

ABSTRACT

The thesis presents results on the synthesis and characterization of diaryl carbonates, poly(arylcarbonate)s and poly(arylester-carbonate)s by carbonate interchange reaction using dimethyl carbonate. The reaction of dimethyl carbonate with aromatic hydroxyl compounds is thermodynamically unfavorable owing to very low K_{eq} of 3×10^{-4} at 453 K. Therefore the achievable efficiency of this reaction is largely controlled by catalysts.

The feasibility of carbonate interchange reaction of phenol was studied at atmospheric pressure using various organotin and titanium compounds as catalysts. The generality of this reaction was explored with various substituted phenols and alcohols. The nature and position of substituent exerted a significant effect on conversion to diaryl carbonates. A maximum of 53 % conversion of phenol to diphenyl carbonate was obtained. Diaryl, substituted diaryl and dialkyl carbonates were characterized by IR, $^1\text{H-NMR}$ and mass spectra.

Carbonate interchange reaction of bisphenol-A with dimethyl carbonate (dimethyl carbonate : bisphenol-A = 2) was studied in the temperature range of 110 - 240°C using di-n-butyltin oxide, 1,3-diphenoxytetrabutyl distannoxane, di-n-butyltin dilaurate, titanium isopropoxide, titanium phenoxide, antimony trioxide, disodium salt of bisphenol-A and sodium borohydride as catalysts. Of these, tin compounds were found to be effective and no reaction occurred in presence of titanium catalysts. Oligo(arylcarbonate)s were characterized by IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, UV spectra and VPO. Few oligo(arylcarbonate)s were characterized by GPC and FAB-MS.

Oligo(arylcarbonate)s with different degree of polymerization were postpolymerized using tin and titanium compounds as catalysts to poly(arylcarbonate)s. Oligo(arylcarbonate)s were also polymerized with diphenyl carbonate and polymers were characterized by viscosity, DSC and UV.

Various bisphenols such as hydroquinone, bisphenol-A, 2,2'bis(4-hydroxy 3-methylphenyl) propane, 1,1'bis(4-hydroxyphenyl) cyclohexane, 4,4'sulfonyldiphenol, 4,4'hexafluoroisopropylidene diphenol and 4,4'biphenol were reacted with excess dimethyl carbonate using 1,3-diphenoxytetrabutyl

distannoxane as catalyst. In all cases, the major product was the mono-methylcarbonate and minor component was the bis-carbonate. These products were characterized by IR, $^1\text{H-NMR}$, mass spectra and elemental analysis.

A new class of di(ester-carbonate) monomers were prepared by reaction of mono-methyl carbonate of bisphenol-A with diacid chlorides at 0°C using triethylamine as acid acceptor and were characterized by spectroscopic techniques. Self polymerization of these monomers in presence of titanium isopropoxide as catalyst resulted in the formation of copoly(arylester-carbonate)s having an ester to carbonate ratio of 2:1. Copoly(arylester-carbonate)s rich in ester and carbonate groups were also prepared by copolymerization. The polymer structure was established by $^1\text{H-NMR}$ and IR spectroscopy. The ordered sequence of ester-carbonate groups in the polymer was established by $^{13}\text{C-NMR}$ spectroscopy. The polymer properties were also evaluated by DSC, TGA and GPC.

Bis-allylether of bisphenols were synthesized by catalytic reaction using $\text{Pd}(0)$ catalyst with allyl and allyl methyl carbonate. The yield of bis-allylether of bisphenols were in the range of 80 - 85 %. These compounds were characterized by elemental analysis, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. Bis-allylether of bisphenol-A was epoxidised with excess m-chloroperbenzoic acid at 0°C . This resulted in the formation of mono- and bis-epoxidised products and were characterized by spectroscopic techniques.