Synthesis and Characterization of Non-isocyanate Polyurethane from Natural Rubber and Poly(lactic acid)

Ruedee Jaratrotkamjorn

A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Polymer Science and Technology

Prince of Songkla University

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Author	Miss Ruedee Jaratrotkamjorn
Major Program	Polymer Science and Technology

Major Advisor

……
(Assoc.Prof. Dr. Varaporn Tanrattanakul)

Co-advisor

……
(Dr. Chuanpit Khaokong)

Examining Committee:

.....……...……Chairperson
(Asst. Prof. Dr. Watchanida Chinpa)

…..……..……..…...Committee
(Assoc.Prof. Dr. Varaporn Tanrattanakul)

..…....……..……...Committee
(Dr. Chuanpit Khaokong)

…...……..……...Committee
(Assoc.Prof. Dr. Pranee Phinyocheep)

…….……..…..….....Committee
(Assoc.Prof. Dr. Nuanphun Chantarasiri)

The Graduate School, Prince of Songkla University, has approved this thesis as fulfillment of the requirements for the Doctor of Philosophy in Polymer Science and Technology

……

(Assoc.Prof. Dr. Teerapol Srichana)
Dean of Graduate School

This is to certify that the work here submitted is the result of the candidate's own investigations. Due acknowledgement has been made of any assistance received.

.....……Signature

(Assoc. Prof. Dr. Varaporn Tanrattanakul)

Major Advisor

.....……Signature

(Miss Ruedee Jaratrotkamjorn)

Candidate

I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

.....……Signature

(Miss Ruedee Jaratrotkamjorn)

Candidate

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Author Miss Ruedee Jaratrotkamjorn

Major Program Polymer Science and Technology

Academic Year 2016

ABSTRACT

Non-isocyanate polyurethane (NIPU) based on natural rubber (NR) and poly(lactic acid) (PLA) were synthesized by polyaddition without catalyst and solvent. Two new oligoisoprenes (amino telechelic natural rubber (ATNR) and cyclic carbonate telechelic natural rubber (CCTNR)) have synthesized from carbonyl telechelic natural rubber (CTNR) obtaining from the control oxidative degradation of NR with the targeted chain length of 1000 and 2000 g/mol. A cyclic carbonate telechelic PLA (CCPLA) was synthesized from lactic acid by melt condensation in the presence of catalyst and succinic acid then it was subsequently reacted with glycerol carbonate in Steglish esterification. The $\bar{M}_n$ of CCPLA was in the range from 1000 to 2000 g/mol. The NIPU from NR were successfully synthesized by two approaches. The first approach was the reaction of ATNR and aromatic or aliphatic dicyclic carbonates corresponding to linear NIPU (NIPU#1). The second approach was the reaction of CCTNR and di- or tri- amines corresponding linear and cross-linked NIPU depending on type of amine (NIPU#2). The homogenous films were obtained in cross-linked NIPU#2. The reaction of CCPLA and various diamines produced NIPU#3. The evolution of the reaction was studied by FTIR analysis. The amide formation did not occur in both of NIPU#1 and NIPU#2 except in NIPU#3. The aminolysis of amine and ester as a side reaction could not prevent from the reaction of NIPU#3; therefore, it has no further analysis. No influence of $\bar{M}_n$ of ATNR, CCTNR and CCPLA on the reactivity to form NIPU was observed. The single T_g was observed in NIPU#1 and NIPU#2 and depended on the molecular weight of ATNR and CCTNR. The types of amine were not influence on T_g. NIPU#2 was a fully amorphous while the NIPU#1 has a low crystallization rate. DMTA analysis of cross-linked NIPU#2 showed the one α transition temperature. Two decomposition steps were found in both NIPU#1 and NIPU#2. The first and second steps were the rupture of urethane linkage and hydrocarbon chain, respectively.

ชื่อวิทยานิพนธ์ การสังเคราะห์และวิเคราะห์คุณลักษณะของพอลิยูริเทนแบบไม่ใช้ไอโซไซยาเนตจากยางธรรมชาติและพอลิแลคติกแอซิด

ผู้เขียน นางสาวฤดี จรัสโรจน์กำจร

สาขาวิชา วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์

ปีการศึกษา 2559

บทคัดย่อ

พอลิยูริเทนแบบไม่ใช้ไอโซไซยาเนต (NIPU) จากยางธรรมชาติ (NR) และพอลิแลคติกแอซิด (PLA) เตรียมผ่านปฏิกิริยาการเติมแบบไม่ใช้ตัวเร่งปฏิกิริยาและตัวทำละลาย โอลิโกเมอร์ที่มีหมู่ปลายสายโซ่เป็นเอมีน (ATNR) และโอลิโกเมอร์ที่มีหมู่ปลายสายโซ่เป็นไซคลิกคาร์บอเนต (CCTNR) สังเคราะห์จาก NR ที่มีหมู่ปลายสายโซ่เป็นคาร์บอนิล (CTNR) ซึ่งเตรียมจาก NR ที่ผ่านปฏิกิริยาย่อยสลายแบบออกซิเดชัน โดยมี $\overline{M}_n$ อยู่ในช่วง 1000 และ 2000 g/mol โอลิโกเมอร์จาก PLA ที่มีหมู่ปลายสายโซ่เป็นไซคลิกคาร์บอเนต (CCPLA) เตรียมจากกรดแลคติกผ่านปฏิกิริยาควบแน่นแบบหลอม โดยใช้ตัวเร่งปฏิกิริยาและกรดซัคซินิก และปฏิกิริยาเอสเทอริฟิเคชัน โดย $\overline{M}_n$ อยู่ในช่วง 1000 และ 2000 g/mol NIPU จาก NR มีวิธีการเตรียม 2 วิธี วิธีที่ 1 คือการเตรียมพอลิยูริเทนแบบเส้นตรง (NIPU#1) จาก ATNR และอะลิฟาติกหรืออะโรมาติกไดไซคลิกคาร์บอเนต และวิธีที่ 2 คือการเตรียมพอลิยูริเทนแบบเส้นตรงและแบบเชื่อมขวาง (NIPU#2) จาก CCTNR และไดเอมีนหรือไตรเอมีน แผ่นฟิล์มพอลิยูริเทนสามารถเตรียมได้จากพอลิยูริเทนแบบเชื่อมขวางเท่านั้น การเกิดปฏิกิริยาของพอลิยูริเทนถูกตรวจสอบด้วยเทคนิค FTIR พบว่าปฏิกิริยาข้างเคียงซึ่งเกิดจากหมู่เอสเทอร์ทำปฏิกิริยากับเอมีนซึ่งเกิดเป็นเอไมด์ไม่ปรากฏในการเตรียมพอลิยูริเทนชนิด NIPU#1 และ NIPU#2 ยกเว้นพอลิยูริเทนชนิดที่ 3 (NIPU#3) ซึ่งเตรียมจาก CCPLA และไดเอมีน ดังนั้น NIPU#3 จึงไม่ได้มีการวิเคราะห์สมบัติด้านอื่นต่อไป จากการศึกษาอิทธิพลของน้ำหนักโมเลกุลของโอลิโกเมอร์ (ATNR CCTNR และ CCPLA) ต่อการเตรียมพอลิยูริเทน พบว่าน้ำหนักโมเลกุลไม่มีผลต่อความไวในการเกิดปฏิกิริยา จากการวิเคราะห์สมบัติทางความร้อน พบว่า NIPU#1 และ NIPU#2 ปรากฏ T_g เพียงค่าเดียว ซึ่งค่า T_g ดังกล่าวขึ้นอยู่กับน้ำหนักโมเลกุลของโอลิโกเมอร์แต่ไม่ขึ้นกับชนิดของเอมีน NIPU#2 เป็นพอลิเมอร์ชนิดอสัณฐาน ขณะที่ NIPU#1 มีอัตราการเกิดผลึกต่ำ จากการวิเคราะห์ด้วยเทคนิค DMTA ในพอลิยูริเทนแบบเชื่อมขวาง (NIPU#2) พบว่า ปรากฏค่า T_g เพียงค่าเดียว การวิเคราะห์ด้วยเทคนิค TGA พบว่าการเสื่อมสลายทางความร้อนของ NIPU#1 และ NIPU#2 มีลักษณะที่เหมือนกัน กล่าวคือในขั้นตอนที่ 1 เป็นการเสื่อมสลายของพันธะยูริเทน ส่วนในขั้นถัดมาเป็นการเสื่อมสลายของสายโซ่ไฮโดรคาร์บอน

ACKNOWLEDGEMENT

Firstly, I would like to special thank my advisor Associate Professor Dr. Varaporn Tanrattanakul for continuous support of my Ph.D study, for her patience, advice, motivation and enthusiasm.

I would like to thank my co-advisor Dr. Chuanpit Khaokong for her advice, correcting and comment of thesis.

I would like to gratefully and sincerely thank Professor Dr. Jean-François Pilard, Assistant Professor Dr. Pamela Pasetto and Dr.Arnaud Nourry for their kindness, patience and suggestion. I would also thank to all techniciens and friends in a IMMM laboralory for their help.

I would like to thank my examining committee, Assistant Professor Dr. Watchanida Chinpa, Associate Professor Dr. Pranee Phinyocheep and Associate Professor Dr. Nuanphun Chantarasiri for accepting my thesis defense, providing the comment and suggestion for my thesis.

I would like to acknowledge PSU. Ph.D. Scholarship, Prince of Songkla University which financially supported. I would like to thank all techniciens and friends in Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University.

Finally, I would like to express thank my parents for supporting, understanding and encouragement. I also thank my younger and youngest brother for their encouragement.

Ruedee Jaratrotkamjorn

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List of abbreviation and symbols

Abbreviation and symbol	Full name
AA	acetic anhydride
AgTFA	silver trifluoroacetate
$Al(OTf)_3$	aluminum trifluoromethanesulfonate
Ar	argon
ATR	attenuated total reflectance
BA	butylamine
BDO	1,4-butanediol
BTMACl	benzyltrimethylammonium chloride
^{t}BuOK	potassium *tert*-butoxide
CaH_2	calcium hydride
CaO	calcium oxide
5CC	five-membered cyclic carbonate
6CC	six-membered cyclic carbonate
7CC	seven-membered cyclic carbonate
CC-CNSL	cyclic carbonate cashew nut shell liquid
$CDCl_3$	chloroform
CO_2	carbon dioxide
COOH	carboxyl group
CSBO	carbonated soybean oil
CTA	chain transfer agent
CTNR	carbonyl telechelic natural rubber
CTPLA	carboxylic telechelic poly(lactic acid)
1D	one dimension
2D	two dimension
DBTL	dibutyltin dilaurate
DCC	*N*,*N*-dicyclohexylcarbodiimide
DCM	dichloromethane
DCU	dicyclohexylurea
DEBDA	*N*,*N′*-diethyl-2-butene-1,4-diamine

List of abbreviation and symbols (Cont.)

DETA	diethylenetriamine
DGEBA	diglycidyl ether of bisphenol A
DMA	dynamic mechanical analysis
DMAc	dimethylacetamide
DMAP	*N*,*N*-dimethyl-4-aminopyridine
DMCOD	1,5-dimethyl-1,5-cyclooctadiene
DMEDA	*N*,*N′*-dimethylethylenediamine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
Ea	activation energy
EDA	ethylenediamine
ELSO	carbonated linseed oil
ENR	epoxidized natural rubber
ESI	electrospray ionization
Et_3N	triethylamine
EtOAc	ethyl acetate
Et_2O	diethyl ether
FTIR	fourier transform infrared spectroscopy
GC	glycerol carbonate
GPC	gel permeation chromatography
HCl	hydrochloric acid
HEMA-$AlEt_3$	tri-(2-hydroxyethyl methacrylate)-aluminium alkoxides
H_5IO_6	periodic acid
HRMS	high resolution mass spectrometry
HTPLA	hydroxyl telechelic poly(lactic acid)
$In(OTf)_3$	indium (III) trifluoromethanesulfonate
K_2CO_3	potassium carbonate

List of abbreviation and symbols (Cont.)

$KMnO_4$	potassium permanganate
KOH	potassium hydroxide
LiBr	lithium bromide
LiOTf	lithium trifluoromethanesulfonate
LLA	L-lactic acid
LNR	liquid natural rubber
MA	maleic anhydride
MALDI-TOF	matrix-assisted laser desorption/ionization time-of-flight
MDI	methylenediphenyl diisocyanate
MeOH	methanol
$MgSO_4$	magnesium sulfate
MNR	maleated natural rubber
MPA	*m*-phosphoric acid
Na	sodium
$NaBH_4$	sodium borohydride
$NaBH(OAc)_3$	sodium triacetoxyborohydride
NaCl	sodium chloride
$NaH(CO_3)$	sodium bicarbonate
NaOH	sodium hydroxide
$Na_2S_2O_3{\cdot}5H_2O$	Sodium thiosulfate pentahydrate
NH_4OAc	ammonium acetate
Ni	nickel
NIPU	non-isocyanate polyurethane
NMP	n-methylpyrrolidone
NMR	nuclear magnetic resonance spectroscopy
NR	natural rubber
P	pressure
$Pb(OAc)_4$	lead tetraacetate
Pd	palladium

List of abbreviation and symbols (Cont.)

PDLLA	poly(D,L-lactic acid)
PHU	polyhydroxyurethane
PLA	poly(lactic acid)
PLLA	poly(L-lactic acid)
POSS	polyhedral oligomeric silsesquioxanes
PPh_3	triphenylphosphine
Pt	platinum
PU	polyurethane
p-XDA	*p*-xylylenediamine
ROMP	ring-opening metathesis polymerization
ROP	ring-opening polymerization
SA	succinic acid
SAH	succinic anhydride
$Sc(OTf)_3$	scandium (III) triflate
SEC	size exclusion chromatography
$Si(OEt)_4$	tetraethyl orthosilicate
$SnCl_2{\cdot}H_2O$	stannous chloride dihydrate
$Sn(Oct)_2$	stannous octoate
TA	terephthalic acid
TAEA	tris(2-aminoethyl)amine
TBAB	tetrabutylammonium bromide
TDI	toluene diisocyanate
TFAA	trifluoroacetic anhydride
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLNR	telechelic liquid natural rubber
TNBT	titanium (IV) butoxide
TPLA	telechelic poly(lactic acid)
TSA	*p*-toluene sulphonic acid
VPO	vapor pressure osmometry

List of abbreviation and symbols (Cont.)

