การสังเคราะห์พอลิคาร์บอเนตแบบโครงสร้างกิ่งโดยปฏิกิริยาทรานส์เอสเตอริฟิเคชันของบิสฟีนอลเอและไดฟีนิลคาร์บอเนต

นางสาวสุนันทา คล้ายโพธิ์สี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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BRANCHED POLYCARBONATE SYNTHESIS FROM MELT TRANSESTERIFICATION OF BISPHENOL-A AND DIPHENYL CARBONATE

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
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Thesis Title	BRANCHED POLYCARBONATE SYNTHESIS FROM MELT TRANSESTERIFICATION OF BISPHENOL-A AND DIPHENYL CARBONATE
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Field of Study	Chemical Engineering
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สุนันทา คล้ายโพธิ์สี :การสังเคราะห์พอลิคาร์บอเนตแบบโครงสร้างกิ่งโดยปฏิกิริยาทรานส์เอสเตอริฟิเคชันของบิสฟีนอลเอและไดฟีนิลคาร์บอเนต. (BRANCHED POLYCARBONATE SYNTHESIS FROM MELT TRANSESTERIFICATION OF BISPHENOL-A AND DIPHENYL CARBONATE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. ศราวุธ ริมดุสิต, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ดร. สุชาดา ตระกูลวิเชียร, 100 หน้า

ในงานวิจัยนี้ได้มีการศึกษาการสังเคราะห์พอลิคาร์บอเนตแบบโครงสร้างกิ่งด้วยปฏิกิริยาทรานส์เอสเตอริฟิเคชันของบิสฟีนอลเอ (BPA) และไดฟีนิลคาร์บอเนต (DPC) ในสภาวะหลอมเหลวภายในเครื่องปฏิกรณ์แบบกะโดยศึกษาผลของอัตราส่วนโมลเริ่มต้นของ DPC ต่อ BPA และการใช้หรือไม่ใช้ตัวเร่งปฏิกิริยาที่มีต่อน้ำหนักโมเลกุลของพอลิคาร์บอเนตที่สังเคราะห์ได้ด้วยเทคนิคเจลเพอร์มีเอชันโครมาโตกราฟี ซึ่งพบว่าอัตราส่วนโมลเริ่มต้นของ DPC ต่อBPA เท่ากับ 1.26 ต่อ 1.00 โดยไม่ใช้ตัวเร่งปฏิกิริยามีความเหมาะสมสำหรับการสังเคราะห์พรีพอลิเมอร์สำหรับสังเคราะห์พอลิคาร์บอเนตแบบกิ่ง เพื่อให้สามารถควบคุมสภาวะในการสังเคราะห์ได้ง่าย นอกจากนั้นแล้วยังมีการศึกษาผลของชนิดและปริมาณของสารก่อกำเนิดกิ่งที่มีต่อน้ำหนักโมเลกุลของพอลิคาร์บอเนตแบบกิ่งที่สังเคราะห์ได้ ซึ่งพบว่า 1,1,1-ทริสพาราไฮดรอกซีฟีนิลอีเทน (THPE), 3,3-บิสไฮดรอกซีฟีนิลออกซินโดนและ 1,1,1-ทริสไฮดรอกซีเมลทิลอีเทน (TME) เป็นตัวเลือกที่เหมาะสมต่อการเตรียมพอลิคาร์บอเนตแบบโครงสร้างกิ่ง โดยการสังเคราะห์พอลิคาร์บอเนตแบบโครงสร้างกิ่งที่อุณหภูมิสูงประมาณ 250 องศาเซลเซียส ความดัน 100 มิลลิเมตรปรอท โดยใช้ THPE ปริมาณ 3 mol% ทำให้ได้พอลิคาร์บอเนตที่มีน้ำหนักโมเลกุลประมาณ 26,294 และพบว่าสารก่อกำเนิดกิ่งชนิด THPE ปริมาณ 3 mol% มีความเหมาะสมมากที่สุดในการสังเคราะห์พอลิคาร์บอเนตแบบโครงสร้างกิ่ง โดย THPE เป็นสารก่อกำเนิดกิ่งที่เหมาะสมที่สุดสำหรับสภาวะการสังเคราะห์ข้างต้น โครงสร้างทางเคมีของพอลิคาร์บอเนตที่สังเคราะห์ได้มีลักษณะเป็นสายโซ่กิ่ง ซึ่งมี THPE เป็นสารก่อกำเนิดกิ่งอยู่ในโครงสร้างโดยยืนยันได้จากการวิเคราะห์ด้วยเทคนิค NMR นอกจากนี้ได้มีการศึกษาค่าความหนืดของพอลิคาร์บอเนตโครงสร้างกิ่งที่ได้ โดยใช้รีโอมิเตอร์แบบแผ่นคู่ขนาน พบว่าพอลิคาร์บอเนตแบบโครงสร้างกิ่งที่ใช้ THPE ปริมาณ 3 mol% มีพฤติกรรมการไหลแบบเชียร์ทินนิ่ง และยังสัมพันธ์กับค่าดัชนีอัตราการหลอมไหลที่ต่ำเทียบเท่ากับค่าที่วัดได้จากพอลิคาร์บอเนตโครงสร้างกิ่งเชิงพาณิชย์ แสดงนัยยะถึงพอลิคาร์บอเนตที่สังเคราะห์ได้เป็นชนิดสายโซ่กิ่งที่ยาว สำหรับการศึกษาคุณสมบัติเชิงความร้อนด้วยเทคนิค DSC และ TGA พบว่าจะมีค่าความเสถียรทางความร้อนที่ดี โดยอุณหภูมิการเปลี่ยนสถานะคล้ายแก้วของพอลิคาร์บอเนตโครงสร้างกิ่งที่สังเคราะห์ได้ใกล้เคียงกับพอลิคาร์บอเนตโครงสร้างกิ่งเชิงพาณิชย์ และยังมีค่ามอดูลัสสะสมซึ่งได้จากเทคนิค DMA เทียบเท่าพอลิคาร์บอเนตโครงสร้างกิ่งเชิงพาณิชย์

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

#5470424721 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : BRANCHED PC / MELT TRANSESTERIFICATION

SUNANTA KLAYPOSRI: BRANCHED PC SYNTHESIS FROM MELT TRANSESTERIFICATION OF BISPHENOL-A AND DIPHENYL CARBONATE. ADVISOR: ASSOC. PROF. SARAWUT RIMDUSIT, Ph.D., CO-ADVISOR: SUCHADA TRAGOONWICHIAN, Ph.D., 100 pp.

In this research, branched polycarbonate (branched PC) was synthesized by melt transesterification of bisphenol-A (BPA) and diphenyl carbonate (DPC) in a batch reactor. The effects of initial mole ratio of DPC/BPA and with or without catalyst on molecular weight of the obtained PC were investigated by gel permeation chromatography. It was found that at initial mole ratio of DPC/BPA at 1.26/1.00 without an addition of catalyst was an appropriate for the preparation of branched PC in a controlled manner. The influence of types and amount of branching agents on PC molecular weight profile were also studied. 1,1,1-tris(p-hydroxyphenyl)ethane (THPE), 3,3-bis(p-hydroxyphenyl)oxindole and 1,1,1-tris(hydroxymethyl)ethane were prove to be candidates as branching agents for branched PC synthesis. The condensation reaction of DPC/BPA with 3 mol% of THPE at temperature up to 250 ^{o}C and pressure of 100 mmHg provided molecular weight of branched PC product about of 26,294. 3 mol% of THPE was found to be the most appropriate and promising choice of branched PC synthesis as can be confirmed by NMR spectroscopy. The melt viscosity of branched PC with 3 mol% of THPE exhibited a high shear sensitivity to that of commercialized branched PC with relatively low melt flow index suggesting a presence of long chain branching in our branched PC. The thermal and thermomechanical properties of branched PC product were also studied using differential scanning calorimetry, thermogravimetric analysis and dynamic mechanical analysis. The thermal properties of synthesized branched PC i.e. glass transition and degradation temperature were close to that of the commercial branched PC. Furthermore, synthesized branched PC possesses mechanical property similar to those commercial PC products.

Department : Chemical Engineering	Student's Signature
Field of Study : Chemical Engineering	Advisor's Signature
Academic Year : 2013	Co-advisor's Signature

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CHAPTER I

INTRODUCTION

1.1 Introduction

Polycarbonates derived from the transesterification process by bisphenol A (BPA) and diphenylcarbonate (DPC) in melt recently gain much attention both academically and industrially due to an environmentally friendly aspect of this process. Polycarbonates are an important class of thermoplastic engineering polymer with high heat resistance, impact resistance, optical clarity, and dimensional stability [1]. The structure of polycarbonates is linear in commercial. It is widely used in data storage devices, structural materials for electrical and electronic applications, automobiles, and construction materials [2]. In processes and applications such as blow molding extrusion of sheet products, it is desirable to use a branched polycarbonate due to its higher melt strengths and melt elasticity [3]. Both of these are important particularly in fabrication by extrusion blow molding.

Melt strength may be simply described as the tenacity of a molten strand and indicates the ability of the melt to support a stress. Melt elasticity is the recovery of the elastic energy stored within the melt from distortion or orientation of the molecules by shearing stresses [4]. It can be expressed by melt flow index. Melt flow index of branched polycarbonate is 2.5 g/10 min. Melt flow index of linear polycarbonate is 12.2 g/10 min. Melt flow index decreased with increasing viscosity [5]. These advantages properties of the branched resins are in large part a result of their non-Newtonian flow characteristics.

In addition, branched polycarbonates will also generally have improved flame retarding behavior. It is shown as the 5% weight loss value of branched polycarbonate and linear polycarbonate 446˚C, 427˚C respectively [6]. The branched polycarbonate has improved chemical resistance compared to linear polycarbonates [7].

Normally, there are three major industrial processes used to produce branched polycarbonates: an interfacial polymerization, by reactive extrusion of a linear or branched polycarbonate with a branching agent, and a melt transesterification by adding branching agents.

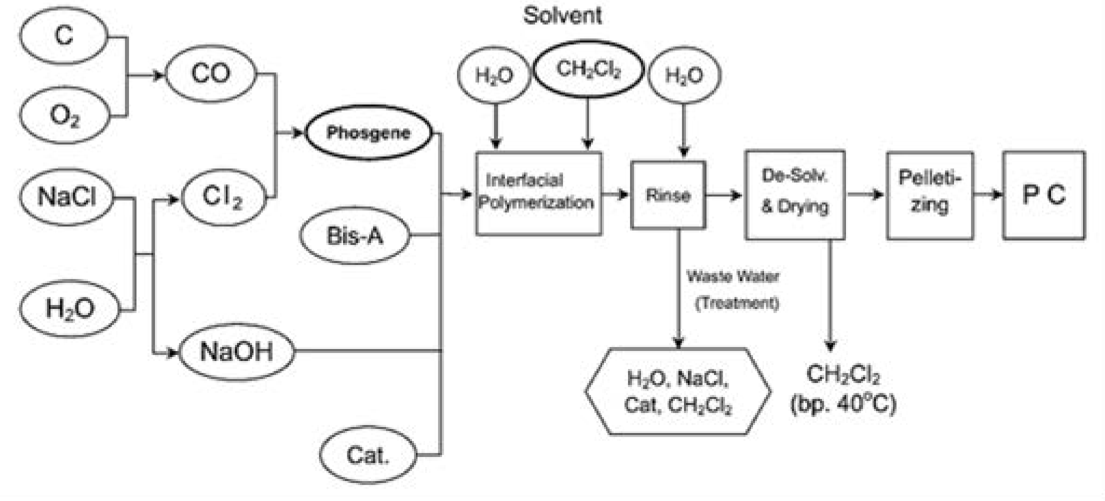


Figure 1.1 Phosgene PC process. [8]

An interfacial polymerization process in shown Fig 1.1 which was basically based on phosgene, bisphenol A to form an oligomer, NaOH in a water/methylene chloride solution, followed by oligomerization with branching agent [9]. However, phosgene is well known to be dangerous while methylene chloride as a polymerization solvent is a low-boiling point solvent with an exposure limit reflecting its carcinogenic properties and it is very difficult to prevent completely the release of the methylene chloride to the atmosphere due to its low boiling point (40○C) [8]. Many attempts have been made to overcome the environmental and cost disadvantages of the phosgene process, both for a production step for a safe monomer of diphenyl carbonate (DPC) to replace phosgene and for a polymerization step to produce branched polycarbonate.

Furthermore, it is possible to produce a polycarbonate possessing a certain degree of branching and molecular weight by melt extruding a linear or branched aromatic polycarbonate reactant with a specific branching agent such as a polyphenol having a molecular weight up to about 3000 and an appropriate catalyst [4]. But it is unsuitable for using in lab-scale because a very large quantity of polycarbonate must be treated and expensive operating cost.

In the transesterification process for producing a branched polycarbonate, an aromatic dihydroxy compound such as bisphenol A (BPA) and a diaryl carbonate e.g. diphenylcarbonate (DPC) are polymerized together with polyfunctional alcohols as branching agents. Alkali metal compounds or alkaline earth metal compounds, as branching inducing catalysts are normally added in the melt polycarbonate oligomer at any stage of the melt process after which the polycarbonate oligomer has reached a weight average molecular weight (Mw) of between 3000 and 30000 g/mole. The branch-inducing catalysts may be added in a melt polycondensation process produces a unique branched polycarbonate composition having increased melt strength [3]. The melt transesterification used to produce branched PC also maintained the environmentally friendly aspect of the process without the use of hazardous phosgene reactant.

Therefore, this research aims to synthesis branched polycarbonate via melt transesterification without using phosgene. The suitable condition for the branched polycarbonate synthesis is investigated. Effects of types of branching agents and their contents on the condensation polymerization process of branched polycarbonate using DPC and BPA as starting reactants as well as the resulting polycarbonate properties will also be examined. The results will also be compared with the commercial branched PC (Makrolon WB1239, Bayer Co. Ltd).

1.2 Objectives

1. To synthesize the branched polycarbonate to yield high molecular weight polycarbonate based on melt transesterification of diphenyl carbonate (DPC) and bisphenol-A (BPA).

2. To investigate the effects of the operating conditions and branching agents on properties of the formed polycarbonate.

1.3 Scopes of the Study

1. Studying on the preparation of branched polycarbonate precursor from BPA and DPC by melt transesterification.

2. Investigating the effect of branched PC using of three different branching agents for example 1,1,1-tris(4-hydroxy-phenyl)ethane (THPE) etc.

3. Examining the viscosity profile of reaction mixture and molecular weight profile of branched polycarbonate by varying.

4. Evaluating the production of branched PC using Na_2CO_3 as a catalysts of transesterification reaction.

5. Evaluating the physical and mechanical properties of the branched polycarbonate obtained from the above polycondensation reactions, i.e.

   - Chemical structure
   - Molecular weight
   - Rheological properties
   - Thermal properties: glass transition temperature, degradation temperature
   - Mechanical properties: dynamic mechanical behaviors.
   - Physical properties: yellowness

6. Summarizing the processing condition, and suitable branching agents of branched PC production based on the reaction of DPC with BPA.

1.4 Procedure of the Study

1. Prepare chemicals and equipment using in this research such as BPA, DPC, catalysts, branching agent (THPE) etc.

2. Compare the effect of types of branching agents on the reaction characteristics and the obtained precursors.

3. Determine the processing condition to produce high molecular weight branched polycarbonate by varying.

4. Determine the physical, mechanical, and thermal properties of the obtained branched polycarbonate product as follows

Chemical characteristics;

- Chemical structure (NMR, FTIR)

Physical properties;

- Viscosity (Rheometry)
- Molecular weight (Gel Permeation Chromatography)

- Melt flow index (Melt Flow Indexer)
- Yellowness index (Spectrophotometer)

Mechanical properties;

- Dynamic mechanical analysis

Thermal properties;

- Glass transition temperature (Differential Scanning Calorimetry)
- Thermal degradation (Thermogravimetric Analysis)

5. Analyze and conclude the experimental results.

6. Prepare the final report.

CHAPTER II

THEORY

2.1 Polycarbonate

Polycarbonate may be defined as polymers containing recurring carbonate groups (-O-CO-C-) in the main chain. The most popular polycarbonate is based on 2, 2-bis (4-hydroxyphenyl) propane, better known as bisphenol-A [10]. The chemical structure of bisphenol-A polycarbonate is shown in Figure 2.1. It was discovered by Schnell, Bottenbruch, and Krimm in 1953 at Farbenfabriken Bayer (now called Bayer), and independently by Fox at General Electric shortly afterward.

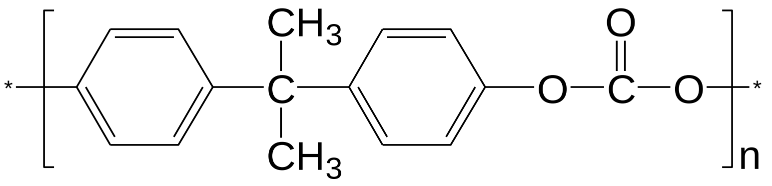


Figure 2.1 Chemical structure of bisphenol-A polycarbonate [10].

The polymer was first produced industrially and introduced to the market in Europe in 1958 by Farbenfabriken Bayer and in the United States in 1960 by Mobay Chemical Corporation (now called Miles Inc.) and General Electric (now called SABIC) [11]. The polycarbonate resin business is global with two dominant producers and three other major producers. Bayer Material Science (Bayer) is the largest worldwide producer, accounting for 30% of world capacity in 2008. The second-largest is SABIC Innovative Plastics (SABIC) with 27%, followed by Teijin, Dow Chemical and Mitsubishi Companies (Mitsubishi Chemical, Mitsubishi Gas Chemical and Mitsubishi Engineering Plastics) with 11%, 9% and 8%, respectively. Bayer, SABIC and Dow have plants in three regions the United States, Western

Europe and Asia; Teijin and Mitsubishi each have multiple plants in Asia. The largest markets for polycarbonate resins are electrical/electronic (including computer and business equipment and optical discs), glazing and sheet usage, and the automotive industry [12].

Applications of Polycarbonate.

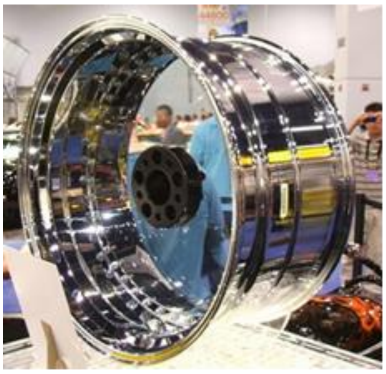
Polycarbonate is becoming more common in housewares as well as laboratories and in industry, especially in applications where any of its main features; high impact resistance, temperature resistance, optical properties are required. It can be injection molded, blow molded, and extruded and it is an ideal engineering plastic with good electrical insulating properties, finding applications in electric meter housings and covers, casket hardware, portable tool housings, safety helmets, computer parts, and vandal-proof windows and light globes. The price of polycarbonate restricts its use to mainly engineering applications.

Other engineering applications include the following [13]:

- equipment housings
- exterior automotive components
- outdoor lighting fixtures
- nameplates and bezels
- nonautomotive vehicle windows
- brackets and structural parts
- medical supply components
- plastic lenses for eyeglasses

www.shell.com/chemicals/dpc

http://www.westernsafety.com



www.automotto.org

Figure 2.2 Applications of polycarbonate.

2.2 Branching and Polymerization in Polycarbonates

The course of the reaction depends on density, T, and the concentration of additives and impurities, and the resultant polymer shows a shear sensitivity that is directly related to the amount of branching agent and inversely related to the amount of the initiator. Figure 2.3 shows an example in the polycarbonate context [14].

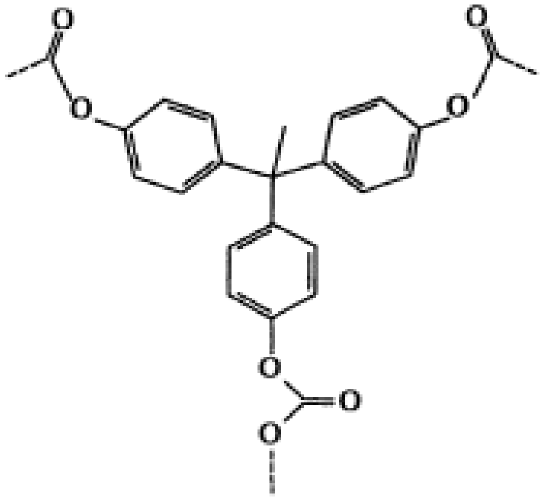


Figure 2.3 Schematic view of the branching center in bisphenol-A polycarbonate produced by the ring-opening polymerization of cyclic oligomers in the presence of small amounts of 1,1,l-tris(4-hydroxyphenyl)ethane, THPE [14].

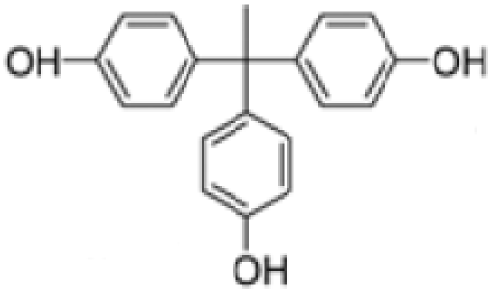


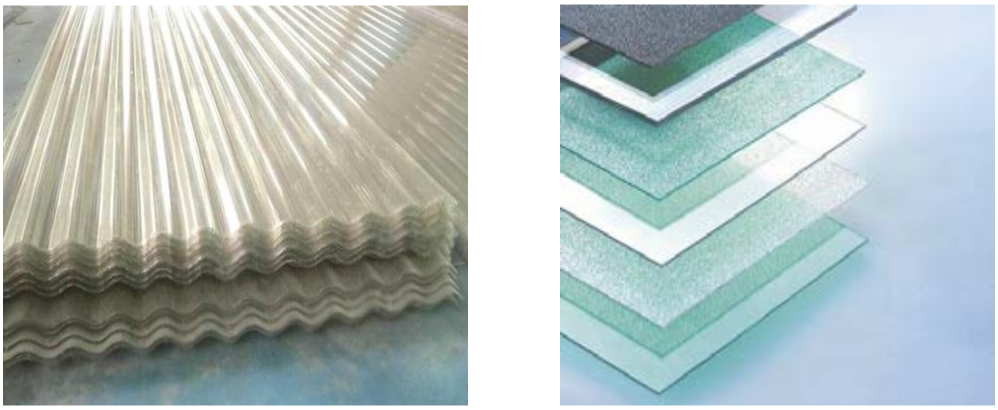
Figure 2.4 Structure of 1,1,l-tris(4-hydroxyphenyl)ethane, THPE [14].

That introducing a small number of trifunctional units could enhance polymerization by allowing the formation of interchain links and aggregates of chain segments; however, the addition of trifunctional particles lowers the degree of polymerization significantly, resulting in a sizable reduction of the average size for molecules with at least one chain termination. The apparent trend towards smaller aggregates is due to the reduction in the molecular extension by branching centers. Lowering temperature reduces the degree of polymerization even in the absence of branching, and trifunctional particles enhance greatly the sensitivity to temperature of both polymer and gel.

Application of Branched Polycarbonate [4]

The branched polycarbonates differ from most thermoplastic polymers in melt rheology behavior.

- automotive (e.g. bumpers, spoilers and ground effects packages)
- extrusion (e.g. wire, cable insulation, extruded bars, pipes, fiber optic buffer tubes, and sheets)
- solid sheets, corrugated sheets



http://www.ytfoam.com. http://www.weiersha.com

Figure 2.5 Applications of branched polycarbonate.

2.2.1 Properties of Branched Polycarbonate

Melt strength is a measurement of how strong a plastic is when it is in a molten state. For plastics which are extruded, melt strength can be especially important. If a plastic has a poor melt strength, it may not be able to hold its shape after extrusion resulting in a product which will deform before it has a chance to cool and harden. Melt strength can also be relevant to injection molding, thermal molding and a wide variety of other processes, depending on the details of the specific process [3]. Melt strength is a measure of the complex rheological properties of the polymer and can be expressed by the Melt Index Ratio (MIR). MIR is the ratio of the Melt Volume Ratio (MVR) measured with a weight of 2.16 kg and the MVR measured with a weight of 21.6 kg. MIR of branched polycarbonate is between 1.9 -2.4 [3]. The increase of long chain branches is essential to enhance its melt strength. For example results of the melt strength of all polypropylene as shown as Table 2.1 and Figure 2.6.

Table 2.1 Melt strength of the PP samples and the PP foams [15].

Code	Melt strength (N)
EPS[a]	0.37
MPP-1[b]	0.56
MPP-2[c]	0.91

[a] EPS (linear polypropylene)

[b, c] MPP-1, MPP-2 (long chain branched polypropylene)

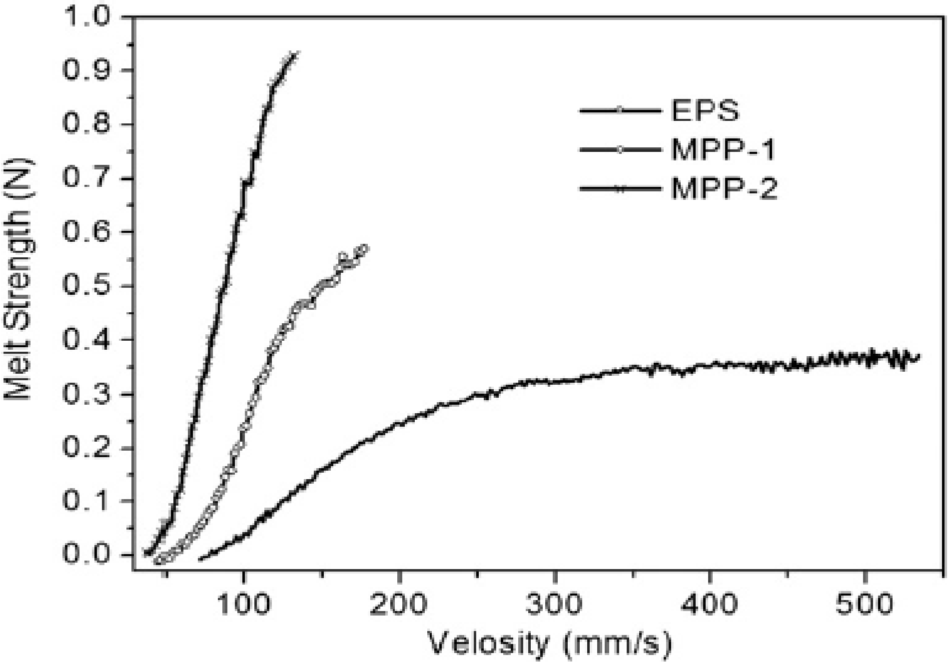


Figure 2.6 Rheoten curves of EPS and LCB PPs at 180 ˚C [15].

