

## Solution Viscosity and Relative Reactivity of Branched and Linear Polycarbonates

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**Abstract** : The relative reactivities of branched and linear polycarbonates were investigated by measuring unreacted chloroformate concentration. It was found that the polymerization for the branched polymer proceeded ca. 10 times faster than that for the linear polymers. The effect of catalyst on a condensation step was studied by changing the amount of TEA (triethylamine) at  $t_0$  and  $t_{90}$  with keeping constant amount of TEA. The viscosity average molecular weight for the obtained branched polycarbonates were measured and compared with those of linear polycarbonates. It was found that the viscosity molecular weights of the obtained polymers decreased nonlinearly as wt % of added oligomer increased. The solution viscosities in methylenechloride for linear and branched polycarbonate increased nonlinearly as the content of polymer increased.

### I. Introduction

Polycarbonates are known to be a tough, clear, and highly impact resistance thermoplastic resin.<sup>1-3)</sup> Branched polycarbonates can be synthesized using any of previous processes by a small amount of polyfunctional branching agent monomer such as triphenols, tetraphenols, dihydric phenols, and hydroxy carboxylic acid.<sup>4-6)</sup> These branched polycarbonates, which differ from most thermoplastic polymers, exhibit the characteristics of the non-Newtonian flow over essentially all melt processing conditions. Branched polycarbonate resins are suitable for blow molding applications such as the production of a large volume of hollow products and large panels which are required high melt strength and high shear sensitivity of polymers as indicated by a melt index ratio (MIR) greater than 20.<sup>7-9)</sup> Polycarbonates with a critical degree of branching are required to achieve such properties.<sup>10, 11)</sup>

Recently, investigations in laboratory have been focused on the synthesis of branched polycarbonates with trihydroxy co-monomers as a

branching agent and the study of their properties.<sup>12)</sup> Cyclic oligomers that are formed in the interfacial polymerization make a significant portion of total oligomer contents in synthesized polymers. In the linear polycarbonate, linear oligomers were formed as much as cyclic oligomers. However, in the branched polycarbonate, the amount of cyclic oligomers is approximately 2 times larger than that of linear oligomers. Thus it can be suggested that these characteristics depend on the trihydroxy functional groups of branching agent. The polymer properties are related to the oligomer content that directly affects molecular weight distribution, degradation, and generation of gases in the molding.<sup>13)</sup>

Important factors in interfacial polymerization are as follows: the ratio of bisphenol A and phosgene, the addition rate of phosgene, reaction temperature, sodium hydroxide concentration, the ratio of methylene chloride and water layers, types and the amount of catalyst, organic and inorganic materials in distilled water, and a polymer content in solution etc. These factors affect reaction rate and polymer properties. Interfacial phosgenation of

bisphenols to form polycarbonates is catalyzed by trialkylamines. Trialkylamines also react with chloroformate-terminated intermediates and form ammonium salts. These salts are important intermediates in the polymerization but also may undergo decomposition to chain-terminating carbamates that contaminate the polymer.<sup>14-21</sup> We proposed that the molecular weight of branched polymers could be controlled in the early condensation stage in which the phenolates in branching agent react well with chloroformate to form branch and cyclic molecular structure.<sup>12</sup> The phenolates in branching agent should have the much more chance of making carbonate bond by trifunctional hydroxy groups than linear polymerization.

In the present study, we describe our efforts to investigate the relative reactivity of branched and linear polycarbonates in condensation polymerization by measuring the unreacted chloroformate concentration and the effect of triethylamine of varying amounts on the condensation steps. In addition, the viscosity average molecular weights of the obtained linear polycarbonates from the different amounts of oligomers added in methylene chloride solution were investigated. We measured solution viscosities of branched polycarbonates in methylene chloride solution for various wt % and compared these values with those of linear polycarbonates.