$ZnCl_2$	zine chloride
%	percent
Å	angstrom
°C	degree Celsius
D	day
Đ	dispersity
Da	Dalton
eq	equivalent
g	gram
g/mol	gram per mole
h	hour
ΔH_f	heat of formation
M	molarity
mbar	millibar
min	minute
mL	millilitre
mol	mole
mmol	millimole
N	normality
Pa	pascal
$\overline{M}_n$	number average molecular weight
$\overline{M}_v$	viscosity average molecular weight
$\overline{M}_w$	weight average molecular weight
S%	degree of scission
T_g	glass transition temperature
T_m	melting temperature
wt%	percentage by weight
%w/v	percentage weight per volume

CHAPTER 1

Introduction

1.1 Background and Rationale

Polyurethane (PU) is a useful polymer which was used in various applications such as foams, adhesives, paints, synthetic leathers, coatings and elastomers due to the good mechanical and physical properties. The conventional PUs usually obtained from the reaction of diols/polyols and diisocyanates/polyisocyanates. Isocyanate was derived from highly toxic phosgene. It caused the environmental hazard and human health (Allport *et al*., 2003). For this reason, the alternative method to produce PUs without isocyanate has been studied. It has been produced via the reaction of dicyclic carbonate and diamine resulting to the non-isocyanate polyurethanes (NIPUs) or polyhydroxyurethanes (PHUs) which contains the hydroxyl group in the polymer side chains. The presence of the intermolecular and intramolecular hydrogen bonds improved the chemical resistance (Kim *et al*., 2015; Figovsky *et al*., 2002; Steblyanko *et al*., 2000) and thermal properties (Kihara *et al*., 1993). The mechanical properties were also improved such as the impact strength (Wang and Soucek, 2013) and tensile strength (Bähr and Mülhaupt, 2012; Wang and Soucek, 2013; Javni *et al*., 2008; Javni *et al*., 2012).

The polyaddition polymerization of bifunctional five-membered cyclic carbonate (5CC) and diamine was usually employed to afford corresponding linear NIPUs. Recently, the commercial available NIPU has been presented under the trade name of Green Polyurethane® which using in the applications of coatings and paints (http://www.hybridcoatingtech.com/company.html, 2015). It was synthesized based on the reaction of multicyclic carbonates and aliphatic amines. It has been reported in the literature reviews that bio-based polymers were used as the starting material for synthesis of NIPU such as, soybean oil (Tamami *et al*., 2004; Javni *et al*., 2008; Javni *et al*., 2012; Bähr and Mülhaupt, 2012; Poussard *et al*., 2016), cashew nut shell liquid (Kathalewar *et al*., 2014) and tannin (Thébault *et al*., 2014; Thébault *et al*., 2015).

Based on the litearature reviews, it has no publication of NIPU based on natural rubber (NR) and poly(lactic acid) (PLA).

Natural rubber (NR) is an eco-friendly material which obtained from a renewable resource. NR is an unsaturated polymer consisting of *cis*-1,4-polyisoprene units. It exhibits the good mechanical properties such as high tensile strength, elongation at break and elasticity. Therefore, it is widely used in various fields, for instance, automobile industry and households.

PLA is an aliphatic, compostable and biodegradable polyester. It is derived from the polymerization of lactic acid (LA) or lactide which obtained from the fermentation of a agricultural renewable resources, for example, corn, wheat and sugar cane. PLA is used in various applications such as nonwovens, biomedical materials, food packaging, industrial packaging and containers.

The aim of this work was the synthesis of two bio-based NIPUs from NR and PLA. Both bio-based NIPUs will be a more environmentally friendly material than the conventional PU which obtained from the production using a toxic isocyanate.

1.2 Objective

The objective of this work was the synthesis and characterization of new bio-based NIPUs based on NR and PLA via the polyaddition reaction.

1.3 Scope of work

1. Two new oligoisoprenes; amino telechelic NR (ATNR) and cyclic carbonate telechelic NR (CCTNR) were synthesized by controlled and oxidative degradation of NR then functionalization of the chain ends which targeting number average molecular weight ($\overline{M}_n$) in the range of 1000 - 2000 g/ mol. The chemical structures were characterized by NMR and FTIR. The MALDI-TOF mass spectrometry was employed to confirm the end group as well as the $\overline{M}_n$. The $\overline{M}_n$ was also determined by NMR and SEC analyses.

2. Two dicyclic carbonates; aliphatic and aromatic dicyclic carbonates were synthesized. The chemical structures were characterized by NMR and FTIR.

3. Low molecular weights of PLA containing carboxylic acid chain ends (cyclic telechelic PLA, CCPLA) was synthesized. The chemical structure was characterized by NMR, FTIR and MALDI-TOF analyses. The molecular weights were also determined by using a ^{1}H-NMR and SEC.

4. Two types of bio-based NIPUs were synthesized. The first type was a NIPU from NR which synthesized by two approches. The first approach was the reaction of oligoisoprene containing amino chain ends and aliphatic or aromatic dicyclic carbonates as referred to NIPU#1. The second one was the reaction of oligoisoprene containing cyclic carbonate chain ends and commercial amines as referred to NIPU#2. The second type was a NIPU from PLA. It was synthesized from the reaction of CCPLA and diamines as referred to NIPU#3.

1.4 Literature reviews

1.4.1 Natural rubber (NR)

NR is an unsaturated polymer consisting of *cis*-1,4-polyisoprene unit. NR obtained from the rubber tree (*brasiliensis hevea*). The chemical structure of NR is presented in Fig. 1.1. In order to increase the elasticity, strength, heat and weather resistances of NR, the chemical process as a vulcanization was used to make a cross-linking by using sulfur and other additives. Therefore, the vulcanized NR is widely used in various applications such as footwears, gloves, wheels and gasket. Normally, it is an amorphous in the normal condition. NR exhibits the good properties such as high tensile strength, resilience and tear resistance and elasticity as well as low heat build-up. The undesirable properties are a low oil, flame, heat and abrasion resistance. These reasons probably caused due to the high unsaturated, molecular weight as well as non-polar character.

NR has a high molecular weight. The molecular weight of NR has been decreased via the mechanical and chemical processes. The mechanical processes were performed in a two-roll mill or internal mixer. The number of mastication and the temperature are the influence on the molecular weight of NR. The chemical processes were performed by cleaving the double bond of isoprene units such as ozonolysis, metathesis reaction and oxidative degradation by chain scission agents.

The periodic acid is usually used as a chain scission agent for NR. Moreover, it was more effective to control the molecular weight.

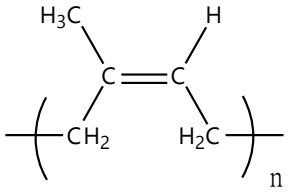
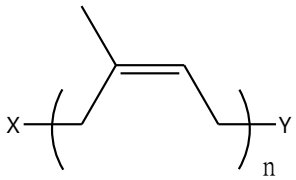


Fig. 1.1 Chemical structure of NR.

1.4.2 Telechelic liquid natural rubber (TLNR)

The telechelic is refered to the oligomer containing two or more terminal groups. The number average molecular weight ($\overline{M}_n$) of TLNR was approximately in the range of 10^2-10^4 g/mol. The chemical structure of TLNR was similar to the NR which containing of isoprene units in the backbone and having the reactive terminal groups as shown in Fig. 1.2. (Nor and Ebdon, 1998).



X and Y = reactive functional group

Fig.1.2 Chemical structure of TLNR (Nor and Ebdon, 1998).

TLNR was obtained by the oxidative degradation of NR. Several methods have been reported for the oxidative degradation such as redox, photochemical and oxidative reactions at high temperature and pressure (Nor and Ebdon, 1998). The presence of complex mechanism and secondary reaction were the limitation of these reactions that it was undesired. Therefore, the alternative methods have been interested such as ozonolysis, metathesis reaction, oxidative cleavage by lead tetraacetate ($Pb(OAc)_4$) and periodic acid (H_5IO_6). Among these methods, H_5IO_6 was a good chain scission agent for NR. In addition, it was cheap and non-toxic material. It has been usually used and reported in the following publications.

Gillier-Ritoit *et al*. (2003) proposed the using of H_5IO_6 to the synthesis of telechelic *cis*-1,4-polyisoprene (TPI) from epoxidized *cis*-1,4-polyisoprene (EPI) and *cis*-1,4-polyisoprene (PI) in tetrahydrofuran (THF) and chloroform ($CHCl_3$) (Fig. 1.3). It was found that the reaction was performed in THF resulting to decrease the molecular weight and give the higher degree of scission (S%) than that $CHCl_3$. The reaction mechanism was involved two steps. The first step, H_5IO_6 reacted with a double bond to form an epoxide or α-glycol. Then epoxide or α-glycol was cleaved with the second equivalent of H_5IO_6 to obtain the telechelic polymer containing with ketone and aldehyde groups at the chain ends (carbonyl telechelic natural rubber, CTNR) (Fig 1.4).

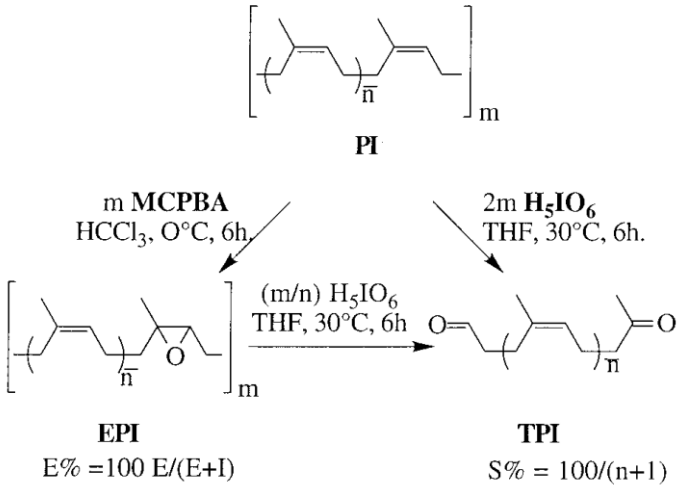


Fig. 1.3 Synthesis of telechelic *cis*-1,4-polyisoprene (Gillier-Ritoit *et al*., 2003).

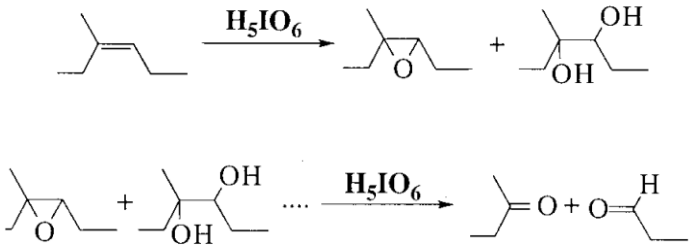


Fig. 1.4 Oxidative degradation mechanism of *cis*-1,4-polyisoprene by using the H_5IO_6 (Gillier-Ritoit *et al*., 2003).

Sadaka *et al*. (2012) described the one step of oxidative process to use the H_5IO_6 for the synthesis of CTNR (Fig. 1.5). This agreed with the two steps mechanism which proposed by Gillier-Ritoit *et al*. (2003).

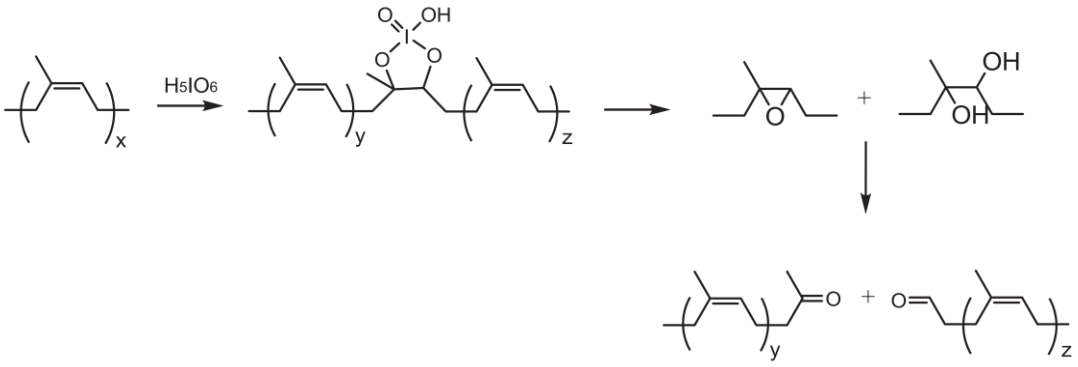


Fig. 1.5 One step of oxidative degradation mechanism by using the H_5IO_6 for the synthesis of CTNR (Sadaka *et al*., 2012).

Phinyocheep *et al*. (2005) proposed the oxidative degradation of epoxidized natural rubber (ENR) by using the H_5IO_6. The double bond of ENR was oxidized by H_5IO_6 resulting to a *vic*-diols then the partial carbon-carbon of *vic*-diols was cleaved with other molecules of H_5IO_6 leading to the chain degradation as shown in Fig. 1.6.

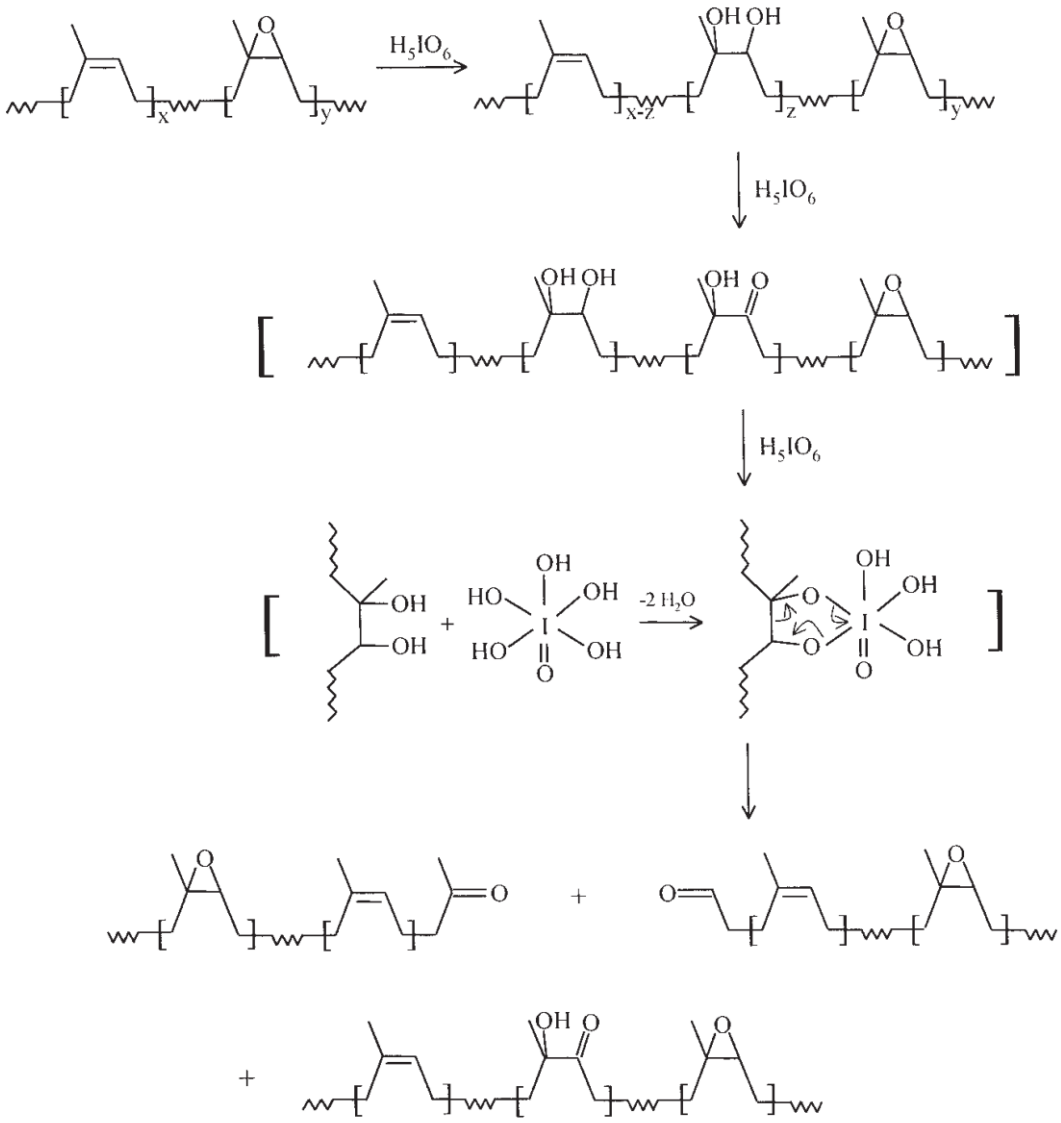


Fig. 1.6 Oxidative degradation mechanism of ENR by using the H_5IO_6 (Phinyocheep *et al*., 2005).