Melt elasticity of polymer melts has been proposed based on the knowledge of the melt flow index, molecular weight distribution and glass transition temperature of the polymer. Melt flow index decreased with increasing viscosity. The melt flow index (MFI) of a polymer is defined as the flow rate in grams extruded in ten minutes under fixed test load conditions through a melt flow apparatus having a die and piston each of specific diameter and length. MFI value is bound by the test temperature and load conditions. In order to make the unified curves independent of temperature and load. It is essential to convert the value of MFI obtained under ASTM conditions to that under the required conditions. The MFI values as calculated according to equation (2.1). A method to do this has been proposed and discussed by Shenoy et al. The characteristics of linear and branched polycarbonates are shown in Table 2.2 [16].

$$\frac{\mathrm{MFI}_{L_2}}{\mathrm{MFI}_{L_1}} = \left(\frac{L_2}{L_1}\right)^{\frac{1}{n}}, \tag{2.1}$$

MFI	melt flow index (g/10 min)
L_1	load (kg) at ASTM test conditions
L_2	load (kg) at required conditions
η	slope of the shear stress vs. shear curve on a log-log scale

Table 2.2 Characteristics of polycarbonate (TRIREX 3022). [5]

Polymer	M_w[a]	Mn[a]	MWD	MI[b] (g/10min)	T_g (°C)
Linear polycarbonate	23,000	9,800	2.3	12.2	148.5
Branched polycarbonate	30,000	15,000	2.0	2.5	151.9

[a] Measured by GPC.

[b] Melt Index, measured with 1.2 kg at 300˚C.

[c] Measured by DSC.

2.2.2 Branched Polycarbonate with Improved Thermal Properties

Branched polycarbonates will also generally have improved thermal stability compared to linear polycarbonates. Thermal decomposition temperature (T_d) measured with thermogravimetric analysis (TGA) at a heating rate of 10°C min^{-1} under a oxygen atmosphere (monitoring range 50-600°C) reported at 5% weight loss revealed T_d value of branched polycarbonate to increase with an increase of branching segments compared to linear polycarbonate [6] as shown in Table 2.3.

Table 2.3 Degradation temperature of linear and branched PC [6].

Polymer	T_d (˚C) at 5% Weight Loss
BPA-PC/Li-PC	427
Branched-PC (Trirex-3026PJ)	446

2.2.3 Characteristics of Non-Newtonian Fluids

A non- Newtonian fluid is a fluid whose flow properties are not described by a single constant value of viscosity. Many polymer solutions and molten polymers are non-Newtonian fluids, as are many commonly found substances such as ketchup, starch suspension, paint, and shampoo. In a non-Newtonian fluid, the relation between the shear stress and the shear rate is nonlinear, and can even be time-dependent. Therefore a constant coefficient of viscosity cannot be defined [17].

2.2.3.1 Shear Thickening Non Newtonian Liquid

A shear thickening liquid, also called a dilatant, is a non-Newtonian fluid where the shear viscosity increases with applied shear stress. This behavior is only one type of deviation from Newton’s law, and it is controlled by such factors as particle size, shape, and distribution. The properties of these suspensions depend on Hamaker theory and Van der Waals forces and can be stabilized electrostatically or sterically. Typical examples of the shear-thickening phenomenon are given in Figure 2.7. It will be observed that the shear-thickening region extends over only about a decade of shear rate [17].

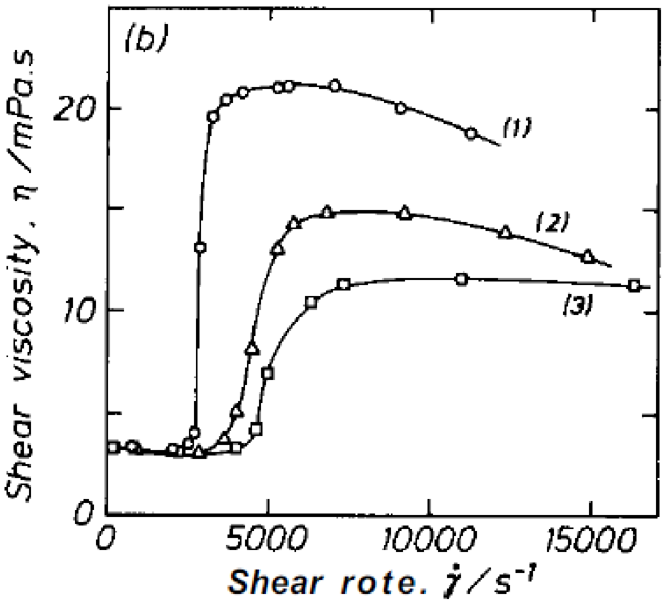


Figure 2.7 Shear-thickening behavior of a non-Newtonian liquid [17].

2.2.3.2 Shear Thinning Non Newtonian Liquid

As soon as viscometers became available to investigate the influence of shear rate on viscosity, workers found departure from Newtonian behavior for many materials, such as dispersions, emulsions and polymer solutions. In the vast majority of cases, the viscosity was found to decrease with increase in shear rate, giving rise to what is now generally called 'shear-thinning' behavior [17]. For shear-thinning materials, the general shape of the curve representing the variation of viscosity with shear rate in shown in Figure 2.8.

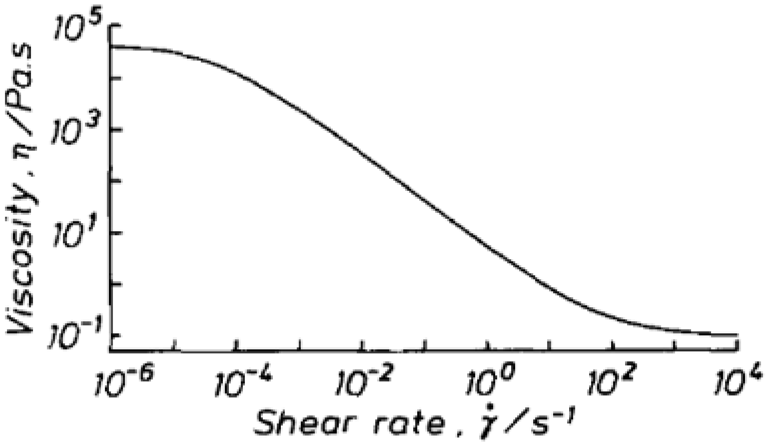


Figure 2.8 Shear-thinning behavior of a non-Newtonian liquid [17].

2.2.3.3 Bingham Non Newtonian Liquid

Bingham plastic is a viscoplastic material that behaves as a rigid body at low stresses but flows as a viscous fluid at high stress. It is named after Eugene C. Bingham who proposed its mathematical form. A common example is toothpaste which will not be extruded until a certain pressure is applied to the tube. Bingham describes the shear rate behavior of many shear-thinning materials at low shear rates, but only over a one-decade range (approximately) of shear rate. Figure 2.9 shows the Bingham behavior of non-Newtonian liquid [17].

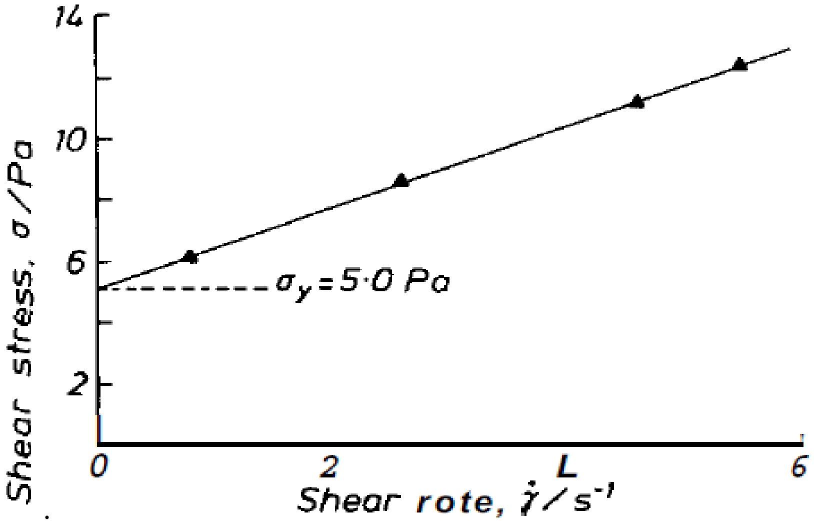


Figure 2.9 the Bingham behavior of non-Newtonian liquid [17].

Figure 2.10 indicates that linear polycarbonate and branched polycarbonate show a shear-thinning behavior. Branched polycarbonate exhibits higher shear sensitivity than linear polycarbonate [6].

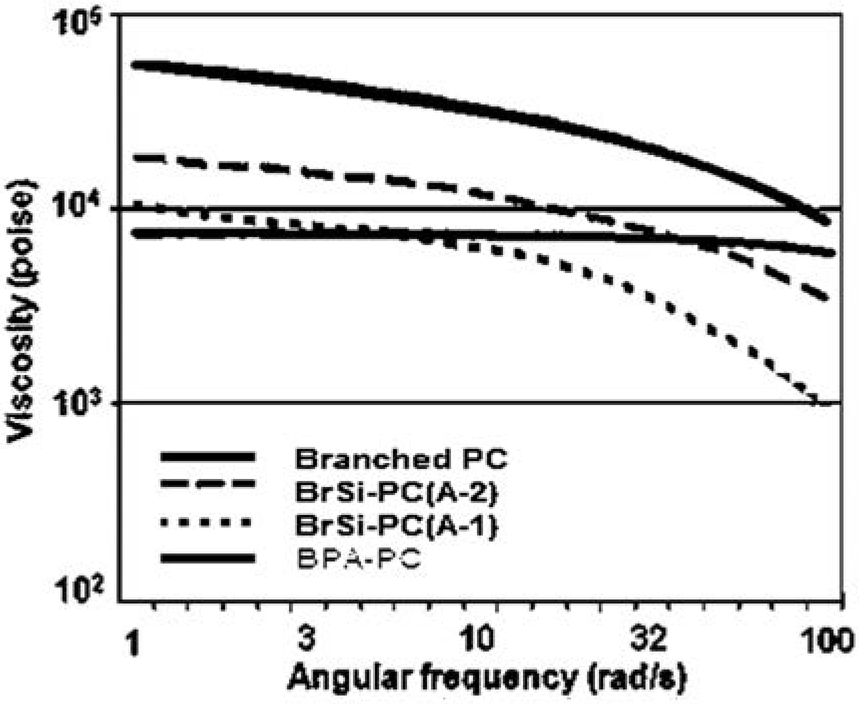


Figure 2.10 Viscosity vs frequency for linear PC-L and branched PC-Bs [6].

2.3 Manufacturing Processes

The melt transesterification method offers many advantages. For example, polycarbonates produced by the melt process are pure due to the absence of any solvents in the reactor, the polymerization reactor can be operated continuously, and the polymers from the reactor can be directly pelletized. However, it has also been known that high molecular weight polycarbonates are more difficult to obtain in the transesterification process than in other processes because the viscosity of the polymer melt increases significantly as the polymer molecular weight increases and thermal degradation reactions occur at high reaction temperatures (e.g., 300°C) [1].

The preparation of BPA polycarbonate from the melt follows the general reaction shown in Figure 2.11. A slight stoichiometric excess of diphenyl carbonate is employed principally for molecular weight control, and also to compensate for any loss due to devolatilization from the reactor. The primary means of controlling the molecular weight is by extent of reaction, with higher molecular weight being achieved as phenol or diphenyl carbonate is removed. Because the equilibrium between diphenyl carbonate and BPA approaches unity, removal of phenol from the system is necessary to drive the reaction. Although the distillation of phenol is trivial in the initial stages of the reaction, in the final stages of the polymerization the reaction becomes mass transfer limited owing to the viscosity of the melt. The increased difficulty of removing phenol from the melt significantly reduces the effective reaction rate. This is partially overcome by increased temperature, vacuum and surface renewal. The reaction is terminated by returning the reactor to ambient pressure when the desired melt viscosity is reached. The result is a polymer endcapped with 60-90% phenyl carbonate moieties, the remaining end groups being BPA-hydroxyl functionalities. The addition of mono-functional phenolic for increased endcap and molecular weight control has been employed successfully although they are not routinely used [14].

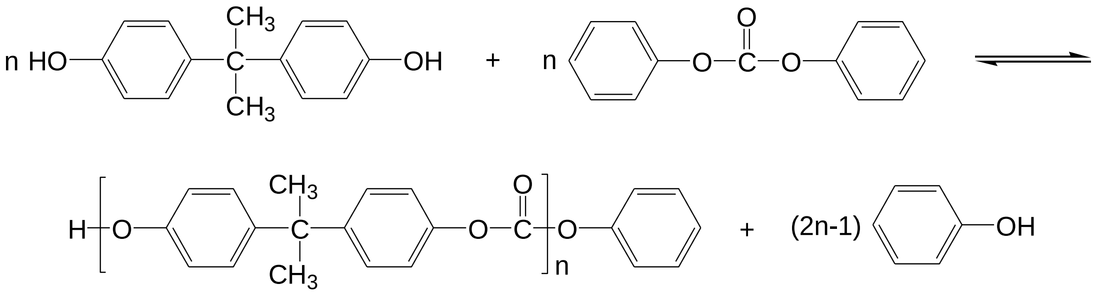


Figure 2.11 General synthesis of BPA-PC by the melt process [14].

The process of manufacturing branched polycarbonates takes place in a reactor. The temperature is increased and the pressure is reduced along the reactor. The reaction is an equilibrium reaction by product phenol is continuously removed from the reactor to ensure the desired molecular weight. The pressure of the reaction is about 0.2-0.6 torr [7]. The branching agent is added in a molten of the linear polycarbonate resin. Advantageously, the temperature is within a range to cause reaction between the polycarbonate and the branching agent a range of 325-350˚C [18].

Branching agents are well- known and may comprise polyfunctional organic compounds containing three or more functional groups, which may be hydroxyl, carboxyl, carboxylic anhydride, and mixture thereof. Some non-limiting examples include tris-p-hydroxyphenylethane,isatin-bis-phenol,pentaerythritol,4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-2-heptene,4,4'-[1-[4-[1-(4-hydroxyphenyl)-1-methylethyl]phenyl]ethylidine]bisphenol,2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol, trimesic acid and benzophenone tetracarboxylic acid [3].

2.4 Molecular Weight and Analysis

BPA polycarbonates are commercially available in a wide range of molecular weights. As the molecular weight increases, melt and solution viscosities increase proportionally. Molecular weights may be determined or inferred by several means, including gel-permeation chromatography, light-scattering, size-exclusion chromatography, measurement of intrinsic or inherent viscosity, and measurements of melt viscosity and flow. Correlation of intrinsic viscosity (IV), or inherent viscosity $[\eta_{inh}]$, with weight-averaged molecular weight (Mw) has been carried out on carefully characterized polycarbonate samples. The following relationship exists when $[\eta_{inh}]$ is in mL/g:

$$[\eta] = (41.2 \times 10^{-3})(M_W^{0.69}) \tag{2.2}$$

Polycarbonate melt viscosity data are scarce. Schnell reported polycarbonate melt viscosity versus molecular weight data at 280˚C and 302°C [6]. These data were fitted by the equation

$$\ln\mu = \left(393.15 - \frac{2.43 \times 10^5}{T}\right) + \left(\frac{2.49 \times 10^4}{T} - 39.8\right)\ln\overline{M_w} \tag{2.3}$$

where T is the melt temperature in Kelvin and Mw is the weight-average molecular weight of the polycarbonate. Figure 2.12 shows the data and the predictions of equation 2.3.

For chemical studies, the chromatographic methods or solution viscosities are methods of preference, but for practical applications, melt flow is most important. Standard injection-molding grades of polycarbonate have intrinsic viscosities in the range of 0.50–0.60 dl/g in chloroform at 30°C, with M_w of 35,000–70,000 and number-averaged molecular weight (M_n) of 15,000–24,000, as determined by gel-permeation chromatography (GPC) using polystyrene standards. The polydispersity ratio, M_w/M_n, of polycarbonate is about 2.3–2.7. The range of molecular weights and viscosities available is shown in Table 2.4.

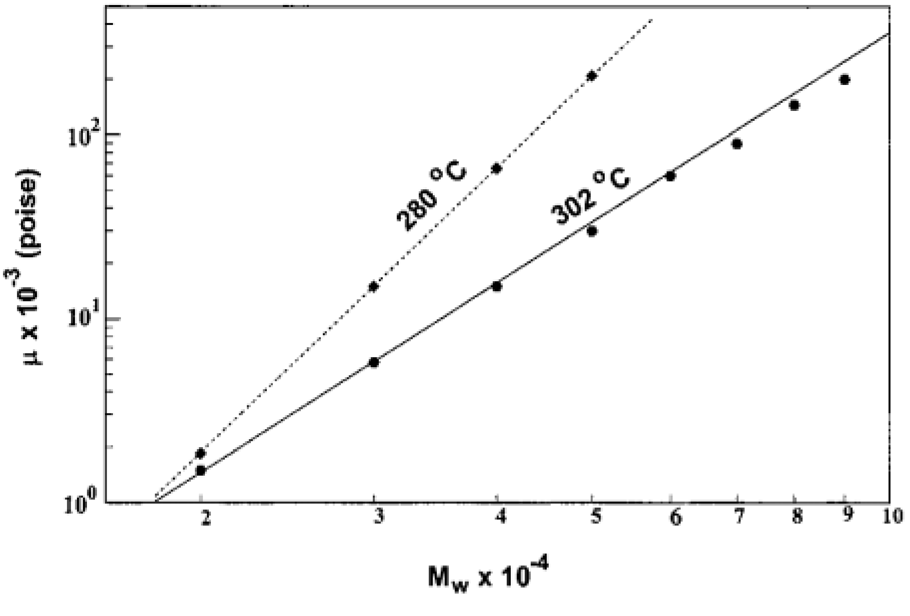


Figure 2.12 Melt viscosity of polycarbonate vs molecular weight [19].

Table 2.4 Molecular weight and viscosity of Lexan resins [20].

Grade	Description	MFI[a]	IV[b]	Mw[c]	Mn[c]	PDI[d]
131	Ultrahigh viscosity	3.1	0.629	72,600	28,100	2.58
1881	Very high viscosity	4.9	0.581	66,100	25,400	2.6
101	High viscosity	6.5	0.551	62,000	25,400	2.44
161	Medium high viscosity	7.4	0.538	60,600	24,400	2.48
141	Medium viscosity	9.2	0.510	57,000	23,900	2.38
141L	Medium low viscosity	11.2	0.493	54,500	22,700	2.40
121	Low viscosity	16.2	0.454	49,800	20,400	2.44
HF1110	High flow	20.9	0.434	46,900	18,400	2.55
SP1110	Superior flow	22	0.53	60,000	24,000	2.50
OQ1020	Optical quality	78	0.35	35,800	13,900	2.57

[a] MFI = melt flow index.

[b] IV = intrinsic viscosity in CH_2Cl_2 at 25°C.

[c] From gel-permeation chromatography using polystyrene standards.

[d] PDI = polydispersivity ratio, Mw/Mn.

2.5 Chemical Structure and Analysis

The degree of branching (DB) of branched aryl polycarbonate can be determined by ^1H NMR spectrum by three different ^1H NMR chemical shifts for the three different methyl groups and two different phenolic protons. To confirm methyl and phenolic protons, which are assigned from linear, branching and chain end units, DB was evaluated using a model compound prepared from the reaction between ditertbutyltricarbonate (DBTC) and 1,1,1-tris(4hydroxyphenyl)ethane(THPE). The reaction can be followed up by direct monitoring using ^1H NMR spectroscopy in THF-dg. The reaction of DBTC and THPE yields three different products, mono(terminal),di(linear) and trisubstituted (branching) structures Figure 2.13 shows an ^1H NMR spectrum with three singlets around 8 ppm assigned to the phenol group and with four singlets around 2 ppm assigned to the methyl group in the early stage.

According to the integration value, the compounds show the characteristic resonance for methyl protons at 2.179, 2.116 and 2.057 ppm for branching, linear and terminal units, respectively whereas linear and terminal units also exhibit distinct phenolic protons at 9.193, respectively. The methyl and phenolic chemical shifts are observed shifted downfield according to the substitution number.

Each model compound shown in Figure 2.13, which was synthesized separately was also investigate by ^{1}H NMR in DMSO-d_6 and showed a similar resonance for the methyl protons at 2.132, 2.071 and 2.012 ppm for branching, linear and terminal units, respectively. The resonances are very similar to the corresponding hyperbranched polycarbonate (HBPC) and are 2.152, 2.090 and 2.032 ppm for branching, linear and terminal units, respectively. As shown in Figure 2.14, this result allows the estimation of DB using ^{1}H NMR in the following equation [21].

$$\mathrm{DB} = \frac{\text{branching units+terminal units}}{\text{branching units+terminal units+linear units}} \tag{2.4}$$

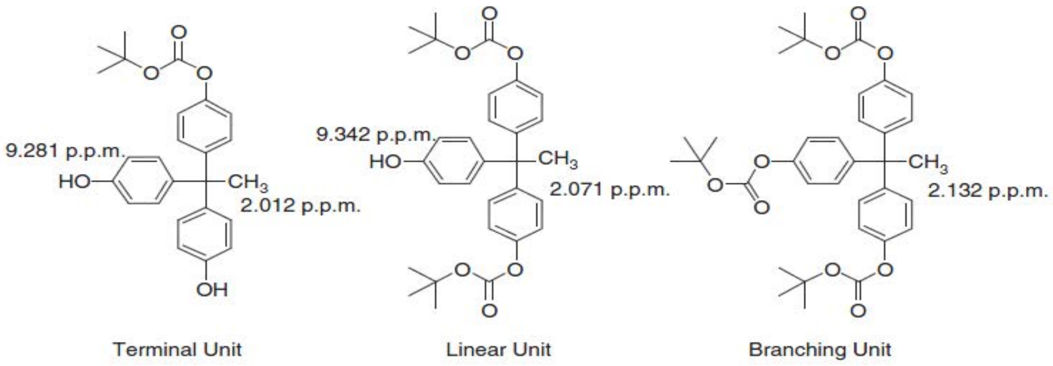


Figure 2.13 Three model compounds(chemical shift in dimethylsulfoxide-d_6) [21]

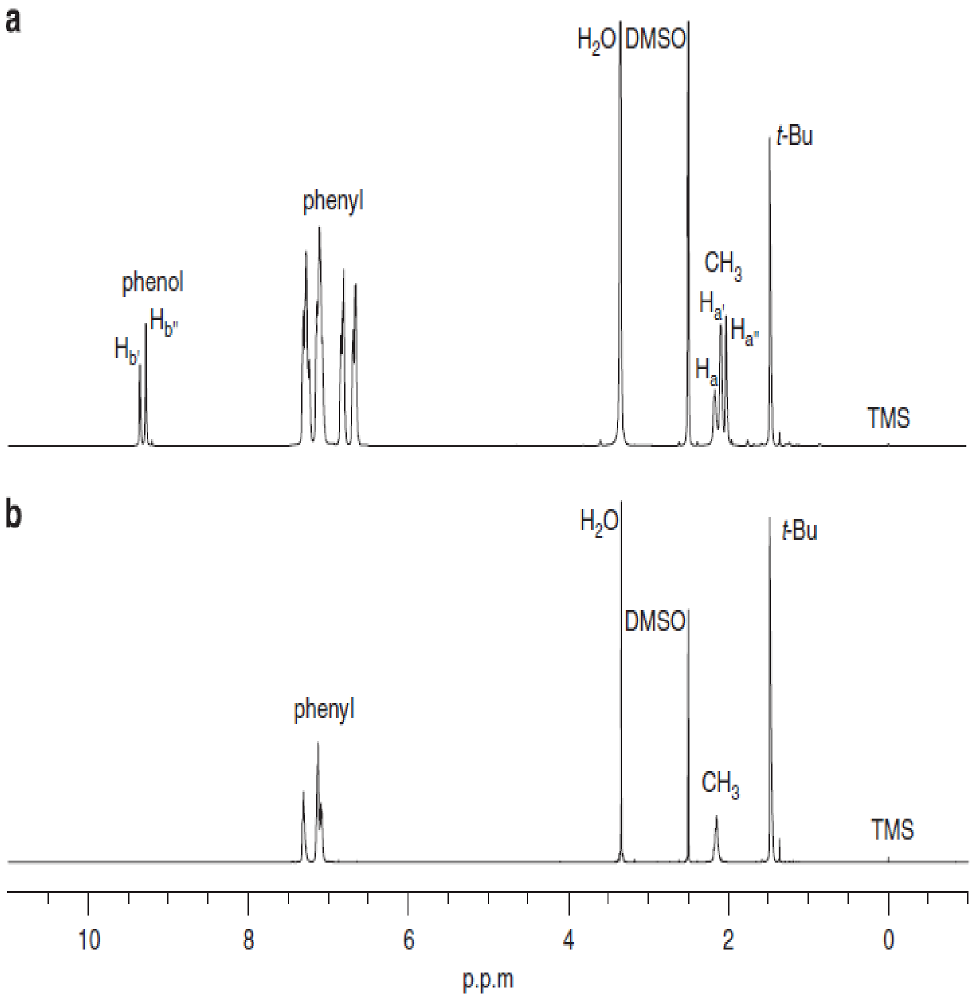


Figure 2.14 ^{1}H NMR spectra (600MHz, dimethylsulfoxide(DMSO)-d$_6$ (a) of hyperbranched polycarbonate(HBPC)-Boc-OH) (b) after introduction of Boc to form HBPC-Boc. The subscript of a, a', (b') and a'' (b'') in Figure 2.14a was assigned to branching linear and terminal units, respectively [21].

