alkylthiol. As known, the van der Waals interaction between alkylchain becomes larger as alkyl chain-length of organomercaptan increases. Therefore, the longer alkylthiol as adsorbate makes desorption more $MH_2Q$ molecules on electrode surface. However, unlike alkylthiols, benzylthiol made displacement only one half of a total amount of the adsorbed $MH_2Q$ even in longer immersion time. This demonstrates that there is no preference in chemisorption of benzylthiol and $MH_2Q$ on gold surface. In fact, $MH_2Q$ molecule has the same chemical structure and size as benzylthiol except two hydroxy groups on benzene ring and their nonpreferential chemisorption is a result from the structural similarity between adsorbate and substituent molecules. However, as shown in Figure 4, the fact that long alkylthiol readily displaces $MH_2Q$ from Au surface states that alkylthiol is preferentially or selectively chemisorbed into $MH_2Q$ layer. In this substitution, the adsorbate and the substituent are not only structurally dissimilar to each other but also different in size. The theoretical calculation[4d] of molecular cross-sectional area ($\sigma$) determined from van der Waals radii by Pauling[8] gives insight on size effect of substituent molecule. According to literature,[4d] the $\sigma$ value (22.5 Å$^2$/molecule) of alkylthiol is only one half of that of benzylthiol (47.4 Å$^2$/molecule). Therefore, it seems to be much easier for alkylthiol to be displaced on gold surface than benzylthiol over the SH functional group of $MH_2Q$. It is nontrivial question whether the two different components in the surface mixture are present homogeneously or heterogeneously. Although this question cannot be answered unambiguously at this moment, hiring of redox-active substituent and adsorbate molecules can provide indications of the heterogeneity of the mixed adsorbed layer from the comparison in the apparent cross sectional areas of substituent and adsorbate.

In conclusion, it is important to take into account the chemical/geometrical structure of substituent molecule in surface-adsorbate displacement reaction which is analogous to ligand exchange on metal substrate. Especially, when the substituent molecule has the same functional group as adsorbate, structural similarities in those molecules play a key role on preferential and nonpreferential coadsorptions of surface ligands on substrate.

**Acknowledgment.** The present studies was supported by the Basic Science Research Institute program, Ministry of Education, Korea, 1997, Project No. 97-3430.

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# Synthesis and Properties of Branched Polycarbonates

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*Received August 13, 1998*

Polycarbonates are one of the major thermoplastic engineering polymers and well known not only their excellent mechanical and electrical properties but also optical and self-extinguish characteristics.[1-4] Most polycarbonates are manufactured by an interfacial polymerization process which offers advantage to modify chemical structure and process. The linear polycarbonate has been severely restricted their use in the production of large hollow bodies by conventional

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extrusion blow molding operations as well as the production of various other shapes by profile extrusion methods.[5-7] Thermoplastic branched polycarbonates exhibit unique properties of non-Newtonian flow, melt elasticity and melt strength which permit them to be used to obtain such articles as bottles, bumper and sheet which were not heretofore easily or readily produced with linear polycarbonates. The branched polycarbonates can be prepared by reacting an aromatic polyhydroxy or polycarboxylicacid. In attempts to provide simple and fast tool to measure the elastic properties of branched polymer at processing conditions such as blown film extrusion, blow molding, forming, and thermoforming Maxwell[8-10] described the concept of the Melt Index (MI) measurement.

Although numerous polycarbonate systems are known to be usable for the interfacial polymerization, few reports[11-13] are available on the reaction kinetics and mechanism. However, in the branched polymers of experimental studies reported in the patents, the studies of reactivity and oligomers occurred in polymerization were not reported. Since branched polycarbonate has different geometry of chemical structure, it is necessary to compare the reactivity with linear polycarbonate. Considering the fact that a precise control of polymer properties and productivity is one of the key issues in designing or optimizing branched polymerization, one need to develop deep understanding of kinetics and associated chemical reactions such as oligomers in polymers. Gel permeation chromatography (GPC) is considered the most appropriate method to characterize a high molecular weight polymer, but limited to analyze the low molecular weight oligomers. Gur'yanova *et al.*[14,15] developed a Liquid chromatography (LC) method for polycarbonate using THF/water solvent system which is able to characterize the oligocarbonate with hydroxy end groups. Gu[16] established new LC method by applying the color development reagent which undertook to analyze the chloroformate containing oligomers, e.g. cyclic and linear oligomers, in the polycarbonate interfacial phosgenation. Oligomers in polymer considerably affect on the properties of polymers.

