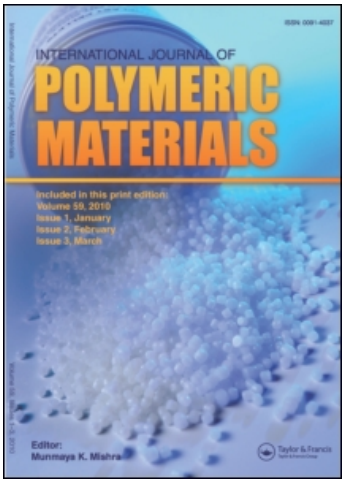

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L. H. Tagle[a]; F. R. Díaz[a]; L. González[a]
[a] Faculty of Chemistry, Catholic University of Chile, Santiago, Chile

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POLYMERIZATION BY PHASE TRANSFER CATALYSIS. 26. SYNTHESIS OF THE POLY(ETHER-ESTER) DERIVED FROM 4,4′-(1,5-NAPHTHALENEDIOXY)-DIBENZOIC ACID AND BISPHENOL *A*

L. H. Tagle, F. R. Díaz, and L. González
Faculty of Chemistry, Catholic University of Chile, Santiago, Chile

The poly(ether-ester) derived from 4,4′-(1,5-naphthalenedioxy)-dibenzoic acid and bisphenol-A was synthetized under phase transfer conditions using quaternary ammonium salts as catalysts. The phase transfer process was effective showing an increase of the yields and η_{inh} values with respect to those obtained without a catalyst. The best results were obtained in CH_2Cl_2, probably due to a higher solubility of the poly(ether-ester) in this solvent.

Keywords: phase-transfer catalysis, polycondensation interfacial polymerization

INTRODUCTION

Phase transfer catalysis has been a powerful tool in the synthesis of different kinds of condensation polymers, such as poly(carbonates), poly(thiocarbonates), poly(ethers) and poly(esters) [1], due to the use of mild conditions and common organic solvents. The principal feature of the phase transfer catalysis is to allow the reagents, present in different phases, to react with the aid of a catalyst, normally quaternary onium salts or crown ethers. The catalyst transfers the dianion in the form of an ion pair from the aqueous phase to the organic one.

In the last years we have focused our attention on the synthesis of polymers containing two functional groups in the repeat unit, and the synthesis of poly(amide-carbonates), poly(amide-thiocarbonates), poly(amide-esters), poly(ester-carbonates), and poly(ester-thiocarbonates) was described [2–6]. Nevertheless the phase transfer process was effective in increasing the yields and viscosity values. The most important limitation was the

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Address correspondence to L. H. Tagle, Faculty of Chemistry, Catholic University of Chile, P.O. Box 306, Santiago, Chile. E-mail: ltagle@puc.cl

insolubility of the polymer in the organic phase, which limited the growth of the polymeric chain.

In this work we describe the synthesis of the poly(ether-ester) derived from a diacic [4,4′-(1,5-naphthalenedioxy)-dibenzoic acid], in which two ether groups are bonded to a bulky group such as a naphthyl one, in order to increase the solubility, as has been described for poly(amides) [7, 8], and bisphenol-*A*, using quaternary ammonium salts as phase transfer catalysts. The effect of several phase transfer catalysts on the yield and inherent viscosity of the poly(ether-ester) was also analyzed.

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 $CDCl_3$ and DMSO-d_6 as solvents and TMS as the internal standard. Viscosimetric measurements were made on a Desreux–Bischof [9] type dilution viscosimeter at 25°C.

Monomer

The 4,4′-(1,5-naphthalenedioxy)-dibenzoic acid was synthetized from the dinitrile derivative according to a procedure described, in which *p*-fluorobenzonitrile reacted with 1,5-dihydroxynaphthalene, and the product was hydrolyzed in a basic media [10].

The 4,4′-(1,5-naphthalenedioxy)-dibenzoic acid chloride (**I**) was synthetized by refluxing the diacid with thionyl chloride and drops of *N*,*N*-dimethyl-formamide. The diacid chloride was purified by recrystallization from a mixture of hexane–toluene.

4,4′-(l,5-naphthalenedioxy)-dibenzoic acid chloride (**I**): m.p.: 155–157°C. IR (KBr) (cm^{-1}): 3075 (H arom.), 1768 and 1739 (C=O), 1594, 1580 and 1493 (arom.) and 839 (*p*-arom.). ^{1}H NMR (δ) (DMSO-d_6): 7.0–8.14 (*m*, arom.). ^{13}C NMR (δ) (DMSO-d_6): 166.6 (C=O), 161.5 (C_{ph}—O), 150 (C_{naph}—O), 129.7, 128, 119.8, 116.2 (C-naphtyl), 131.6, 125.8, 117.4 (C-phenyl).

Poly(Ether-Ester)

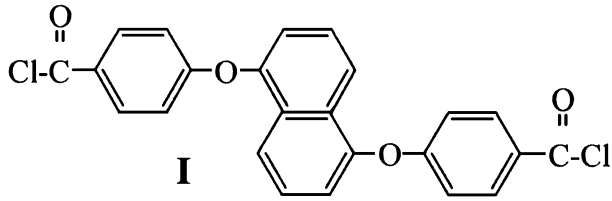
The poly(ether-ester) was synthetized according to the following general procedure: 0.228 g (1 mmol) of bisphenol-*A* and the catalyst (5% mol) were

dissolved in 10 mL of 0.5 M NaOH and 20 mL of water at 20°C. Then, 0.437 g (1 mmol) of the diacid chloride dissolved in 30 mL of the organic solvent was added. The mixture was stirred for one hour and then poured into 400 mL methanol. The poly(ether-ester) was filtered, washed with methanol, dried to constant weight, and characterized.