2.6 Rheological Analysis

Rheological properties have also been used to distinguish linear and branched PC. In the report by Lie et al., a commercial branched polycarbonate was melt pressed at 260˚C into 1 mm thick plates, and cut into small disks about 25 mm diameter. The rheological measurements were performed with 25 mm parallel plate geometry and a 1 mm sample gap. Thermal stability of samples during the rheological testing was also checked by a time sweep. The selected samples gave a stable G' signal for at least 100 min at 260˚C. The dynamic viscoelastic properties were determined with frequencies from 0.1 to 500 rad/s by using strain values determined with a stress sweep to lie within the linear viscoelastic region (LVR). All measurements were carried out in nitrogen atmosphere at temperatures 260˚C as shown in Figure 2.15 [13].

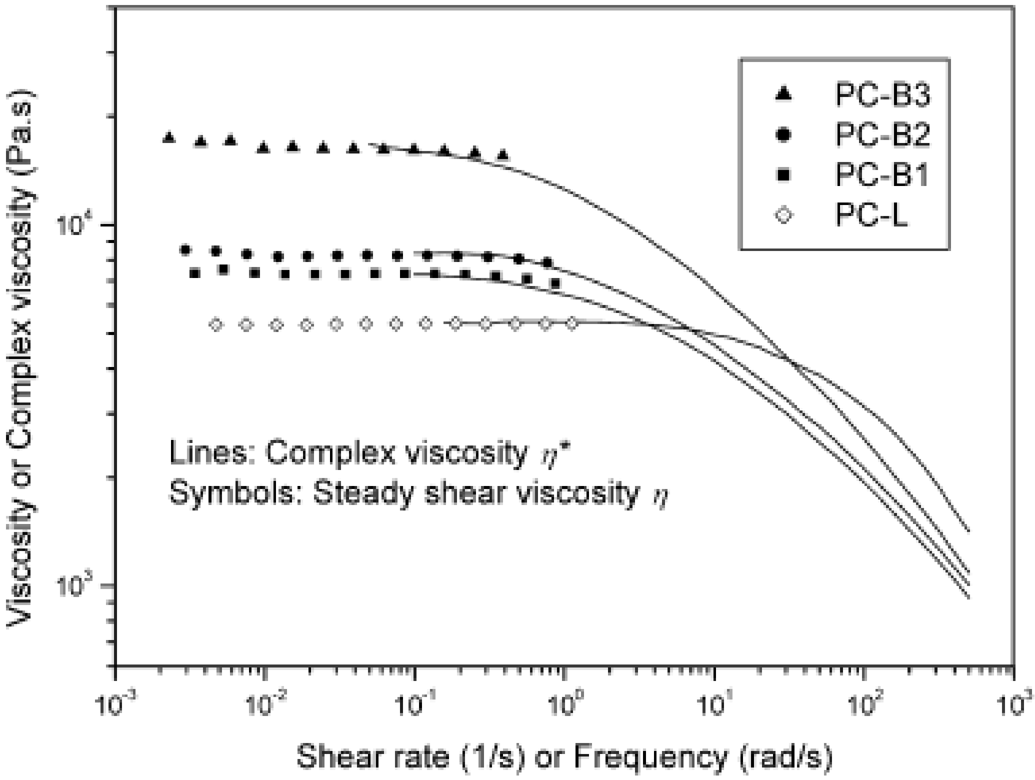


Figure 2.15 Viscosity vs shear rate of linear PC-L and branched PC-Bs

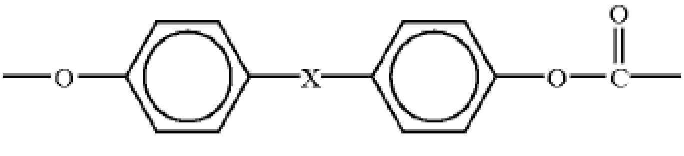
at 260 ˚C [13].

CHAPTER III

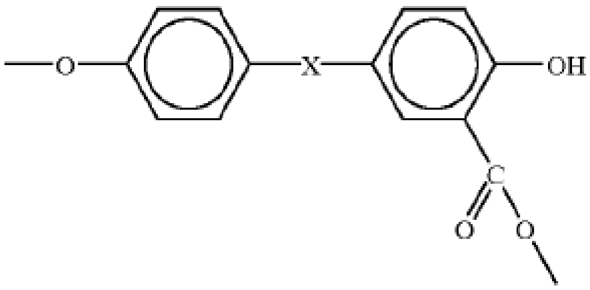
LITERATURE REVIEWS

3. Literature Reviews

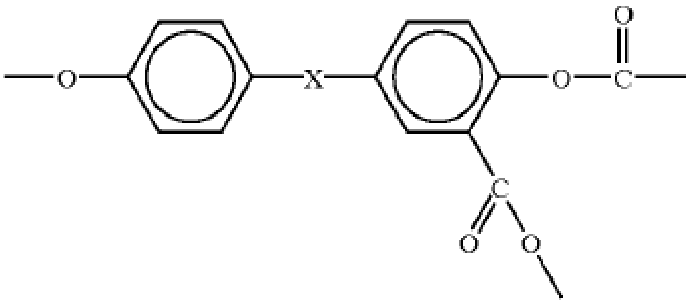
Karlik et al. in 2003 [3] studied a method for the production of a branched polycarbonate composition having increased melt strength by late addition of branch-inducing catalysts to the polycarbonate oligomer in a melt polycondensation process. Branching can be induced in the polycarbonates by the addition of branch-inducing catalysts, such as alkali metal compounds and alkaline earth compounds in the melt process. The addition of these catalysts not only generates the linear polycarbonate compound A but also such products as B and C after a rearrangement reaction known as the “Fries” rearrangement: Linear Fries products (B) and branched or extended Fries products (C) are shown in Figure 3.1.



(a)



(b)



(c)

Figure 3.1 Chemical structure of linear polycarbonate (a), linear Fries products (b), and branched or extended Fries products (c) [3].

The branch-inducing catalysts may be added together or separately in any combination of the stages where the polycarbonate oligomer has reached an Mw of at least 3,000 g/mole. It is preferable about 5,000-6,000 g/mole. If the branch-inducing catalysts are added after the molecular weight of the oligomers is too high, not as much Fries products are generated, and the Fries products that are generated are more linear or not as effectively branched. The mobility of the larger oligomers is too low or the concentration of reactive free OH (endcap level) is too low for high activity. If the branch-inducing catalysts are added too early, branches on branches are generated on the smaller oligomers producing insoluble and unmeltable gels.

Mestanza et al. in 1999 [4] studied the synthesis of branched polycarbonates by the reaction of a linear or branched polycarbonate with a branching resin having a molecular weight up to about 3,000. The branching of the linear polycarbonate resin is affected advantageously by an equilibration reaction. Reaction was conducted by heating the mixed reactant resins to an equilibration temperature within the range of about 200-250° C. The reaction preferably takes place in the presence of a carbonate equilibration catalyst.

Md. Monirul Islam, Dong-Wan Seo, Ho-Hyoun Jang, Young-Don Lim, Kyung Moo Shin, and Whan-Gi Kim in 2011 [6] studied the synthesis of Br-Allyl-

PCs using a bisphenol-A (BPA) based linear oligomer and 3,3'3"-triallyi-1,1,1-tris(4-hydroxy-phenyl)ethane(triallyl-THPE) through an interfacial polymerization process. The structures of the synthesized compounds were characterized by FTIR and ^{1}H NMR. The sequential disappearance and appearance of a broad peak for the-OH stretching vibration at 3500 cm^{-1} in the FTIR spectrum indicates the successful conversion of THPE to its ether form followed by triallyl-THPE, respectively, as shown in Figure 3.2.

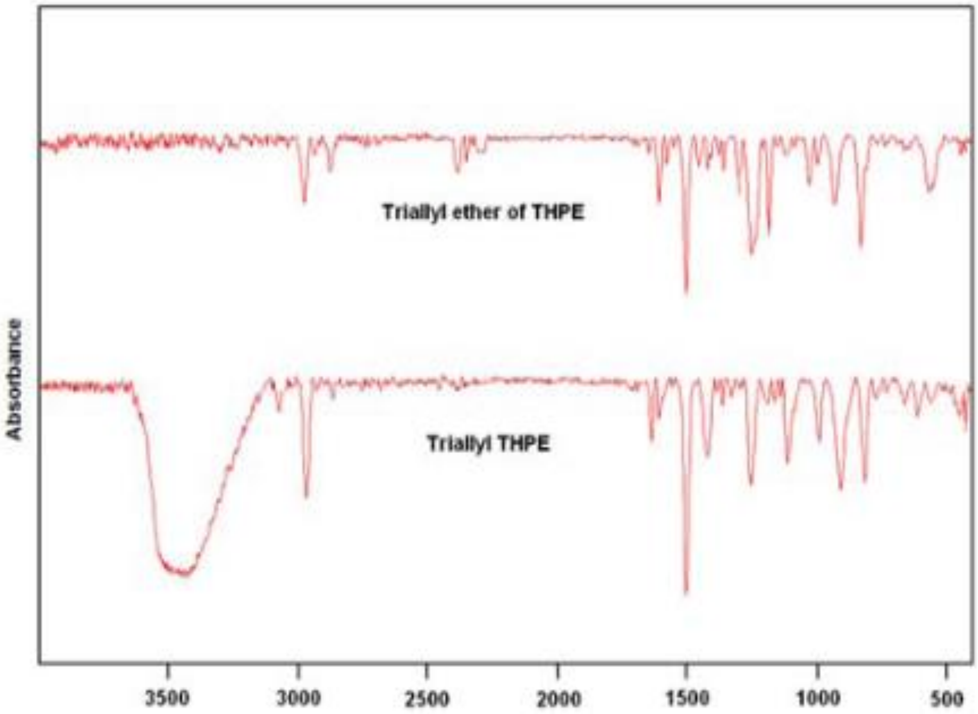


Figure 3.2 FTIR spectra of triallyl-THPE [6].

The ^{1}H NMR spectra also confirmed the result because they showed all the peaks of the protons positioned as expected as shown in Figure 3.3(a). The attachment of a triallyl-THPE monomer to the main backbone of the polymer and successful silicone grafting were determined by ^{1}H NMR spectroscopy which are represented sequentially in Figure 3.3 (b)

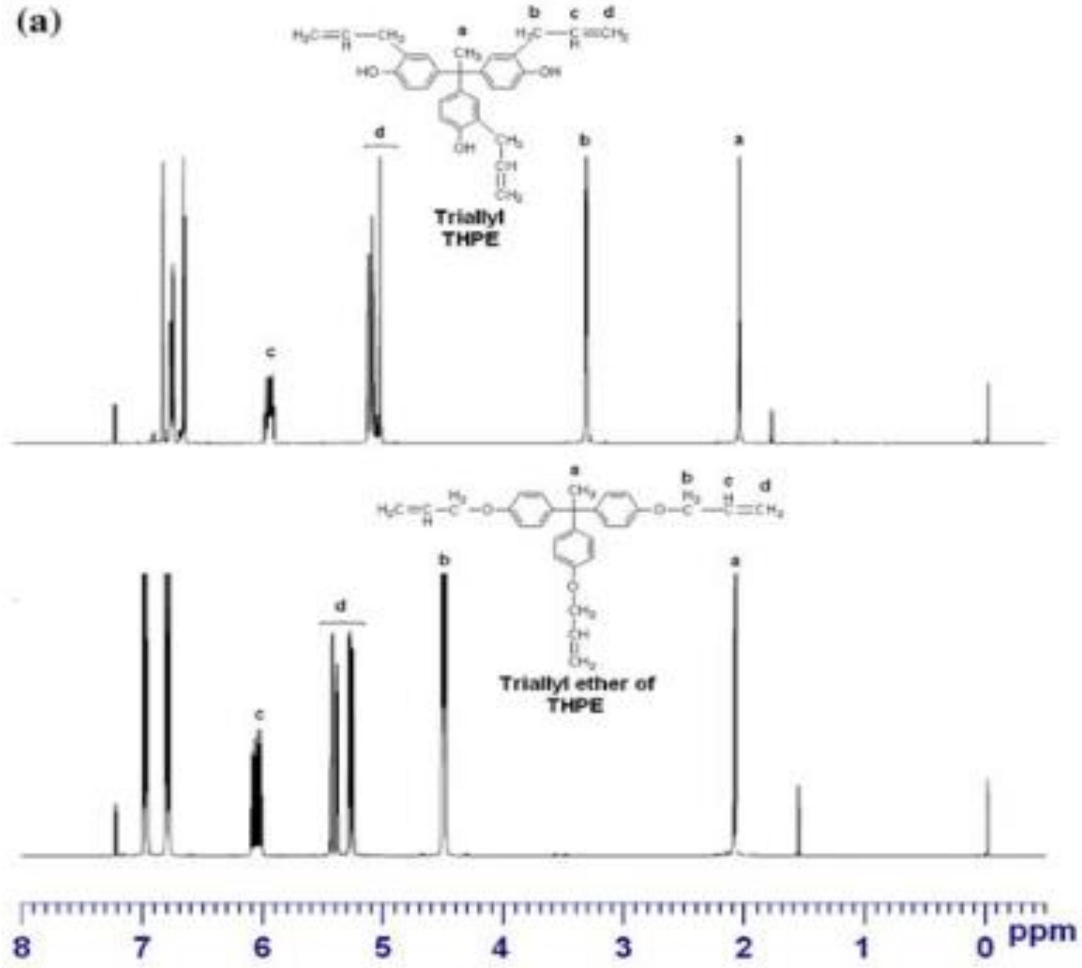


Figure 3.3 (a) ^{1}H NMR spectra of the triallyl ether of THPE and triallyl-THPE [6].

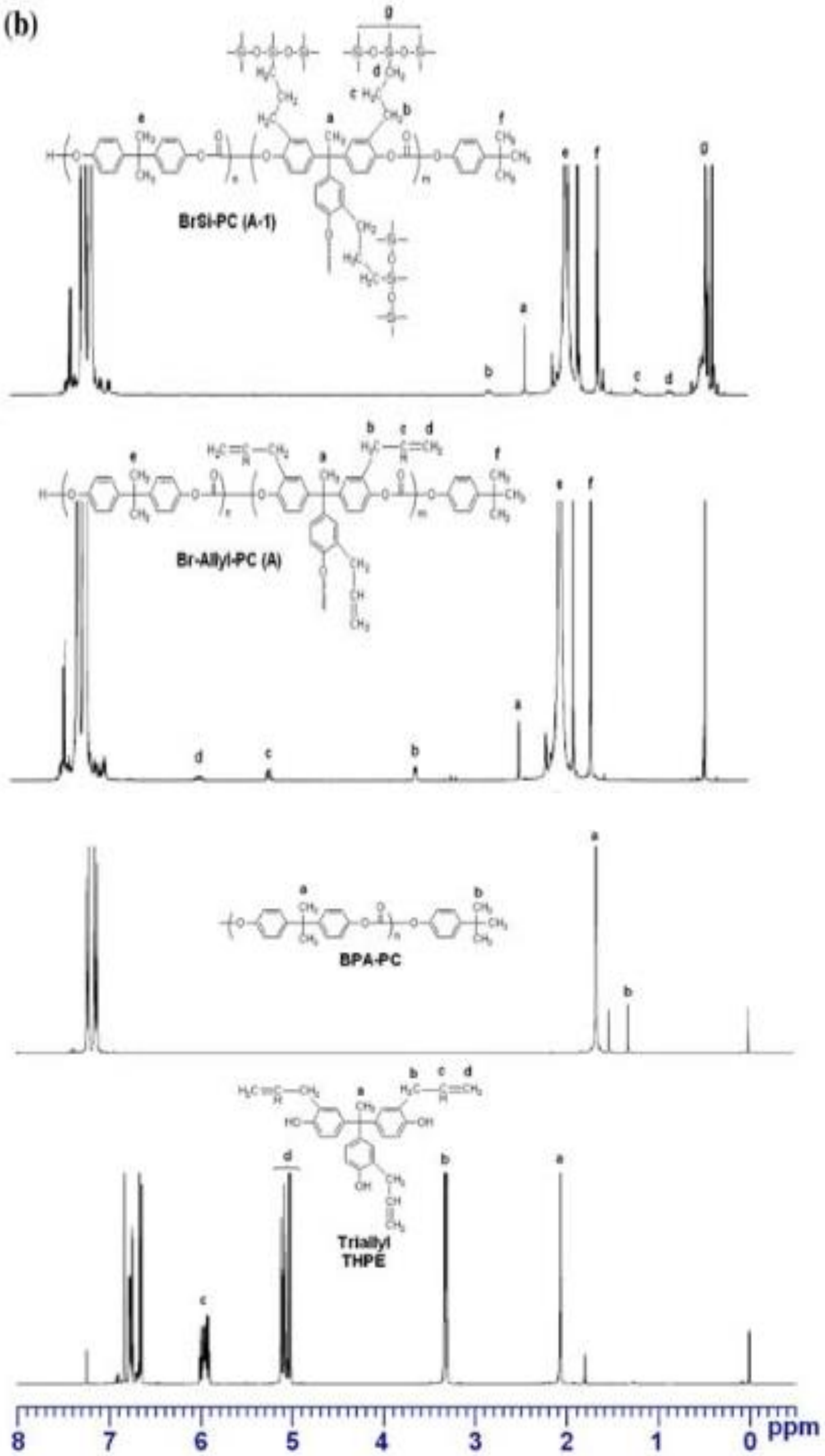
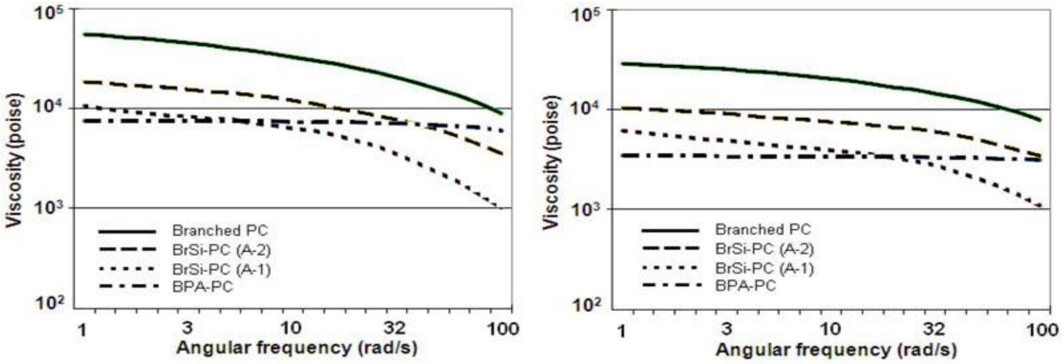
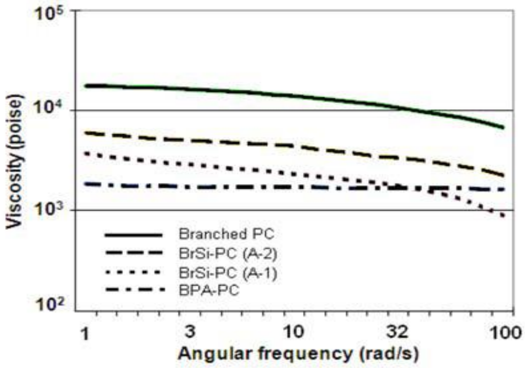


Figure 3.3 (b) ^{1}H NMR spectra of triallyl-THPE, BPA-PC, Br-allyl PC and BrSi-PC [6].

The complex viscosity of the synthesized branched grafted silicone polycarbonates (BrSi-PCs) shows in Figure 3.4. The viscosities of the polymers expectedly decrease with increasing temperature. The BrSi-PCs exhibited higher and lower shear viscosities than BPA-PC and branched-PC because of the strong non-Newtonian characteristics. The complex viscosity of BrSi-PCs decreased more significantly than that of BPA-PC and branched-PC at higher frequencies. High molecular weight or branched molecules have a lower relaxation or diffusion speed than low molecular weight or linear molecules, which result in higher shear thinning behavior. Low molecular weight short chain grafted BrSi-PC shows better flow properties than long chain grafted BrSi-PC. The shear thinning behaviors are less pronounced when temperature increases.



(a) Temperature at 260 °C (b) Temperature at 280 °C

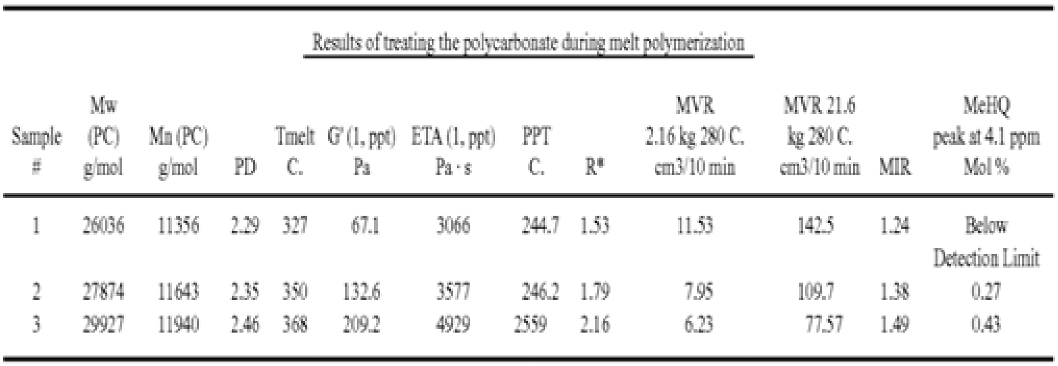


(c) Temperature at 300 °C

Figure 3.4 Complex viscosity curves of the linear, branched, and branched-Si polycarbonates: (a) at 260 °C, (b) at 280 °C, and (c) 300 °C [6].

Brack et al. in 2010 [7] studied a method of increasing the branching and polydispersity of a polycarbonate by reactive extrusion. The example and results are summarized in Table 3.1 below. It is observed that increasing the temperature of a reactive extruder operating under melt polymerization conditions increases the branching and polydispersity of the resulting polycarbonate derived from alkylated monomers.

Table 3.1 Results of treating the polycarbonate during melt polymerization [7].



Results of treating the polycarbonate during melt polymerization

Sample #	Mw (PC) g/mol	Mn (PC) g/mol	PD	Tmelt C.	G' (1, ppt) Pa	ETA (1, ppt) Pa · s	PPT C.	R*	MVR 2.16 kg 280 C. cm3/10 min	MVR 21.6 kg 280 C. cm3/10 min	MIR	MeHQ peak at 4.1 ppm Mol %
1	26036	11356	2.29	327	67.1	3066	244.7	1.53	11.53	142.5	1.24	Below Detection Limit
2	27874	11643	2.35	350	132.6	3577	246.2	1.79	7.95	109.7	1.38	0.27
3	29927	11940	2.46	368	209.2	4929	2559	2.16	6.23	77.57	1.49	0.43

As the melt temperature is increased, it can be seen that the both the R* and MIR values systematically increased. R* is the ratio between the complex melt viscosity at 1 rad/s over the complex melt viscosity at 100 rad/s. MIR is ratio of the melt volume rate measured with a weight of 2.16 kg and the melt volume rate measured with a weight of 21.6 kg. R* and MIR value indicates a melt strength.

Sang Pil Kim, Jae-Silk Lee, Suo-Ho Kim, Bong-Hee Lee, Sang Hern Kim, and Whan-Gi Kim in 1999 [9] have investigated the branched polycarbonates were synthesized by interfacial polymerization of linear oligomer (Mv=1000), which was based on Bisphenol A (BPA) and phosgene, and followed by oligomerization with 1,1,1-tris-p-hydroxyphenylethane (THPE) as a branching agent, and p-t-butylphenol (PTBP) as a molecular weight controller in a batch reactor. Chemical structures of the branched polycarbonate were identified by ^{1}H NMR. ^{1}H NMR Spectra of branched polycarbonates are shown in Figure 3.5. The aromatic proton peaks of the branching agent in branched polycarbonate containing 0.35 mol% of THPE were not detected in the ^{1}H NMR spectrum. In the case of branched polycarbonate with 2 mol% of THPE the methyl proton peaks of branching agent were observed at 1.65 ppm and the peaks of aromatic ring protons of the branching agent were observed at 6.6-6.7 ppm. Hydroxy groups of bisphenol A and the branching agent were observed at 4.9 ppm because the reaction was stopped in the oligomerization stage.