1.4.3 Chemical modifications of carbon-carbon double bond

The chemical modification of carbon-carbon double bonds could be produced the new NR derivatives and usually made from a synthetic polyisoprene with the specific reaction such as, epoxidation, hydroboration, maleinization, carbonization, chlorophosphonylation, phosphorylation, silylation and metalation (Fig. 1.7) Some reactions have been used with NR and NR derivatives, espectially liquid natural rubber (LNR) and epoxidized liguid natural rubber (ELNR). LNR and

ELNR were the starting materials to afford the new specific polymer by chemical modification. Fig. 1.8 represent some of chemical modification of ELNR. This reaction allow to convert the epoxide group to new functional groups, for instance alcohol, carboxylic acid, amine and phosphoric acid derivatives.

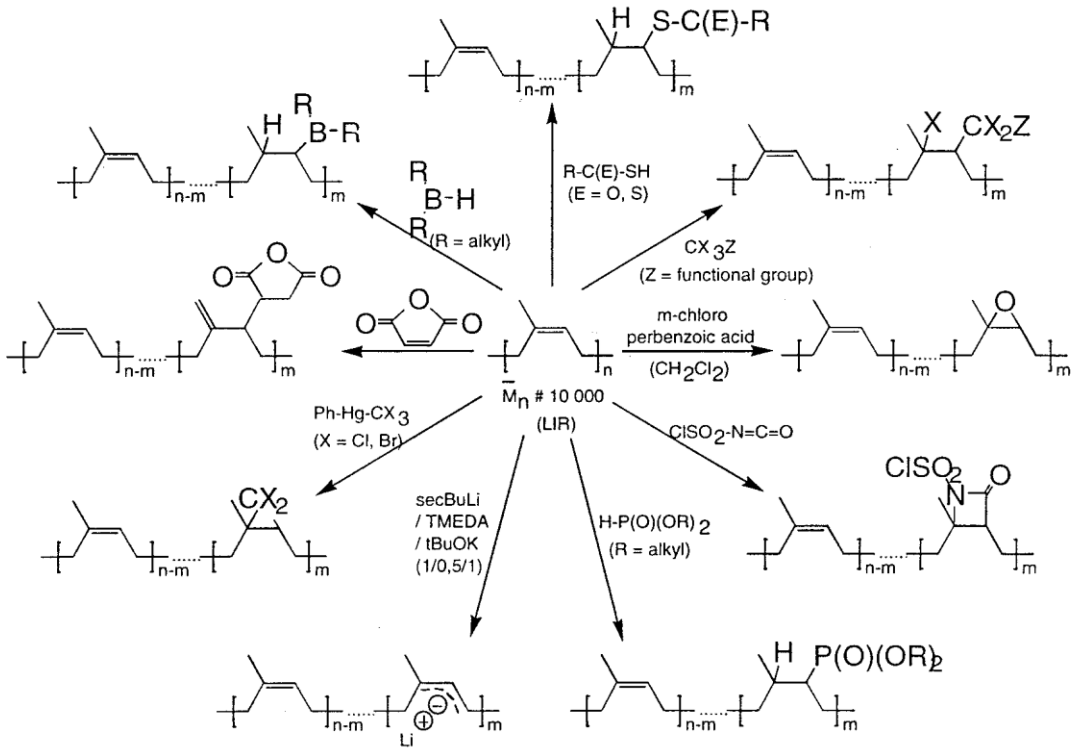


Fig. 1.7 Chemical modifications of double bond in liguid natural rubber (Brosse *et al*., 2000).

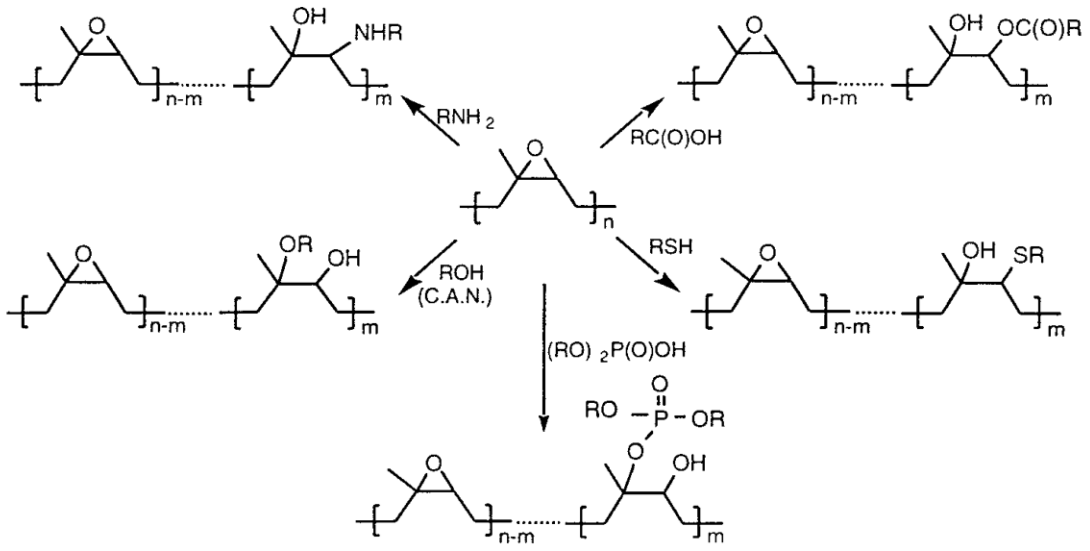


Fig. 1.8 Chemical modifications of epoxidized liguid natural rubber (Brosse *et al*., 2000).

1.4.4 Chemical modification of chain ends

Kébir *et al*. (2005) reported the two methods for the synthesis of amino telechelic NR based on CTNR**.** The first pathway was the synthesis of oligoisoprene containing the primary amine chain ends (amino telechelic *cis*-1,4-oligoisoprene). This partway has been synthesized through many steps to obtain the amino telechelic *cis*-1,4-oligoisoprene. The yield of reaction was too low for the large scale. Therefore, the direct reductive amination was presented to obtain the oligoisoprene containing secondary amine chain ends (nButyl amino telehelic cis-1,4-oligoisoprene). The last pathway was not only one step but also giving the higher yield (Fig. 1.9).

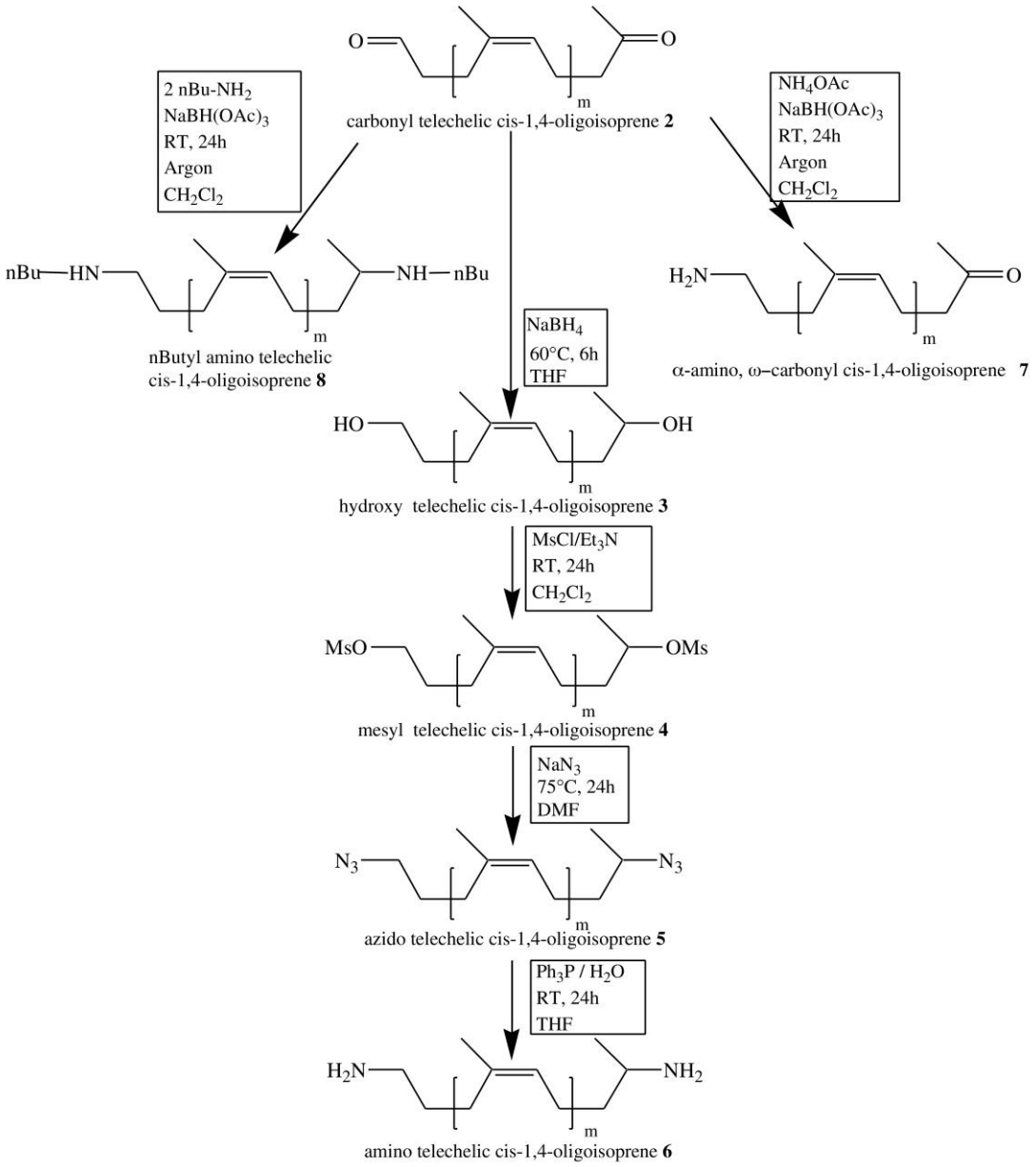


Fig. 1.9 Synthesis of amino telechelic *cis*-1,4-oligoisoprene (Kébir *et al*., 2005).

Morandi *et al*. (2007) reported the direct selective amination of CTNR to produce the amine chain ends (Fig. 1.10). The first reaction was performed with excess butylamine leading to the secondary amine functional end groups (product 3), whereas the mixture of oligomer (product 2, 4-7) was obtained when using the sodium triacetoxyborohydride ($NaBH(OAc)_3$) as a reducing agent. This reaction occurred only aldehyde group even activation with acetic acid due to the less reactive amine.

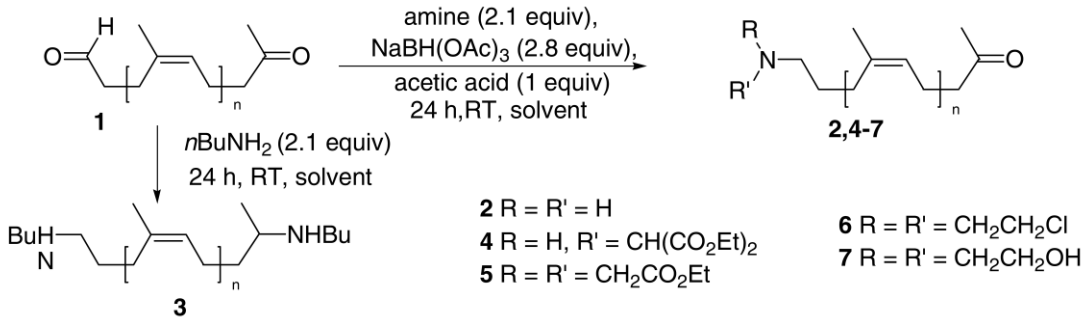


Fig. 1.10 Direct reductive amination of CTNR (Morandi *et al*., 2007).

Saetung *et al*. (2011) synthesized the α-trithiocarbonyl-ω-carbonyl-*cis*-1,4-polyisoprene based on NR (Fig. 1.11). The first step was the synthesis of CTNR (product 1) via the oxidative degradation of NR by using the H_5IO_6. Then CTNR was reacted with the ammonium acetate (NH_4OAc) to obtain the α-amino-ω-carbonyl-*cis*-1,4-polyisoprene (product 2). Finally, the α-amino-ω-carbonyl-*cis*-1,4-polyisoprene was reacted with S-1-dodecyl-S'-(α-α'-dimehyl-α"-acetic acid) trithiocarbonate (compound 3) in the presence of oxalyl chloride resulting to the α-trithiocarbonyl-ω-carbonyl-polyisoprene (product 4).

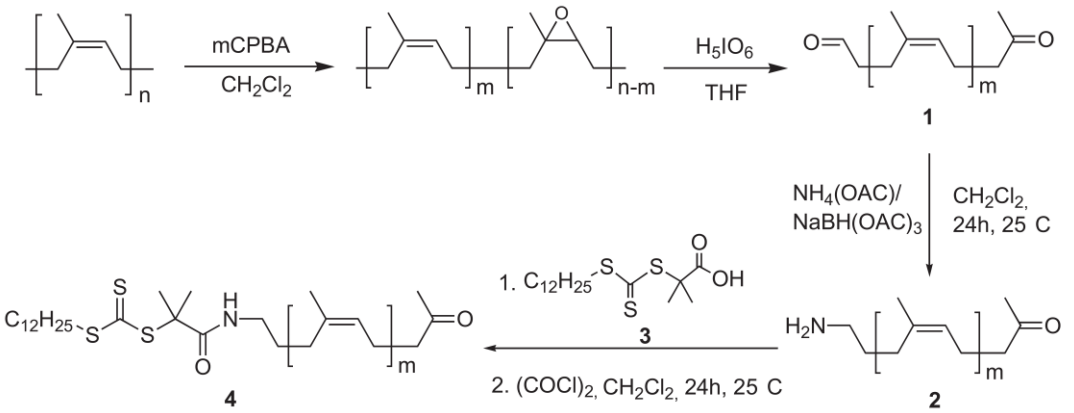


Fig. 1.11 Synthesis of α-trithiocarbonyl-ω-carbonyl-*cis*-1,4-polyisoprene based on NR (Saetung *et al*., 2011).

1.4.5 Poly(lactic acid) (PLA)

Polylactide or PLA was discovered in 1932 by Carothers. It is an aliphatic polyester deriving from renewable resource such as corn, sugarcane, wheat and starch. Lactic acid (2-hydroxy propionic acid) was a monomer of PLA which have the two optically active configurations (Fig. 1.12). The L(+)-and D(-)-lactic acid rotate the plane of polarized light clockwise and counterclockwise, respectively (Rasal *et al*., 2010). The ratio of L and D isomers influence on the properties of PLA such as glass transition temperature (T_g), melting temperature (T_m), mechanical properties and crystallinity (Carrasco *et al*., 2010). Lactic acid can be produced by chemical synthesis or fermentation. Some substrates and microorganisms for the production of lactic acid are listed in Table 1.1.

