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A convenient laboratory preparation of aromatic polycarbonate

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Summary

An experimentally simple method for the synthesis of aromatic polycarbonates is described. Reaction of commercially available *p*-nitrophenyl chloroformate with bisphenol A afforded BPA polycarbonate in good yields with M_n = 26,000 g/mol. This laboratory procedure avoids the use of phosgene or phosgene equivalents in the laboratory. The process requires the use of 2 equivalents of triethylamine and a catalytic amount of 4-dimethylaminopyridine.

Introduction

Older industrial methods for aromatic polycarbonates utilize phosgene as a carbonate source.[1] This toxic gas is often a common element in syntheses. In an effort to eliminate the risk associated with the use of this reagent, several alternatives have been investigated.[2-7] It was our goal to develop an alternative synthetic route that combines experimental simplicity while eliminating laboratory exposure to conventional phosgene sources for the synthesis of bisphenol A (BPA) polycarbonate. Traditional industrial processes for manufacture of aromatic polycarbonate include 1) an interfacial, 2-phase phosgene-based process that uses a phase transfer catalyst, 2) transesterification in the melt using a carbonate ester and aromatic diols as starting materials, and 3) a solution process involving phosgenation of an aromatic bisphenol in a chlorinated solvent.[1] None of these methods are experimentally simple and generally suitable for small-scale laboratory syntheses.

Bis(trichloromethyl)carbonate, or triphosgene, is a stable solid which is safely handled and has been used as a phosgene substitute in polycarbonate synthesis. Yields of 75% have been reported for BPA polycarbonate synthesized at 20ºC in dichloromethane using the triethylamine as nucleophilic catalyst. [2] However, phosgene is produced as an intermediate in this reaction scheme and therefore, care must still be taken to ensure decomposition of the toxic gas as it is formed *in situ*. Sun and coworkers[3] synthesized fully aromatic liquid crystalline polycarbonates from triphosgene and aromatic diols, including BPA, *via* both interfacial and solution polycondensation. High molecular weight polymer was obtained through interfacial methods when an excess of triphosgene was used. When solution polymerization was employed, the yield of polymer and its inherent viscosity were both found to be dependent on the amount of triphosgene used.

Recently, relatively high molecular weight polycarbonate was prepared *via* transesterification of dimethylcarbonate (DMC) and BPA. Transesterification of BPA with diphenylcarbonate is a known method of polycarbonate synthesis where the diphenylcarbonate is prepared from DMC.[4] DMC can be synthesized industrially from carbon monoxide and methanol using copper catalysts.[5] Haba and coworkers[4] synthesized BPA bis(methyl carbonate) while continuously removing by-product methanol with molecular sieves. Subsequent melt polymerization of this intermediate yielded polycarbonate with a molecular weight M_n = 20,000 g/mol.

Fréchet and coworkers[6] reported the synthesis of allylic and benzylic copolycarbonates, which underwent instantaneous and irreversible degradation when heated to 200-210ºC or when treated with a catalytic amount of acid. Carbon dioxide and other small molecules were released upon degradation. These copolymers were synthesized without the laboratory use of phosgene. Commercially available *p*-nitrophenyl chloroformate was reacted with a diol to form a copolycarbonate of BPA and bis(4-nitrophenyl)-2-cyclohexen-1,4-ylene dicarbonate under phase transfer conditions. Once the intermediate was isolated and recrystallized, it underwent phase transfer catalyzed polycondensation with the diol BPA, 1,1'-(1,4-phenylene)diethanol, or 1,4-phenylenedimethanol.

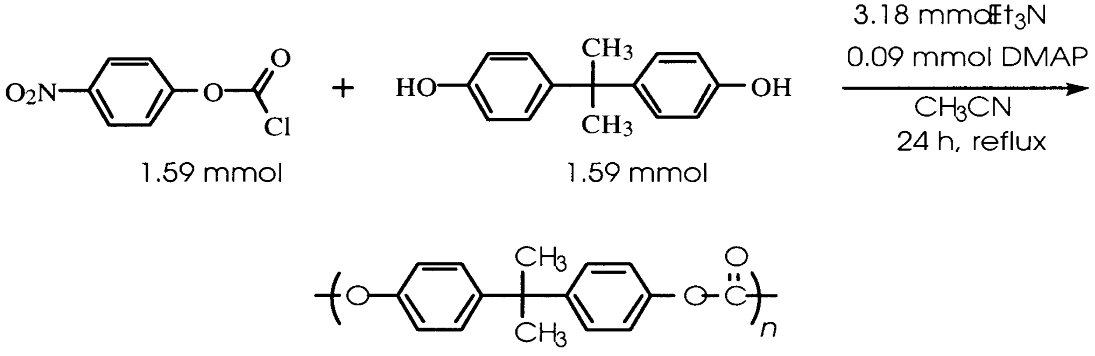
In a closely related study, Brunelle[7] used *o*-nitrophenyl carbonate for the preparation of aromatic polycarbonates. A wide variety of different polycarbonates were prepared; reasonable molecular weights were obtained at room temperature with reaction times of 1 – 20 h. The primary disadvantage of Brunelle's method is that *o*-nitrophenyl carbonate is not commercially available.