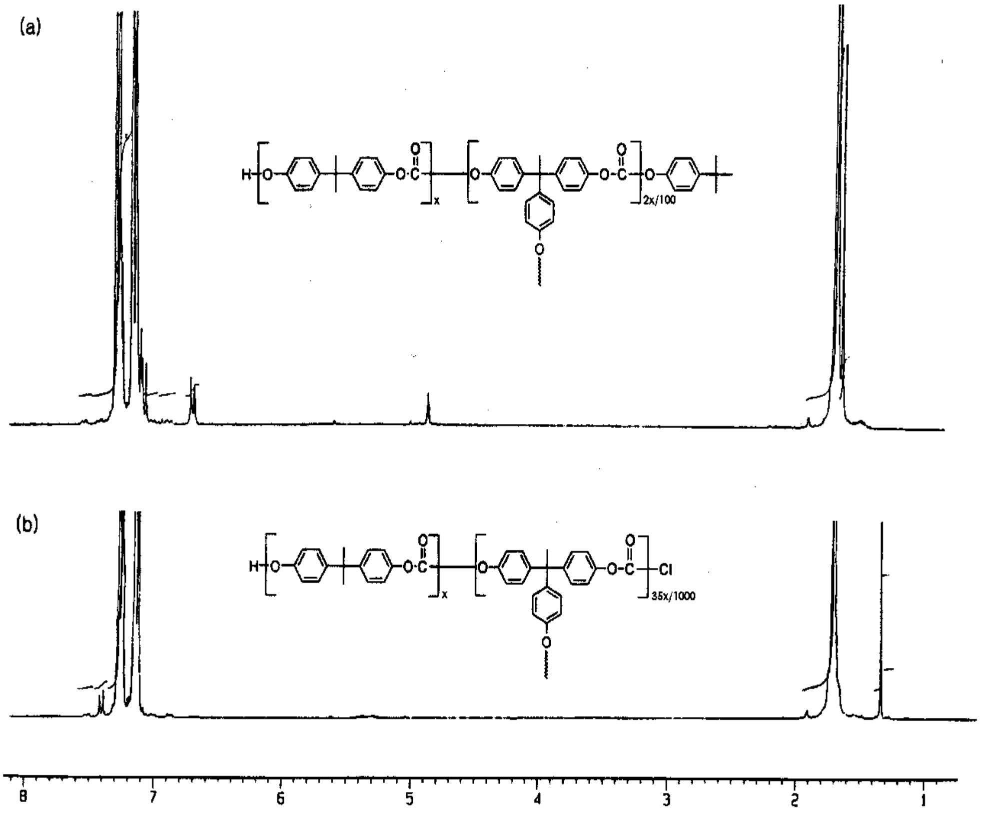
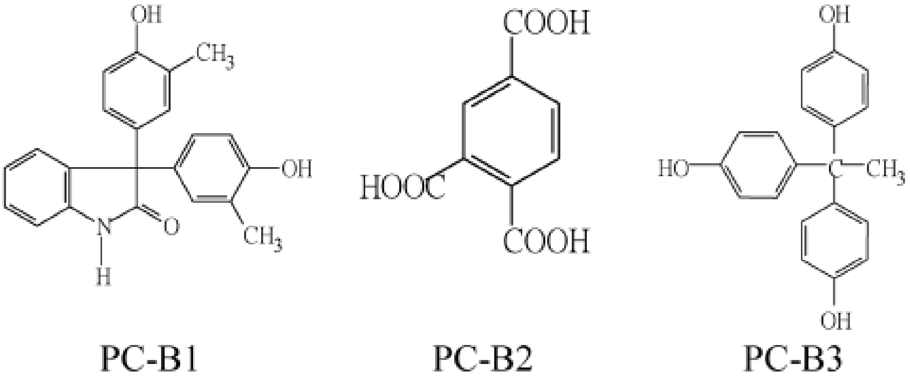


Figure 3.5. ^{1}H NMR Spectra of branched polycarbonates (a) with 2 mol% and (b) 0.35 mol% of THPE based on bisphenol A without PTBP [9].

Chenyang Liu, Chaoxu Li, Peng Chen, Jiasong He, and Qingrong Fan in 2004 [13] studied the similar molecular weight and molecular weight distribution of linear polycarbonate and branched polycarbonate. The PC-Bs have different branching agents, which was observed to be the same as shown in Figure 3.6.



(a) (b) (c)

Figure 3.6 Chemical structures of three different branching agents for PC-Bs. Branching agent as: (a) 3,3-Bis(3-methyl-4hydroxyphenyl)oxyindole, (b) Trimellitic acid , and(c) 1,1,1-Tris(4-hydroxyphenyl)ethane [13].

Furthermore, Figure 3.7 exhibits dynamic viscosity curves for linear and branched polycarbonate at 260˚C. At low shear rate, the viscosities of all branched PC-Bs are much higher than that of PC-L in contrast to at high frequency the viscosities of all PC-Bs are lower than that of PC-L. The phenomenon of decreasing in viscosity was observed for all of PC-L and PC-Bs when shear rate increased.

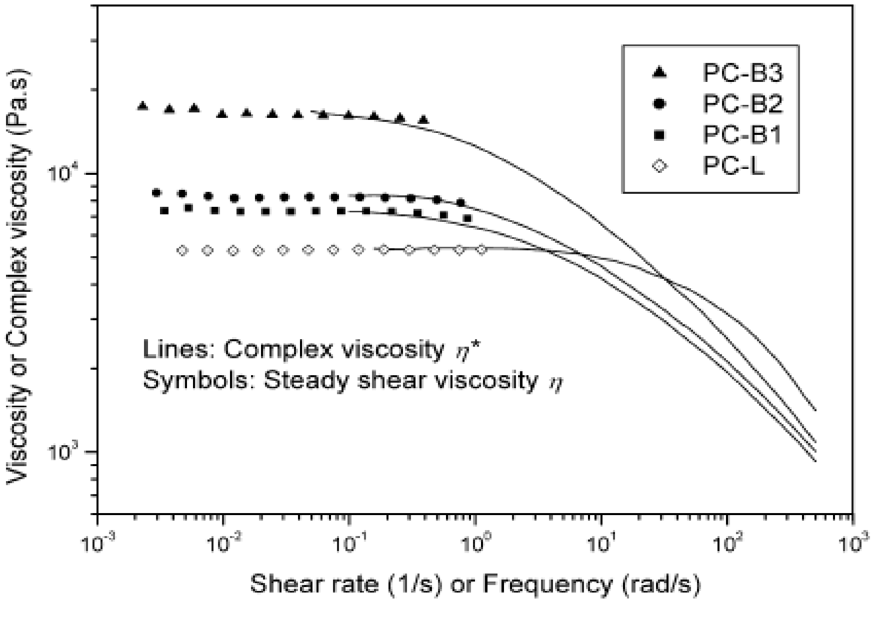


Figure 3.7 Viscosity vs shear rate of Linear PC-L and

branched PC-Bs at 260 ˚C [13].

The characteristic frequencies of three branched PC-Bs are 1-2 decades lower than that of PC-L indicating that the branched PC-Bs exhibit higher shear sensitivities. The extent of shear thinning and the shear rate for shear thinning are related with two factors chain branching and MWDs. However, the branched PC-Bs exhibit higher zero-shear viscosities and more significant shear thinning which is consistent with an amount of long-chain branches (LCBs). At low shear rates, polymer with long chain branches would have higher viscosity than linear polymers. The branched polymer is easier to be disentangled under shear than the linear polymer. Thus, shear thinning becomes more noticeable with increasing long chain branch density. The shear thinning of the branched PC-Bs indicates that the modified polycarbonates prepared by incorporating 0.3-0.5 mol% branching agents have chain branches long enough to produce molecular entanglements.

Hess et al in 1999 [22] described the syntheses of both linear and branched PETs. Branched PETs were obtained via the ester-interchange route starting from DMT and a 2.5 M excess of EG. The reactions were performed in a stainless-steel reactor with different amounts (0.07 to 0.43 mol% with respect to DMT) of trimethylolpropane (TMP) present during the transesterification step. Transesterification was catalyzed with the addition of manganese acetate at a maximum temperature of 230°C. Following transesterification, polycondensation was catalyzed by antimony acetate at a maximum temperature of 290°C under vacuum.

Boo-Gon Woo, Kyu Yong Choi, Kwang Ho Song, and Sang Ho Lee in 2001 [23] studied the melt transesterification of bisphenol-A and diphenyl carbonate in a semibatch reactor. In the melt polymerization process, a partial loss of diphenyl carbonate occurs as the reaction by-product phenol is removed from the reactor. To obtain a high molecular weight polymer under high temperature and low pressure conditions, a stoichiometric mole ratio of the two reactive end groups needs to be maintained during the polymerization. The weight average molecular weight values calculated for different initial DPC/BPA mole ratios are shown in Figure 3.8. It is seen that the highest molecular weight is obtained when the initial mole ratio is 1.05.

When the initial mole ratio is 1.01, the polymer molecular weight after 150 min is only 50% of the molecular weight when the initial mole ratio of 1.05 is used. It is also seen that the polymer molecular weight keeps increasing only when the ratio of the functional end groups is almost unity during the course of polymerization (e.g., initial DPC/BPA mole ratio is 1.05).

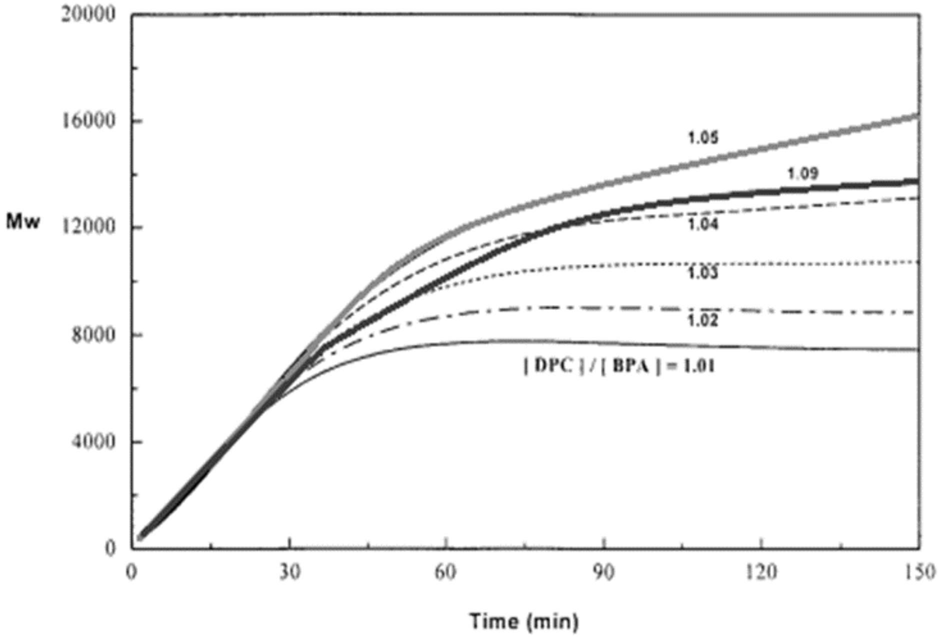


Figure 3.8 Effect of initial DPC/BPA mole ratios on polymer molecular weight (230°C; 5 mmHg; reflux column temperature, 82°C) [23].

Namba Nobutsugu and Hachiya Hiroshi in 2011 [24] studied the branched polycarbonate synthesis from diphenyl carbonate and bisphenol-A (BPA) via melt transesterification as disclosed in EP 2592102 A1. The continuous system of production was developed in order to produce branched polycarbonate without phosgene and to avoid fish eye formation. From the invention, the synthesis reaction mainly divided into 2 zones. The first zone which consisted of 4 stirred tank polymerization reactors was used to synthesize linear prepolymer polycarbonate whereas the second zone was used to produce branched polycarbonate via two wire-contact polymerization reactors.

The synthesis condition to produce branched polycarbonate using the polyfunctional compound, 1,1,1-tris(4-hydroxyphenyl)ethane or THPE was schematically illustrated in Figure 3.9. As seen in the figure, the first two reactors in the first zone were operated at temperature of 180°C and at atmospheric pressure for 4 hours. After that, the prepolymer was then fed into reactor no. 2 which was operated at increased temperature of 230°C and reduced pressure of 13.3 kPa. The reactor no.3 at temperature of 265°C and pressure of 2.66 kPa was connected to reactor no.2 and the molten polymer was transported into reactor no.3. Polycarbonate was further polymerized in wire-contact reactors at temperature of 265°C and pressure of 800 Pa. THPE was continuously added to the outlet of the wire-contact fluidized first polymerization reactor, in an amount of 0.1-0.95 mol% with respect to BPA. The polymer was then pumped into the wire-contact fluidized second polymerization reactor at temperature of 265°C and pressure of 120 Pa.

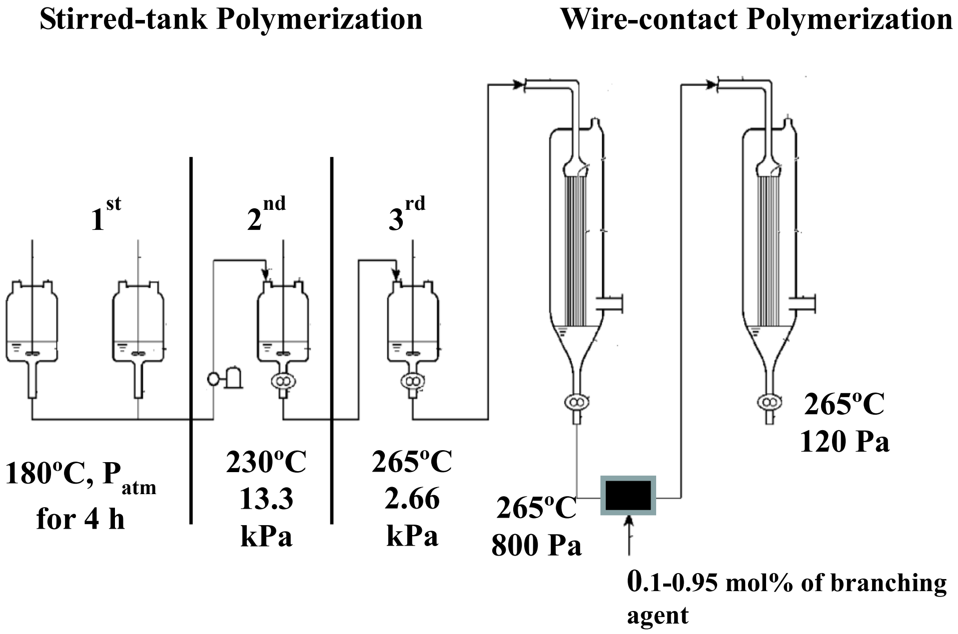


Figure 3.9 The synthesis condition to produce branched polycarbonate using the polyfunctional compound, 1,1,1-tris(4-hydroxyphenyl)ethane or THPE [24

CHAPTER IV

EXPERIMENTAL

4.1 Materials

Bisphenol-A (BPA, 99.97% purity) and diphenyl carbonate (DPC, 99.9% purity) as a co-monomer were supplied by PTT Phenol Company Limited and Aldrich, respectively. Sodium carbonate (Na_2CO_3, 99.9% purity) as catalyst was purchased from Rankem. Tetrahydrofuran (THF, HPLC grade) and Chloroform (AR grade) were purchased from RCI Labscan. 1,1,1-Tris(p-hydroxyphenyl)ethane (THPE), 3,3-Bis(p-hydroxyphenyl)oxindole, Trimellitic acid and 1,1,1-Tris(hydroxymethyl)ethane were purchased from Aldrich. The commercial branched polycarbonate was supplied as pellets by Bayer Material Science AG. The commercial linear polycarbonates (wonderilite PC 110 and PC 175) were used as a reference, obtained from Chi Mei Co.Ltd.

4.2 Synthesis of Branched Polycarbonate via Melt Transesterification Reaction

Batch melt transesterification for synthesis of polycarbonate was carried out using a 250-ml round-bottomed four-neck flask as a reactor equipped with a mechanical stirrer. The reactor was immersed in silicon oil bath in which the temperature was set and controlled by a PID controller. The two reactants of BPA and DPC were inserted into the reactor at temperature of 180°C and pressure of 760 mmHg under nitrogen atmosphere at a flow rate of 2 ml/min. The reactants was left to melt for about 3 minutes. Branching agent was then added into the reactor and meahcnically stirred at 200 rpm to ensure good mixing of the reactants. The reaction was proceeded for about 60 minutes. After that, the temperature was raised to 200°C for about 30 minutes. Then, the reduced pressure of 100 mmHg was set in order to remove a by-product i.e. phenol. The vapor was traped by passing the outgasing products through the vacuum trap. Small amounts of samples were withdrawn at different reaction times for characterizations. The synthesis condition was summerized in Table 4.1 and the experiment apparatus was shown in Figure 4.1

Table 4.1 Experimental reaction conditions.

Step No.	Time (min)	Temperature (^oC)	Pressure (mmHg)
1	0-60	180	760
2	60-90	180-200	760
3	90-240	200	100

Figure 4.1 Experimental setup for melt transesterification of DPC and BPA.

4.3 Characterization Methods

4.3.1 Differential Scanning Calorimeter (DSC)

Glass transition temperature was studied by a differential scanning calorimeter (DSC) model 2910 from TA Instruments. Each specimen was sealed in an aluminum pan with lid. The specimen was heated from 30°C to 200°C using a heating rate of 10°C/min under nitrogen purging.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structures of as-synthesized PC were studied by FT-IR spectroscopic technique. FTIR spectra were recorded on a Spectrum GX FTIR spectrometer from Perkin Elmer instrument at a resolution of 4 cm^{-1}, in transmittance mode with the frequency range of 4000 to 400 cm^{-1}. The samples were prepared on thin films, obtained from $CHCl_3$ solution casting onto potassium bromide (KBr) plates by spontaneous evaporation of the solvent at room temperature.

4.3.3 Gel Permeation Chromatography (GPC)

Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity index (PDI) of as-synthesized PC were measured by Gel Permeation Chromatography (GPC) technique. The GPC system consisted of Waters 600 E chromatographer, Waters 410 refractometer and three Waters Styragel columns (HR-4, HR-3 and HR-2). The mobile phase was tetrahydrofuran (THF) maintained at 40°C, and at a flow rate of 1.0 ml/min. The GPC was calibrated with narrow polydispersity polystyrene standards, and molecular weights of the obtained products were reported as polystyrene equivalents.

4.3.4 Rheological Properties Measurement

Rheological properties of as-synthesized PC were examined using a Rheometer (Haake Rheo Stress 600, Thermo Electron Cooperation) equipped with 25 mm parallel plate geometry. The measuring gap was set at 1 mm. For dynamic temperature sweep mode, samples were heated from 180 to 300°C at a constant frequency of 1 Hz. For dynamic frequency sweep mode, the dynamic viscoelastic properties were determined with frequencies ranging from 0.01 to 100 Hz at temperatures 260°C.

4.3.5 Nuclear Magnetic Resonance Spectroscopy (NMR)

Chemical structures of synthesized PC were also studied by ^{1}H and ^{13}C NMR. NMR experiments were performed using a Varian Unity Inova 500 MHz Spectrometer. The NMR probe was tuned to ^{1}H and ^{13}C frequency, which is 500.15 and 125.76 MHz for the 500 MHz spectrometer. The NMR samples were prepared by dissolving each sample in deuterated chloroform ($CDCl_3$). Prior to the NMR measurements, The obtained PC was purified by dissolving it in dichloromethane and then precipitating it using acetone. The polymer was then dried in a vacuum oven at 40°C for at least 1 day.

4.3.6 Thermogravimetric Analysis (TGA)

For investigation of the degradation temperature (T_d) and char yield of the synthesized PC samples and commerical PCs were determined using a thermo gravimetric analyzer (TGA/SDTA 851e, Mettler Toledo, Germany). All measurements were performed with a heating rate of 20°C/min from room temperature to 800°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained at 50 ml/min. The sample weight was 8-12 mg. Weight loss of the samples was measured as a function of temperature. Values for residues were taken at the end of the main decomposition step. The degradation temperature (T_d) was reported at 5% weight loss and the char yield were reported at 800 °C.

4.3.7 Melt Flow Index Measurement (MFI)

Melt flow index or MFI is a measure of an ease of flow of the melt of PC using a melt flow indexer (MI-4 Gottfert Instruments). It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of an orifice with a diameter of 2.095 mm and orifice length of 8.0 mm according to ASTM D 1238 standard at 300°C/1.2kg load for PC. All these are preheat for 30 seconds.

4.3.8 Yellowness Index (YI) Measurements (YI)

The yellowness index (YI) were measured by spectrophotometer (Utra Scan Pro Hunter Lab Instruments), in accordance with ASTM E313[D65/10°]. In order to set the yellowness index for air equal to 0.0. The sample reflectance area is 25 mm × 4 mm. Transmittance path lengths up to 80 mm was used in the measurement. The purified PC samples were prepared as thin film, obtained from $CHCl_3$ solution casting onto glass plates followed by evaporation of the solvent at room temperature.

4.3.9 Dynamic Mechanical Analysis (DMA)

A Dynamic mechanical analyzer (DMA), model DMA 242C, NETZSCH was used to investigate dynamic mechanical properties and relaxation behaviors of the synthesized PC i.e. storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta$) data. The glass transition temperature (T_g) was taken as the maximum point on the loss modulus and $\tan\delta$ curve in the DMA thermogram. All PC film was measured in a tension mode. In the single frequency temperature-sweep experiment, a frequency of 1 Hz was used while the temperature was scanned from 30°C to about 200°C with a heating rate of 2°C/min

CHAPTER V

RESULTS AND DISCUSSION

5.1 Operating Conditions for Linear PC Precursor Synthesis

5.1.1 Effect of Operating Conditions and Mole Ratios of DPC/BPA on Molecular Weight of Linear Polycarbonate Precursor

In the first stage of branched PC synthesis, we began with the preparation of linear PC precursor. It is desirable to prepare a long chain branching PC for desirable melt strength and rheological properties therefore, a linear precursor of a molecular weight of at least 5,000 [25] which is a critical molecular weight of our PC was firstly synthesized. The critical molecular weight (M_c) is the minimum molecular weight at which a polymer chain entangles. This level of branches molecular weight could improve melt strength of the polycarbonate which makes it particularly suitable for such types of polymer processing procedures as blow molding of large, hollow containers, corrugate sheet and the extrusion of complex profile forms as discussed by Hoeks et al. [18]. In this first stage, we were attempting to synthesize PC with a molecular weight in a range of 5,000 to 10,000 before an introduction of a branching agent to produce branched PC. When too high molecular weight of linear PC precursor i.e. > 10,000 was used, we experienced difficulty in mixing or dispersion of the branching agent in the obtained PC precursor and those molecular weight was avoided based on this reaction set-up.

Reaction condition for transesterification of bisphenol-A (BPA) and diphenyl carbonate (DPC) for linear PC precursor preparation in this work is shown in Figure 5.1. In practice, it is desirable to minimize the loss of DPC by maintaining the polycondensation of the transesterification reaction at a temperature of 180^{o}C for about 60 min. At this stage, the monomers will be converted to a less volatile oligomer with higher molecular weight thus suppressing the loss of the DPC above. Any loss of DPC during the reaction will cause significant variations in the concentration of reactive end groups and the resulting molecular weight of the PC. As the polymerization reaction proceeds, molecular weight of polymer increases and the melt viscosity also increases rapidly. Hence the reaction temperature was raised from 180°C to 200°C to reduce the melt viscosity of the reaction mixture for better mixing. Too high temperature is to be avoided in the synthesis to prevent side reaction, particularly, gelation of the obtained PC. During the polycondensation of BPA and DPC, the reaction by-product, i.e. phenol, is produced. The phenol by-product needs to be distilled off continuously to facilitate the forward chain growth reaction. In our case, phenol was removed from the reaction by applying a high vacuum.

The molecular weight profile of PC as a function of time was investigated in order to find the proper reaction time to reach the critical molecular weight value above.

Moreover, the molecular weight profile of the polycondensation polymer also varies with the initial mole ratio of the reactants. Thus the investigation on molecular weight profile of our PC by varying the initial mole ratio between BPA and DPC was carried out in our work. The initial mole ratio of DPC/BPA at 1.05/1.00, which was reported to provide the maximum molecular weight of linear PC [23], and the off-stoichiometric initial mole ratio at 1.26/1.00 as estimated according to Carothers' equation (1) were used for an investigation of the molecular weight profile of our PC.

$$\bar{X}n = \frac{1+r}{1-r} \qquad (1)$$

Where $\bar{X}n$ is the number average degree of polymerization. In this case, the critical molecular weight of polycarbonate is 5,000 g/mole [25]. The molecular weight of repeating units of polycarbonate is 254.3 g/mole and r is stoichiometric imbalance (a limiting reactant is BPA).

Figure 5.2 shows the molecular weight profiles of the synthesized polycarbonate at the initial mole ratios of DPC/BPA of 1.05/1.00 and 1.26/1.00 without using any catalyst. It was observed that the polymer molecular weight increased with reaction time and changed significantly with the variation in the initial mole ratios of the two reactants. The more rapid increase in PC molecular weight with reaction time was noticed when the initial mole ratio of DPC/BPA used was 1.05/1.00 whereas the weight-average molecular weight of PC with mole ratio of DPC/BPA of 1.26/1.00 was also increased with the reaction time but with a lower rate. The linear PC precursor with DPC/BPA of 1.05/1.00 reached its critical molecular weight of 5,000 g/mole with less than 120 min of reaction time. Its molecular weight continually increased to about 20,000 g/mole at the reaction time of 240 min. For the PC using DPC/BPA at 1.26/1.00 initial mole ratio, PC precursor reached its critical molecular weight at about 150 min then slightly increased to 8,000 g/mole at the end of reaction of 240 min. Theoretically, the highest molecular weight is obtainable when the concentrations of the two functional end groups are equal during the polymerization i.e. at the molar ratio of 1.00/1.00 as reported by Woo et al [23]. The off-stoichiometric amount of the reactants can evidently be used to control the molecular weight of our PC precursor.

Therefore, the PC prepolymer at the initial DPC/BPA mole ratio of 1.26:1.00 was found to be appropriate for the preparation of the PC precursor in a more controllable manner because it provided a linear PC with desirable molecular weight in the range of 5,000 and also gave sufficient time for an addition of a branching agent for branched PC synthesis in the next step.

