

## Ring opening polymerization of ethylene carbonate with base as initiator

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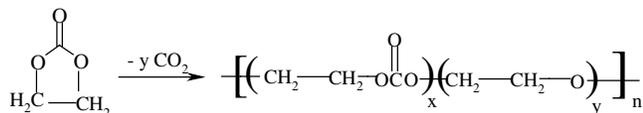
The study presents synthesis of industrially important polymer, polyethylene ether carbonate, via ring opening polymerization of ethylene carbonate using KOH as initiator at 200°C for 7 h. The molecular weight (1200-3400) and yield (40-80%) of the polymer were determined. The structure analysis using IR and NMR techniques showed the presence of carbonate and ether linkages in the polymer.

**Keywords:** Polycarbonate, Ethylene carbonate, Ring opening polymerization

**IPC Code:** C 08 G 64/02

### Introduction

Polycarbonate, one of the important classes of engineering plastics, is known for its higher mechanical properties especially impact strength. It is generally prepared by using phosgene<sup>1,2</sup>. Aliphatic polycarbonates (APs), though can be obtained from urea and diols, however, transesterification of dialkyl carbonates and diols is commonly used for commercial production<sup>3</sup>. APs are not generally useful materials for engineering thermoplastics due to their thermal instability and lack of ductility. APs are now gaining importance in the fields of medicinal, pharmaceutical and polymer synthesis. New applications of APs and their co-polymers with glycolide or lactide serve as biodegradable materials for medical sutures and drug delivery systems. Decomposition of APs with  $\beta$ -hydrogens leads to olefins, CO<sub>2</sub> and alcohol<sup>4</sup>. AP diols are found to be useful in synthesis of polyurethanes having exceptional properties derived from carbonate linkage only<sup>5-9</sup>.



The ring opening polymerization of cyclic carbonates is an alternative route to obtain polycarbonate. Ethylene and propylene carbonates are

unique in ring opening polymerization with their ceiling temperature below 25°C. Even though they are customarily polymerized above 100°C, polymerization is normally accompanied by decarboxylation and the final polymer obtained is typically a polyether carbonate<sup>10</sup>. The loss of CO<sub>2</sub> depends on mechanism of polymerization (cationic or anionic) and makes the entropy of the polymerization positive, causing polymerization thermodynamically possible at high temperatures. Ethylene carbonate could be polymerized using different Lewis acids, transesterification catalysts, as initiators<sup>11,12</sup>. Using such initiators, normally resultant polymers contained 40-50 percent carbonate units. The polymerization of ethylene carbonate with basic catalysts is studied very rarely<sup>13</sup>.

The paper reports on polymerization of ethylene carbonate with KOH as initiator and the polymerization behavior.

### Experimental Details

#### Materials

Ethylene carbonate (E Merck Ltd, Germany) was used as procured. KOH was dried at 110°C for three days and grounded into powder, which was directly used as initiator. The other chemicals were obtained from S D Fine chemicals Pvt Ltd, Mumbai and used without further purification.

#### Polymerization

The reaction vessel (10 ml) was flame dried. Measured quantities of ethylene carbonate and KOH (mole ratio, 1000:1) were placed into flask.

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Polymerizations were carried out without any solvent. The reaction flask was flushed with  $N_2$ . The flask was immersed in oil bath at  $200^\circ\text{C}$ . The reaction was carried out for predetermined time (7 h).

#### Isolation of Polymers

The reaction mixture was cooled and dissolved in ethanol and the solution was poured into excess of ether, whereupon viscous polymer precipitated while monomer remained dissolved in the ether. The ether layer was then decanted and polymer was washed with ether.

#### Characterization

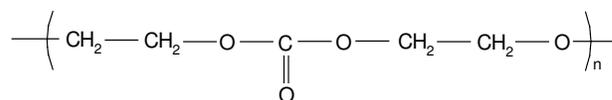
The polymer was analyzed for IR and  $^1\text{H}$  NMR. The composition of the polymer was determined using Jeol NMR spectrometer (90 MHz), while spectra for IR frequencies were scanned on Shimadzu 8000 spectrophotometer.

#### Results and Discussion

Ethylene carbonate was bulk polymerized with KOH with different mole ratios to get higher molecular weight at temperatures  $150$ ,  $180$  and  $200^\circ\text{C}$  to obtain higher yield in less reaction time. Out of three different ratios (1000:1, 500:1 and 200:1), the mole ratio (1000:1) performed best with all three-reaction temperatures. Around 98 percent monomer is converted to polymer during 7-8 h and further heating causes depolymerization reaction<sup>14</sup>. Similar results were observed in this study. The longer reaction time caused lowering in molecular weight of the product. Hence, the polymerization was carried out for 7 h and stopped by cooling the flask to room temperature at once. Out of three temperatures,  $200^\circ\text{C}$  was efficient for better yield in 7 h reaction time.