## II. Experimental

### 1. Materials and Instrumentation

Bisphenol A, THPE (1,1,1-tris-*p*-hydroxyphenylethane), TEA (triethylamine), and PTBP (*p*-*tert*-butylphenol) were purchased from Aldrich Chemical Co. Common reagents such as sodium hydroxide, methylene chloride, aniline, and phenolphthalein, were used without further purification. TEA was used as a solution of 15 wt% in aqueous solution, and PTBP was used as a solution of 24wt% in methylene chloride solution. The <sup>1</sup>H NMR spectra were collected on a Bruker DRX (300MHz) spectrometer. Deuterated methylene chloride was used as a solvent, and

tetramethylsilane (TMS) as an internal standard. Average viscosity molecular weights ( $M_v$ ) of polymer solution (0.5g/dL) in methylene chloride were obtained by measuring five satisfactory readings of efflux time using an Ubbelohde viscometer at 20°C.

### 2. Preparation of branched polycarbonate

To a 3 L three-necked round bottomed flask fitted with a nitrogen inlet and an ice jacket, were added bisphenol A (0.5mol, 114g) and 5.4wt % aqueous NaOH solution (1.12mol, 44.8g). Phosgene (0.65mol, 64.35g) dissolved in 950mL of methylene chloride was slowly added to the solution and stirred for 30 min. Methylene chloride and water layers were separated from the reaction mixture. The molecular weight of obtained oligomer in methylene chloride was 1,000. To a 1L three-necked round bottomed flask were placed 200mL of methylene chloride layer (bisphenol A, 0.17mol), 300mL of water layer and added 3.73mL of *p*-*tert*-butylphenol (24 wt%, 6mmol) as a molecular weight controller, 0.073g of TEA (15 wt%), 0.266 g of THPE (0.35mol % of bisphenol A) dissolved in NaOH (0.25g/10 mL H<sub>2</sub>O) solution. The reaction mixture was maintained for 30 min. at room temperature. The methylene chloride layer was then separated. To a solution of the separated methylene chloride were added 0.1 g of TEA, 80mL of methylene chloride, 8.2g of NaOH in 57mL of distilled water, and the mixture was reacted for 150 min. The obtained polymer solution was washed with distilled water (3×250mL), neutralized with HCl, and poured into 800 mL of mixture of acetone and distilled water (50/50, v/v) to give a white granular polymer.  $T_g=150$  °C, <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ 1.35 (s, -C(CH<sub>3</sub>)<sub>3</sub>),  $\delta$ 1.65 (s, -CH<sub>3</sub>, THPE),  $\delta$ 1.7 (s, -CH<sub>3</sub>),  $\delta$ 6.6-6.7 (m, THPE, aromatic H),  $\delta$ 7.1-7.3 (m, bisphenol A aromatic H). MIR=23,  $M_w=25500$ , and polydispersity ( $M_w/M_n$ ,  $M_w=95400$ ,  $M_n=29800$ ) = 3.20; MIR=25,  $M_w=26,500$ , and polydispersity ( $M_w/M_n$ ,  $M_w=98500$ ,  $M_n=30000$ ) = 3.28.