In this work we have studied the relative reactivities between linear and branched polycarbonate prepared from branching agents containing multi-hydroxyphenyl, and have analyzed the types and contents of oligomers in branched polycarbonate, as well as compared with those of linear polycarbonate.

## Experimental

$^1$H NMR spectra were taken in $CD_2Cl_2$ solution on a Brucker DRX (300 MHz). Bisphenol A, THPE (1,1,1-tris-*p*-hydroxyphenylethane), TEA (triethylamine) and PTBP (*p-tert*-butylphenol) were purchased from Aldrich Chemical Co.. Common reagents, e.g. sodium hydroxide, methylenechloride, were used without further purification. TEA was used 15 wt% in aqueous solution and THPE also was used 24 wt% in methylenechloride solution.

Viscosity molecular weights ($M_v$) of polymer solution (0.5 g/dL) in methylenechloride were obtained by measuring five satisfactory readings of the efflux time (polymer, t; solvent, $t_0$) with a Ubbelohde viscometer at 25 °C. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were performed with Perkin-Elmer TGA7 and DSC7 at a heating rate of 20 °C/min under a gas flow rate of 50 mL/min. Melt index ratios (MIR) were measured by Gottfert MPX 62.92 under weight of 21.6 kg and 2.16 kg at 260 °C, which is the ratio of melt flow rates at two different shear levels, and is a measure of non-Newtonian property of the polymer.

**Preparation of Branched Polycarbonate.** To a 3 L three-necked round bottom flask, fitted with a nitrogen inlet and ice jacket, were added bisphenol A (0.5 mol) and 5.4 wt% NaOH solution (1.12 mol). Phosgene (0.65 mol) dissolved in methylenechloride (950 mL) was slowly added and stirred for 30 min. Methylenechloride and water layers were separated from the reaction mixture. The molecular weight of obtained oligomer in methylenechloride was 1,000. To a 1 L three-necked round flask were placed methylenechloride layer 200 mL (bisphenol A 0.17 mol), water layer 300 mL and added *p-tert*-butylphenol (24 wt%, 4.17 mL, 6.7 mmol) as a molecular weight controller, TEA (15 wt%, 100 μL), THPE (0.3 mol% of bisphenol A, 0.228 g) dissolved in NaOH solution and maintained for 30 min at room temperature. After the reaction methylenechloride layer was separated. To a solution of the separated methylenechloride, TEA 146 μL, and methylenechloride 80 mL, NaOH 8.2 g in distilled water 57 mL was added and reacted for 90 min. The obtained polymer solution was washed with distilled water (3×250 mL), neutralized with HCl and precipitated in 800 mL mixture solution of acetone and distilled water (50 : 50, V/V) to give a white granule polymer. $T_g$=150 °C, $^1$H NMR ($CD_2Cl_2$) $\delta$ 1.35 (s, -C($CH_3$)$_3$), $\delta$ 1.65 (s, -C$CH_3$), $\delta$ 1.7 (s, -$CH_3$), $\delta$ 6.6-6.7 (m, THPE, aromatic H), $\delta$ 7.1-7.3 (m, bisphenol A aromatic H). MIR=21, $M_v$=23,000, MWD=3.3.

**Preparation of Linear Polycarbonate.** This reaction was carried out as in branched polycarbonate at room temperature without THPE as a branching agent. $T_g$=150 °C, $^1$H NMR ($CD_2Cl_2$) $\delta$ 1.35 (s, -C($CH_3$)$_3$), $\delta$ 1.7 (s, -$CH_3$), $\delta$ 7.1-7.3 (m, aromatic H). MIR=11, $M_v$=21,000, MWD=1.9.