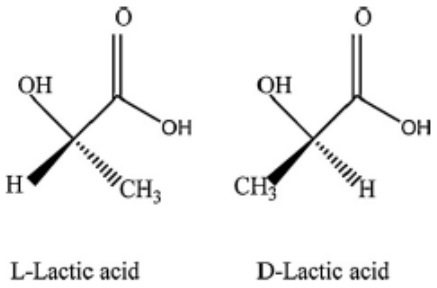


Fig. 1.12 L(+) and D(-) stereoisomers of lactic acid (Rasal *et al*., 2010).

Table 1.1 Substrate and microorganism for the production of lactic acid (Nampoothiri *et al*., 2010)

Substrate	Microorganism	Lactic acid yield
Wheat and rice bran	Lactobacillus sp.	129 g/l
Corncrob	Rhizopus sp.MK-96-1196	90 g/l
Pretreated wood	Lactobacillus delbrueckii	48-62 g/l
Cellulose	Lactobacillus coryniformis ssp. torquens	0.89 g/g
Barley	Lactobacillus casei NRRLB-441	0.87-0.98 g/g
Cassava bagasse	L. delbrueckii NCIM 2025, L casei	0.9-0.98 g/g
Wheat starch	Lactobacillus lactis ssp. Lactis ATCC 19435	0.77-1 g/g

Table 1.1 Substrate and microorganism for the production of lactic acid (Nampoothiri *et al*., 2010) (cont.)

Whole starch	Lactobacillus lactis and Lactobacillus delbrueckii	0.93-0.95 g/g
Potato starch	Rhizopus oryzae, R. arrhhizuso	0.87-0.97 g/g
Corn, rice, wheat starches	Lactobacillus amylovorous ATCC 33620	<0.70 g/g
Corn starch	L. amylovorous NRRL B-4542	0.935 g/g

1.4.6 Synthesis methods of PLA

PLA has been synthesized by many methods: direct condensation polymerization, azeotropic dehydration condensation and lactide ring-opening polymerization, as shown in Fig. 1.13.

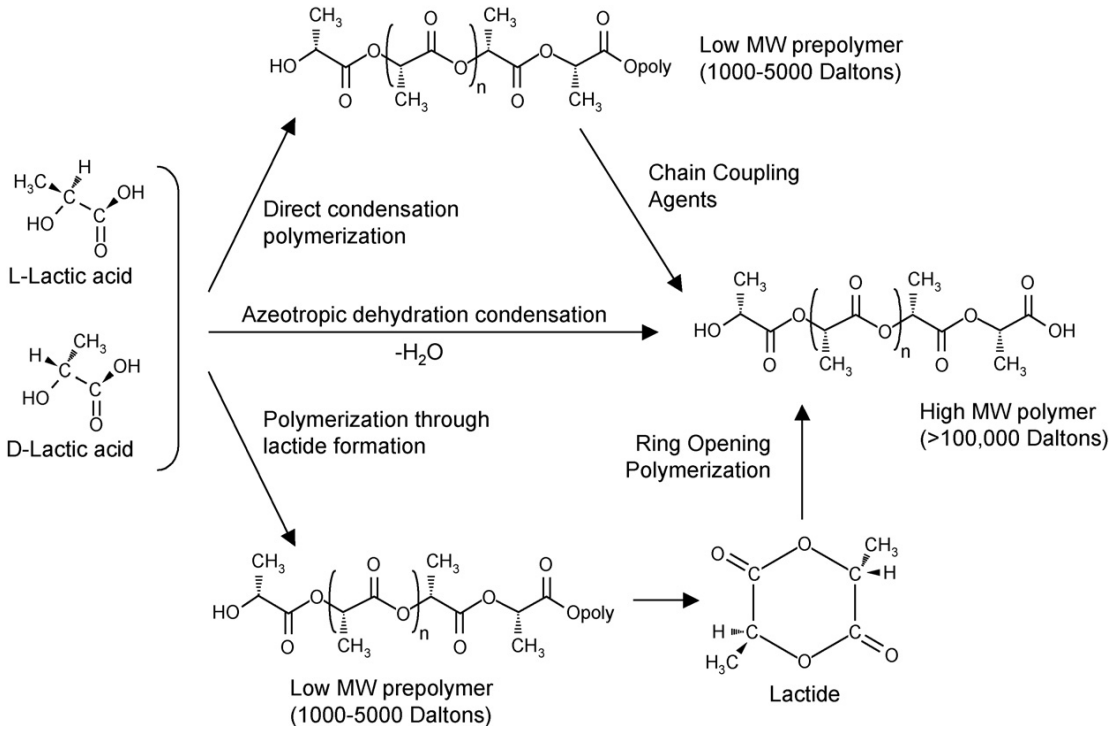


Fig. 1.13 Synthesis routes of PLA (Lim *et al*., 2008).

1.4.6.1 Direct condensation polymerization

The direct condensation polymerization was performed in the presence of catalyst under reduced pressure. Single catalyst system was used for the preparation of PLA, such as stannous octoate ($Sn(Oct)_2$) (Zhou *et al*., 2004), titanium(IV) butoxide (TNBT) (Chen *et al*., 2006) stannous chloride dihydrate ($SnCl_2 \cdot H_2O$) (Laonuad *et al*., 2010) and *p*-toluene sulphonic acid (TSA) (Pivsa-Art *et al*., 2011).

A binary catalyst system consists of a metal ion catalyst ($SnCl_2.H_2O$ or $Sn(Oct)_2$) and a proton acid catalyst (TSA). The metal ion (Lewis acid) catalysts have the multiple protons that it is generally believed to promote the dehydration polymerization resulting to increase the molecular weight of the polymer. The proton acid catalysts prevent the side reactions including discoloration and racemization. Thus the binary catalyst system with both Lewis acid and proton acid is believed to be a good combination for the producing a high molecular weight with a little discoloration and racemization.

The disadvantage of direct condensation polymerization is difficulty to produce the high molecular weight of PLA because each step of polymerization process presents the one molecule of water as shown in Fig.1.14. The water causes the degradation of polymer chains resulting to decrease the molecular weight of PLA.

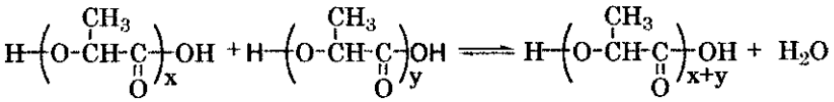


Fig. 1.14 Condensation polymerization of PLA (Moon *et al*., 2000).

1.4.6.2 Azeotropic dehydration condensation

The azeotropic dehydration condensation was a method to obtain the high molecular weight of PLA without using the chain extender. A general method was performed in aprotic solvent under reduce pressure (Garlotta, 2001).

1.4.6.3 Ring-opening polymerization (ROP)

The common production of high molecular weight PLA was performed by ROP of lactide in the presence of catalyst. Lactide was a cyclic dimer that it was formed by the depolymerization of low molecular weight of PLA under pressure to afford the three stereoforms: L-lactide, D-lactide, or *meso*-lactide (Fig. 1.15). The common catalysts for the synthesis of PLA are listed in Table 1.2. The content of stereoisomer depended on the lactic acid isomer feedstock, temperature and catalysts (Garlotta, 2001). The commercial available high molecular weight PLA were the poly(L-lactic acid) (PLLA) and poly(D,L-lactic acid) (PDLLA) which produced from L-lactides and D,L-lactides, respectively (Lim *et al*., 2008).

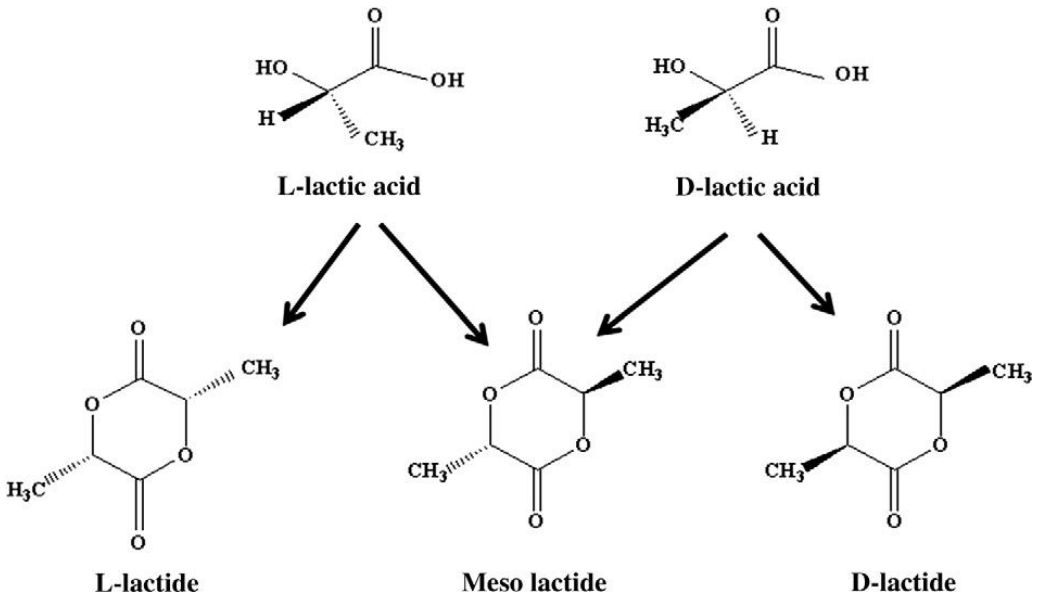


Fig. 1.15 Stereoforms of lactide (Nampoothiri *et al*., 2010).

Table 1.2 Common catalysts for the synthesis of PLA (Nampoothiri *et al*., 2010)

Polymer	Catalysts	Solvent	Molecular weight
D, L PLA/ L-PLA	Aluminium Isopropoxide	Toluene	$\overline{M}_n$ = 90,000
D-L PLA	Stannous octoate	Alcohols	$\overline{M}_w$ < 3,500,000

Table 1.2 Common catalysts for the synthesis of PLA (Nampoothiri *et al.*, 2010) (cont.)

L-PLA	Stannous octoate	Alcohols, carboxylic acid	$\overline{M}_n$ = 250,000
L-PLA	Stannous octoate and compounds of titanium and zirconium	Toluene	$\overline{M}_n$ = 40,000 – 100,000
D-PLA	Stannous trifluoromethane	Ethanol	-
L-PLA	Sulfonate, scandium (III)	Ethanol	-
D-L PLA	Trifluoromethane sulfonate	Ethanol	-
L-PLA	Mg, Al, zn, Titanium alkoxides	Methylene chloride	-
L-PLA	Yttrium tris (2,6-di-tert butyl phenolate) (in toluene)	2-propanal, butanol, ethanol	$\overline{M}_n$ < 25,000
D-L PLA	Zn lactate	No solvent	$\overline{M}_n$ = 212,000
D-L PLA	Butylmagnesium, Grignard reagent	Ethers	$\overline{M}_n$ < 300,000
L-PLA	Potassium naphthalenide	THF, toluene	$\overline{M}_n$ < 16,000
L-PLA	Complexes of iron with acetic, butyric, siobutyric and dichloroacetic acid	No solvent	$\overline{M}_w$ = 150,000

1.4.7 Synthesis of telechelic PLA (TPLA)

The low molecular weight of PLA has been modified to obtain the telechelic poly(lactic) acid (TPLA). Typically, the TPLAs were terminated with hydroxyl (OH) or carboxyl (COOH) groups as shown in Fig. 1.16.

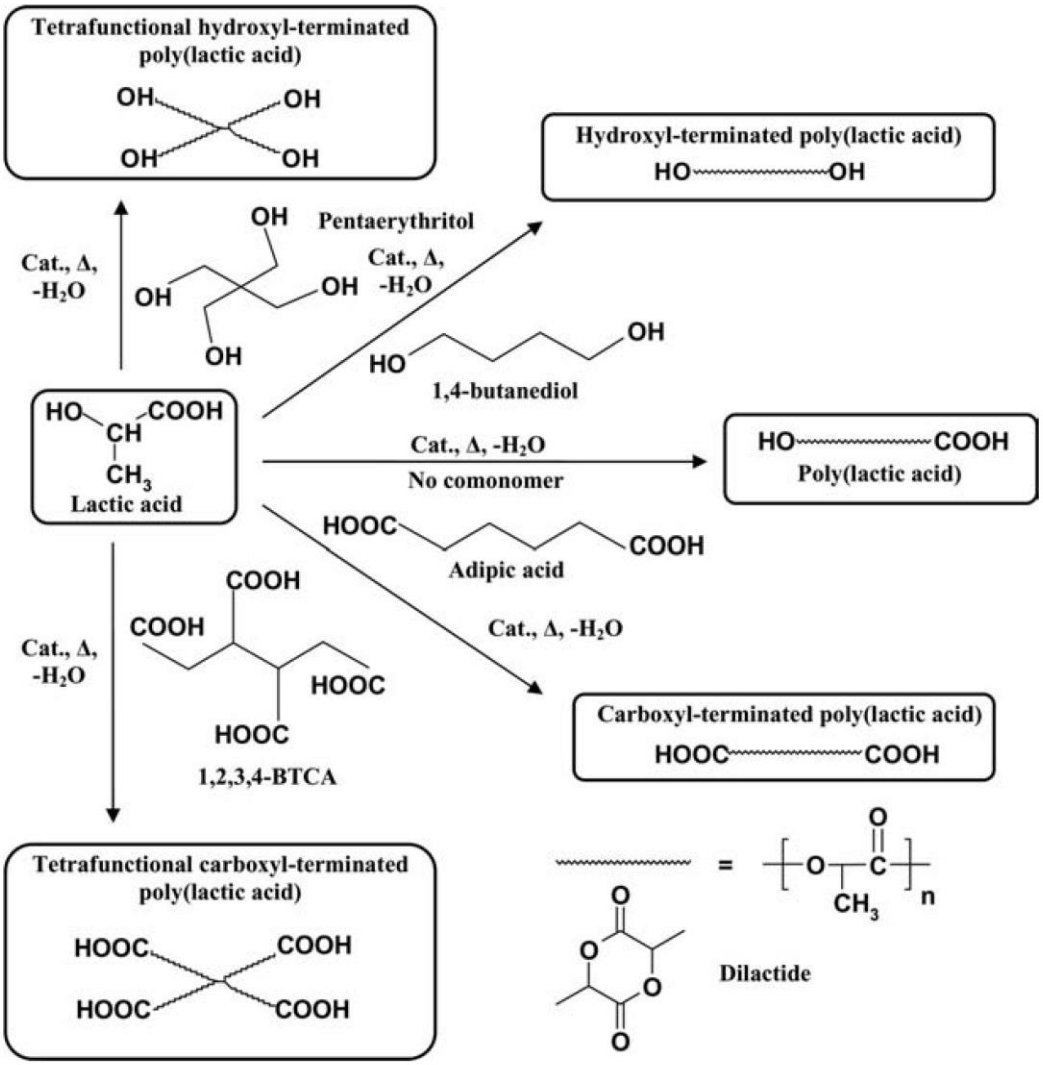


Fig. 1.16 Synthesis routes of telechelic poly(lactic) acid (Inkinen *et al*., 2011).