### 3. Preparation of linear polycarbonate

To a 3 L three-necked round bottomed flask

fitted with a nitrogen inlet and an ice jacket, were added bisphenol A (0.5mol, 114g) and 5.4 wt % aqueous NaOH solution (1.12mol, 44.8g). Phosgene (0.65mol, 64.35g) dissolved in 950 mL of methylene chloride was slowly added to the solution and stirred for 30 min. Methylene chloride and water layers were separated from the reaction mixture. The molecular weight of obtained oligomer in methylene chloride was 1,000. To a 1 L three-necked round bottomed flask were placed 200mL of methylene chloride layer (bisphenol A, 0.17mol), 300mL of water layer and added 3.73 mL of p-tert-butylphenol (24 wt %, 6 mmol) as a molecular weight controller, 0.073g of TEA (15 wt %). The reaction mixture was maintained for 30min at room temperature. The methylene chloride layer was then separated. To a solution of the separated methylene chloride were added 0.1g of TEA, 80mL of methylene chloride, 8.2g of NaOH in 57mL of distilled water, and the mixture was reacted for 150 min. The obtained polymer solution was washed with distilled water (3× 250mL), neutralized with HCl, and poured into 800mL of mixture of acetone and distilled water (50/50, v/v) to give a white granular polymer.  $T_g = 150\text{ }^\circ\text{C}$ ,  $^1\text{H NMR (CD}_2\text{Cl}_2)$   $\delta$ 1.35 (s,  $-\text{C}(\text{CH}_3)_3$ ),  $\delta$ 1.7 (s,  $-\text{CH}_3$ ),  $\delta$ 7.1-7.3 (m, aromatic H).  $\text{MIR}=10$ ,  $M_v=30,000$ , and polydispersity ( $M_w/M_n$ ,  $M_w=54200$ ,  $M_n=28200$ ) = 1.92 :  $\text{MIR}=11$ ,  $M_v=21000$ , and polydispersity ( $M_w/M_n$ ,  $M_w=44500$ ,  $M_n=23400$ ) = 1.9.

#### 4. Measurement of unreacted chloroformate concentration

During polymerization, 10mL of methylene chloride layer was subsequently collected at 0 min ( $t_0$ ), 60min ( $t_{60}$ ), 90min ( $t_{90}$ ), 120min ( $t_{120}$ ) and 150min ( $t_{150}$ ) of reaction. To each collected solution, were added 2mL of aniline, 30mL of distilled water, and 1-2 drops of phenolphthalein indicator. The chloroformate concentration was measured by titration with NaOH (0.5 N) solution.

#### 5. Viscosity average molecular weight and solution viscosity

The solution viscosity of polymers was measured on a Haake Model VT 550 and Brookfield Model

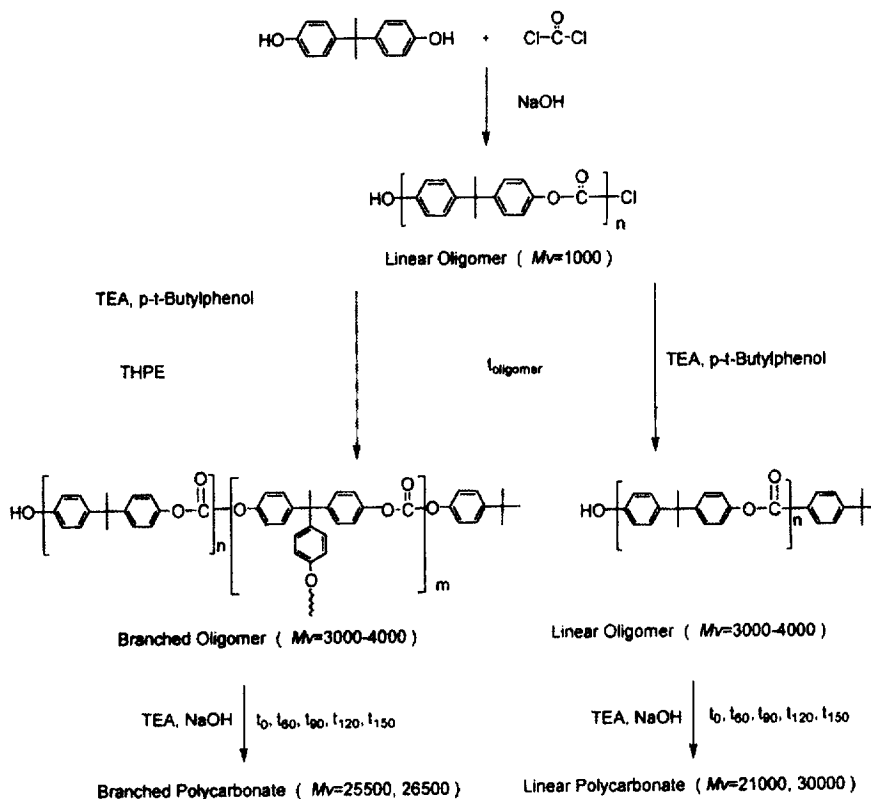
DV-II viscometers. We studied viscosity molecular weight of the obtained polymers after polycondensation for various amounts of oligomers (10, 12, 15, 18, and 21 wt %) in methylene chloride solution. We also investigated solution viscosity vs. wt % (10, 15, 18, 20, 21, 23, and 24 wt %) of linear ( $M_v=21,000$  and 30,000) and branched polycarbonates ( $M_v=25,500$  and 26,500) in methylene chloride solution

