Efficient method for polymerization of diallycarbonate and hexa(allylcarbonate) monomers and their thermal properties

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Abstract
Polymers have had a significant increase in the industrial field, and polycarbonates (PCs) are an example. PCs have important properties such as high impact resistance, high heat capability, hardness, toughness, optical clarity, heat resistance, abrasion resistance and high refractive index. PCs with these properties have a variety of applications, for example, astronaut helmets, CDs/DVDs, automobile parts, bulletproof windows, ophthalmic lenses and welding masks. In the present work we report the synthesis and characterization of network polycarbonates, based (1,1'-biphenyl)-4,4'-diylallylcarbonate (I) and hexa(4-allylcarbonatephenoxy) cyclotriphosphazene (III). The polycarbonates were obtained by bulk polymerization technique. The polymers obtained with thermal initiators showed degrees of cross-linking greater than 80%. The PCs obtained have thermal stability to 250 °C. The polycarbonate obtained from the monomer III showed a limiting oxygen index of 46.3%, therefore this polymer can be considered potentially useful as flame-retardant.

1. Introduction
Polycarbonates have been synthesized by different synthetic routes such as: reaction of diols with phosgene, copolymerization of epoxides with carbon dioxide in the presence of organometallic catalysts, ring opening polymerization of cyclic carbonate monomers, condensation of diols with CO2, and radical polymerization of the vinyl or allyl carbonate monomers.1-3 Monoallylic compounds do not form homopolymers of high molecular weight under free-radical initiation. However, the reactivity of the allylcarbonate monomers is enhanced with the increase of allylic groups, triallylcarbonate>diallylcarbonate >monoallylcarbonate. The radical polymerizations of allylcarbonate monomers have been studied using different initiators, such as peroxide, azo and peroxydicarbonate compounds, but due to their relatively low reactivity of this allyl compounds, high concentrations of initiators are needed (>3%) to be polymerized in a reasonable time. Other alternative for synthesis of PCs via free radical is the use of UV-Vis radiation and high energy radiation (gamma and electron radiation). In this work we are reporting the syntheses of allylcarbonate monomers, the syntheses of polycarbonates network, and thermal stability of network. The polycarbonates were obtained by bulk polymerization technique using benzoyl peroxide as initiator.
2. Experimental Section

2.1 Materials

All of the chemicals and solvents were reagent grade. Hydroquinone, hexachlorocyclotriphosphazene and 4,4'-biphenol were used as received without further purification. Allyl chloroformate and pyridine were distilled before use. Acetone was dried with potassium carbonate and distilled prior to use. Allyl(4-hydroxyphenyl) carbonate (II) was synthesized in the lab as described in the literature.

2.2 Instruments

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer FT-IR System 2000, using a KBr plate. $^1$H NMR (400MHz), $^{13}$C NMR (400MHz), and $^{31}$P NMR (400MHz), spectra were obtained with a Varian Mercury spectrometer. As convention, the $^1$H NMR and $^{13}$C NMR spectra were referenced to tetramethylsilane, chloroform CDCl$_3$ or acetone-d$_6$ as the solvent. Thermogravimetric study was carried out on a Mettler–Toledo (851) equipment with nitrogen as the purge gas at a 10 °C min$^{-1}$ scanning rate from 25 to 800 °C. Elemental analysis was obtained with a Perkin Elmer analyzer (2499 C, H, N, Serie II), using acetonitrile reference.

2.3 Synthesis of (1,1'-biphenyl)-4,4'-diylidiallylcarbionate monomer (I)

The compound I was synthesized by a Schotten-Baumann reaction, Figure 1a. A solution of 4,4'-2,4'-pentamethylene-bis(4-hydroxyphenyl) (2499 C, H, N, Serie II), using acetanilide reference.

2.4 Synthesis of hexa(4-allylcarbonatephenoxy)cyclotriphosphazeno monomer (III)

The compound III was synthesized in two steps, Figure 1b. In the first step, the compound II was prepared, as described in the literature.

2.5 Synthesis of the 1,1'-biphenyl-4,4'-diallylcarbionate homopolymer (IV)

The compound II was polymerized in sealed pyrex tubes using benzoyl peroxide as initiator (5 weight %). The tubes were degassed by the usual freezing and thawing technique under vacuum and then sealed off. Tubes were taken out at different times and then the polymerized samples (cured monomer or castings) were analyzed. The percentage of insoluble crosslinked polycarbonate formed (gel...
content) was obtained by extracting the soluble part (sol fraction) from the cured monomer with CH$_2$Cl$_2$ and filtration. After the extraction, the gel content was dried to a constant weight. Gel content is taken as the weight percent of polymer formed, % gel. Sol and gel fractions were characterized by IR and elemental analysis. All the reaction systems were homogeneous before polymerization as well as at the end of polymerizations. FTIR (cm$^{-1}$): 3080 ($\nu$C-H), 2950 ($\nu$C-H), 1761 ($\nu$C=O), 1602 ($\nu$C=C aromatic), 1272 ($\nu$-C-O-C-), 933 ($\nu$ aromatic).