1.4.7.1 Hydroxy telechelic PLA (HTPLA)

Wang *et al*. (2006) synthesized the HTPLA in the toluene. The reaction was performed at 125°C for 24 h in the presence of $Sn(Oct)_2$ and 1,4-butanediol (BDO). The $\overline{M}_n$ determining by ^{1}H-NMR was 3000, 5000 and 10000 g/mol. Wang *et al*. (2011) synthesized the HTPLA by the ROP of D,L-lactide in the presence of $Sn(Oct)_2$ and BDO. The reaction was performed at 140°C for 24 h under vacuum. The $\overline{M}_n$ determining by ^{1}H-NMR was 3592 g/mol. Selukar *et al*. (2012) synthesized

the HTPLA via the dehydropolycondensation of L-lactic acid with 2,5-hexanediol in the presence of tetraphenyltin. The reaction was carried out in xylene at 144°C. The molecular weight determined by ^{1}H-NMR and vapor pressure osmometry (VPO). The $\overline{M}_n$ determining by ^{1}H-NMR were 4320 and 5544 g⁄mol. The $\overline{M}_n$ determining by VPO were 4400 and 5692 g⁄mol. Ali *et al*. (2014) synthesized the HTPLA in the presence of $Sn(Oct)_2$ and BDO. The reaction was performed in toluene at 160°C for 6 h under nitrogen atmosphere. The molecular weight and polydispersity index were 1400 g/mol and 1.70, respectively.

1.4.7.2 Carboxylic telechelic PLA (CBPLA)

Huh and Bae (1999) synthesized CBPLA by the condensation reaction of L-lactic acid in the presence of succinic acid (SA). The molecular weight was controlled by changing a feed ratio between L-lactic acid and SA. The molar ratio of L-lactic acid and succinic acid was in the range from 6/1 to 50/1. The $\overline{M}_n$ and polydispersity of the dicarboxylated PLLA obtained from gel permeation chromatography (GPC) ranged from 1000 to 6000 g/mol and 1.27 to 1.67, respectively. Zhou *et al*. (2007) synthesized PLLA with the reaction of succinic anhydride with L-lactic acid prepolymer by melt polycondensation. PLLA and epoxy resin based on diglycidyl ether of bisphenol A (DGEBA) copolymers were prepared by chain extension of dicarboxylated PLLA with DGEBA. The amount of carboxyl group of L-lactic acid prepolymer and dicarboxylated PLLA was 3.7×10^{-4} and 7.2×10^{-4} g⁄mol, respectively. The viscosity average molecular weight ($\overline{M}_v$) of PLLA/DGEBA copolymer reached 87900 g⁄mol when reaction temperature, reaction time, and molar ratio of dicarboxylated PLLA to DGEBA was 150°C, 30 min, and 1:1, respectively. Zhao *et al*. (2012) synthesized CBPLA prepolymer in the presence of SA at 180 °C for 48 h under high vacuum, and the temperature was gradually increased to 180°C within 12 h. Two kinds of CTPLA prepolymers with average molecular weights of 1000 (PLA1000) and 2000 (PLA2000**)** were prepared by changing the molar ratio of lactic acid/SA.

1.4.8 Non-isocyanate polyurethane (NIPU)

Polyurethane (PU) is one of the polymers which exhibited the excellent physical and mechanical properties. Therefore, PU is widely used in numerous fields such as elastomers, adhesives, coatings and foams. The classical PUs are synthesized from the polyaddition of diols/ polyols and isocyanates/ polysiocyanates (Fig. 1.17). Isocyanate is usually derived from toxic phosgene which causes the environmental hazards and human health such as skin irritation, eye irritation and asthma (Guan *et al*., 2011). As a result, the alternative methods have been more attractive in order to avoid the using of isocyanate.

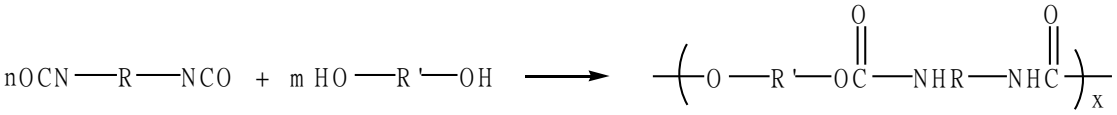


Fig.1.17 Reaction of diols/polyols and isocyanates/polyisocyanates.

It has been reported that the preparation of PU by polyaddition of diisocyanates and diol could not prepare the PU consisting hydroxyl group in the polymer side chain (Tomita et al., 2001e review by Whelan et al., 1963; Mikheev et al., 1983; Rokicki and Czajkowska, 1989). Due to the presence of hydroxyl group in the polymer side chains of NIPU, the intermolecular and intramolecular hydrogen bonds could form through the carbonyl and hydroxyl group at the *β*-carbon atom resulting to improve the chemical resistance (Steblyanko *et al*., 2000; Kim *et al*., 2001; Figovsky *et al*., 2002), glass transition temperature (Kihara *et al*., 1993) as well as increased the modulus and tensile strength (Javni *et al*., 2012; Bähr *et al*., 2012; Javni *et al*., 2012). The absence of biurets and allophanetes units led to enhance the thermal stability (Tomita *et al*., 2001d). For these reasons, NIPU has been used for various applications such as adhesives, coatings and sealents.

NIPUs have been synthesized via three methods: polyaddition, polycondensation and ring opening polymerization (Rokicki *et al*., 2015). The most common method is the reaction between five-membered cyclic carbonates (5CC) and diamines as shown in Fig. 1.18. The synthesis methods of 5CC are presented in Fig

1.19. The common method is an insertion of CO_2 into an oxirane ring in the presence of catalyst (Fig. 1.20. and Table 1.3). Another method is the functionalization of the molecules containing Cl or COOH at chain ends by using the commercial available glycerol carbonate (GC) (Fig. 1.21) (Helou *et al*., 2011; Benyahya *et al*., 2012; Carré *et al*., 2014; Duval *et al*., 2016).

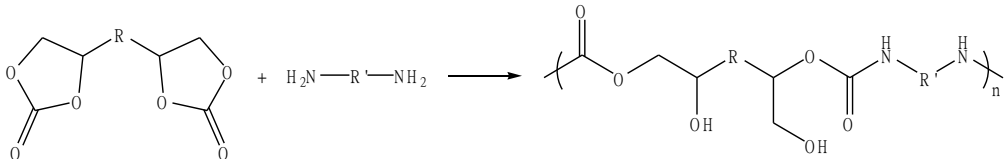


Fig. 1.18 Reaction of dicyclic carbonate and diamine (Tomita *et al*., 2001a).

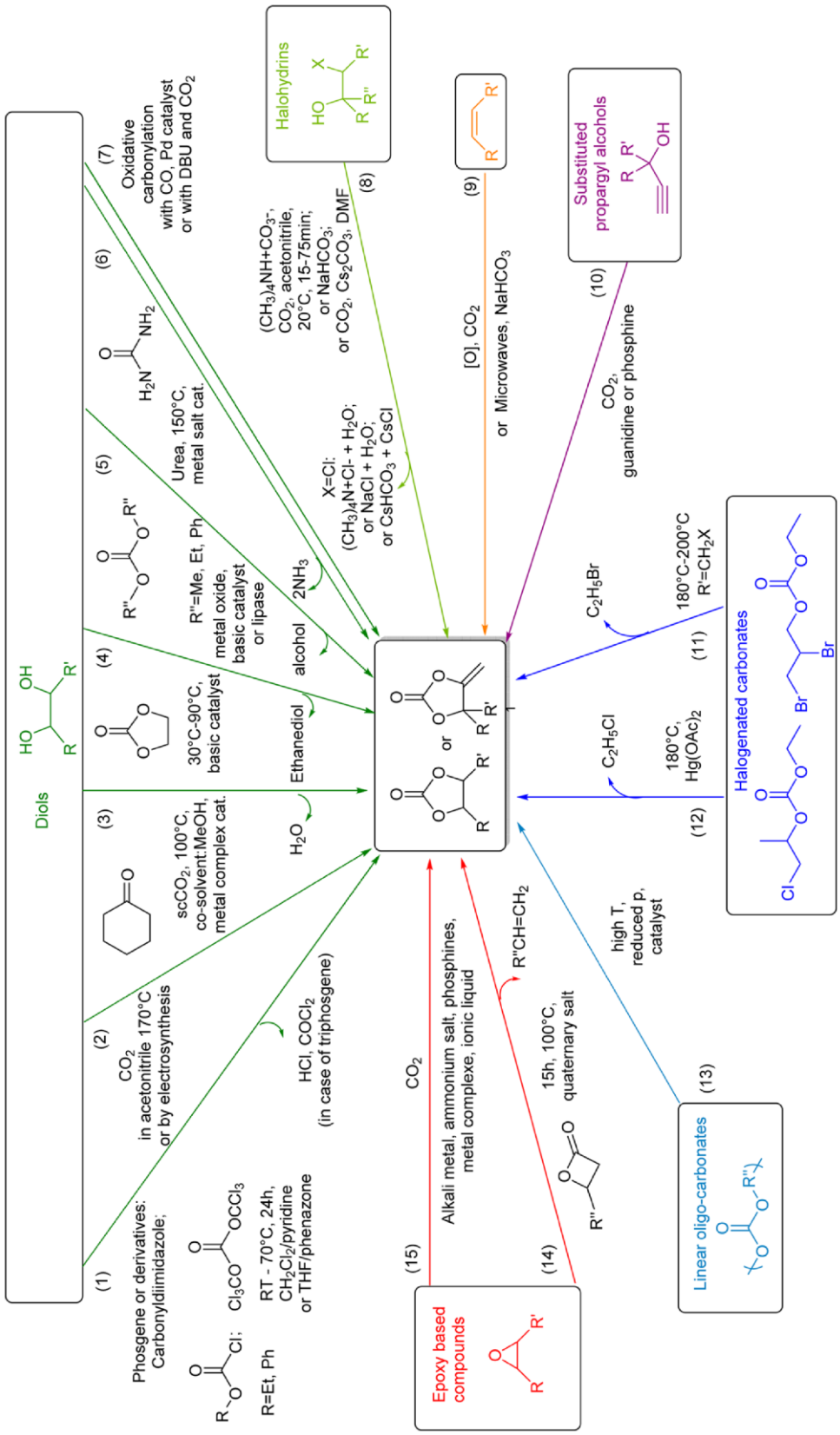


Fig 1.19 Schematic methods for synthesis of 5CC (Maisonneuve *et al*., 2015).

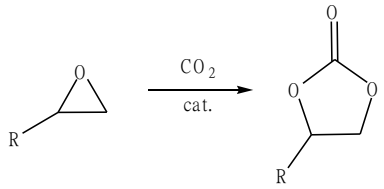
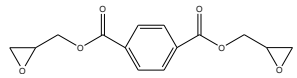
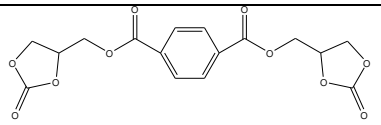
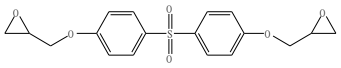
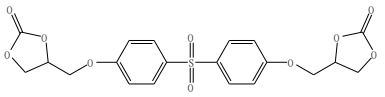
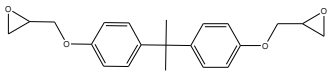
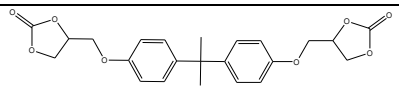
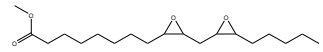
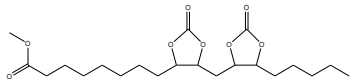
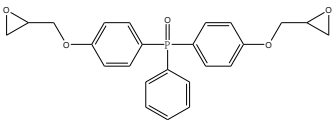
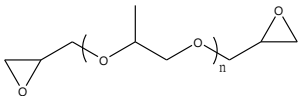
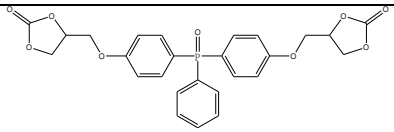
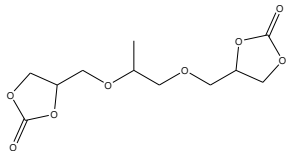
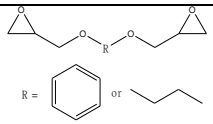
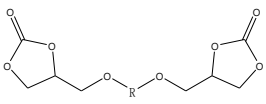


Fig 1.20 Synthesis of 5CC by insertion of CO_2 into oxirane ring (Guan *et al*., 2011).

Table 1.3 Synthesis of 5CC by insertion of CO_2 into an oxirane ring

Materials	Conditions	5CC	References
	Libr, NMP, 100°C		Steblyanko *et al*., 2000
	BTMACl, NMP, 100°C, 24 h		Kim *et al*., 2001
	LiCl, NMP, 100°C, 24 h		Ochiai *et al*., 2005
	TBAB, 100°C, 15 h		Helou *et al*., 2011
 	TBAB, 80°C, 3 h	 	Hosgor *et al*., 2012
	LiBr, 80°C, 24 h		Camara *et al*., 2014

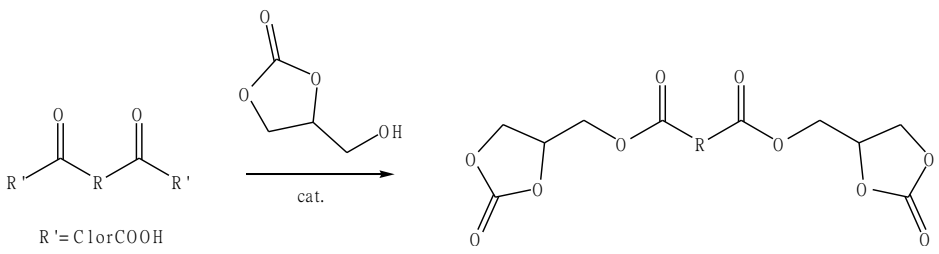


Fig 1.21 Synthesis of 5CC by using a glycerol carbonate.

1.4.9 Mechanism of NIPU formation

Two mechanisms for the formation of NIPU have been proposed. The first mechanism was proposed by Tomita *et al*. (2001b) (Fig. 1.22). The reaction formed through the intermediate and transition state (A and A') corresponding to the product 1 or 1'. A and A' were more stable after substitute by electron-withdrawing group (R). The transition state A was more stable than A' because of the absence of methylene group between the negatively charged oxygen and the R.

The second mechanism was proposed consisting of three stages (Guan *et al*., 2011 review by Garipov *et al*., 2003a and Garipov *et al*., 2003b) (Fig. 1.23) In the first stage, a nucleophilic was attacked by amine at the carboxyl group in cyclic carbonates corresponding to the formation of a tetrahedral intermediate. In second stage, the hydrogen ion on the amine at the tetrahedral intermediate was removed. Finally, the C-O bond was broken up by the strong electron-withdrawing of nitrogen atoms and the new generated alkyl-oxygen ion combines with hydrogen ions resulting in a rapid formation of the NIPU (Guan *et al*., 2011 review by Garipov *et al*., 2003a and Garipov *et al*., 2003b).