### III. Results and discussion

#### 1. Unreacted chloroformate concentration

Reactivity of polycarbonates was studied by monitoring the unreacted chloroformate concentrations in polymers at 0min ( $t_0$ ), 60min ( $t_{60}$ ), 90min ( $t_{90}$ ), 120min ( $t_{120}$ ) and 150min ( $t_{150}$ ) (Scheme 1). The chloroformate concentration was measured by titrating methylene chloride solution containing polymers with NaOH (0.5 N) solution until the solution changed from colorless to pink. The branching agent appeared to affect significantly the polymerization rate and change the chloroformate concentrations in polymer. In Figure 1, the chloroformate concentrations for two linear and one branched polycarbonates are shown as a function of reaction time. At the oligomerization stage ( $t_{\text{oligomer}}$ ), the chloroformate concentrations for all three samples were the same. At the early condensation stage, the chloroformate concentrations decreased for all three polycarbonates. However, the decrease in the concentration for a branched polycarbonate, i.e. from 1000  $\mu\text{eq}$  to 30  $\mu\text{eq}$ , was more drastic than those for linear polycarbonates (from 1000  $\mu\text{eq}$  to ca. 300  $\mu\text{eq}$ ). It was found that the polymerization for the branched polymer proceeded ca. 10 times faster than that for the linear polymers.

In the branched polycarbonate polymerization, the early condensation stage was important to determine polymer properties such as the formation of cyclic oligomers, molecular weights, and molecular weight distributions. At this stage, phenolates reacted easily with chloroformates of other chains, resulted in the formation of high molecular weight polymers when the amount of



Scheme 1. Synthesis of linear and branched polycarbonates

sodium bisphenolates was large. In the case of the polymerization for linear polycarbonate, when the reaction time increased from 60 min ( $t_{60}$ ) to 90 min ( $t_{90}$ ), for the low molecular weight polycarbonate ( $M_v=21,000$ ) the amount of the unreacted chloroformate decreased gradually, whereas it decreased rapidly for the high molecular weight polycarbonate ( $M_v=30,000$ ). The molecular weight distributions of linear polycarbonates were in the range of 1.9-2.3, while those of branched polycarbonates significantly increased to the range of 3.2-3.5. From the above findings, it could be concluded that in the branched polymer system the branching agent was effective in the formation of cyclic oligomers and branches in the polymer chain.

## 2. Effect of catalyst

In the present work, the relative reactivity studies in the branched polycarbonate system showed that at the polycondensation stage the

reaction rates were higher than that in the linear polycarbonate system. Therefore, the effect of varying concentrations of catalyst on a condensation step was studied. The reaction was

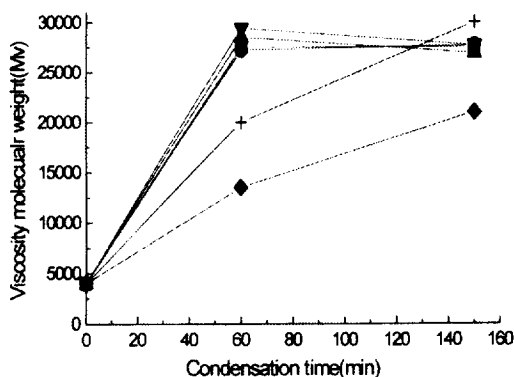


Figure 1. A plot of unreacted chloroformate concentration vs. reaction time in batch polymerization ●: linear PC ( $M_v=21,000$ ), ■: linear PC ( $M_v=30,000$ ), ▲: branched PC ( $M_v=25,500$ ).