2.6 Synthesis of the phosphazene-cyclomatrix homopolymer (V)

100 mg of the compound III and 5 mg de benzoyl peroxide (5 weight %) were placed in two necked flask, equipped with a stirrer, thermometer and argon inlet. The temperature of the reaction mixture was increased to 90 °C and stirred for 72 h. The polymer was formed as a white solid. The solid obtained was separated by filtration. The polymer was washed in acetone in order to remove the residual monomer. FT-IR (cm$^{-1}$): 2960 ($\nu$C-H), 1758 ($\nu$C=O), 1500 ($\nu$C=C Aromatic) 1262 ($\nu$-C-O-C-), 1196, 1178 and 1165 ($\nu$P=N) 856 ($\nu$cyclotriphosphazene ring).

3. Results and discussion

3.1 Monomers characterization

The compound (1,1’-biphenyl)-4,4'-diyldiallylcarbonate monomer is a white solid (90% yield). The hexa(4-allylcarbonatephenoxy)cyclotriphosphazeno monomer (III) is a colorless, viscous liquid. It was obtained with a purity of 99.8% and 60% yield. The chemical structures of monomers I and III were characterized by FTIR spectroscopy, $^1$H, $^{13}$C and $^{31}$P NMR spectroscopy. Results are present in the experimental section.

Formation of allylcarbonate monomers is evident from their $^1$H NMR spectra (Figure 2). The most important signals for both allylcarbonate monomers were the multiplets assigned to the protons of CH$_2$= (H$_D$) allylic group at 5.36 and 5.47 ppm for compound I, and at 5.33 and 5.20 ppm, for the monomer III, besides the signal of -CH- allyl group (H$_C$) was found in the range 6.08-5.96 ppm for the monomer I and in 5.95-5.83 ppm for the monomer III.

3.2 Polymers characterization

Bulk polymerization of monomers I and III using 5 weight % of benzoyl peroxide as initiator were studied at 90 °C. After polymerization, the cross-linked polycarbonates obtained from compounds I and II were practically colorless and insoluble in organic solvents. For the polymer IV the crosslinking was 96% after three hours of polymerization, whereas using reaction times lower than two hours the degree of crosslinking was negligible. The homopolymer V was obtained in 34 h, its formation was evident from typical FTIR. The absorption bands at 1205, 1176 and 1159 cm$^{-1}$ were attributed to P=N and P-N bonds in phosphazene rings. The absorption band at 1260 cm$^{-1}$ was attributed to the $\nu$C-O-C- ester group. Other evidence in FTIR was the absence of the signal at 1649 cm$^{-1}$ corresponding to the $\nu$C=C of allyl group.

Figure 1. Synthetic route of (1,1’-biphenyl)-4,4'-diyldiallylcarbonate (a), and cyclomatrix phosphazene hexa(4-allylcarbonatephenoxy)ciclotriphosphazene (b)
Figure 2. Spectra $^1$H NMR of monomers (1,1'-biphenyl)-4,4'-diyldiallylcarbonate (a), and cyclomatrix phosphazene hexa(4-allylcarbonatephenoxy)ciclotriphosphazene (b)

Thermal properties of the polymers obtained were analyzed by TGA. Figure 3 shows a comparison between the TGA curves of the polymers obtained. The polycarbonates exhibit good thermal stability as is reported in the literature.\(^{(5)}\) The polymer IV is stable to 250 °C, while the polymer V begins to decompose at 240 °C. Also is interesting the behavior at 800 °C, polymer IV has lost 90% of its total weight, whereas the Polymer V has lost 28% of its weight. The result show that the polycarbonate with cyclomatrix has highest thermal stability, and the polycarbonate \(V\) could present the property of the flame retarder.\(^{(6)}\) The limiting oxygen index (LOI) calculated via char yield data at 800 °C, using the semi-empirical formula proposed by Ven Krevelen,\(^{(7)}\) was 46.3%.

Figure 3. TGA of 1,1'-biphenyl-4,4'-diallylcarbonate homopolymer (red) and phosphazencyclophosphazene homopolymer (black)

4. Conclusions

(1,1'-biphenyl)-4,4'-diallylcarbonate and cyclomatrixphosphazene hexa(4-allylcarbonatephenoxy) ciclotriphosphazene were easily synthesized in high yields and were bulk polymerized by thermal crosslinking with free radical initiators such as benzoyl peroxide. The PCs obtained have thermal stability to 250 °C. The polycarbonate V showed a limiting oxygen index of 46.3%, therefore this polymer can be considered potentially useful as flame-retardant.

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