5.1.2 Effect of Na_2CO_3 Catalyst on Synthesis of Linear Polycarbonate Prepolymer

The effects of a catalyst on molecular weight profile of synthesis PC were also investigated. According to our previous report [26], sodium carbonate (Na_2CO_3) was proved to be one suitable catalyst by giving the highest weight average molecular weight of linear polycarbonate via melt-transesterification reaction. The synthesis of polycarbonate prepolymer using Na_2CO_3 as a catalyst was studied experimentally in a batch reactor at the same synthesis condition as used in section 5.1. Figure 5.3 illustrates molecular weight profiles of as-synthesized polycarbonate using Na_2CO_3 as a catalyst. The molecular weight of the obtained PC precursor was observed to drastically increase with increasing reaction time and reached the value of about 20,000 g/mole at the reaction time of 240 min. Moreover, it was found that gelation frequently occurred in this catalyzed system. In the case of gelled PC, the solid product is white and opaque and insoluble in tetrahydrofuran (THF) at 40°C.

It is believed that the Na_2CO_3 could act as a branch-inducing catalyst and might cause Fries rearrangement which provides branched structure as reported by Karlik et al. [3]. The formation of Fries product was schematically presented in Figure 5.4. Fries rearrangement of the linear aromatic polycarbonate in Figure 5.4(a) yields, initially, a substituted phenyl salicylate product as shown in Figure 5.4(b), which can then undergo polymerization by reaction of the pendant salicylate hydroxyl group with DPC and BPA to yield a branched aromatic polycarbonate as shown in Figure 5.4(c) [27]. The polycarbonate oligomers, to which the branch-inducing catalysts are added, have Fries branch point structures. If the content of Fries branch point structures in the polycarbonate oligomer is too high, then the chain lengths between branch points in the final resin will be short. This was reported to give rise to insoluble gel particles which clog filters and produce poor optical properties in the PC product. In our case, to be able to control the branching reaction of polycarbonate from mainly the added branching agent and to suppress the rearrangement reaction hypothesized above, the synthesis condition of PC without Na_2CO_3 catalyst will be used.

In this work, the linear PC precursor without the use of Na_2CO_3 catalyst was reproduced several times to determine the reaction time to produce PC with molecular weight in the range of 5,000. As seen in Figure 5.5, molecular weight of PC gradually increased with reaction time and reached the molecular weight of 5,000 g/mole after 210 min. At this reaction time, the branching agent was added in the reactor to generate branched PC. However, by introducing branching agent at this time, it required an additional reaction time of at least 120 min for the branching reaction to proceed. This rather long reaction time, totally of more than 330 min (see Figure 5.6) resulted in an unexpectedly frequent gelation of the PC with a chance of greater than 50%. The rather long reaction time might raise a possibility of rearrangement process to promote gelation. This is also probably due to low reaction rate between the viscous PC precursor and the branching agent added. In order to avoid the gel formation due to long reaction time, branching agent for branched PC synthesis was simultaneously introduced into the reactor right after the melting of the BPA and DPC reactants.

5.2 Operating Conditions for Branched PC Synthesis

5.2.1 Effect of Type of Branching Agents on Molecular Weight and Molecular weight Distribution of the Synthesized Polycarbonate

Branched polymers are characterized by a presence of branched point or a presence of more than two end groups, thus constitute a class of polymers between linear polymers and polymer networks [28]. The most common method for synthesizing branched polycarbonate is via the additional of small amount of trifunctional or multifunctional agents to the polymerization to obtain long-chain branched polymer. Unlike short chain branches, a long chain branch is long enough to entangle with other chains in the melt resulting in an increase in their melt strength as well as shear sensitivity.

Branched PCs are very useful for a wide range of applications such as extrusion blow molding processes for a production of profiles, solid sheets, muti-wall sheets or corrugated sheets. Synthesis of branched PC is via the addition of appropriate amounts of a multifunctional branching agent to the polymerization. Branching agents are well known and may comprise of polyfunctional organic compounds containing three or more functional groups, which may be hydroxyl, carboxyl, carboxylic anhydride, and mixtures of those [3]. 1,1,1-tris(p-hydroxyphenyl)ethane (THPE) is one of the most utilized branching agents for branched PC production. THPE is normally more preferable as the compound is readily available at competitive cost [29]. Additionally, 3, 3-bis (p-hydroxyphenyl)oxindole, and 1,1,1-tris (hydroxymethyl)ethane (TME) and tricarboxylic acid are also used as branching agents for the synthesis of branched PC in this work [13, 30]. The chemical structure of each branching agents was shown in Table 5.1.

Initially, the amount of these branching agents was fixed at 0.35 mol% with respect to BPA. The mole ratio between DPC/BPA is maintained at 1.26/1.00. The branching agent was introduced in the reactor right after the two reactants were melted as suggested in the previous section. Branched PC was synthesized from different types of branching agents based on the condition shown in Figure 5.1. The reaction time to reach the same level of viscosity, i.e. before gel formation, of branched PC synthesis using THPE, 3,3-bis(p-hydroxyphenyl)oxindole, TME and tricarboxylic acid as branching agents was 240, 120, 180 and 170 min, respectively and was summarized in Table 5.2. Similarly, linear PC without an addition of branching agent was also prepared based on the same temperature and pressure profile using the reaction time of 240 min. This polymer is defined as a controlled PC. The molecular weight and molecular weight distribution of the obtained branched PCs are listed in Table 5.3.

The number average molecular weight (M_n), weight average molecular weight (M_w) and molecular weight distribution of the controlled PC were determined to be 3,091, 5,308 g/mole and 1.71, respectively. With an addition of branching agents in the branched PC synthesis, Mw and molecular weight distribution of the obtained PC were found to be higher compared to those of the controlled linear PC.

The synthesis of branched PC using THPE as a branching agent provided a greater M_w and molecular weight distribution of synthesized PC compared to those of the controlled PC. The Mw of the obtained branched PC is in the range of 7,057 to 9,380 g/mole with the molecular weight distribution to be in the range of 1.85-1.98.

A higher in Mw and molecular weight distribution of branched PC synthesis using 3,3-bis(p-hydroxyphenyl)oxindole compared to those of the linear PC was also observed. In this case, the Mw of the resulting branched PC was determined to be in the range of 5,933 to 10,345 g/mole while the molecular weight distribution was found to be in the range of 1.85-1.93. An addition of TME into the synthesis also provided a greater molecular weight with the value between 8,154 and 9,752 g/mole and the molecular weight distribution of 1.70-1.72.

In the case of tricarboxylic acid, as this type of branching agent possesses carboxylic functional group, the initial mole ratio of DPC/BPA was set at 1.00/1.26 for the better chance of the branching agent to be incorporated into the PC structure. However, no high molecular weight polymer was obtained using this branching agent. This might be due to the reactivity of the carboxyl group of this branching agent with the hydroxyl group of BPA is lower than that between the hydroxyl group of the other three branching agents with the phenoxy group of DPC. Therefore, it can be concluded that THPE, 3,3-bis(p-hydroxyphenyl)oxindole, and TME are potential branching agents for further investigation of branched PC synthesis via melt transesterification.

5.2.2 Effect of Concentration of Branching Agents on Molecular Weight and Polydispersity of the Synthesized Polycarbonate

The effect of the amount of branching agent of 0.35, 2.00 and 3.00 mol% with respect to BPA on the synthesis of branched PC was also investigated. In this study, THPE and 3,3-bis(p-hydroxyphenyl)oxindole were evaluated as branching agents for our branched PC synthesis. The same reaction condition as mentioned in section 5.2 was used for this investigation. The reaction times for branched PC synthesis using THPE and 3,3-bis(p-hydroxyphenyl)oxindole at various amount of branching agent were 240 and 120 min, as suggested in Table 5.2. From the GPC analysis, an increase in THPE content from 0.35 to 3.00 mol% based on BPA resulted in a steady increase in molecular weight and molecular weight distribution of the obtained PC as evidently seen in Table 5.4. From the table, the increasing content of THPE from 0.35 to 2.00 mol% with respect to BPA provided an increase in the resulting PC molecular weight from 7,057 to 11,166 and the molecular weight distribution from 1.98 to 2.11. The use of 3.00 mol% of THPE also provided a higher in molecular weight up to 15,032 with a molecular weight distribution of 2.27. Whereas the increase in the amount of 3,3-bis(p-hydroxyphenyl)oxindole from 0.35 to 3.00 mol% with respect to BPA provided no significant difference in molecular weight in the synthesized polycarbonate as shown in Table 5.4. The molecular weights of the synthesized PC using 0.35, 2.00 and 3.00 mol% of 3,3-bis(p-hydroxyphenyl)oxindole are 10,345, 12,870 and 10,429 and the molecular weight distributions of these PC are 1.85, 2.26 and 1.98, respectively.

5.2.3 Chemical Structure of Synthesized Branched Polycarbonate

Chemical structures of the branched polycarbonate were characterized by ^{1}H NMR. The peak characteristics of the branching agents, in the branched polycarbonate containing 0.35, 2 and 3 mol% of each branching agent, were examined in the ^{1}H NMR spectrum. Figure 5.7 shows the ^{1}H NMR spectra of branched polycarbonate with 0.35, 2 and 3 mol% of THPE based on bisphenol A.

In the spectra, the methyl proton peaks of bisphenol A were observed at 1.67 ppm whereas the peak of methyl proton of THPE was observed at 2.18 ppm. The peaks of aromatic ring protons of the THPE were observed at 7.00-7.30 ppm. These assignments are in good agreement with those of PC using THPE as a branching agent as reported by Kim et al [9]. From those ^{1}H NMR spectra, the characteristic chemical shifts in our PC samples were observed with an addition of 0.35, 2 and 3 mol% of THPE indicating a presence of branched structure from this type of branching agent in our synthesized PC.

Furthermore, the characteristic NMR peaks of branched polycarbonate containing 0.35, 2 and 3 mol% of 3,3-bis(p-hydroxyphenyl)oxindole as a branching agent is shown in Fig 5.8. It was found that the methyl proton peaks of bisphenol A were observed at 1.70 ppm and the peaks of aromatic protons of bisphenol A were found at 7.00-7.42 ppm. However, no characteristic peak due to 3,3-bis(p-hydroxyphenyl)oxindole branching agent was observed in the spectra. From the above results, THPE is thus clearly the promising candidate as a branching agent to synthesize branched PC via melt-transesterification process. This finding is also consistent with the information disclosed in the patent by Namba and Hachiya [24].

5.2.4 Rheological Properties of Synthesized Polycarbonates Compared with Commercial Polycarbonates

Complex viscosities of commercial linear PC (Chi Mei, M_w=49,171) and commercial branched PC (Makrolon, M_w=55,804) were determined isothermally at 260°C in the frequency range of 0.01-100 Hz as displayed in Figure 5.9. At low shear frequency, the viscosity of the commercial branched PC is much higher than that of linear PC likely due to the greater degree of entanglement of the branched PC compared to its linear counterpart. However with increasing frequency, the viscosity of branched PC is reduced at a faster rate than that of the linear PC. In other words, commercial branched PC exhibited stronger shear thinning that the linear polymer. The viscosity of the commercial linear polymer was found to decrease from 1,155

Pa.s at a frequency of 0.01 Hz to the value of 537 Pa.s at a frequency of 100 Hz. In the case of commercial branched PC, the viscosity of the polymer was observed to decrease from 4,987 Pa.s at frequency of 0.01 Hz to the value of 638 Pa.s at a frequency of 100 Hz. Shear thinning is a reduction of the flow resistance due to the arrangement of the polymer molecules parallel to the flow direction. The degree of shear thinning is related to the structure of the molecules, molecular weight, molecular weight distribution, and relaxation or diffusion speed. Therefore, the branched polymer tends to possess less relaxation or diffusion speed compared to the linear one, and this gives a stronger time dependent shear thinning flow behavior [32].

Temperature dependence of complex viscosity of both types of commercial PC samples was examined in a temperature range of 180-300°C and at a frequency of 1 Hz. From Figure 5.10, the complex viscosity of both commercial PCs expectedly decreases with increasing temperature. In the case of the commercial linear PC, the viscosity decreased from 43,440 Pa.s at 190°C to 314 Pa.s at 300°C. Whereas in the commercial branched PC, the viscosity decreased from 77,540 Pa.s at 190°C to 671 Pa.s at 300°C. In principle, as the polymer heats up, there is more free volume created. The molecules are able to flow freely and past one another more easily as more free volume is present [33]. This behavior is common to both linear and branched polymers.

The complex viscosities of synthesized branched PC with an addition of THPE as a branching agent were also carried out in a similar fashion as that of commercial linear PC or PC-L (M_w=30,115) and commercial branched PC or PC-B (M_w=55,804). Figure 5.10 shows the complex viscosity of the three branched PC using THPE as a branching agent at 0.35, 2 and 3 mol% i.e. PC-BT1, PC-BT2, PC-BT3, as well as PC-B and PC-L' measured at 260°C. In this study, the commercial linear PC with lower molecular weight, i.e. 30,115, was selected for the test as this molecular weight is closer to the molecular weight of our synthesized branched PCs. From the figure 5.11, PC-BT3 and PC-B exhibited higher shear viscosities than PC-BT1, PC-BT2 and PC-L with strong non-Newtonian flow characteristic. That is the complex viscosity of PC-BT3 and PC-B decreased more strongly than that of PC-BT1, PC-BT2 and PC-L at higher frequencies. From the results, the synthesized branched PC using 3 mol% of THPE clearly shows rheological behaviors imitating commercial branched PC which is produced from interfacial polymerization process. This behavior suggested the successful formation of branched PC when 3 mol% of THPE is used as a branching agent. The long chain branching is thus expected to be presented in this PC. Though the NMR results suggested the presence of THPE in the obtained PC, less entanglement probably due to a formation of short chain branches may be the reason for the observed low shear sensitivity of the synthesized PCs using 0.35 mol% and 2 mol% THPE.

In addition, complex viscosities of as-synthesized branched PC with an addition 0.35 mol%, 2 mol%, and 3 mol% of 3,3-bis(p-hydroxyphenyl)oxindole i.e. PC-BO1, PC-BO2, and PC-BO3 were also determined at 180°C in the frequency range of 0.01-100 Hz and the results are displayed in Figure 5.12. From this figure, the zero-shear viscosity of PC-BO1, PC-BO2, and PC-BO3 were found to be lower than PC-L' because the molecular weights of PC-BO1, PC-BO2, and PC-BO3 polycarbonate are lower than PC-L. PC-BO1, PC-BO2 and PC-BO3 also exhibited lower shear sensitivity than PC-L'. From these results, it is likely that this type of branching agent cannot provide branched PC or might provide rather short branches in the obtained PC.

From the aforementioned findings, the synthesized branched PC with 3 mol% of THPE with respect to BPA exhibited strong shear sensitivity similarly to that of commercialized branched PC implying the formation of long chain branching PC was successfully produced via melt-transesterification process using the condition described above.

5.2.5 Preparation and Characterizations of Branched PC Prepared at Elevated Temperature

From the previous experiment, branched PC synthesis was prepared at relatively low temperature of up to 200°C in order to minimize side reaction particularly gelation. However, as a polymerization reaction proceeds, molecular weight of polymer increases correspondingly. This also causes the melt viscosity to increase rapidly and the polymerization rate tends to decrease due to the transformation of the kinetic control process to the diffusion controlled mode. Hence the reaction temperature is normally raised to reduce the melt viscosity and to facilitate the further chain growth reaction. In typical melt-transesterification of PC, the temperature of the reactor can be raised up to 300°C. The reaction temperature greater than this will cause a significant change in the sample color and promote undesirable side reactions including Fries arrangement to form branched structure [34].

The branched PC synthesis at elevated temperature was used to produce the PC sample with higher molecular weight and the condition is shown in Figure 5.13. The esterification was conducted using a 1.26 to 1.00 mole ratio of DPC to BPA with 3 mol% of THPE. In the first step, the reaction temperature was held at temperature of 180°C and atmospheric pressure for 60 min. Then, the reaction temperature was raised from 180 to 220°C for 30 min. After that, the pressure was reduced to 100 mmHg and the temperature was held at 220°C for 60 min. The reaction temperature was further raised to 250°C. In a similar manner, the reaction was terminated before the gel formation occurred. At 240 min of reaction time, branched PC synthesis with 3 mol% of THPE at elevated temperature provided a higher molecular weight of up to 26,294 g/mole and a molecular weight distribution of 3.76. The average molecular weight of the synthesized branched PC are relatively close to that of the commercial linear PC (Wonderlite PC 175) i.e. 30,115 g/mole. Consequently, this branched PC was further characterized to compare its properties with the commercial Wonderlite PC 175.

Figure 5.14 presents complex viscosity of the synthesized branched PC (M_W=26,294 g/mole), commercial branched PC (Makrolon WB 1239, M_W= 55,804 g/mole) and commercial linear PC (wonderlite PC 175, M_W=30,115 g/mole) measured at 260°C. It was found that at low frequencies, the viscosities of the synthesized branched PC and commercial branched PC are much higher than that of commercial linear PC. However, at high frequency range, the viscosities of the synthesized branched PC and commercial branched PC are lower than that of commercial linear PC and the viscosities of the formers start to decrease at much lower frequency than that of the latter, indicating that the synthesized branched PC exhibit high shear sensitivity comparable to the commercial branched PC and greater than the commercial linear PC. The extent of shear thinning and the onset shear rate for shear thinning is related with two factor; chain branching and molecular weight distribution [35, 36]. The commercial linear and the synthesized branched PCs have similar molecular weights and MWDs. However, the branched PC exhibits higher zero-shear viscosities and more significant shear thinning, which is consistent with the rheological behaviors of polyethylene or polyester possessing long chain branches [28]. There are two effects of the long chain branches on the viscosity curves of polymers. On one hand, long chain branches are more helpful to molecular entanglement than the linear polymer of the same molecular weight, if they have the same chemical structure. At low shear rates, polymers with long chain branches would have higher viscosity than linear polymer. On the other hand, the branched polymer is easier to be disentangled under shear than the linear polymer [35, 36]. Consequently, shear thinning becomes more noticeable with increasing long chain branch density [13]. The notable shear thinning of our synthesized branched PC indicates that the modified PCs prepared by incorporating 3 mol% THPE as branching agent has chain branches long enough to produce molecular entanglements. Thus, the synthesized branched PC is expected to impart high melt strengths and high shear sensitivities which will provide better processabilities particularly in blow molding applications etc.

5.3 Spectroscopic Characterization of Synthesized Branched PC

FTIR spectra of commercial linear polycarbonate, commercial branched polycarbonate and the synthesized branched polycarbonate are shown in Figure 5.15. The CH_3 absorption bands at 2970 cm^{-1} and 2874 cm^{-1} corresponded to asymmetric and symmetric CH_3 stretching vibrations, and the bands at 1465, 1387 and 1365 cm^{-1} corresponded to asymmetric and symmetric CH_3 deformation vibrations; the carbonate absorption bands at 1773 cm^{-1} assigned to the free carbonyl stretching vibration, the bands at 1235 cm^{-1}, 1194 cm^{-1}, 1164 cm^{-1} assigned to C-O stretching vibration, the bands at 1081 cm^{-1}, 1015 cm^{-1}, 831 cm^{-1} assigned to C-H deformation vibration of ring hydrogen, the bands at 1602 cm^{-1} and 1506 cm^{-1} assigned to C-C stretching vibration, the bands at 1387 cm^{-1} and 1365 cm^{-1} assigned to $C(CH_3)_2$ asymmetric bending vibration substituted phenyl, and the weak band at 757 cm^{-1} assigned to ring deformation vibration. The obtained FTIR absorption bands of the commercial linear polycarbonate, commercial branched polycarbonate and the synthesized branched polycarbonate are relatively similar**.** These assignments are in good agreement with those of linear and branched PC reported by Delpech et al. [37]. The assignment of the main absorption of PC is also listed in Table 5.5.

5.4 Thermal Properties of Synthesized Branched PC

Thermal behaviors of all polycarbonate samples were examined by differential scanning calorimetry (DSC). In theory, the glass transition temperature ($T_{g)}$ of polymer increases with a decrease in free volume due to increasing molecular weight by the increasing number of connected mers in the system [38]. The T_g values of commercial branched PC, the synthesized branched PC and commercial linear PC were determined to be 153,143 and 141°C, respectively. The T_g values are also poltted in the corresponding Figure 5.16. The T_g value of the synthesized branched PC is lower than that of commercial branched PC because the synthesized branched PC has lower molecular weight than that of the commercial branched PC. The higher the molecular weight, the lower the free volume thus the higher the T_g.

5.5 Thermogravimetric Analysis of the Synthesized PC

Figure 5.17 shows TGA curves of the synthesized PC, commercial linear PC (Wonderlite PC175), and commercial branched PC (Makrolon WB 1239). Whereas Table 5.6 summarizes the 5% weight loss values of the synthesized PC, commercial branched PC and commercial linear PC. The TGA data reveal that polycarbonates exhibited relatively high thermal stability. The thermal degradation temperature of the commercial branched PC and the synthesized branched PC were determined to be 500°C and relatively higher than that of the commercial linear PC having the value of 468°C. However, the char yields of all three polycarbonates were observed to be the same. Our synthesized branched PC therefore shows thermal stability characteristics comparable to its commercial benchmark.

5.6 Thermomechanical Properties of the Synthesized PC

The themomechanical properties of the synthesized PC, commercial branched PC (Makrolon WB1239) and commercial linear PC (Wonderlite PC175) were investigated by dynamic mechanical analysis (DMA). Figure 5.18 illustrates a comparison of storage modulus for the synthesized PC, commercial branched PC and commercial linear PC at a frequency of 1 Hz. The storage modulus at 30°C were determined to be approximately 1,090, 1,026 and 884 MPa for the synthesized PC, commercial branched PC and commercial linear PC, respectively. Our synthesized branched PC thus possesses mechanical property similar to those commercial PC products suggestion its high molecular weight characteristic with sufficient entanglement effect.

The loss tangents for the synthesized PC, commercial branched PC and commercial linear PC are shown in Fig 5.19. The α-relaxation peaks or T_gs were determined to be 162,168 and 172°C for commercial linear PC, synthesized branched PC and commercial branched PC, respectively. It was also observed that the T_g of the synthesized branched PC was close to that of the commercial branched PC and commercial linear PC confirming the formation of high molecular weight PC based on our synthesis condition.

5.7 Melt Flow Index (MFI) of the Polycarbonate Samples

In this measurement, the PC samples were tested at 300°C by an applied load of 1.2 kg in order to compare the MFI values with those reported in the specification sheets of each polymer. The MFI results were determined to be 1.6, 2.3 and 60.8 g/10 min for the PC, the synthesized PC, commercial branched PC (Makrolon WB 1239) and commercial linear PC (Wonderlite PC 175) respectively. The values are in good agreement with the literature values of 2.5 and 62 g/10 min for of both commercial

PCs. It was found that the MFI value of the synthesized PC and commercial branched PC are much lower than that of the commercial linear PC. The complex rheological properties of the polymer can be expressed by Melt Flow Index (MFI). The values of MFI decreased with increasing the complex viscosity as suggested by Dutta [39]. Consequently, the synthesized PC and commercial branched PC exhibit higher viscosity than the commercial linear PC. The chain branching in the synthesized PC and commercial branched PC are helpful to promote molecular entanglement than the commercial linear PC. Those MFI values of the PC, the synthesized PC, commercial branched PC and commercial linear PC are also summarized in Table 5.7.

5.8 Yellowness Index of the Polycarbonate Samples

The color of all polycarbonate samples was reported quantitatively by measuring yellowness index as calculated by measuring changes in L*, a* and b* color values relative to clear air. It could be seen that the yellowness index value of our synthesized PC is relatively higher than that of the commercial branched PC (Makrolon WB 1239) and commercial linear PC (Wonderlite PC175). The yellowness index values of the synthesized PC, commercial branched PC and commercial linear PC were measured to be 1.23, 0.80 and 0.65, respectively. The high degree of branching of our PC was achieved without the usual formation of compounds having a high degree of yellowing reported by Mason et al. [40]. The yellowing index of the synthesized PC, commercial branched PC and commercial linear PC are also summarized in Table 5.8. The transparency of the synthesized PC, commercial branched PC and commercial linear PC are relatively similar. Their visual appearance is illustrated in Figure 5.20.

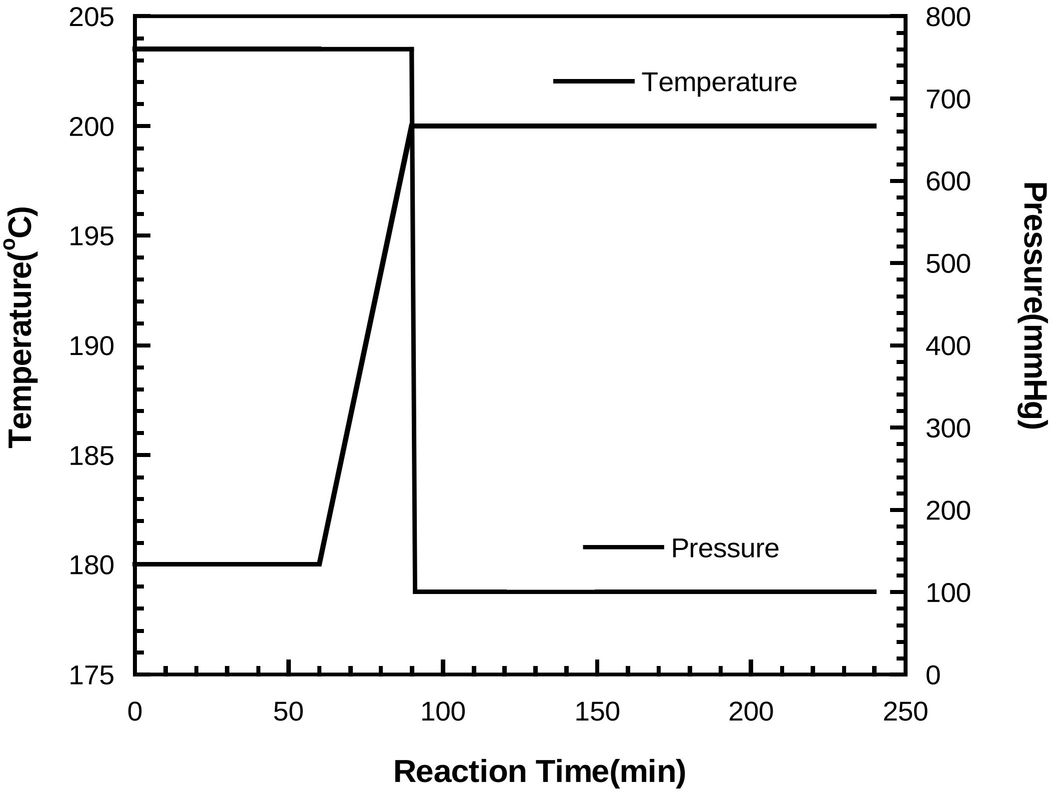


Figure 5.1 Synthesis condition of linear polycarbonate precursor preparation.