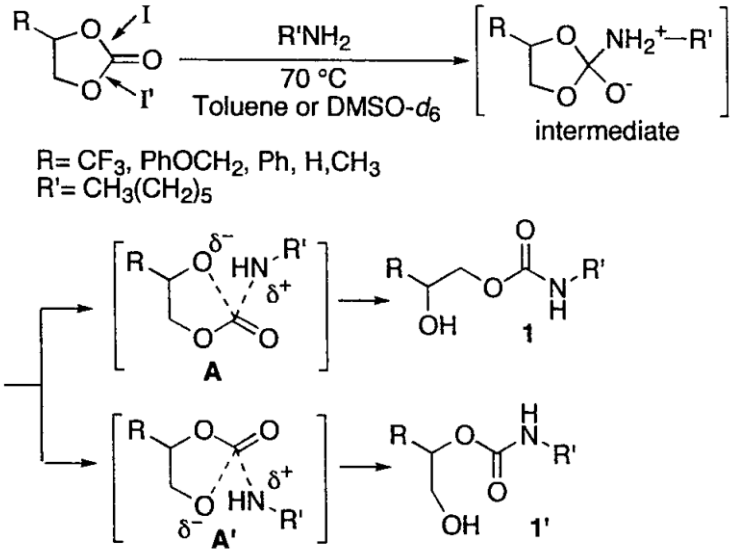


Fig. 1.22 The mechanisms of NIPU formation (Tomita *et al*., 2001b).

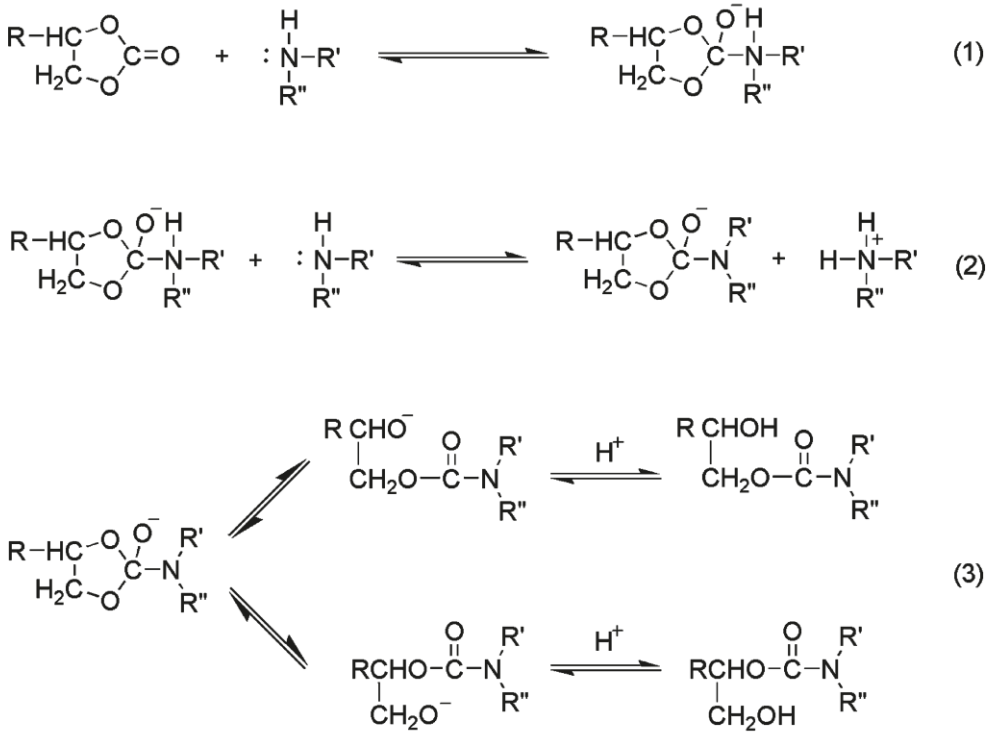


Fig. 1.23 Schematic mechanisms of NIPUs formation (Guan *et al*., 2011 review by Garipov *et al*., 2003a and Garipov *et al*., 2003b).

1.4.10 Selectivity of the reaction

The reaction of five-membered cyclic carbonate reacts with diamine to afford the NIPU with primary and secondary hydroxy groups. The formation ratio of primary and hydroxyl groups in NIPU have been studied.

Steblyanko *et al*. (2000) proposed the model reaction from the reaction of monofunctional cyclic carbonate (2m) with benzylamine corresponding hydroxyurethane with product A and B (Fig. 1.24). They found that the molar ratio of product B was predominant than product A. In addition, they also studied the stability of NIPU with product A and B via the heat of formation (Fig. 1.25). It was determined by using the *ab initio* molecular orbitals calculations. The heat of formation of product B was lower (ΔH_f = -9.77 kcal/mol) than the product A (ΔH_f = -8.10 kcal/mol). This means the product B was higher stability than product A resulting to the predominant formation of product B than product A.

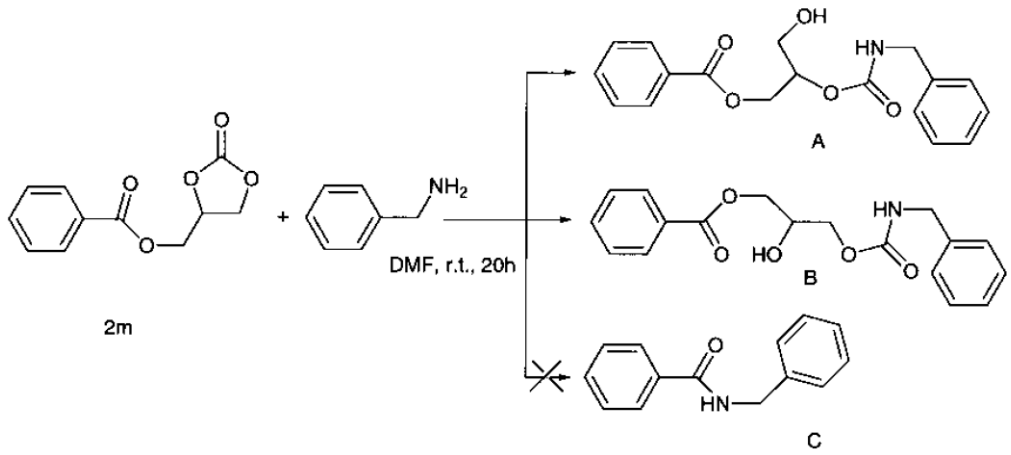


Fig. 1.24 Model reaction of hydroxyurethane from the reaction of monofunctionl cyclic carbonate and benzylamine (Steblyanko *et al*., 2000).

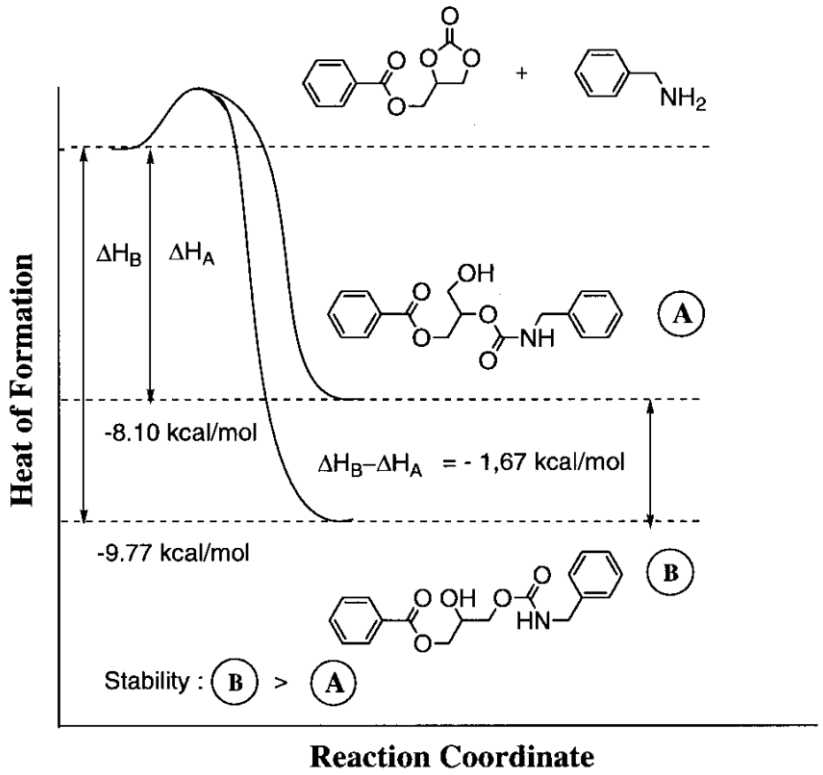


Fig. 1.25 The heat of formation values of NIPUs (Steblyanko *et al*., 2000).

Tomita *et al*. (2001b) proposed the model reaction from the reaction of five-membered cyclic carbonate and diamines corresponding NIPU with primary and

secondary hydroxyl groups as shown in Fig. 1.26. The ^{1}H-NMR showed that NIPU with the secondary hydroxyl groups were predominantly formed in the reaction.

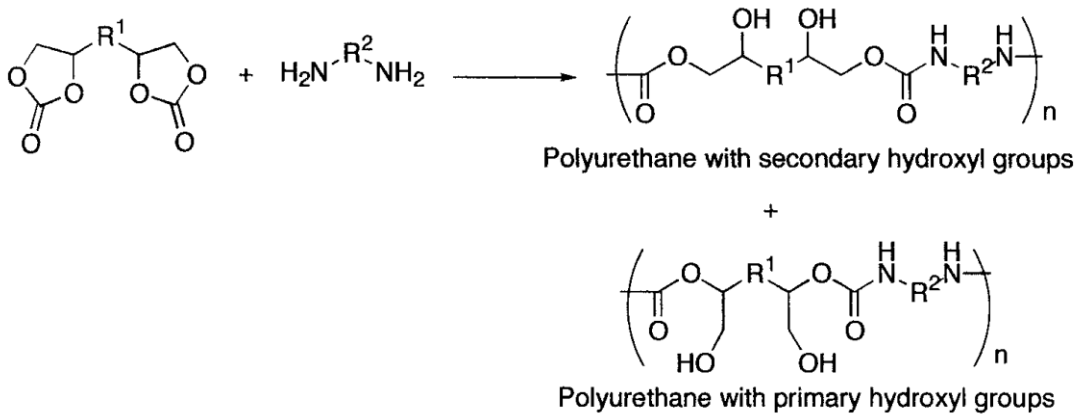


Fig. 1.26 Model reaction of NIPU from the reaction of five-member cyclic carbonate and diamine (Tomita *et al*., 2001b).

1.4.11 Reactivity of amine

The reactivity of amine depends on the chemical structure of amine. Normally, the primary amines are more reactive than the secondary amines. However, the less reactive secondary amine could react with cyclic carbonate to form NIPU (Camela *et al*., 2014). The chemical structure and molecular weight of amines have an influence on the reactivity. The reactivity was directly associated with the existence of bulky and/or strong electron withdrawing groups in α or β-position in respect to the reactive amino groups (Diakoumakos and Kotzev, 2004) (Fig. 1.27). The lower basicity and steric hindrance of benzyl group also influence on the reactivity of amine (Tomita *et al*., 2001c).

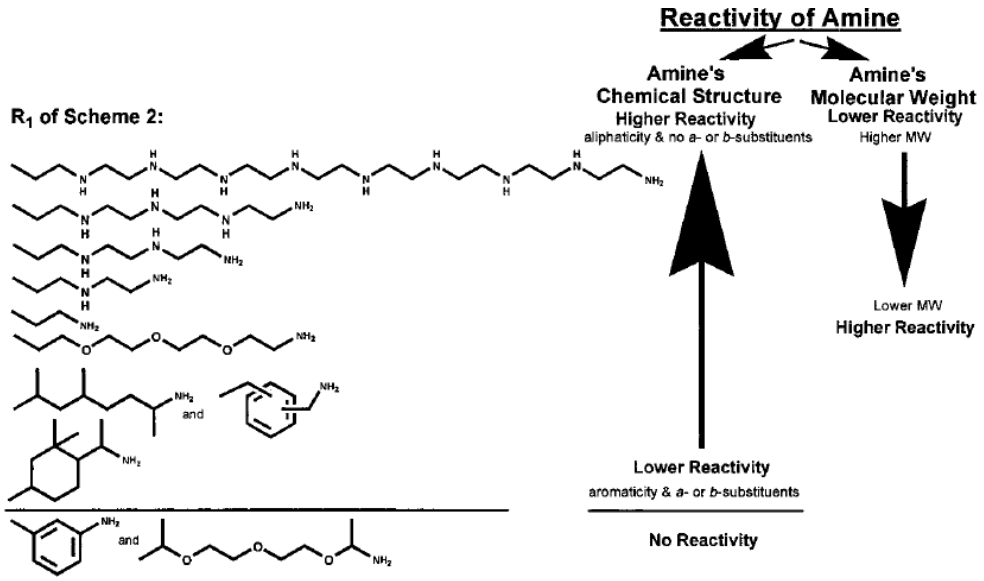


Fig. 1.27 The reactivity of various amines (Diakoumakos and Kotzev, 2004).

1.4.12 Catalysts for synthesis of NIPU

The organic catalysts, organometallic catalysts and salts using for the synthesis of NIPU are summarized in Fig. 1.28. The effect of various catalysts such as lithium bromide (LiBr), zinc chloride ($ZnCl_2$), potassium *tert*-butoxide (^tBuOK), lithium trifluoromethanesulfonate (LiOTf), scandium (III) triflate ($Sc(OTf)_3$), $Al(OTf)_3$, indium (III) trifluoromethane- sulfonate ($In(OTf)_3$) or dibutyltin dilaurate (DBTL) on the conversion was studied by Annunziata *et al*. (2014). Among this catalyst, LiBr was the most efficient one. It has reported the 45-80% of conversion was arose from the using of 5 mol% of LiBr. Lambeth and Henderson (2013) also revealed the organocatalysts increasing the reaction rate and molecular weight of NIPU.

