the synthesis of these poly(amide-ester)s was their insolubility in the reaction media, because the growth of the polymeric chain was hindered. On the other hand, the increase of the yields with respect to those obtained without a catalyst, was not very high. This fact may be due to a hydrolytic process of the polymeric chains that has been shown in the synthesis of other polymers, and which is influenced by the nature of the catalyst [2, 13]. However, it is possible to conclude that phase-transfer catalysis was a suitable technique for the synthesis of these poly(amide-ester)s, due principaly to the mild conditions used, and the good results obtained.

ACKNOWLEDGEMENTS

The authors acknowlege the support of this research by “Fondo Nacional de Investigación Científica y Tecnológica” through grant 8970011.

REFERENCES

1.- L.H. Tagle, F.R. Diaz and W. Campbell, Eur. Polym. J., **29**, 1069 (1993).
2.- L.H. Tagle and F.R. Diaz, Eur. Polym. J., **23**, 109 (1987).
3.- L.H. Tagle, F.R. Diaz, J.C. Vega and P. Alquinta, Makromol. Chem., **186**, 915 (1985).
4.- L.H. Tagle, F.R. Diaz and P. Riveros, Polymer J., **18**, 501 (1986).
5.- Y. Imai, T.Q. Nguyen and M. Ueda, J. Polym. Sci., Polym. Lett. Ed., **19**, 205 (1981).
6.- E.V. Dehmlow and E.S. Dehmlow, “Phase Trasnfer Catalysis”, 3rd ed., Verlag Chemie, Weinheim, 1993.
7.- L.H. Tagle, F.R. Diaz, R. Concha and H. Cisternas, Inter. J. Polymeric Mater., **20**, 159 (1993).
8.- L.H. Tagle, F.R. Diaz and H. Cisternas, Bol. Soc. Chil. Quim., **39**, 279 (1994).

9.- L.H. Tagle, F.R. Diaz and A. Donoso, J. Macromol. Sci., Pure Appl. Chem, **A33**, 1643 (1996).

10.- L.H. Tagle, F.R. Diaz and A. Godoy, Polym. Bull., **36**, 717 (1996).

11.- R. Bar, L. Karpug-Bar, Y. Sasson and J. Blum, J. Anal. Chim. Acta, **154**, 203 (1986).

12.- V. Desreux and F. Bischoff, Bull. Soc. Chim. Belg, **59**, 93 (1950).

13.- L.H. Tagle, F.R. Diaz and M.P. De La Maza, Polym. Bull., **18**, 485 (1987).