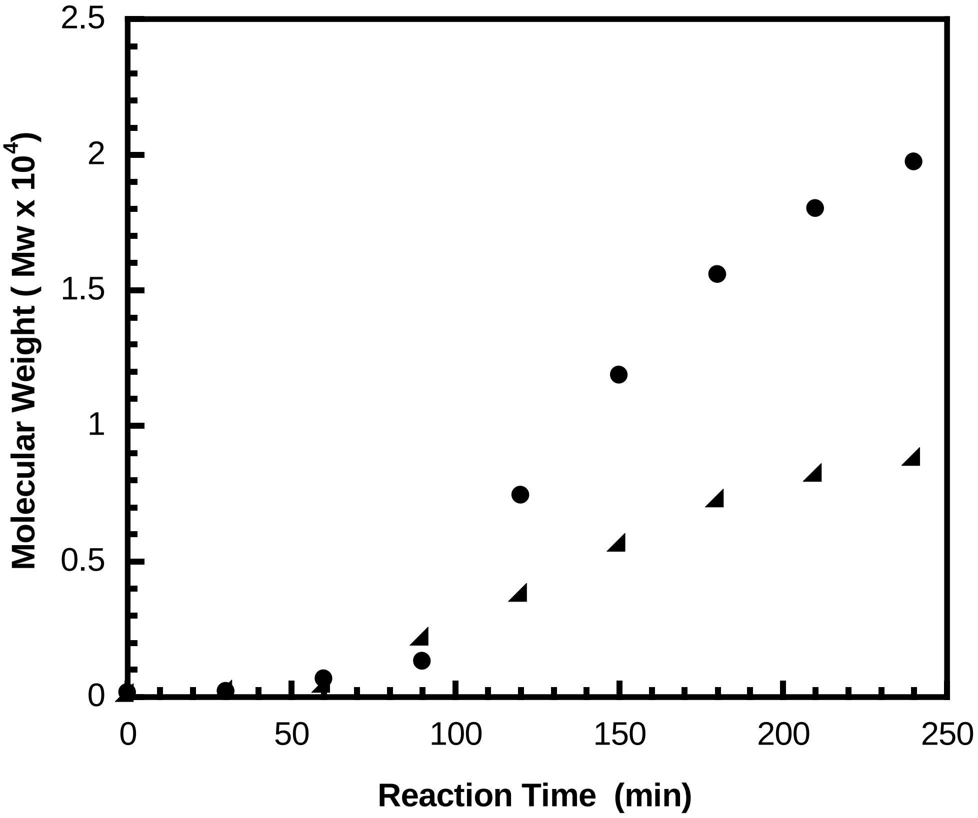


Figure 5.2 Molecular weight profiles of synthesized polycarbonate at initial mole ratios of DPC/BPA; (•) 1.05/1.00 and (◢) 1.26/1.00.

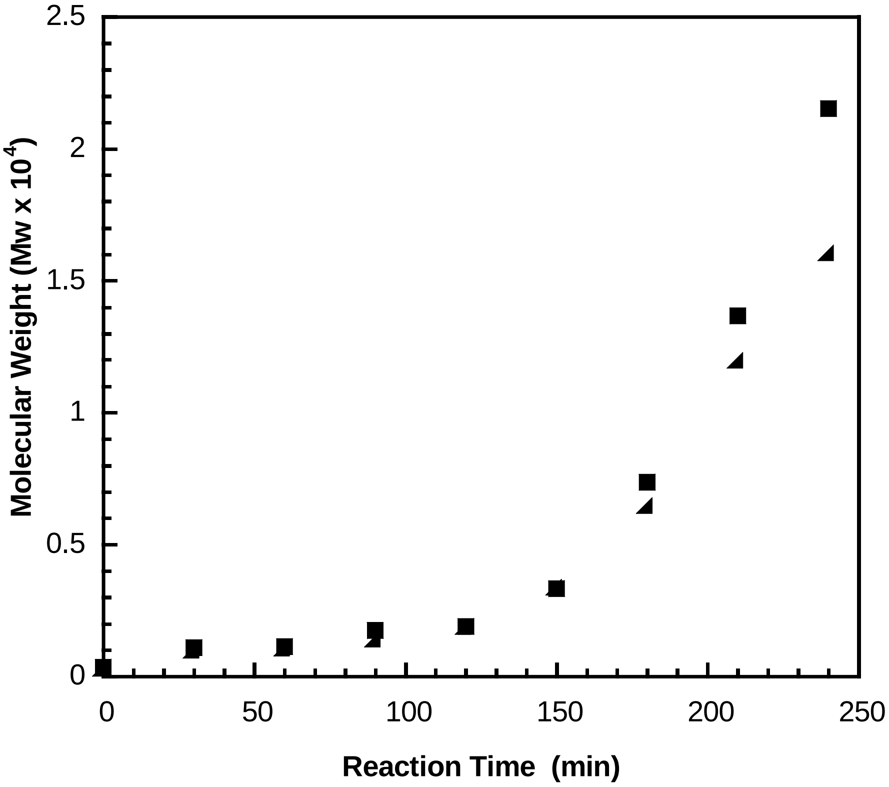


Figure 5.3 Molecular weight profiles of synthesized PC using Na_2CO_3 as a catalyst; (■) Run 1 and (◢) Run 2 (the case without gelation).

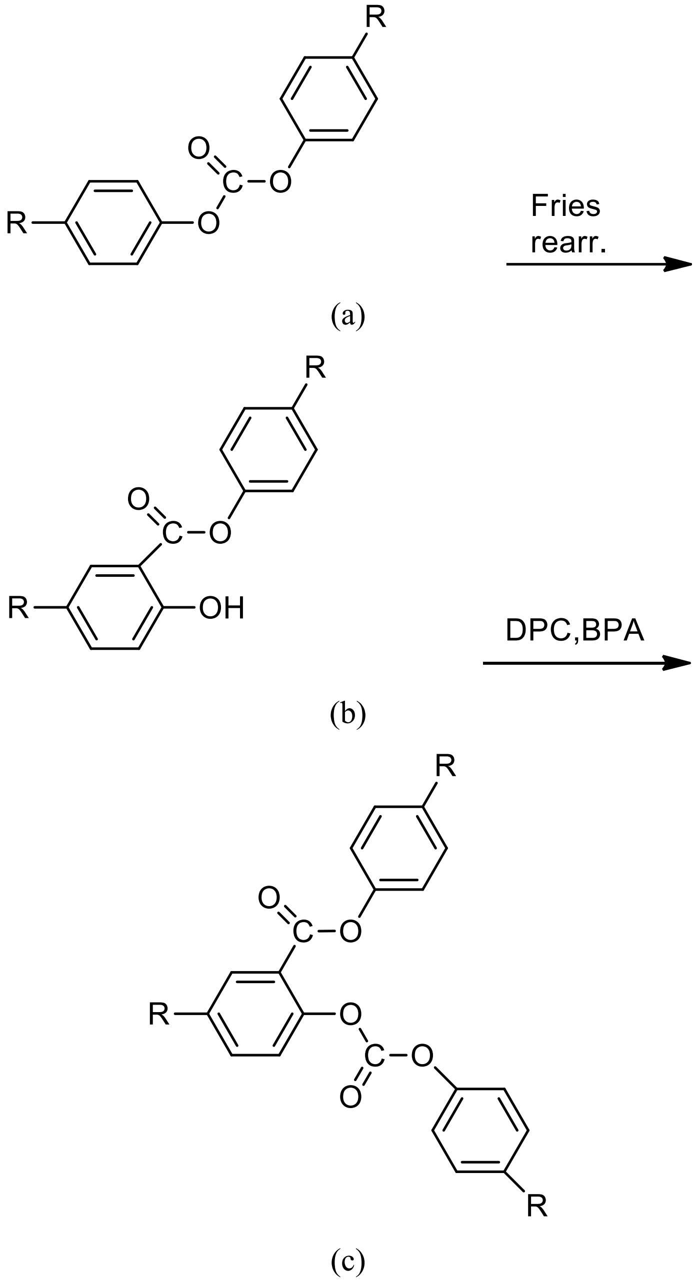


Figure 5.4 Structure of Fries rearrangement Products; (a) Linear aromatic polycarbonate (b) Primary Fries product and (c) Branched aromatic polycarbonate.

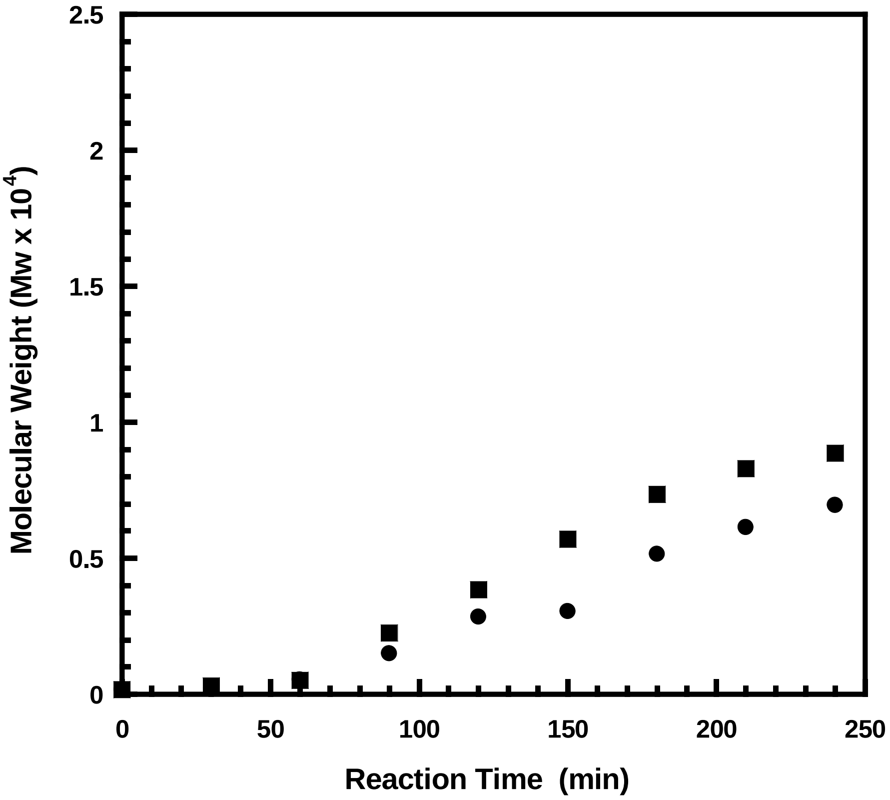


Figure 5.5 Molecular weight profiles of synthesized PC with initial mole ratio of DPC/BPA at 1.26/1.00 without a catalyst; (■) Run 1 and (•) Run 2.

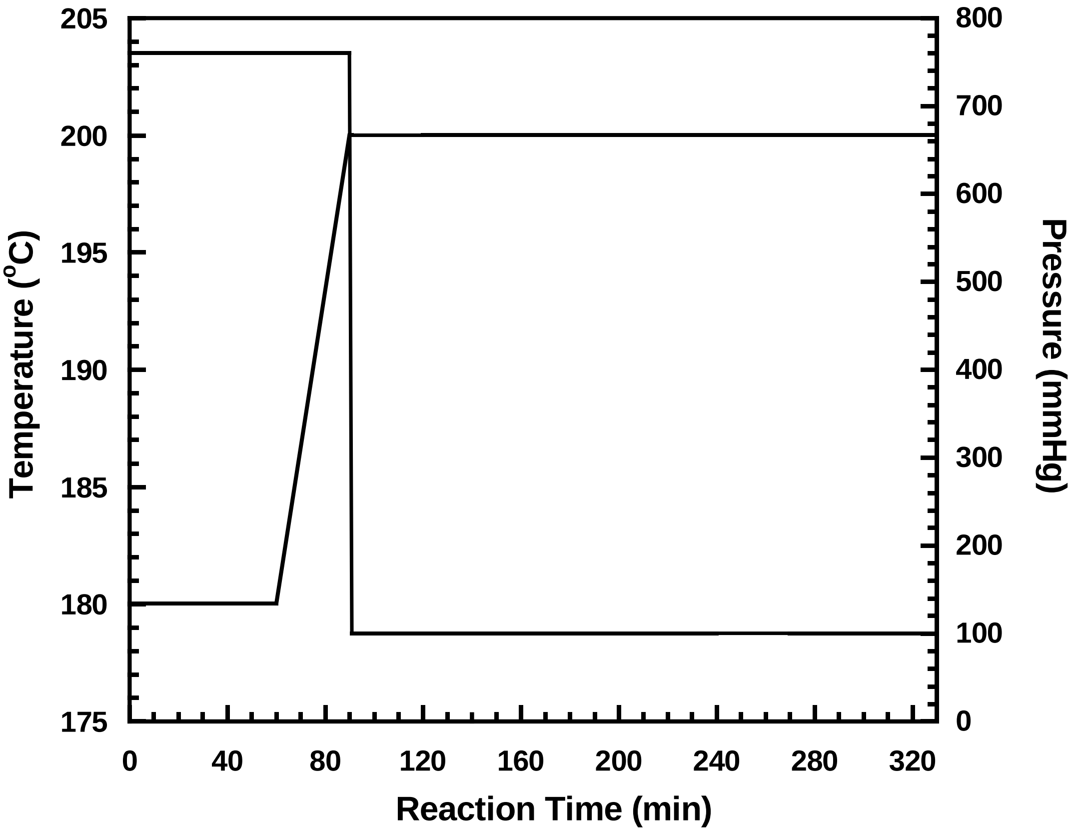


Figure 5.6 Synthesis condition of branched PC (the case no simultaneous mix)

Table 5.1 Chemical structure of branching agents used for branched PC synthesis in this report [31].

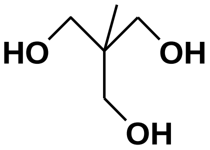
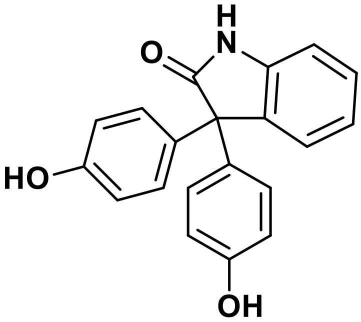
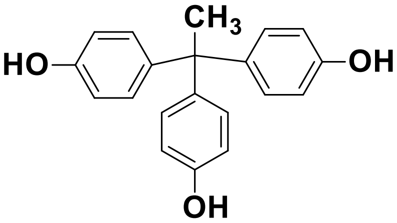
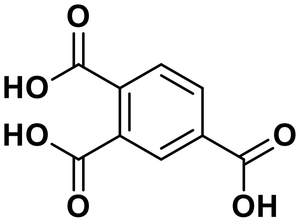
Types of branching agent	**Chemical structure**	**Molecular weight (g/mole)**
1,1,1-tris(hydroxymethyl)ethane (TME)		120.15
3,3-bis(p-hydroxyphenyl)oxindole		317.34
1,1,1-tris(4-hydroxyphenyl)ethane (THPE)		306.35
Tricarboxylic acid		210.14

Table5.2 Reaction time of each branching agents used for branched PC synthesis.

Types of branching agents	**Reaction time (min)**
1,1,1-tris(hydroxymethyl)ethane (TME)	180
3,3-bis(p-hydroxyphenyl)oxindole	120
1,1,1-tris(4-hydroxyphenyl)ethane (THPE)	240
Tricarboxylic acid	170

Table 5.3 Weight average molecular weight (M_w) and number average molecular weight (M_n) as well as polydispersity index (PDI) of the resulting branched PC.

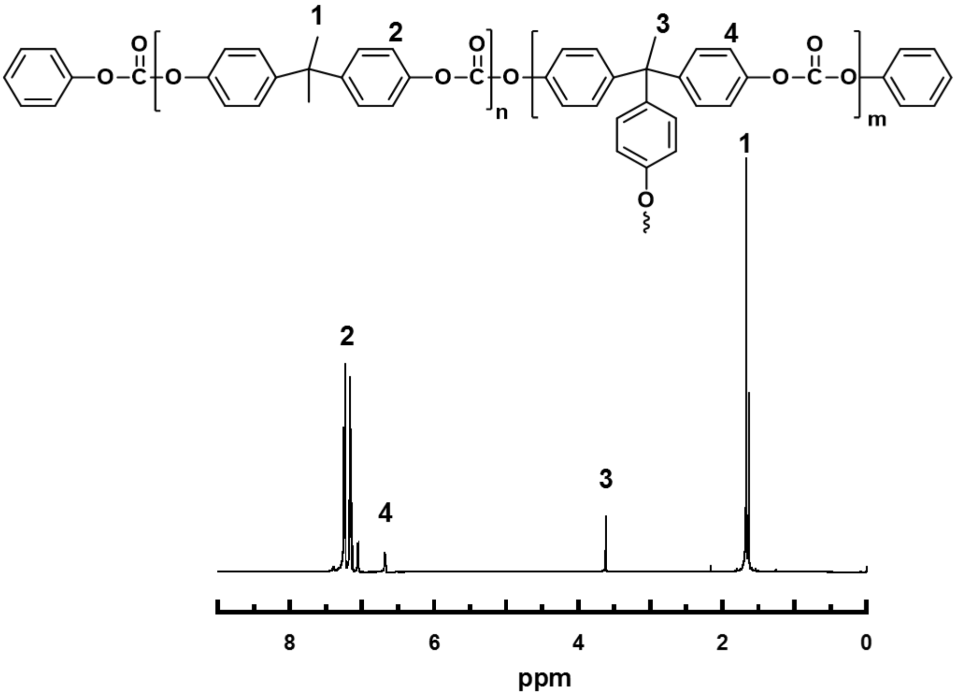
Sample	**Types of branching agents**	**M_n[a]**	**M_w[b]**	**PDI[c]**
PC-L	-	3,091	5,308	1.71
PC-BT	THPE	3,561-5,059	7,057-9,380	1.85-1.98
PC-BTM	TME	4,723-5,726	8,154-9,752	1.70-1.72
PC-BO	BPO	3,073-5,587	5,933-10,345	1.85-1.93
PC-BTi	TCA	No high Mw polymer was formed.		

[a] Number-average molecular weight.
[b] Weight-average molecular weight.
[c] Polydispersity index.
THPE=1,1,1-tris(4-hydroxyphenyl)ethane
TME=1,1,1-tris(hydroxymethyl)ethane
BPO=3,3-bis(p-hydroxyphenyl)oxindole
TCA=Tricarboxylic acid

Table 5.4 Molecular weights (M_w) and polydispersity (PDI) of the synthesized polycarbonate using THPE and 3,3-bis(p-hydroxyphenyl)oxindole as branching agents.

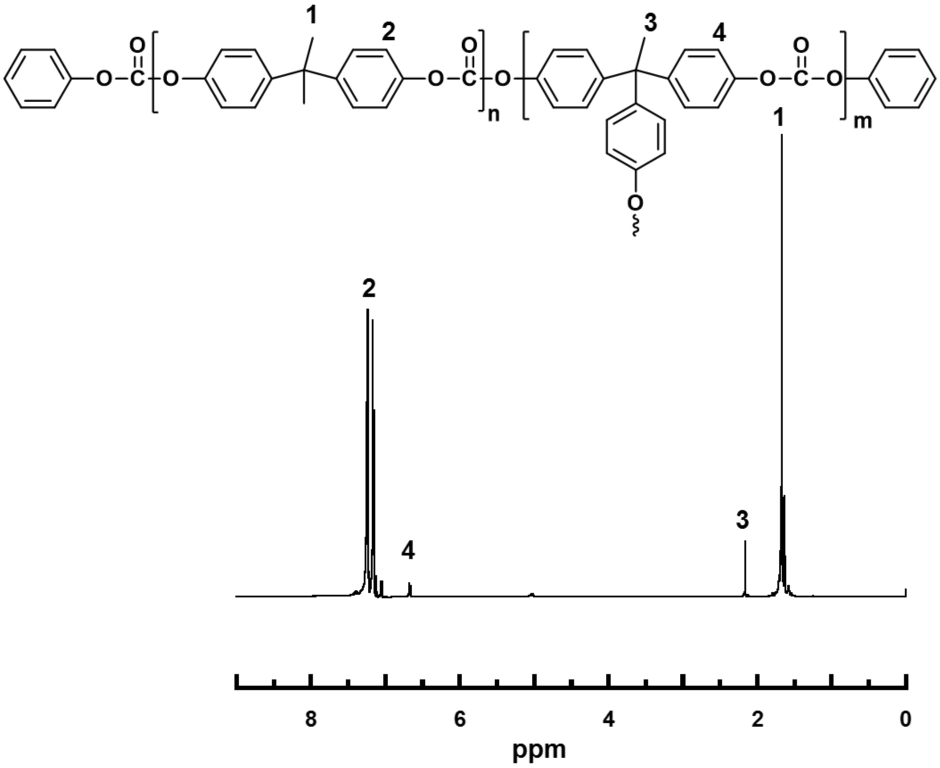
Sample	**Branching agent**	**Content (mol% of BPA)**	**M_n[a]**	**M_w[b]**	**PDI[c]**
PC-BT1	1,1,1-tris(4-hydroxyphenyl)ethane	0.35	3,561	7,057	1.98
PC-BT2	1,1,1-tris(4-hydroxyphenyl)ethane	2.00	5,280	11,166	2.11
PC-BT3	1,1,1-tris(4-hydroxyphenyl)ethane	3.00	6,633	15,032	2.27
PC-BO1	3,3-Bis(p-hydroxyphenyl)oxindole	0.35	5,587	10,345	1.85
PC-BO2	3,3-Bis(p-hydroxyphenyl)oxindole	2.00	4,864	12,870	2.26
PC-BO3	3,3-Bis(p-hydroxyphenyl)oxindole	3.00	5,261	10,429	1.98

[a] Number-average molecular weight in g/mole
[b] Weight-average molecular weight in g/mole
[c] Polydispersity index.



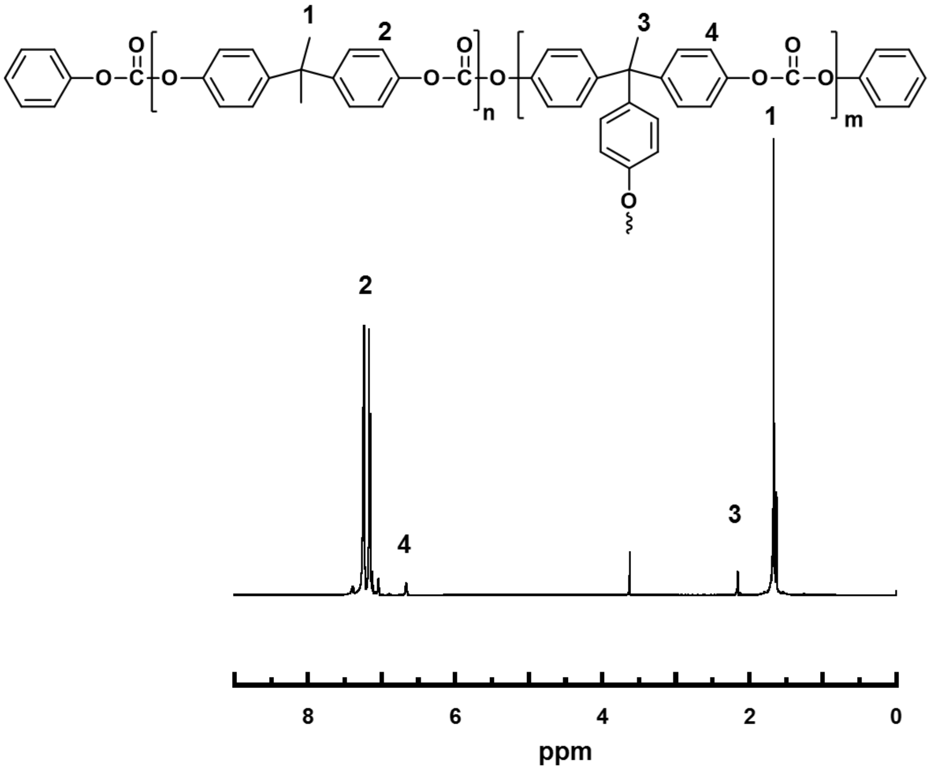
(a)

Figure 5.7 ^{1}H NMR spectra of the synthesized PC using THPE as a branching agent; (a) PC-BT1.



(b)

Figure 5.7 ^{1}H NMR spectra of the synthesized PC using THPE as a branching agent; (b) PC-BT2.



(c)

Figure 5.7 ^{1}H NMR spectra of the synthesized PC using THPE as a branching agent; (c) PC-BT3.