Results and Discussion

The work of Fréchet and coworkers[6] served as the inspiration for this report. We felt that *p*-nitrophenyl chloroformate might serve as a convenient phosgene substitute for a generalized polycarbonate synthesis. The synthetic scheme used for the preparation of BPA polycarbonate is shown in Scheme 1. Our early research followed the same experimental procedure of Fréchet and coworkers where we substituted BPA for 2-cyclohexen-1,4-diol. The dicarbonate intermediate formed from BPA and *p*-nitrophenyl chloroformate could not be recrystallized prior to the polymerization step unlike the literature dicarbonate intermediate. The ^{1}H NMR spectrum of our BPA adduct indicated 60% monosubstituted compound and 30% disubstituted product. The experimental molecular weight (gel permeation chromatography in THF) of our intermediate was never greater than M_n = 3900 g/mol with a polydispersity index (PDI) = 1.4. In an attempt to improve this experimental result, the *p*-nitrophenyl chloroformate was rigorously purified by sublimation. Also, two equivalents of freshly distilled triethylamine were substituted for pyridine. Our anhydrous dichloromethane was evaluated via Karl Fischer titration to minimize chloroformate hydrolysis. In an attempt to decrease stoichiometric error, volumetric techniques were employed. Preparation of stock solutions of the *p*-nitrophenyl chloroformate and BPA in anhydrous dichloromethane was unsuccessful due to the insolubility of BPA in the solvent. Brunelle[7] reports retarded polycarbonate formation due to the low solubility of bisphenols in dichloromethane. The solubility of the bisphenols in dichloromethane increases steadily with molecular weight as the reaction proceeds.

We used anhydrous acetonitrile as the solvent for the starting materials.

Scheme 1



Equimolar amounts of *p*-nitrophenyl chloroformate and BPA were reacted with 2 equivalents of triethylamine and a 6 % stoichiometric equivalent of dimethylaminopyridine (DMAP). DMAP was used in addition to triethylamine to catalyze the condensation reaction. Brunelle[8] investigated the role of DMAP on the rate of transesterification of *o*- and *p*-nitrophenyl carbonates. He reported a quantitative yield of diphenylcarbonate from *o*-nitrophenyl carbonate and phenols at ambient temperature using only catalytic DMAP. We observed a slight rate enhancement when *p*-nitrophenyl carbonate was reacted with 2 equivalents of triethylamine and 1 % DMAP compared to the same reaction performed in the absence of DMAP.

The addition of triethylamine to a reaction flask containing the BPA and *p*-nitrophenyl chloroformate effected a bright yellow color formation due to the byproduct *p*-nitrophenoxide. Almost immediately after mixing, a suspension was formed as the polymer precipitated out of solution. After a 24 h reflux at 70-75°C, the precipitate was isolated and washed with methanol to remove the residual *p*-nitrophenoxide. A molecular weight value of M_n = 26,000 g/mol and a PDI = 1.88 were obtained relative to polystyrene standards. The polycarbonate was not end-capped. DSC analysis indicated T_g = 146 °C which is only slightly lower than the literature value of 150°C.[9] We do not have an explanation for the lower T_g.

In summary, we have found that using *p*-nitrophenyl chloroformate as carbonate-source is a simple and convenient laboratory method for the synthesis of BPA polycarbonate. This method avoids the direct use of phosgene or the potential exposure of a researcher to the phosgene byproduct generated during the use of di- and triphosgene. We successfully syntheBPA polycarbonate that closely corresponded to commercial samples. We believe that this method is general and could be easily extended to other polycarbonates.

Experimental

Materials

Acetonitrile (99.8% anhydrous) and 4-*N*,*N*-dimethylaminopyridine (DMAP) (99 + %) were used as received from Aldrich. Glacial acetic acid was used as received from

Fisher Scientific. Triethylamine (Aldrich) was distilled from calcium hydride; bisphenol A (99 + % Aldrich) was recrystallized from glacial acetic acid and water (1:1, v/v) and dried *in vacuo* prior to use; *p*-nitrophenyl chloroformate (97% Aldrich) was sublimed prior to use.

Characterization

Size exclusion chromatography was performed using a Waters 501 HPLC pump, 2 PLgel (Polymer Laboratories) mixed D columns (5 µ), and a Waters 410 differential refractometer. The eluent was THF and the flow rate = 0.5 mL/min. Data analysis was performed using EZChrom software (Scientific Software, Inc.) and the molecular weights were determined relative to polystyrene standards. Differential scanning calorimetry measurements were done with a TA instruments DSC 2910 in nitrogen. A ramp rate of 20°C/min to 200°C was used.

Synthesis of bisphenol A (BPA) polycarbonate

A 0.318 M stock solution was prepared from 1.8 g of bisphenol A in 25 mL of anhydrous acetonitrile in a volumetric flask. A 0.318 M volumetric stock solution of 1.6 g of dry, sublimed *p*-nitrophenyl chloroformate was also prepared in 25 mL of anhydrous acetonitrile. 5 mL of the bisphenol A stock solution (1.59 mmol) and 5 mL of the *p*-nitrophenyl chloroformate stock solution (1.59 mmol) were added *via* syringe to a 25 mL round bottom flask containing 0.011 g (0.09 mmol) of 4-dimethylaminopyridine. 0.44 mL (3.18 mmol) of distilled triethylamine was added *via* syringe and the mixture was heated to reflux under an argon atmosphere. After 24 h the polymer was isolated by filtration to afford a 77% yield of polymer; M_n = 26,000 g/mol; PDI=1.88; T_g = 146°C; T_m = 235°C. The polymer was not end-capped.

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