**Oligomer Analysis.** Oligomers in linear and branched polycarbonates were separated by using LC (liquid chromatography) with column Spherisorb (ODS; 15 cm×4.6 mm, 5 μL) and detected in UV 270 nm. Typical sample preparation is carried out by dissolving 1.5 wt% of the polycarbonate in THF. It is preferable to analyze the freshly prepared sample immediately to avoid any undesirable side reaction that may occur in the solution. LC solvent for this developed method was run from THF/distilled water 50 : 50 (V/V) ratio in the initial time to THF 100% in the terminal time. A flow rate of 1.0 mL/min was used and column temperature was maintained 40 °C.

**Reactivity Measurement.** Polymerizations was assayed by monitoring the viscosity molecular weight ($M_v$) at that condensation time 30, 60, and 120 min respectively in order to compare reactivity with linear and branched polycarbonate. In attempt to describe the effect of PTBP polymerizations were carried out with changing content of PTBP at constant branching agent (0.3 and 0.5 mol% of bisphenol A).

## Results and Discussion

Branched polycarbonates were prepared by interfacial polymerization of oligomer ($M_v$=1,000) based upon phosgen-

ation of bisphenol A, and followed by condensation with *p-tert*-butylphenol as molecular weight controller and THPE as a branching agent in the presence of triethylamine as catalyst in batch reactor. In a preferred variant of the polymerization process, the branching agent is added in the form of an aqueous solution of its alkali metal salt. One advantage of this process is that the polyphenolic branching agent has the same reactivity profile as the bisphenol A used to make the linear chains. The polymerization was studied with changing branching agent in amounts of 0.3 and 0.5 mol% relative to mol of bisphenol A employed. The viscosity molecular weight and MIR of obtained polymers were in the range of 24,000-28,000, and 20-25 respectively, which are applicable to blow molding. To get accurate molecular weights we have obtained intrinsic viscosity which is the most useful of the viscosity designations because it can be related to molecular weight by the Mark-Houwink equation.

$$[\eta]=K M_v^a$$

$K$ and a values of linear polycarbonate were obtained $1.11\times 10^{-5}$ and 0.82 respectively in methylenechloride solution, and also obtained $1.23\times 10^{-5}$ and 0.83 in branched polycarbonate. The 0.3 mol% of branching agent in branched polycarbonate did not affect on solution viscosity as compare with linear polycarbonate.

**Oligomers in Polymers.** The content of oligomers is dependent on several process parameters such as temperature, phosgene feeding rate, and amine catalyst.[17] In the linear polycarbonate polymerization, oligomers increase if the amine catalyst is abundant. Cyclic polycarbonate oligomers are formed in the interfacial polymerization, which make up the significant portion of total oligomer contents in synthesized polymers. Referring to Table 1, in linear polycarbonate linear oligomers were formed as much as cyclic oligomers. In contrast, cyclic oligomers of branched polycarbonate were significantly increased twice as much as linear ones. It has been demonstrated that these characteristics are dependent on the tri-hydroxy functional groups of branching agent. In the early stages of polymerization when the sodium bisphenolates are abundant especially in branched polymer compared with that of linear polycarbonate the phenolates easily react to the close neighbor chloroformates and formed cyclic oligomers as shown in Figure 1. The polymer properties are related to the content of oligomers which directly effect on molecular weight distribution, degradation, and generation of gases in the molding. The molecular weight distribution of linear polycarbonates were in the range of 1.9-2.3, but those of branched polycarbonates were significantly increased to in the range of 3.2-3.5. This result

**Table 1.** Oligomers in linear/branched polycarbonate*

| Oligomers* | $LO_1$ | $LO_2$ | $LO_3$ | $LO_4$ | $CO_3$ | $CO_4$ | $CO_5$ | $CO_6$ |
|---|---|---|---|---|---|---|---|---|
| Linear Polycarbonate (ppm) | 2,500 | 700 | 2,300 | 1,200 | 1,600 | 2,700 | 2,100 | 1,500 |
| | 6,700 | | | | 7,900 | | | |
| Branched Polycarbonate (ppm) | 700 | 900 | 500 | 1,100 | 2,000 | 3,700 | 3,200 | 2,700 |
| | 3,200 | | | | 11,600 | | | |

*LO: linear oligomer, CO: cyclic oligomer, 1, 2, 3, .....: number of repeating unit.