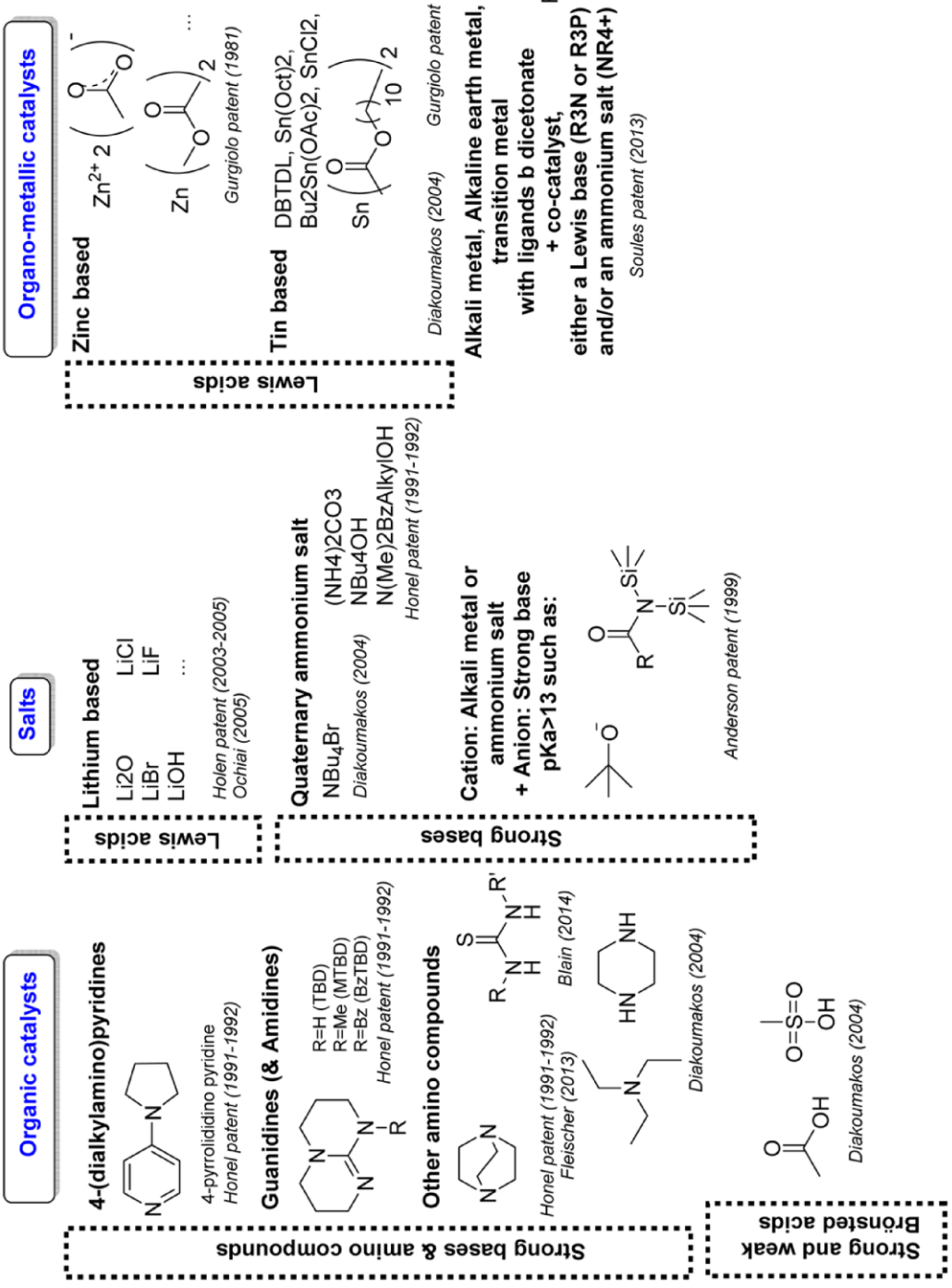


Fig. 1.28 Catalysts for synthesis of NIPU (Maisonneuve *et al*., 2015).

1.4.13 Linear and cross-linked NIPU

The linear or cross-linked NIPU depended on the functionality of cyclic carbonate and amine. Generally, the linear NIPU was synthesized by the reaction of dicyclic and diamine. Synthetic conditions and thermal properties of various linear NIPUs are summarized in Table 1.4. The cross-linked NIPU has been synthesized from the reaction between multifunctional cyclic carbonates and/ or polyamine. The multifunctional cyclic carbonates have been used such as trifunctional 5CC (Suzuki *et al*., 2004; Camara *et al*., 2014) and polyhedral oligomeric silsesquioxanes (POSS) cyclic carbonate (Blattmann and Mülhaupt, 2016).

Table 1.4 Synthetic methods and thermal properties of linear NIPUs

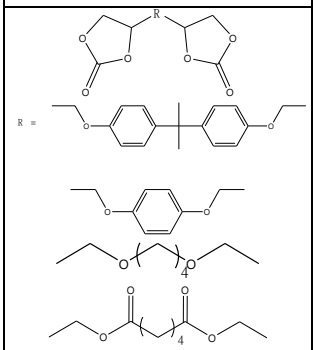
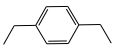
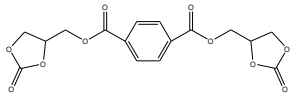
Cyclic carbonates	Amines	Conditions	Thermal properties (°C)	Authors
	$H_2N—R—NH_2$ R= $(CH_2)_6$, $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_{12}$ 	100°C, 24 h DMSO	-	Kihara and Endo, 1993
	$H_2N—R—NH_2$ R= $(CH_2)_2$, $(CH_2)_3$, $(CH_2)_5$, $(CH_2)_6$ 	RT, 20 h, DMF	T_g = 3-29 T_d = 177-277	Steblyanko *et al*., 2000

Table 1.4 Synthetic methods and thermal properties of linear NIPUs (cont.)

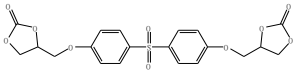
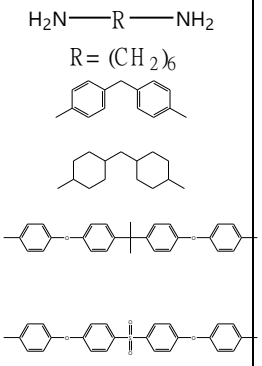
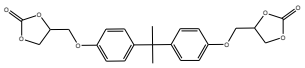
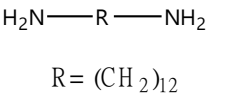
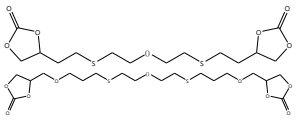
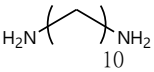
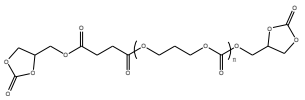
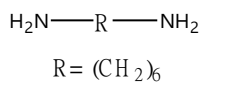
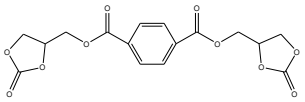
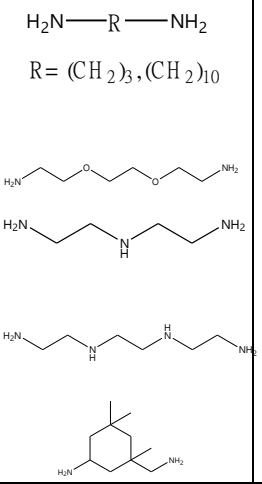
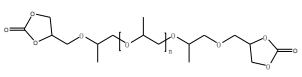
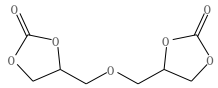
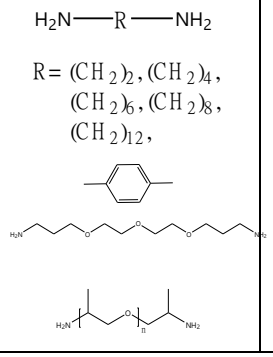
		100°C, 24 h DMSO	T_g = 50-102 T_d = 339-388	Kim *et al*., 2001
		70°C, 8 h	-	Ochiai *et al*., 2005
		75°C, 48 h DMF	T_d = 227-249	Benyahya *et al*., 2011
		70°C, 5 d	T_g = 6	Helou *et al*., 2011
		75°C, 48 h	T_g = 4-78 T_d = 177-277	Benyahya *et al*., 2012
	Jeffamine EDR 176	80°C, 72 h	-	Annunziata *et al*., 2014

Table 1.4 Synthetic methods and thermal properties of linear NIPUs (cont.)

		150°C, 8 h	T_g = -20-38 T_d = 260-335	Tryznowski *et al*., 2015

1.4.14 Bio-based NIPU

Recently, the renewable resources have been interested to prepare NIPU due to the environmental concerning. Some of renewable resources have been used for example, vegetable oils and tannin. Among the vegetable oils, soybean oil was the most ones that it was widely used. The molecules of triglycerides consist of three fatty acids and one glycerol (Fig. 1.29). The double bonds, allylic carbons and ester groups were the active sites that it was converted to another functional group (Khot *et al*., 2001) (Fig. 1.30). Soybean oil containing the carbonate chain ends (carbonated soybean oil, CSBO) was used as a starting material for the synthesis of bio-based NIPUs. The carbonated linseed oil (ELSO), cyclic carbonate cashew nut shell liquid (CC-CNSL) were also used. The bio-based NIPUs synthesizied from the vegetable oils are summarized in Table 1.5.

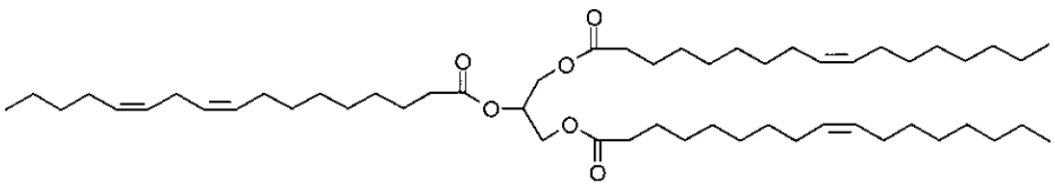


Fig. 1.29 Chemical structure of triglyceride (Khot *et al*., 2001)

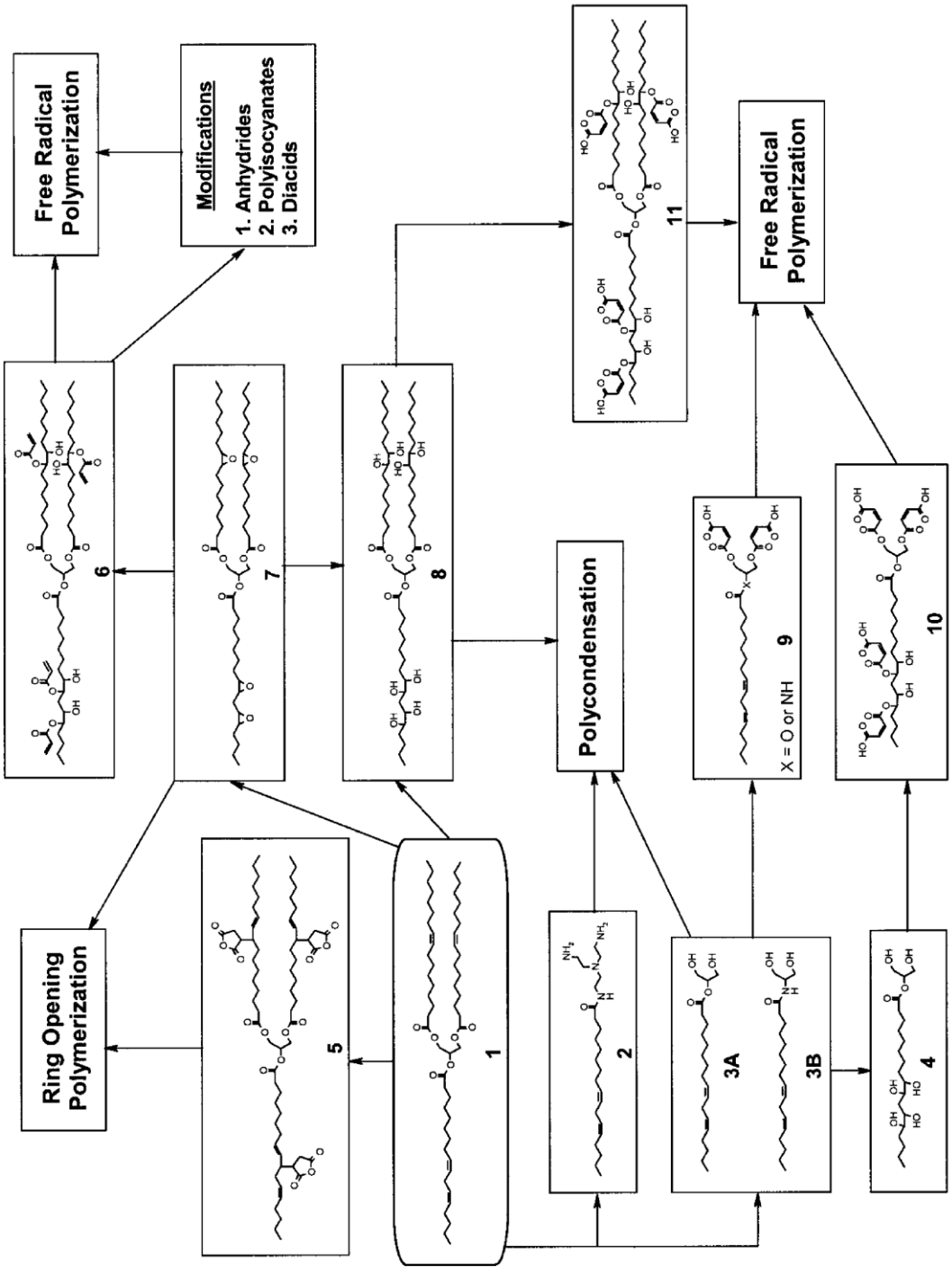


Fig. 1.30 Modification routes of soybean oil (Khot *et al*., 2001).

Table 1.5 Bio-based NIPUs synthesized from vegetable oils

Cyclic carbonates	Conditions	Thermal properties (°C)	Authors
CSBO	70°C, 10 h	$T_{g\ (DSC)}$ = 2.3-22.5 $T_{g\ (DMA)}$ = 8.5-40.1	Javni *et al*., 2008
CSBO	70°C, 10 h	$T_{g\ (DSC)}$ = -6.4-26.1 $T_{g\ (DMA)}$ = 16.3-46.1	Javni *et al*., 2012
CSBO, CLSO	70°C, 10 h	$T_{g\ (DMA)}$ = 17-60	Bähr and Mülhaupt, 2012
CC-CNSL	120 and 150°C 1 h	$T_{g\ (DSC)}$ = 30-35	Kathalewar *et al*., 2014
CSBO	LiCl, 70°C, 3 h	-	Lee and Deng, 2015
CSBO	120°C, 3 h	$T_{g\ (DMA)}$ = -14-18	Poussard *et al*., 2016

CHAPTER 2

Materials and Methods

2.1 Materials

1. Natural rubber (NR, STR5LCV60) was produced by Jana Concentrated Latex Co., Songkhla, Thailand.

2. Periodic acid (H_5IO_6, ≥99%) was purchased from Aldrich.

3. Ethane-1,2-diamine (EDA, ≥99%) was purchased from Aldrich.

4. Butane-1,2-diamine (BDA, 99%) was purchased from Aldrich.

5. *p*-Xylylenediamine (*p*-XDA, 99%) was purchased from Aldrich.

6. Tris(2-aminoethyl)amine (TAEA, 96%) was purchased from Aldrich.

7. 4-(Hydroxymethyl)-1,3-dioxolan-2-one (≥90%) or glycerol carbonate (GC) was purchased from TCI chemicals.

8. Succinic acid (SA, ≥99%) was purchased from Aldrich.

9. Terephthalic acid (TA, ≥97%) was purchased from Aldrich.

10. Succinic anhydride (SAH, ≥99%) was purchased from Aldrich.

11. Succinyl chloride (95%) was purchased from Acros organics.

12. Terephthaloyl chloride (≥99%) was purchased from Aldrich.

13. Acetic anhydride (AA, ≥99%) was purchased from Aldrich.

14. Triethylamine (Et_3N, ≥99%) was purchased from Aldrich.

15. *N*,*N*-dimethyl-4-aminopyridine (DMAP, ≥99%) was purchased from Aldrich.