carried out in a batch reactor with adding the amount of TEA at  $t_0$  and  $t_{60}$ . Figure 2 shows the viscosity molecular weights of branched polymers produced from the batch experiments when TEA were added 0.1 g at  $t_0$  and 0 g at  $t_{60}$  in 1L of methylene chloride which were denoted by 0.1/0 in Figure 2. For the various TEA weight ratios such as 0.1/0, 0.01/0.09, 0.02/0.08, and 0.03/0.07 with keeping constant total amount of TEA, the viscosity molecular weights for the obtained branched polymers were measured. It was found that molecular weights of linear polycarbonates ( $M_v = 21,000$  and  $30,000$ ) increased when TEA of 0.01 g and 0.09 g in 1 L methylene chloride was added at  $t_0$  and  $t_{60}$ , respectively. However, in the same condition, molecular weight of branched polymer increased fully at the first condensation step ( $t_0$ ) and decreased at the final condensation step ( $t_{60}$ ). It is because at this step the molecular weight of branched polymers could be controlled by phenolates in branching agent which reacted well with chloroformate to yield a maximum molecular weight. At this point, it should be noted that high pH and free TEA caused the decrease in molecular weight at final condensation step. The condensation rate of branched polycarbonate was so faster than that of linear polycarbonate at the early condensation stage that a TEA content did not affect the branched polycarbonate polymerization rate. After  $t_{60}$  molecular weight for branched polycarbonate decreased slightly. Therefore, it is proposed that in the case of branched polycarbonate the polymerization rate could be influenced by the branching agent rather than the TEA concentration.

### 3. Viscosity average molecular weight and solution viscosity

In condensation, washing, and granulation steps, the wt % of polymer in methylene chloride solution was an important factor that affects the reaction rate and molecular weight.<sup>21</sup> In case of high solution viscosity the bulk density of polymer was low because evaporation rate is slow, and low solution viscosity results in high bulk density. The former condition had a low productivity and the latter one had a packaging problem. Figure 3

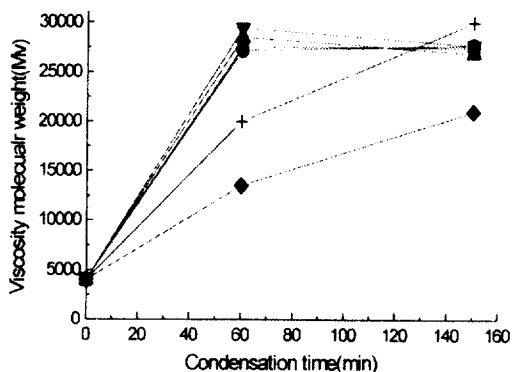


Figure 2. Viscosity molecular weights as functions of condensation time and weights of the added TEA in 1 L of methylene chloride at  $t_0$  and  $t_{60}$ . Branched PC; TEA weights at  $t_0$  and  $t_{60}$  (0.1/0,  $\blacktriangledown$ ), (0.03/0.07,  $\blacktriangle$ ), (0.02/0.0,  $\bullet$ ), (0.01/0.09,  $\blacksquare$ ), Linear PCs ; ( $M_v=21,000$ ,  $\blacklozenge$ ) and ( $M_v=30,000$ ,  $+$ ) ; TEA content (0.01/0.09). (0.1/0 means weights of the added TEA in 1 L of methylene chloride at  $t_0$  and  $t_{60}$ )