Poly (carbonyl-1,4-phenylene-oxy-1,5-naphthalene-oxy-1,4-phenylene-carbonyl-oxy-1,4-phenylene-2,2-propyl-1,4-phenylene-oxy): IR (KBr) (cm^{-1}): 3060 (H arom.), 1736 (C=O), 1595 and 1499 (arom.).

RESULTS AND DISCUSSION

The poly(ether-ester) derived from the diacid chloride **I** and bisphenol *A* was synthetized under phase transfer conditions, using several ammonium quaternary salts in a biphasic system organic solvent/0.5 M NaOH at 20°C, and characterized by IR spectroscopy and elemental analysis, and the results are in agreement with the proposed structure (Scheme 1).



I

SCHEME 1

In the poly(ether-ester) it was possible to see a new band at 1736 cm^{-1} corresponding to the C=O of the ester group. The poly(ether-ester) was insoluble in all common organic solvents as well as in *N*,*N*-dimethyl-formamide, *N*,*N*-dimethyl-acetamide, dimethylsulfoxide, 1,2-dichloro-benzene, and chloroform, but soluble in *N*-methyl-pirrolidone, and it was impossible to obtain the NMR spectra.

In the synthesis of this poly(ether-ester) only the nature of the catalyst and the solvent were considered; reaction time, catalyst and base concentration, and temperature remained constant.

Polymerization takes place when the diphenolate is transferred to the organic phase as a ionic pair with the catalyst. Table 1 shows the yields and inherent viscosity values (η_{inh}) obtained for the poly(ether-ester) derived from the diacid chloride **I**.

Essays without catalyst were made in the two solvents to evaluate the behavior of the interphase. In both solvents the poly(ether-ester) was obtained due to an interfacial polycondensation process between the diphenolate dissolved in the aqueous phase and the diacid chloride dissolved

TABLE 1 Yields and inherent viscosities obtained for the poly(ether-ester) **I**

Solvent	CH_2Cl_2		1,2-*diCl*-C_6H_4	
Catalyst	%	η^*	%	η^*
none	22	0.10	3	0.10
TBAB	79	0.29	56	0.20
ALIQUAT	88	0.38	99	0.20
BTEAC	39	0.24	20	0.20
HDTMAB	79	0.24	99	0.24

* Inherent viscosity in NMP at 25°C ($c = 0.3$ g/dL).

in the organic one. The low yields obtained in these conditions would be indicative of the low reactivity of this diacid chloride.

When the catalysts were used, both values increased, showing the efficiency of the transfer process. In spite of an increase of both parameters, BTEAC showed the lowest efficiency in both solvents, especially in the yields, due to its hydrophilic characteristics [11] which does not permit an adequate transfer process of this diphenolate, which has been described in other polymer syntheses [1–6]. The low increase of the yields plus the low efficiency of this catalyst for transporting the diphenolate would be indicative of the low reactivity of this diacid chloride in the interface.

ALIQUAT was a very efficient catalyst in CH_2Cl_2, showing an important increase of both parameters. This catalyst has more lipophilic characteristics and is suitable for transporting this diphenolate. Also in 1,2-diCl-C_6H_4, ALIQUAT was efficient in obtaining the poly(ether-ester) with a quantitative yield and an increase of the η_{inh}. In this solvent the distribution constant of the catalysts is very low, in spite of its higher polarity with respect to CH_2Cl_2. In the equilibrium a small percentage of the ion pairs can be transferred to the organic phase, so the reaction will be retarded. However if lipophilic cations as ALIQUAT are used, this effect can be compensated and it is possible to obtain a high yield [12]. Also the lower solubility of the poly(ether-ester) in this solvent limited the growth of the polymeric chain, and as a consequence the η_{inh} value was lower.

When HDTMAB was used, in both solvents there was an important increase of the yields but with the same values of η_{inh}. The increase of the yields showed the efficiency of this catalyst for transporting the diphenolate, but the similar η_{inh} can be due to the insolubility of the poly(ether-ester) which does not permit the growth of the polymeric chain specially in 1,2-diCl-C_6H_4. However, HDTMAB has micelar agent characteristics [13] and formed emulsions in the reaction media, but this effect apparently does not influence the results. When TBAB was used as catalyst the obtained values were higher in CH_2Cl_2 than in 1,2-diCl-C_6H_4. It has been described that this catalyst has a very low extraction constant in 1,2-diCl-C_6H_4 (< 0.1) [12],

but this does not exclude this solvent as unsuitable for this reaction and in spite of this value, during the reaction a small percentage of the ion pair can be transferred to the organic phase and the poly(ether-ester) can be obtained.

In general, it is possible to see that the best results were obtained in CH_2Cl_2, due probably to a higher solubility of the poly(ether-ester) in this solvent, because the η_{inh} were higher than those obtained in 1,2-diCl-C_6H_4. It is also possible to indicate that the reactivity of this diacid chloride in the interfacial system is low, and is dramatically increased by using the phase transfer catalysts, with the only limitation of the solubility being the poly(ether-ester) in the organic phase.

Finally, the phase transfer process was efficient in the synthesis of this poly(ether-ester) in both solvents, obtaining an increase of the yields and η_{inh} values with respect to those obtained without catalyst.

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