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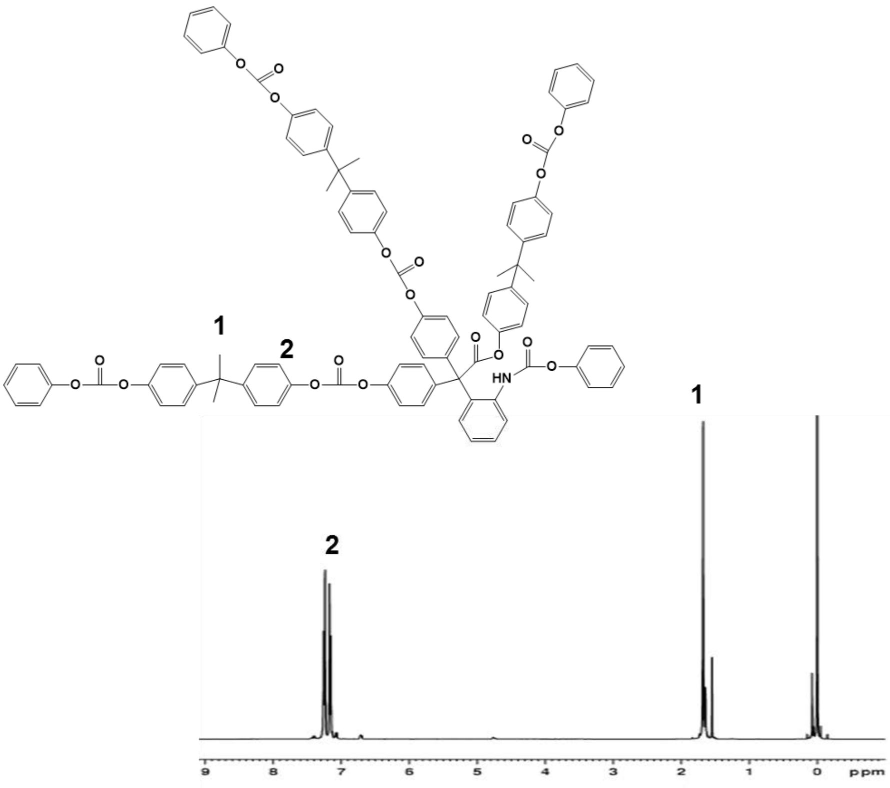
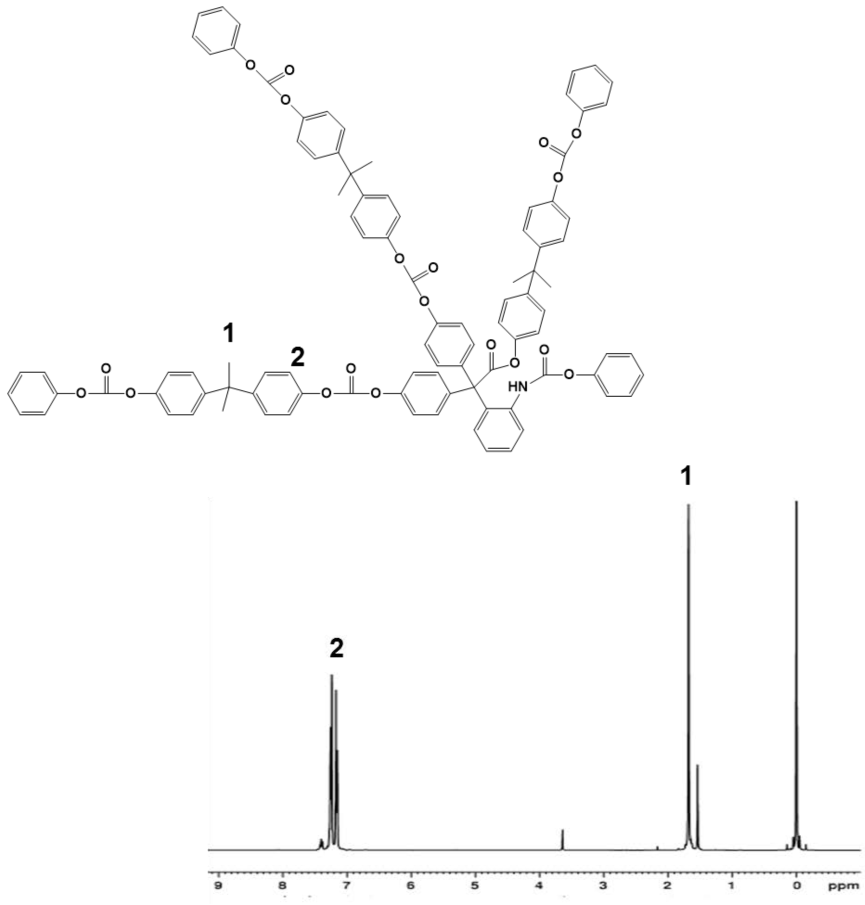


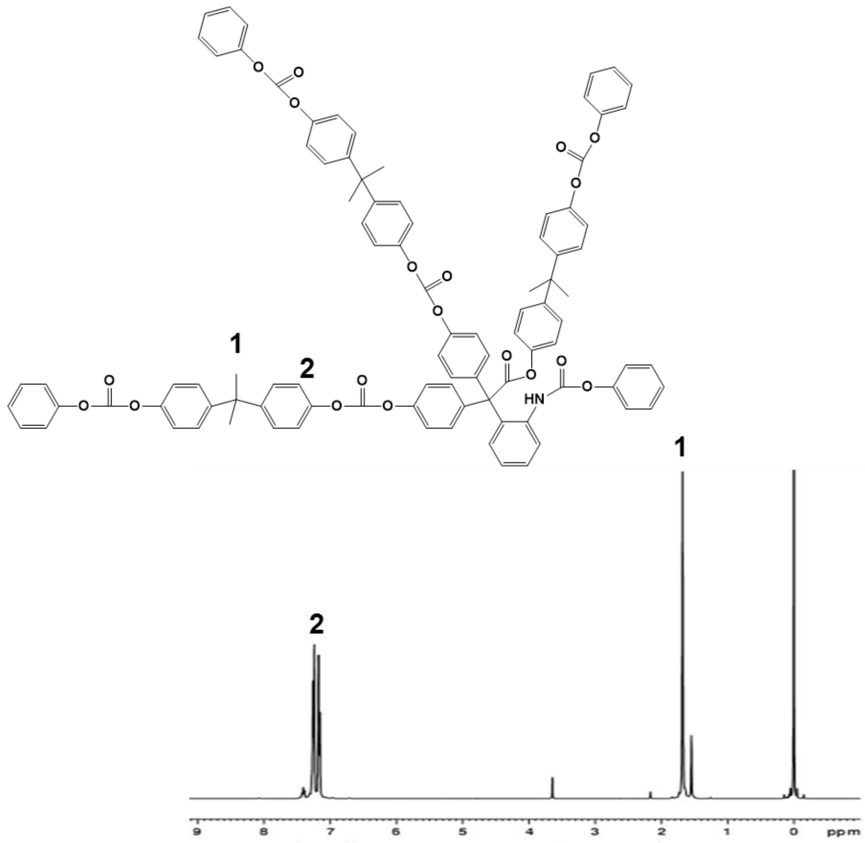
(a)

Figure 5.8 ^{1}H NMR spectrum of the synthesized PC using 3,3-bis(p-hydroxyphenyl)oxindole as a branching agent; (a) PC-BO1.



(b)

Figure 5.8 ^{1}H NMR spectrum of the synthesized PC using 3,3-bis(p-hydroxyphenyl)oxindole as a branching agent; (b) PC-BO2.



(c)

Figure 5.8 ^{1}H NMR spectrum of the synthesized PC using 3,3-bis(p-hydroxyphenyl)oxindole as a branching agent; (c) PC-BO3.

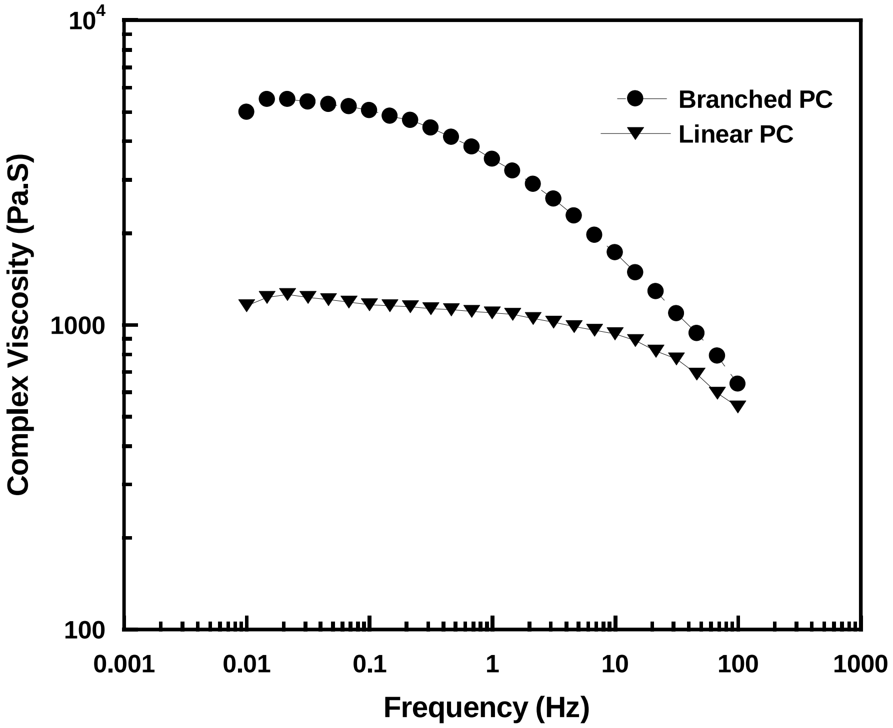


Figure 5.9 Complex viscosity versus frequency for commercial PC samples measured at 260°C; (•) Branched PC (Mw 55,804) and (▼) Linear PC (Mw 49,171).

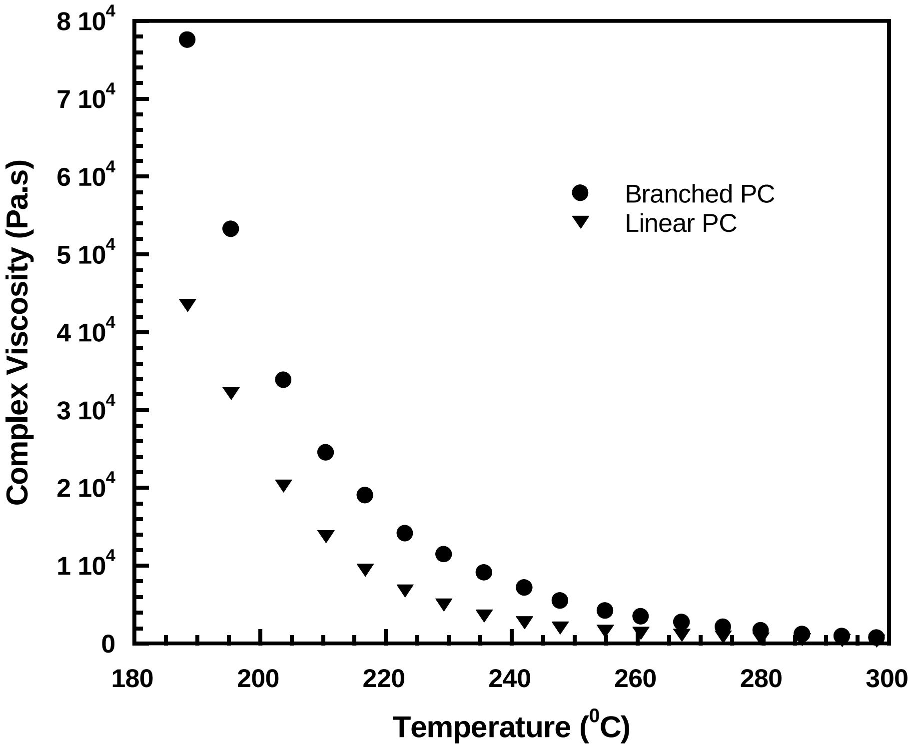


Figure 5.10 Complex viscosity as a function of temperature for commercial PC samples: (•) Branched PC (M_w 55,804) and (▼) Linear PC (M_w 49,171).

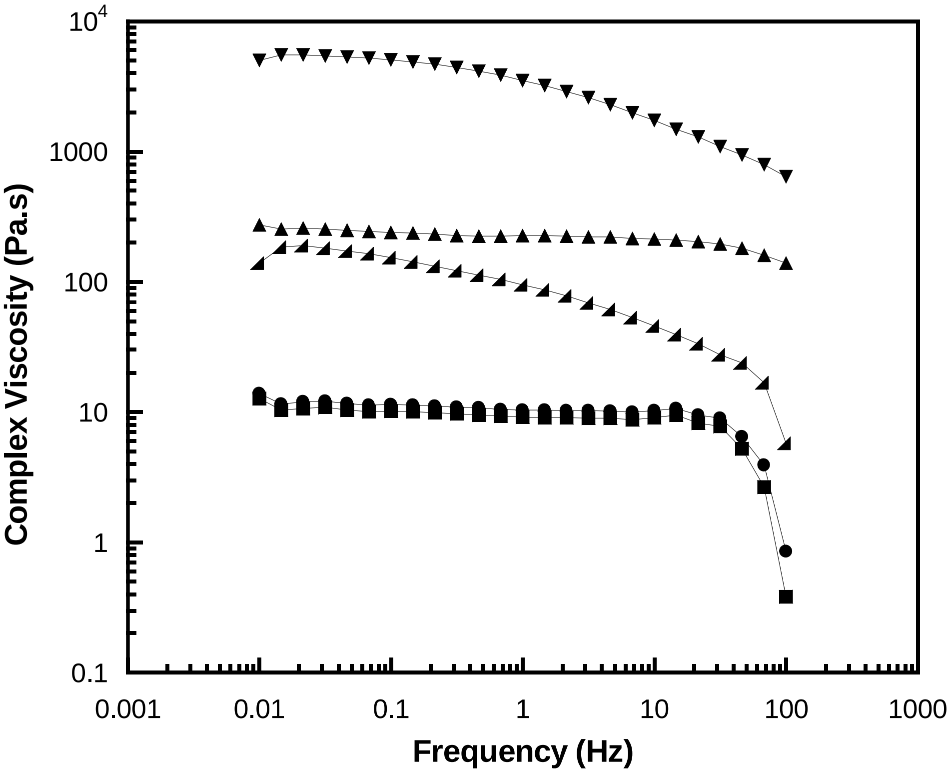


Figure 5.11 Complex viscosity versus frequency for branched PC samples at 260°C; (■) PC-BT1, (♦) PC-BT2, (◢) PC-BT3 (▲) PC-L, and (▼) PC-B.

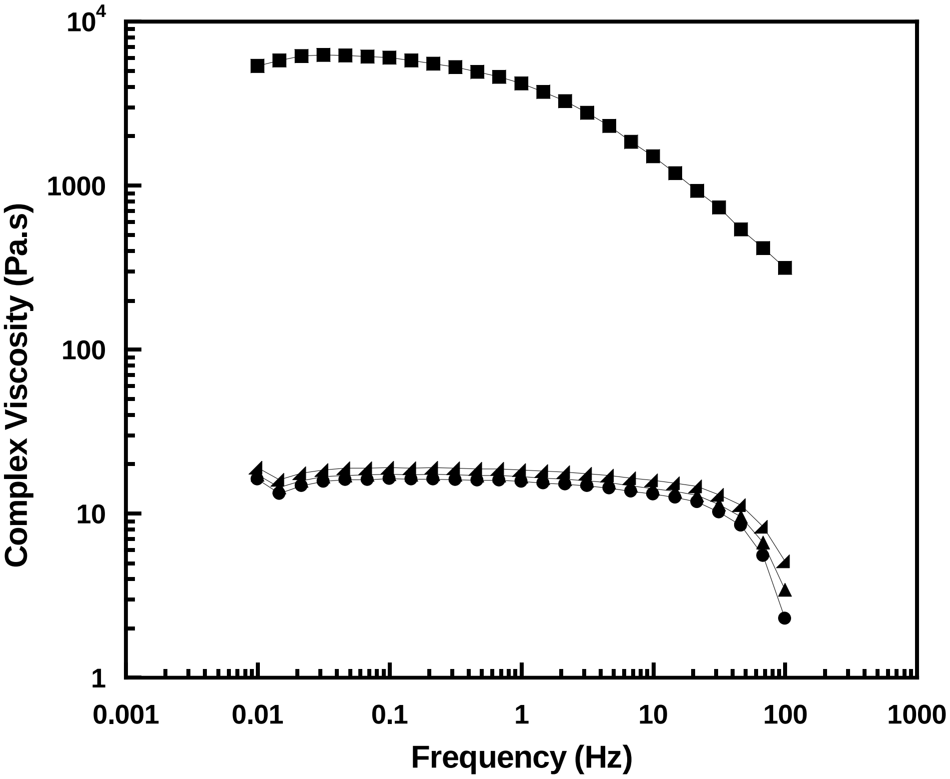


Figure 5.12 Complex viscosity versus frequency for branched PC samples at 180°C; (●) PC-BO1, (◢) PC_BO2, (▲) PC-BO3, (■) PC-L.

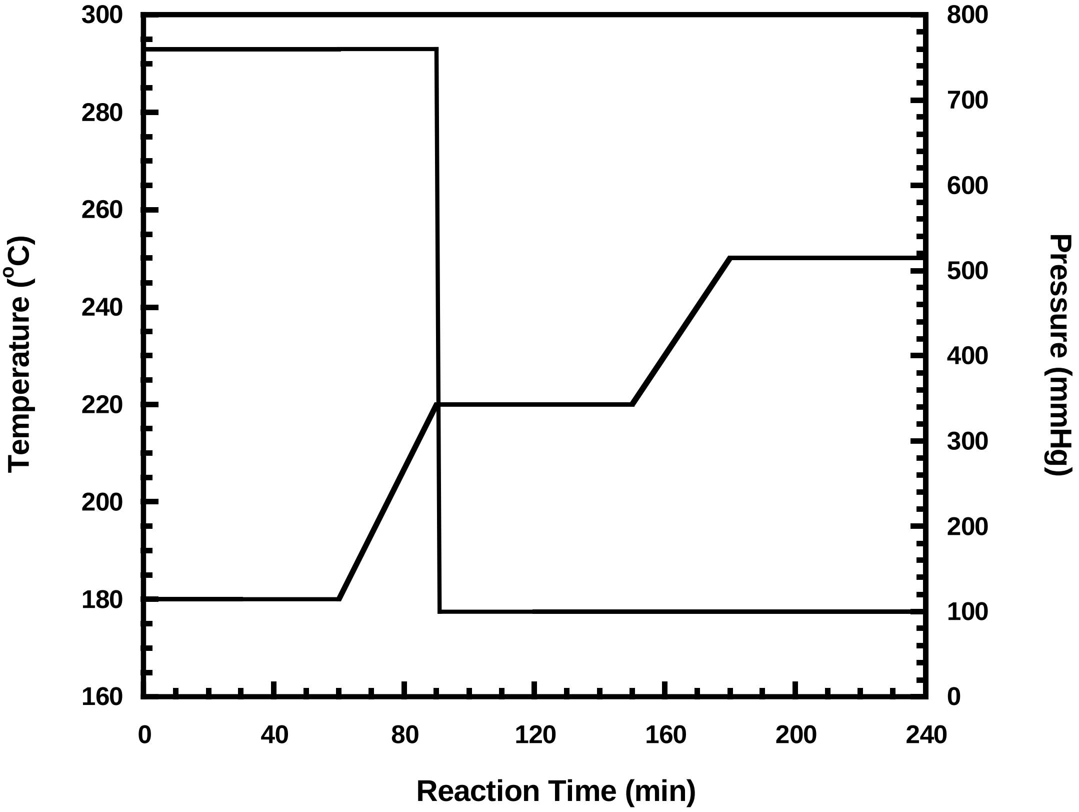


Figure 5.13. Synthesis condition for high molecular weight branched PC.

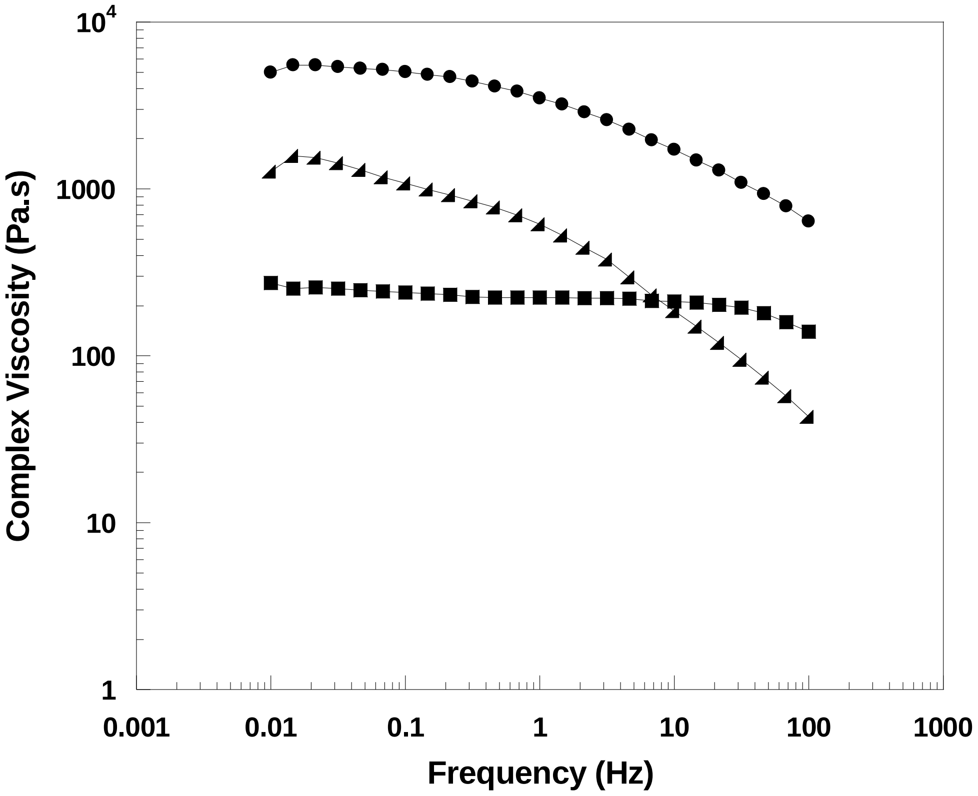


Figure 5.14 Complex viscosity versus frequency for branched PC samples at 260°C; (◢) the synthesized branched PC, (●) PC-B and (■) PC-L.

Table 5.5 Assignments of FTIR spectra of commercial linear polycarbonate, commercial branched polycarbonate and the synthesized branched polycarbonate.

Frequency (cm^{-1})	Bonds	Vibrational mode
2970	C-H (methyl groups)	Symmetrical stretching
1773	O-(C=O)-O (carbonyl)	Stretching
1602	C=C (aromatic ring)	Stretching
1506	C-H (aromatic ring)	In-plane bending
1387	C-H (methyl groups)	Symmetrical bending
1232	C-O-(C=O)-O-C	Asymmetrical stretching
757	C-H (aromatic ring)	Out-of-plane bending
667	C=C (aromatic ring)	Out-of-plane bending

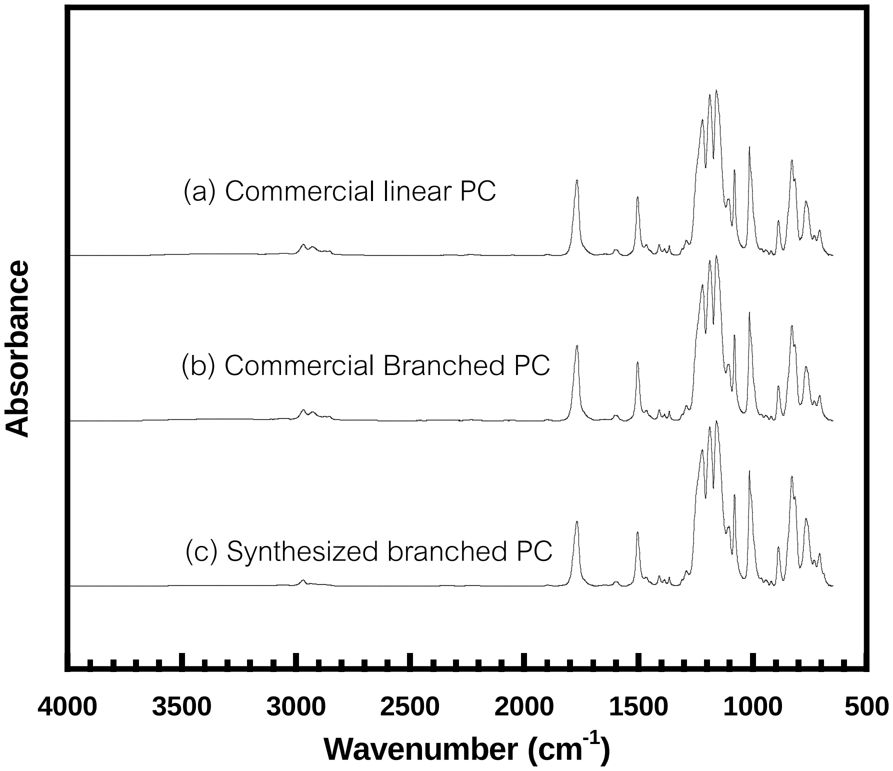


Figure 5.15 FTIR spectra of PC samples; (a) commercial linear PC, (b) commercial branched PC and (c) synthesized branched PC.