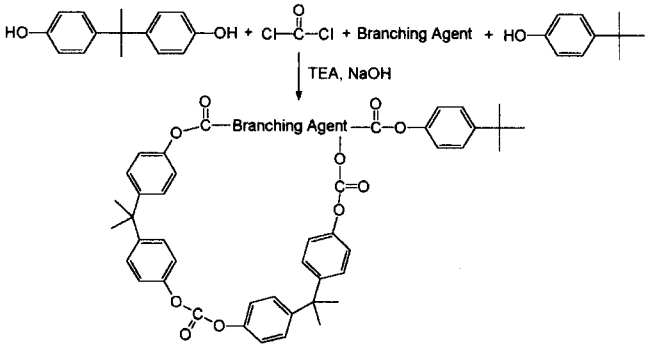



**Figure 1.** Molecular structure of cyclic oligomers.

clearly indicates that in branched polymer system branching agent effects on consisting cyclic oligomers and branching in the polymer chain.

**Relative Reactivity.** In this study we employed branching agent to study whether it could effect the reactivity and how much increase molecular weight. The branching agent seems considerably to affect on the polymerization rate by operating competitively and simultaneously. As shown the reactivity of polymers in Figure 2, in oligomerization stage, the molecular weights of branched polymers are shown same as those of linear polymers ($M_v$= 3,000-4,000). In the condensation stage branched polymerization is faster than linear polymerization and affords somewhat higher molecular weights. It is fact that the molecular weight of branched polymers could be controlled in the early condensation stage in which phenolates of branching agent react well with chloroformate to form branch and cyclic molecular structure as described. We also trust that the phenolates of branching agent should have the much more chance of making carbonate bond by trifunctional hydroxy groups than linear polymerization under the same condition. The effects of PTBP are shown in Figure 3; as indicated there, the molecular weights of linear

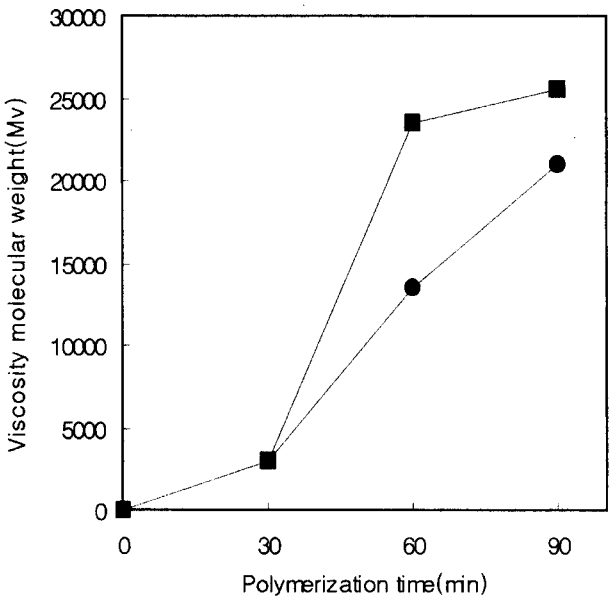



**Figure 2.** Effects of relative reactivity on polymerization time of branched (■) and linear polycarbonates (●).

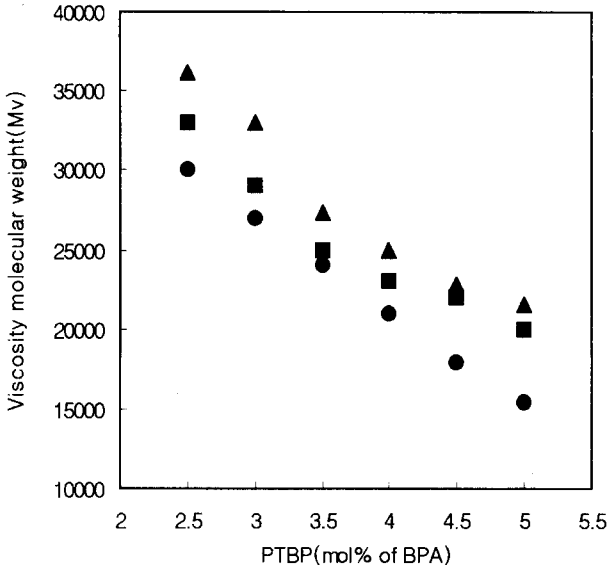



**Figure 3.** Effects of PTBP mol% on viscosity molecular weight of branched (■: THPE 0.3 mol , ▲: THPE 0.5 mol) and linear polycarbonates (●).