On heating the reaction mixture, KOH started to dissolve in the reaction medium and after 30 min all the KOH got dissolved. The colour of reaction mixture changed from colourless to yellow. The polymer was isolated by pouring reaction mixture in diethyl ether. The isolated polymer was characterized by IR and NMR (Figs 1 & 2). IR spectrum shows absorption at  $1710\text{ cm}^{-1}$ , which is indicative for carbonyl groups while  $1350\text{-}1300\text{ cm}^{-1}$  and  $1100\text{-}1150\text{ cm}^{-1}$  are attributed to carbonyl-oxygen stretching of carbonate linkage and carbon-oxygen stretching of ether linkage, respectively. A broad peak at  $3450\text{ cm}^{-1}$  was attributed to terminal  $-\text{OH}$  confirming the diol end groups of the polymer. This elucidated the

structure of polymer with ether and carbonate linkage as shown below:



The NMR spectrum shows two peaks at  $\delta$  4.31 and 3.75 ppm. The peak at  $\delta$  4.31 ppm is shown by the methylene protons in structure, which is shifted from its value 3.4 ppm due to deshielding, which is observed due to adjacent electron withdrawing carbonate group. The ether linkage shielded the protons of methylene group (b) and located at down field (3.75 ppm).

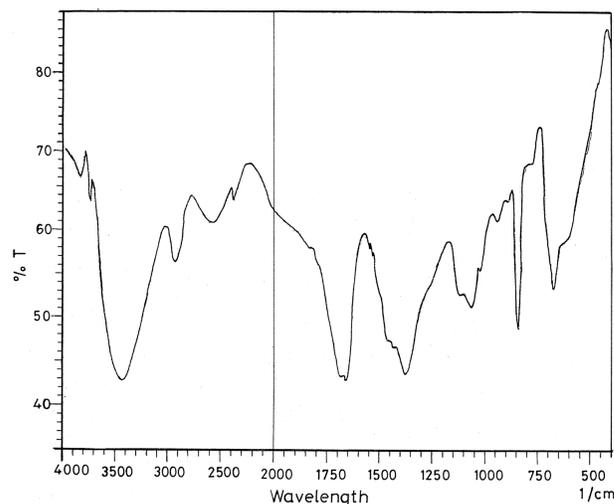


Fig. 1—IR spectrum of polyethylene ether carbonate

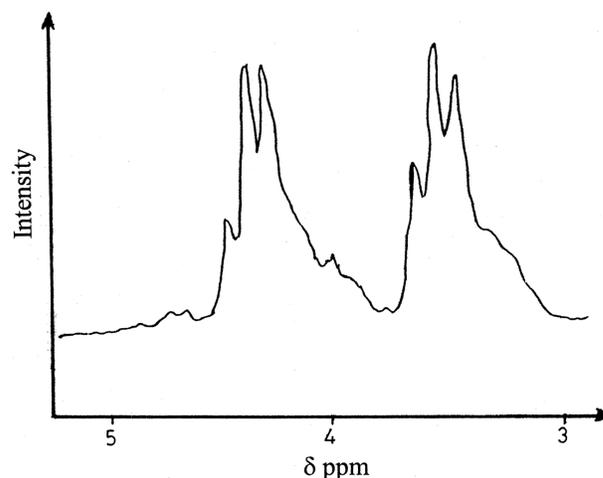
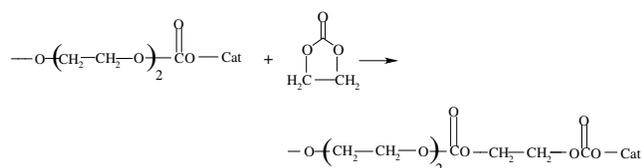


Fig. 2—NMR spectrum of polyethylene ether carbonate

As the reaction proceeded, the peak intensity of proton decreased due to monomer ethylene carbonate i.e. singlet at 4.54 ppm decreased. During polymerization, a fraction of the ethylene carbonate units decarboxylated so that a copolymer of ethylene carbonate and ethylene oxide was obtained.

The NMR results show that the polymer contains about 50 percent ether linkage and 50 percent carbonate linkages. The ethylene carbonate content in the polymer could be varied from 10 to 50 percent; however, in no case it was found to be higher than 50 percent. Polymerization occurred above the ceiling temperature for pure polyethylene carbonate and that propagation occurred via monomer insertion between the growing polymer chain end and a catalyst fragment.



The ring opening polymerization of ethylene carbonate with KOH initiator was found advantageous in terms of less reaction time required for polymerization compared to Lewis acid catalysts which required reaction time >50 h to get products with 40-50 percent carbonate linkages<sup>13</sup>.

### Conclusions

Ring opening polymerization of ethylene carbonate using KOH shows that the produced polymer contains 50 percent carbonate and 50 percent oxide linkages. The monomer to initiator mole ratio (1000:1) was effective to get higher molecular weight products. Out of three temperatures (160, 180 and 200°C), highest yield (80%) was obtained at 200°C. The reaction time of 7 h was sufficient to get high molecular weight product with good enough yield.

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