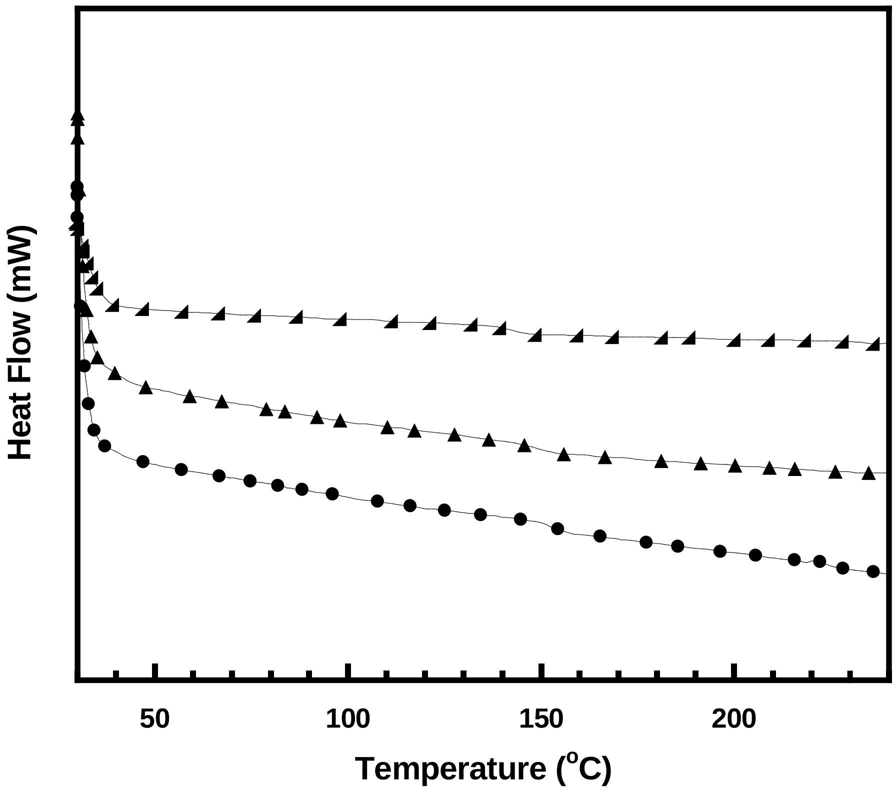


Figure 5.16 DSC thermograms of PC products; (■) commercial linear PC (●) synthesized branched PC and (▲) commercial branched PC.

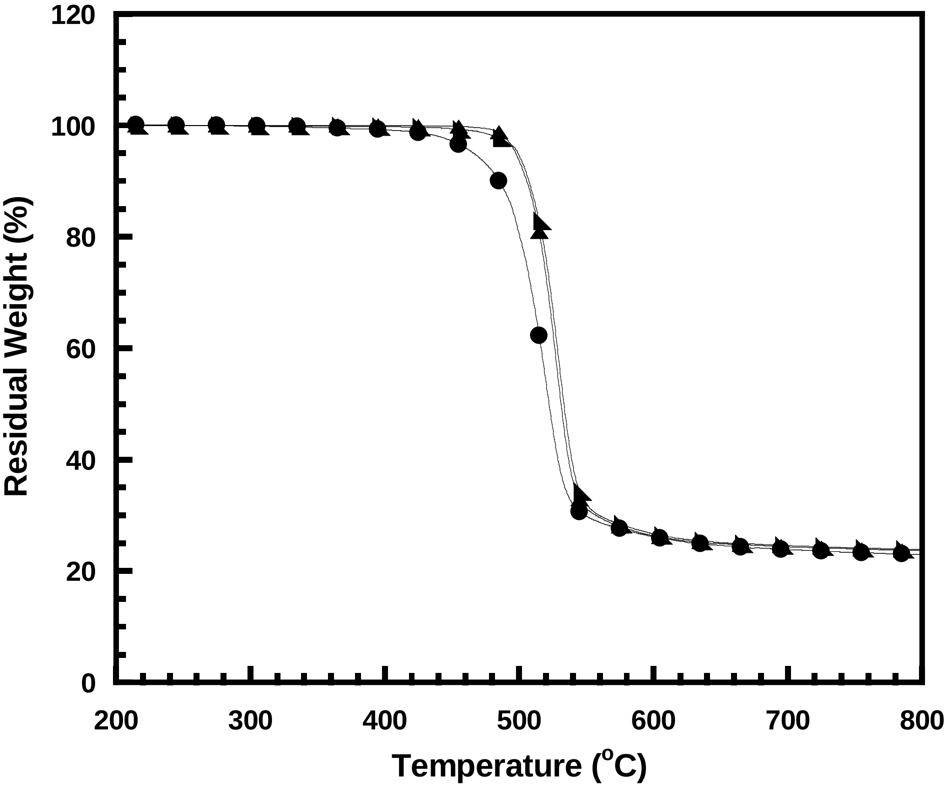


Figure 5.17 Thermogravimetric analysis of the PCsamples; (◢) Synthesized PC, (•) PC-L and (▲) PC-B.

Table 5.6 Thermal degradation temperature of commercial and the synthesized PCs.

Sample No.	**Mn**	**Mw**	**T_d (°C)**	**Char yield (%)**
Commercial linear PC (PC 175)	15,332	30,115	468	23.0
Commercial branched PC (WB 1239)	25,400	55,804	500	23.7
Synthesized PC	6,985	26,294	500	23.9

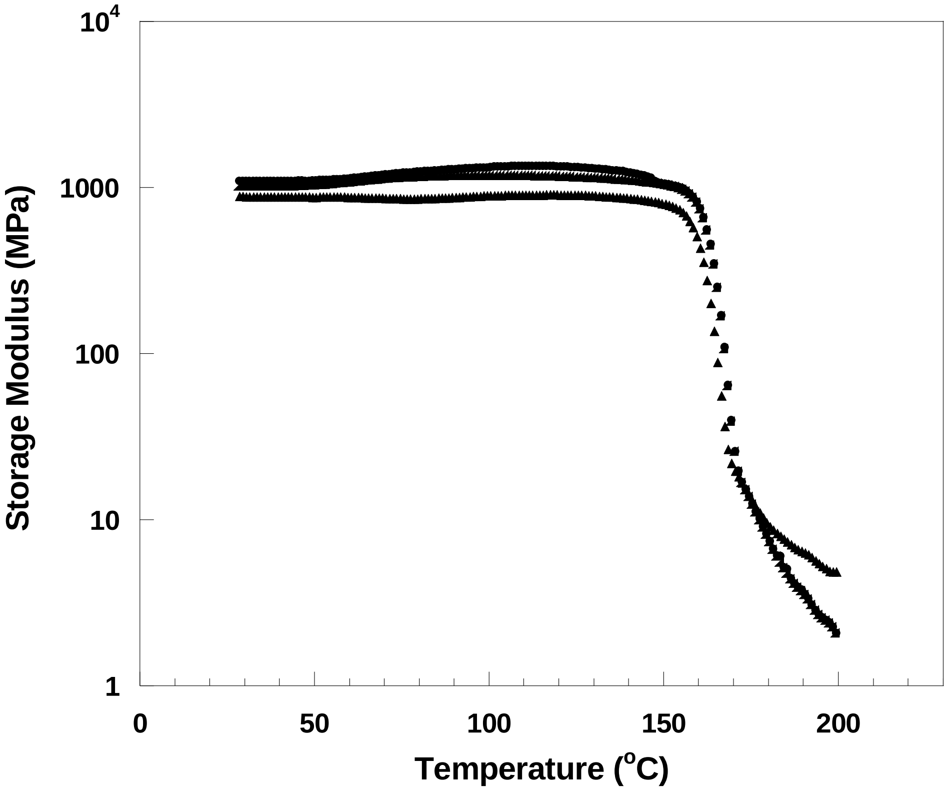


Figure 5.18 Storage modulus as a function of the temperature of PC samples; (•) Synthesized PC, (◢) PC-B and (▲) PC-L.

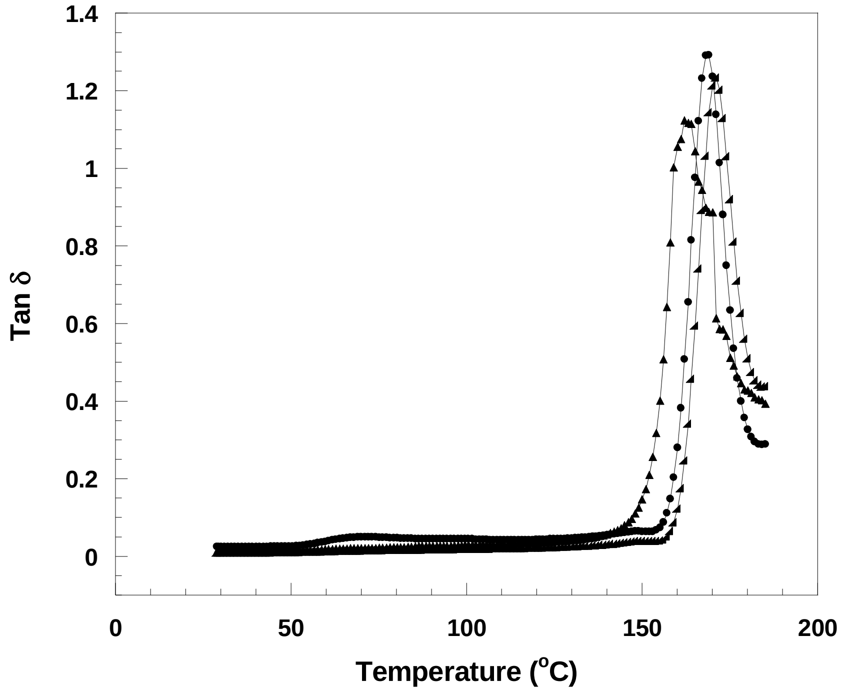


Figure 5.19 Loss tangent as a function of temperature of PC samples; (●) Synthesized PC, (◢) PC-B and (▲) PC-L.

Table 5.7 Melt flow index of the synthesized PC, commercial branched PC and commercial linear PC.

Sample	**Melt flow index (g/10min)**
Synthesized PC	1.6
Commercial branched PC (WB 1239)	2.3
Commercial linear PC (PC 175)	60.8

Table 5.8 Yellowness index of the PC, the synthesized PC, commercial branched PC and commercial linear PC.

Sample	Yellowness Index
Synthesized PC	1.23
Commercial branched PC (WB 1239)	0.80
Commercial linear PC (PC 175)	0.65

(a)

(b)

(c)

Figure 5.20 Transparency of PCs; (a) synthesized PC (b) commercial branched PC and (c) commercial linear PC.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In this work, branched polycarbonate was successfully synthesized by melt transesterification of bisphenol-A with diphenyl carbonate. The initial mole ratio of DPC/BPA at 1.26:1.00 was found to be appropriate for the preparation of branched PC in a more controlled manner. The uncatalyzed condensation reaction at temperature up to 250°C and pressure of 100 mmHg is suitable for the branched PC synthesis providing a relatively high molecular weight value of up to 26,300 g/mole. It was also found that a branching agent could be added simultaneously with DPC and BPA in the preparation of the branched PC. Additionally, THPE, TME and 3, 3-bis (p-hydroxyphenyl)oxindole were proved to be potential candidates as branching agents for branched PC synthesis under melt transesterification process and THPE was found to be the most appropriate among those branching agents based on the above synthesis condition as confirmed by NMR spectroscopy.

Various properties of our synthesized branched PC (Mw=26,294 g/mole) were characterized and the properties were compared with commercial linear PC (Wonderlite PC175, Mw=30,115 g/mole) and commercial branched PC (Makrolon WB1239, Mw=55,804 g/mole). From, rheological test, branched PC with 3 mol% of THPE exhibited high shear sensitivity similarly to that of commercialized branched PC (Makrolon WB1239) with relatively low melt flow index suggesting a presence of long chain branching in our branched PC. Thermomechanical, thermal and physical properties of our branched PC i.e. T_g, T_d, char content, storage modulus, melt flow index, and yellowness index were observed to be comparable to the benchmarking commercial branched PC.

6.2 Recommendations

The synthesis condition used in this research is suitable specifically for branched PC synthesis using THPE as a branching agent. However, it is suggested that the more appropriate synthesis conditions should be further evaluated to suit each type of branching agent i.e. TME, 3, 3-bis (p-hydroxyphenyl)oxindole and tricarboxylic acid as the types of functional groups present in these branching agents are different from THPE. Consequently, variation in the synthesis condition for each branching agent is expected.

Gelation was frequently observed in this transesterifcation process thus the polymerization reaction should be closely monitored particularly the reaction at relatively high temperature or at high amount of branching agents.

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APPENDIX

APPENDIX A

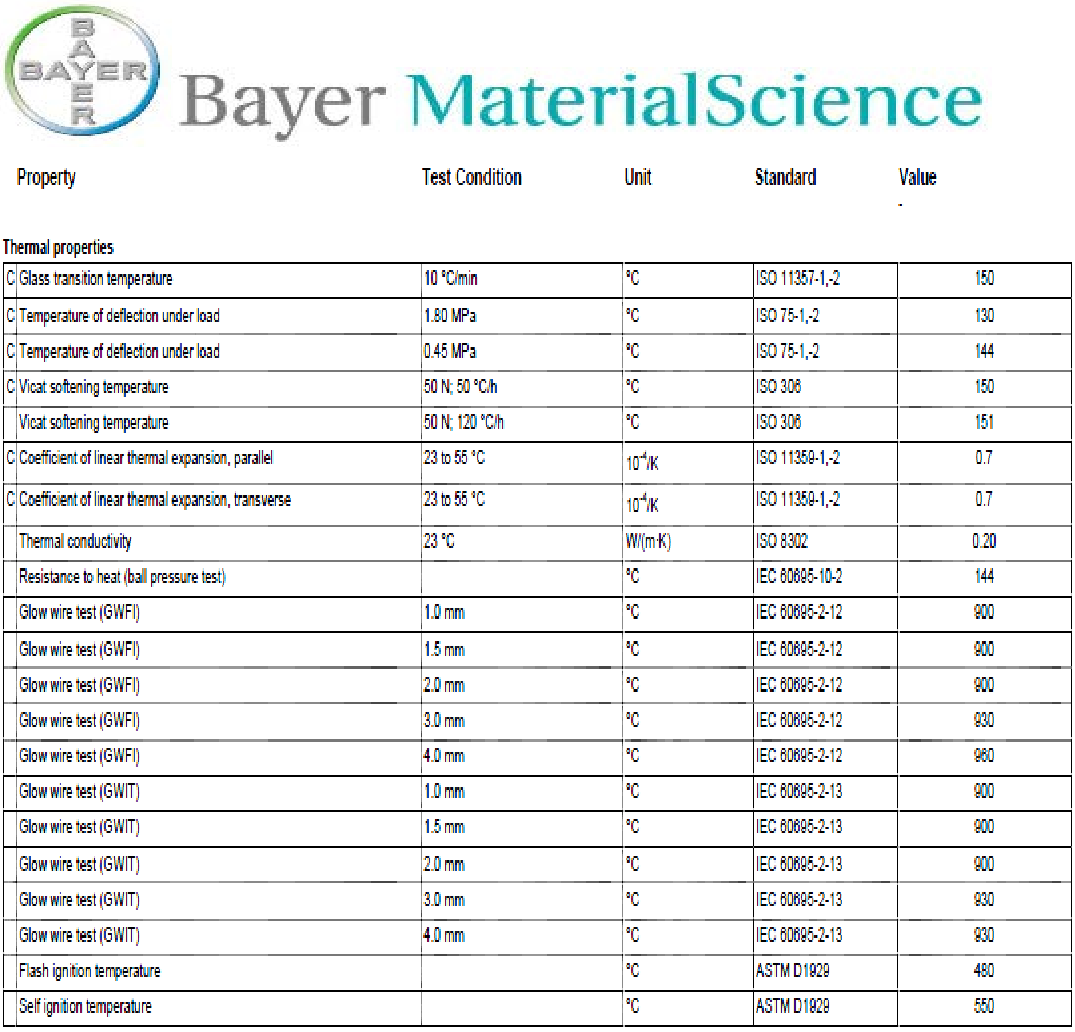
Table A. GPC analysis of various commercial polycarbonates.

Company	**Trade Name**	**Mw**	**Mn**	**PDI**
Bayer.Co.th	MAKROLON®	25,400	55,804	2.19
Chi Mei Corp.	WONDERLITE®	28,065	49,171	1.75
Chi Mei Corp.	WONDERLITE®	15,332	30,115	1.96

APPENDIX B

Table B. Properties of Makrolon ®WB 1239 and Wonderlite ®PC-110,175.

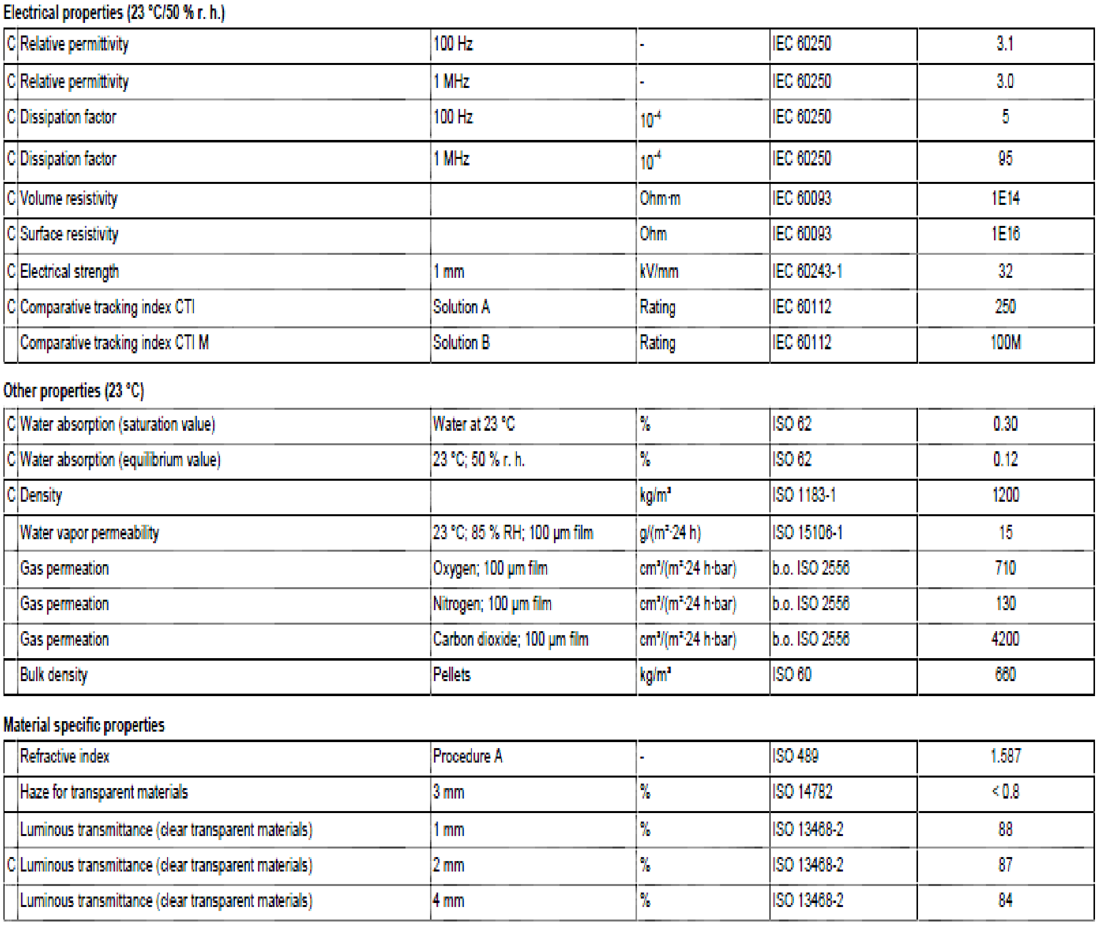
Typical Properties of MAKROLON® (WB1239)



Bayer MaterialScience

Thermal properties

	Property	Test Condition	Unit	Standard	Value
C	Glass transition temperature	10 °C/min	°C	ISO 11357-1,-2	150
C	Temperature of deflection under load	1.80 MPa	°C	ISO 75-1,-2	130
C	Temperature of deflection under load	0.45 MPa	°C	ISO 75-1,-2	144
C	Vicat softening temperature	50 N; 50 °C/h	°C	ISO 306	150
	Vicat softening temperature	50 N; 120 °C/h	°C	ISO 306	151
C	Coefficient of linear thermal expansion, parallel	23 to 55 °C	10^{-4}/K	ISO 11359-1,-2	0.7
C	Coefficient of linear thermal expansion, transverse	23 to 55 °C	10^{-4}/K	ISO 11359-1,-2	0.7
	Thermal conductivity	23 °C	W/(m·K)	ISO 8302	0.20
	Resistance to heat (ball pressure test)		°C	IEC 60695-10-2	144
	Glow wire test (GWFI)	1.0 mm	°C	IEC 60695-2-12	900
	Glow wire test (GWFI)	1.5 mm	°C	IEC 60695-2-12	900
	Glow wire test (GWFI)	2.0 mm	°C	IEC 60695-2-12	900
	Glow wire test (GWFI)	3.0 mm	°C	IEC 60695-2-12	930
	Glow wire test (GWFI)	4.0 mm	°C	IEC 60695-2-12	960
	Glow wire test (GWIT)	1.0 mm	°C	IEC 60695-2-13	900
	Glow wire test (GWIT)	1.5 mm	°C	IEC 60695-2-13	900
	Glow wire test (GWIT)	2.0 mm	°C	IEC 60695-2-13	900
	Glow wire test (GWIT)	3.0 mm	°C	IEC 60695-2-13	930
	Glow wire test (GWIT)	4.0 mm	°C	IEC 60695-2-13	930
	Flash ignition temperature		°C	ASTM D1929	480
	Self ignition temperature		°C	ASTM D1929	550



Electrical properties (23 °C/50 % r. h.)

C	Relative permittivity	100 Hz	-	IEC 60250	3.1
C	Relative permittivity	1 MHz	-	IEC 60250	3.0
C	Dissipation factor	100 Hz	10^{-4}	IEC 60250	5
C	Dissipation factor	1 MHz	10^{-4}	IEC 60250	95
C	Volume resistivity		Ohm·m	IEC 60093	1E14
C	Surface resistivity		Ohm	IEC 60093	1E16
C	Electrical strength	1 mm	kV/mm	IEC 60243-1	32
C	Comparative tracking index CTI	Solution A	Rating	IEC 60112	250
	Comparative tracking index CTI M	Solution B	Rating	IEC 60112	100M

Other properties (23 °C)

C	Water absorption (saturation value)	Water at 23 °C	%	ISO 62	0.30
C	Water absorption (equilibrium value)	23 °C; 50 % r. h.	%	ISO 62	0.12
C	Density		kg/m³	ISO 1183-1	1200
	Water vapor permeability	23 °C; 85 % RH; 100 µm film	g/(m²·24 h)	ISO 15106-1	15
	Gas permeation	Oxygen; 100 µm film	cm³/(m²·24 h·bar)	b.o. ISO 2556	710
	Gas permeation	Nitrogen; 100 µm film	cm³/(m²·24 h·bar)	b.o. ISO 2556	130
	Gas permeation	Carbon dioxide; 100 µm film	cm³/(m²·24 h·bar)	b.o. ISO 2556	4200
	Bulk density	Pellets	kg/m³	ISO 60	660

Material specific properties

	Refractive index	Procedure A	-	ISO 489	1.587
	Haze for transparent materials	3 mm	%	ISO 14782	< 0.8
	Luminous transmittance (clear transparent materials)	1 mm	%	ISO 13468-2	88
C	Luminous transmittance (clear transparent materials)	2 mm	%	ISO 13468-2	87
	Luminous transmittance (clear transparent materials)	4 mm	%	ISO 13468-2	84

CHIMEI
奇美實業股份有限公司
CHI MEI CORPORATION

Typical Properties of WONDERLITE® (PC)

Typical Properties		Test Method	Unit	Condition	WONDERLITE® (PC)		
					Optical	Extrusion	Injection
					PC-175	PC-108 PC-108U	PC-110 PC-115 PC-122
Melt Flow Index		ASTM D1238	g/10min	300°C, 1.2 kg	62	6.5	10 15 22
Specific Gravity		ASTM D792	-	23/23°C	1.20	1.20	1.20
Water Absorption		ASTM D570	%	24hr at 23°C	0.2	0.2	0.2
Light Transmission		ASTM D1003	%	3 mm thick	89	89	89
Haze		ASTM D1003	%	3.2 mm thick	<0.8	<0.8	<0.8
Refractive Index		ASTM D542	-	-	1.585	1.585	1.585
Tensile Strength at Yield		ASTM D638	Kg/cm^2	23°C	640	630	630
Elongation	Yield	ASTM D638	%	23°C	6	6	6
	Break				70	110	110 110 90
Flexural Strength		ASTM D790	Kg/cm^2	23°C	920	920	920
Flexural Modulus		ASTM D790	Kg/cm^2	23°C	24,000	24,000	24,000
Izod Impact Strength (Notched)		ASTM D256	Kg cm/cm	1/4″	-	15	15
				1/8″	-	90	87 87 80
Rockwell Hardness		ASTM D785	M Scale	-	M-77	M-77	M-77
Compressive Strength		ASTM D695	Kg/cm^2	-	-	780	780
Heat Distortion Temperature (unannealed)		ASTM D648	°C	4.6 Kg/cm^2, 120°C /hr	-	136	136
				18.6 Kg/cm^2, 120°C /hr	-	125	125
Vicat Softening Temperature		ASTM D1525	°C	1 Kg, 50°C /hr	-	150	150
Coefficient of Linear Expansion		ASTM D696	×10^{-5} cm/cm/°C	40~100°C	6~8	6~8	6~8

Typical Properties	Test Method	Unit	Condition	**WONDERLITE® (PC)**		
				Optical	Extrusion	Injection
				PC-175	PC-108 PC-108U	PC-110 PC-115 PC-122
Thermal Conductivity	ASTM C177	W/m°C	-	0.2	0.2	0.2
Dielectric Constant	ASTM D150	-	60 Hz	-	2.95	2.95
			10^6 Hz	-	2.9	2.9
Dissipation Factor ($\tan\delta$)	ASTM D150	-	60 Hz	-	0.0004	0.0004
			10^6 Hz	-	0.009	0.009
Dielectric Strength	ASTM D149	kV/mm	1.6mm	-	30	30
Arc Resistance	ASTM D495	sec	-	-	110	110
Characteristics/Principal Applications				Optical Disc	Sheet Extrusion	General Purpose

VITA

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