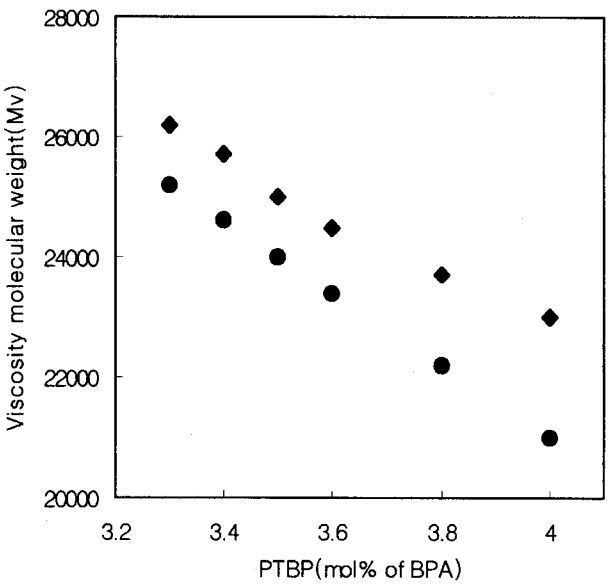
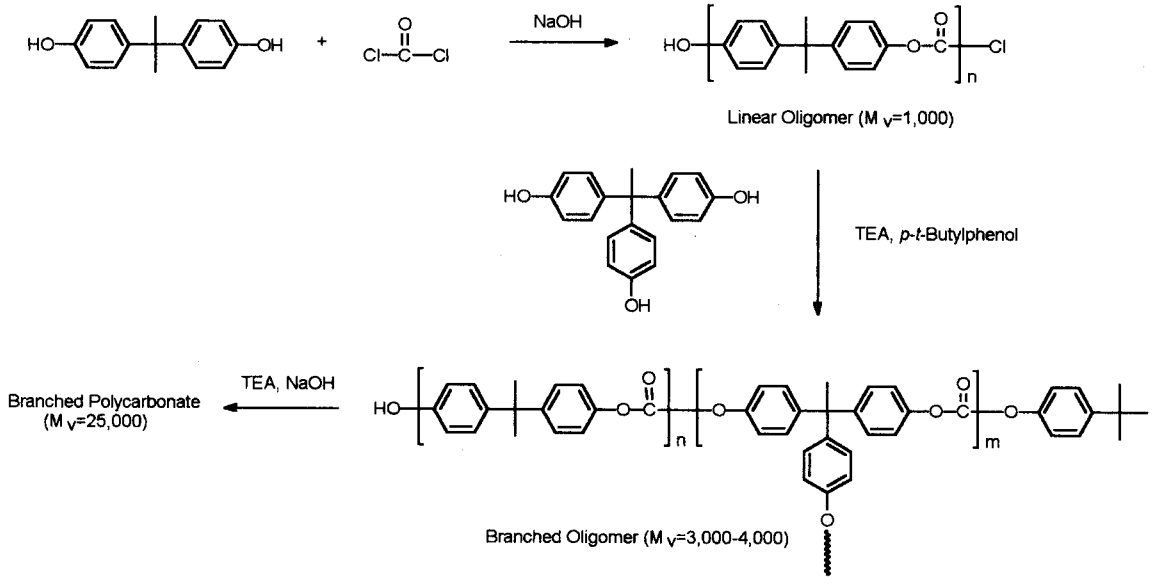