shows the viscosity molecular weights of the obtained linear polycarbonates from the different amounts of oligomers in methylene chloride solution, i.e. 10, 12, 15, 18, and 21 wt %. The figure shows that molecular weights of the obtained polymers decreased nonlinearly as wt % of added oligomer increased. However, in a commercial process, proper content (21 wt %) was needed for a better productivity. In the interfacial polymerization of polycarbonate, an organic layer containing polymers is a continuous phase, while a water layer is a dispersed phase. If the phases are reversed, polymerization and washing rates dramatically decrease. Therefore, we investigated the solution viscosities of linear and branched polymers to obtain the proper conditions. Figure 4 shows the solution viscosities for the various polymer solutions (10, 15, 18, 20, 21, 23, and 24 wt % in methylene chloride solution). At a low concentration, the solution viscosities were similar to each other. However, the solution viscosity increased nonlinearly as the wt% of polymer increased. It should be pointed out that the 24 wt% of polymer ( $M_v=30,000$ ) solution could not be prepared owing to the low solubility of polymer. From the figure, it was found that the

proper condition to obtain branched polycarbonates ( $M_v=25,500$ ) was 18 wt% in methylene chloride solution at which the solution viscosity was ca. 300 cP. It should be mentioned that, in the case of linear polycarbonate ( $M_v=21,000$ ), the 21 wt% sample showed a similar solution viscosity.

#### IV. Conclusions

The rate of polymerization for the branched polymer was ca. 10 times faster than that for the linear polymers by measuring the unreacted

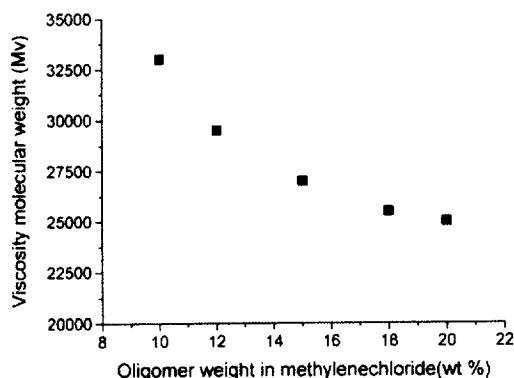


Figure 3. Effects of oligomer content in solution on viscosity molecular weights of the obtained polymers from the various content of oligomer.

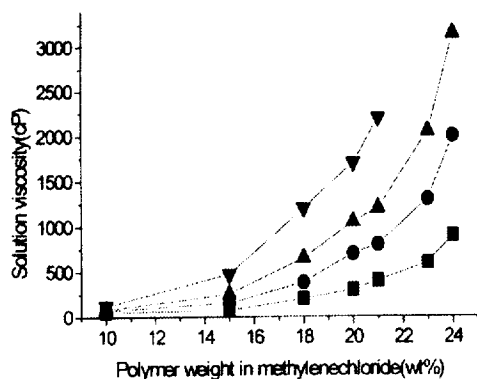


Figure 4. Relationship between the polymer content and solution viscosity in methylene chloride :  $\blacktriangledown$  : linear PC ( $M_v=30,000$ ),  $\blacktriangle$  : branched PC ( $M_v=26,500$ ),  $\bullet$  : branched PC ( $M_v=25,500$ ),  $\blacksquare$  : linear polycarbonate ( $M_v=21,000$ ).

chloroformate concentration. The effect of catalyst on a condensation step was studied by changing the amount of TEA at  $t_0$  and  $t_{60}$  with keeping constant amount of TEA. The viscosity molecular weights of branched polymers produced were measured. The molecular weight of branched polymer increased fully at the first condensation step ( $t_0$ ) and decreased at the final condensation step ( $t_{60}$ ). It is proposed that in the case of branched polycarbonate the polymerization rate could be influenced by the branching agent rather than the TEA concentration. It was found that the molecular weights from the obtained polymers decreased nonlinearly as wt % of added oligomer increased. The solution viscosity increases nonlinearly as the wt% of polymer increases. It was found that the proper condition to obtain branched polycarbonates ( $M_v=25,500$ ) is 18 wt % in methylene chloride solution at which the solution viscosity is ca. 300 cP. It should be mentioned that, in the case of linear polycarbonate ( $M_v=21,000$ ), the 21 wt % sample showed a similar solution viscosity.

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