**Figure 4.** Effect of PTBP mol% on the viscosity molecular weight of branched (◆) and linear polycarbonates (●).

polycarbonates are linearly increased as the amount of PTBP decreased. However as observed with decreasing the amount of PTBP molecular weights of branched polycarbonates are non-linearly increased. The results have been obtained for branched polymers containing 0.3 and 0.5 mol% of THPE. Interestingly branched polymers obtained from 3-4 mol% of PTBP had lower molecular weight than the expected ones and also increment of molecular weight per PTBP mol% increased with decreasing PTBP. For example, in case of 0.3 mol% of THPE with PTBP mol% change (5→4.5→4), the molecular weights of branched polymers increased from 20,000 through 22,000 to 23,000, while those for the branched polymer with PTBP mol% change (3.5→3→2.5), molecular weights increased from 25,000 through 29,000 to 33,000. In 0.5 mol% of THPE the results were observed similar behavior as shown. The net molecular weights change at low concentration of PTBP (3.5→2.5) increased 3,000-4,000 while those at high concentration (5→4) increased 1,000-2,000. A possible explanation for different reactivities according to the different concentration of PTBP is that the free phenolates of THPE provide for excess molecular weight controller at middle area which reduces molecular weights, and also affects the reactivity in terms of different geometric structure of the branching agent at low and high concentration of PTBP. At low concentration of PTBP THPE predominantly reacts with chloroformate relative to PTBP and makes an offer to more branching effect. To see the precise effect of the amount of PTBP we studied branched polymers containing 3.2-4 mol% of PTBP. The changes of molecular weight are shown in Figure 4. It was found that the branching effect decreased at 3.2-3.6 mol% of PTBP. In order to get the desirable molecular




**Scheme 1.** Synthesis of branched polycarbonate.

weight we could consider the ratio of branching agent to molecular weight terminator.

In summary, this work describes the polymerization of branched polycarbonate with bisphenol A and trihydroxyphenyl co-monomers in batch reactors. The polymerization was based upon phosgenation, followed by condensation with triethylamine as a catalyst. The relative kinetic studies of branched polycarbonate system show that in polycondensation stage the reaction rates are faster than the corresponding linear polycarbonate. Branched polycarbonate was predominantly formed cyclic oligomers due to trihydroxyphenyl co-monomer. $M_v$ (viscosity molecular weight)s of branched polycarbonate were obtained non-linear dependence on PTBP concentrations. The branching agent appeared to competitively and concurrently function as both molecular terminator and branching factors in polymerization.

**Acknowledgment.** This work was supported by the Korea Science and Engineering Foundation through the Advanced Material Research Center for Better Environment at Taejeon National University of Technology and partly by Sam Yang Group Research Center.

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# The Effect of Bases on the Reaction of (S)-Naproxen Chloride with Nucleophiles without Racemization

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Two enantiomers of racemic drugs often show different pharmacological activities in living systems.[1] Consequently, individual enantiomers of chiral drugs should be studied for their own pharmacological properties during the process of marketing or developing chiral drugs according to the guidelines recently issued by the drug regulatory bodies around the world.[2] In this instance, the techniques of assaying the enantiomeric purity of chiral drugs are essential. For this purpose, various techniques are available.[3] However, liquid chromatographic separation of enantiomers on chiral stationary phases (CSPs) have been known the most convenient and accurate means in assaying the enantiomeric purity of chiral drugs.[4]

$\alpha$-Arylpropionic acids such as naproxen are well known non-steroidal anti-inflammatory profen drugs. The two enantiomers of these chiral drugs have been known to show different metabolic pathway and different pharmacological activity.[5] Consequently, much attention has been given to the liquid chromatographic analytical resolution of $\alpha$-arylpropionic acid enantiomers.[6,7] The resolution of profen drugs on Pirkle-type CSPs has been performed with their $\pi$-acidic or $\pi$-basic aromatic amide derivatives in order to utilize the $\pi$-$\pi$ donor acceptor interaction between the profen derivatives and the CSPs.[6] Derivatization of racemic profen drugs has been usually done by treating $\alpha$-arylpropionic acid chlorides with a $\pi$-acidic or a $\pi$-basic aromatic amino compound in the presence of a base such as triethylamine or without a base.[6] However, in some cases, the derivatization has experienced severe problem of racemization, which deteriorates the usefulness of the liquid chromatographic CSPs in determining the enantiomeric purity of optically active profen drugs. For example, the reaction of (S)-naproxen chloride with 3,5-dinitroaniline in the presence of triethylamine was found to afford partially racemized 3,5-dinitroanilide derivative of naproxen.[8] In order to overcome the racemization problem, in this study, we systematically