16. *N*,*N*-dicyclohexylcarbodiimide (DCC, ≥99%) was purchased from Aldrich.

17. Sodium borohydride ($NaBH_4$, 98%) was purchased from Acros organics.

18. Sodium triacetoxyborohydride ($NaBH(OAc)_3$, 97%) was purchased from Aldrich.

19. Acetic acid (CH_3COOH, ≥99%) glacial was purchased from Aldrich.

20. Lithium bromide (LiBr) was purchased from Janssen Chimica.

21. Stannous octoate ($Sn(Oct)_2$, 95%) was purchased from Aldrich.

22. L(+)-lactic acid (LLA), 90% solution in water was purchased from Acros organics.

23. Benzophenone (99%) was purchased from Aldrich.

24. Sodium (Na) metal stored under mineral oil.

25. Calcium hydride (CaH_2) was purchased from Aldrich.

26. Calcium oxide (CaO) was purchased from Aldrich. It was used as a drying agent for amine.

27. Potassium hydroxide (KOH) was purchased from Aldrich.

28. Hydrochloric acid (HCl, 37%) was purchased from Aldrich.

29. Sodium hydroxide (NaOH) was purchased from Aldrich.

30. Sodium bicarbonate ($NaHCO_3$) was purchased from Fisher Scientific.

31. Sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) was purchased from Fisher Scientific.

32. Sodium carbonate (Na_2CO_3) was purchased from Fisher Scientific.

33. Sodium chloride (NaCl) was purchased from Fisher Scientific.

34. Anhydrous magnesium sulfate ($MgSO_4$) was purchased from Fisher Scientific.

35. Potassium permanganate ($KMnO_4$)

36. Potassium carbonate (K_2CO_3) was purchased from Aldrich.

37. Silica gel (Kieselgel 60, 230–400 mesh) was purchased from Merck.

38. *n*-Hexane (97%) was purchased from Aldrich.

39. Dimethyl sulfoxide (DMSO, ≥99%) was purchased from Aldrich.

40. Ethyl acetate (EtOAc, 99.8%) was purchased from Aldrich.

41. Methanol (MeOH) was a technical grade.

42. Cyclohexane was purchased from Aldrich.

43. Diethyl ether (Et_2O) was a technical grade.

44. Petroleum ether was a technical grade. It was used as a solvent.

45. Dioxane (≥99%) was purchased from Aldrich.

46. Dichloromethane (DCM) was purchased from Aldrich.

47. Tetrahydrofuran (THF) was purchased from Aldrich.

48. Chloroform-*d* ($CDCl_3$) was purchased from Aldrich.

49. Dimethyl sulfoxide-d_6 (DMSO-d_6) was purchased from Aldrich.

50. 4 Å molecular sieves were purchased from Aldrich. It was activated at 250°C for 2 h before using.

2.1.1 Purification methods

The chemicals were purified before using as a following description. The other chemicals were used without purification.

EDA (200 mL) was dried over activated 4 Å molecular sieves (70 g) for overnight under argon atmosphere and continuous stirring. Then it was filtered and dried over with a mixture of CaO (10 g) and KOH (3 g) under an argon atmosphere and continuous stirring. Before distillation, it was filtered to remove CaO and KOH. Finally, it was distilled under argon (Fig. 2.1). The distilled EDA was stored with 4 Å molecular sieves under argon atmosphere.

TAEA was dried over activated 4 Å molecular sieves for overnight under argon atmosphere and continuous stirring. Then it was filtered before distillation under reflux and argon atmosphere. The distilled TAEA was stored under argon atmosphere.

DMSO was dried over in the small amount of CaH_2 with continuous stirring under reflux for 1 h. The distillation was performed under vacuum ($P \approx 200$ mbar) (Fig. 2.2). The distilled DMSO was stored under argon atmosphere.

Dioxane was distilled using Na metal and benzophenone. The distillation was performed under argon atmosphere (Fig. 2.3). The distilled dioxane was stored in the 4 Å molecular sieves under argon atmosphere.

Fig. 2.1 Distillation apparatus of EDA.

Fig. 2.2 Distillation apparatus of DMSO.

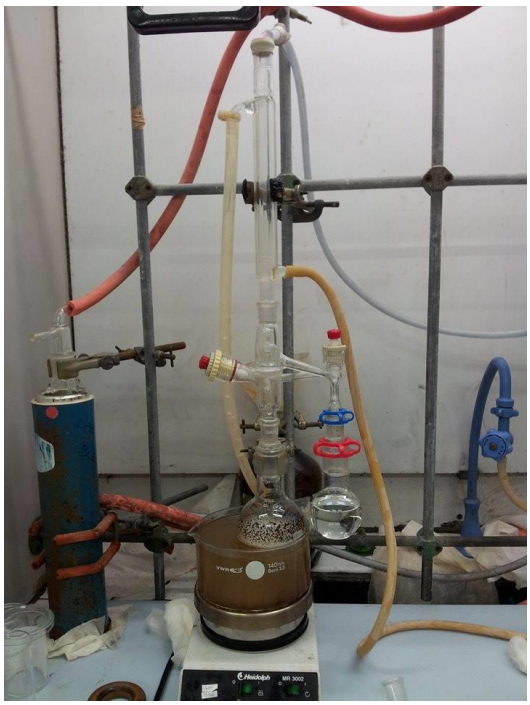


Fig. 2.3 Distillation apparatus of dioxane.

2.2 Instruments

1. Nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR, 200 MHz and 400 MHz), Bruker®

2. Fourier transform infrared spectroscopy (FTIR), Nicolet® 6700.

3. Size exclusion chromatography (SEC), SpectraSYSTEM® AS 1000 autosampler

4. High-resolution mass spectrometry (HRMS), Bruker® MicroTof-Q-III

5. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, Bruker® UltraFlex II

6. Differential scanning calorimetry (DSC), Perkin Elmer® DSC8500

7. Thermogravimetric analysis (TGA), Perkin Elmer® STA8000

8. Dynamic mechanical thermal (DMTA) analysis, Rheometric Scientific® DMTA V

9. Contact angle measurement, OCA® 15EC

2.3 Methods

2.3.1 Synthesis of oligoisoprenes

Two oligoisoprenes containing amino chain end (amino telechelic natural rubber ATNR) and cyclic carbonate chain end (cyclic carbonate telechelic natural rubber, CCTNR) were described in this part. The targeted chain lengths as referred to number-average molecular weight ($\overline{M}_n$) of both ATNR and CCTNR were 1000 and 2000 g/mol.

2.3.1.1 Synthesis of carbonyl telechelic natural rubber (CTNR)

CTNR was synthesized according to previous work (Sadaka *et al*., 2012). 44.50 g (0.65 mol) of NR were dissolved in 1090 mL of THF (0.6 M) in a reactor for overnight (Fig. 2.4). The H_5IO_6 (3.2 eq., 16.39 g, 0.07 mol) was dissolved in 180 mL of THF (0.4 M) and added dropwise in the reactor using a dropping funnel. The solution was stirred at 30ºC for 6 h. The organic solution was filtered and washed with saturated aqueous solutions of 70% in volume of $NaHCO_3$ (770 mL) and 30% in volume of NaCl (330 mL). Then it was washed again with the solutions of 50% in volume of $Na_2S_2O_3$ (20% w/v) (550 mL) and 50% in volume of NaCl (550 mL). Finally, the organic phase was dried over $MgSO_4$ for 1 h, and after filtration the organic solution was evaporated in a rotary evaporator and dried in a vacuum oven until a constant weight was obtained.

Fig. 2.4 Synthesis apparatus of CTNR.

2.3.1.2 Synthesis of amino telechelic natural rubber (ATNR)

Distilled EDA (15 eq., 4.33 g, 0.07 mol) was dissolved in 20 mL of dry DCM (3.59 M). A 0.03 M solution of CTNR (9.94 g, $\overline{M}_{n,\ NMR}$ = 2070 g/mol, 4.80 mmol) in 150 mL (0.032 M) of dry DCM was added dropwise to the reaction mixture, and then $NaBH(OAc)_3$ (10 eq., 10.17 g, 0.05 mol) and 0.27 mL (1 eq., 0.29 g, 4.80 mmol) of glacial CH_3COOH were dropped successively. The reaction mixture was stirred 6 at 30°C for 24 h under argon atmosphere. The organic solution was then washed with 1 N NaOH aqueous solution (150 mL) and the aqueous solution was extracted once with Et_2O (150 mL). The combination of organic layer was dried over $MgSO_4$ for 1 h and processed similarly to the method used for CTNR.

2.3.1.3 Synthesis of hydroxy telechelic natural rubber (HTNR)

HTNR was synthesized according to previous work (Kébir *et al*., 2005). CTNR (10.35 g, $\overline{M}_{n,\ NMR}$ = 2070 g/mol, 4.99 mmol) was dissolved in 160 mL (0.03 M) of dry THF and $NaBH_4$ (6 eq., 1.13 g, 0.03 mol) was added in the reactor. The reaction was carried out at 60ºC for 6 h under argon atmosphere with continuous stirring and, then, hydrolyzed with ice (50 g). The mixture was evaporated to remove THF. Then the oligomer was dissolved in 160 mL of DCM and washed with an aqueous NaCl saturated solution (140 mL). The final organic phase was dried over $MgSO_4$ for 1 h and processed similarly to the method used for CTNR.

2.3.1.4 Synthesis of carboxylic telechelic natural rubber (CBTNR)

HTNR (4.23 g, $\overline{M}_{n,\ NMR}$ = 2130 g/mol, 1.98 mmol) was dissolved in 40 mL of dry DCM (0.05 M). DMAP (2 eq., 0.48 g, 3.96 mmol), Et_3N (2 eq., 0.55 ml, 3.96 mmol) and succinic anhydride (3 eq., 0.59 g, 5.94 mmol) were added to the reaction mixture. The reaction was stirred at 25ºC for 24 h under argon atmosphere. The solution was washed thrice with 2 N HCl solution (3*40 mL), twice with distilled water (2*40 mL) and NaCl saturated solution (35 mL). The final organic phase was dried over $MgSO_4$ for 1 h and processed similarly to the method used for CTNR.

2.3.1.5 Synthesis of cyclic carbonate telechelic natural rubber (CCTNR)

CBTNR (2.58 g, $\overline{M}_{n,\,NMR}$ = 2200 g/mol 1.17 mmol) was dissolved in 24 mL of dry DCM (0.05 M). Glycerol carbonate (GC) (3 eq., 0.46 g, 3.52 mmol), DMAP (1.5 eq., 0.22 g, 1.76 mmol) and DCC (3 eq., 0.73 g, 3.52 mmol) were added in the reactor. The mixture was stirred at 25ºC for 24 h under argon atmosphere. The suspension was filtered to remove dicyclohexylurea (DCU). The organic solution was washed successively with 2 N HCl solution (2*20 mL), distilled water (2*20 mL) and NaCl saturated solution (20 mL) then dried over $MgSO_4$ for 1 h and further process was done as performed in CTNR. The crude product was further purification by column chromatography as a following procedure (Fig. 2.5)

1. The cotton and sand were packing in the column. Then the 29 g of slurry (silica gel) in DCM was gradually loading.

2. The sample (1.96 g) was dissolved in DCM before loading into a column. The DCM, EtOAc and MeOH were used as the eluent. The polarity of solvent was gradually increase (DCM, DCM:EtOAc; 1:0.5, 1:1, EtOAc, EtOAc+10% MeOH). The same oligomer solution fraction was combined and evaporated to remove the solvent. Finally, the oligomer was dried in a vacuum oven until a constant weight was obtained.

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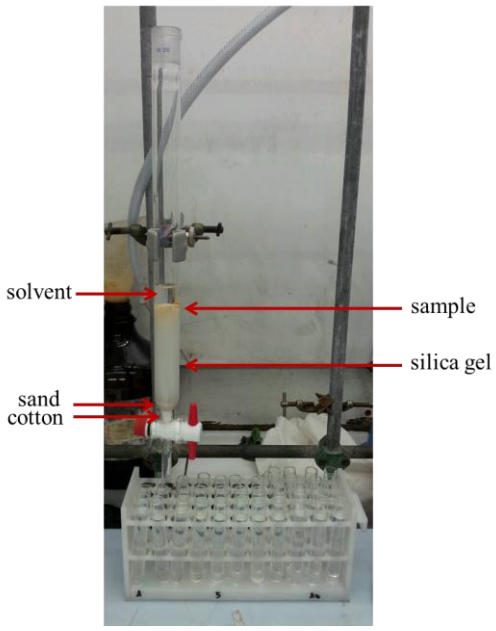

Fig. 2.5 Purification of CCTNR by column chromatography.

2.3.2 Synthesis of aromatic and aliphatic dicyclic carbonates

The synthesis route of aromatic dicyclic carbonate (dicyclic carbonate#1 and aliphatic dicylclic carbonate (dicyclic carbonate#2) were described.

2.3.2.1 Synthesis of 4-methylterephthalate-1,3-dioxolan-2-one (dicyclic carbonate #1)

Two methods have been carried out for the synthesis of aromatic dicyclic carbonates (dicyclic carbonate #1).

I. Synthesis of dicyclic carbonate#1 from terephthalic acid (TA)

TA (3.17 g, 0.02 mol) was dissolved in 90 mL of dry DCM (0.22 M) before adding GC (3 eq., 6.73 g, 0.06 mol) and DMAP (0.5 eq., 1.16 g, 0.01 mol). DCC (3 eq., 11.76 g, 0.06 mol) in 20 mL of dry DCM (3.0 M) was added dropwise successively at 0°C for 1 h. The reaction was performed at 25°C for 24 h under argon atmosphere. The reaction mixture was filtered through a filter paper to remove DCU as a by-product. The reaction mixture was washed twice with 2 N HCl solution (2*100 mL), twice with Na_2CO_3 saturated solution (2*100 mL). The reaction mixture was dried over $MgSO_4$, filtered and evaporated to remove the solvent. The crude product was further purification by column chromatography on siliga gel (EtOAc/cyclohexane: 1:1) as described in 2.3.1.5.

II. Synthesis of dicyclic carbonate#1 from terephthaloyl chloride

At 0°C, Et_3N (2 eq., 6.12 g, 0.06 mol) was added to a solution of GC (2 eq., 7.90 g, 0.06 mol) which dissolved in 54 mL of dry DCM (1.11 M), and terephthaloyl chloride (1 eq., 6.12 g, 0.03 mol) in 9 mL of dry DCM (3.19 M) was added dropwise successively. The reaction mixture was refluxed for 3 h under argon atmosphere then was washed with distilled water (50 mL) and $NaHCO_3$ saturated solution (50 mL). The reaction mixture was dried over $MgSO_4$ and filtered. The solvent was removed by using as evaporator. The crude product was purified by recrystallization technique as a following procedure.

The crude product was dissolved in a minimum volume of hot EtOAc. Then the small volume of petroleum ether was added and the mixture was slowly cool

to crystallize in ice bath. Finally, the purified product was separated by vacuum filtration and was rinsed with small volume of cold petroleum ether. It was dried in a vacuum oven until a constant weight was obtained.

2.3.2.2 Synthesis of 4-methylsuccinate-1,3-dioxolan-2-one (dicyclic carbonate #2)

Two methods have been tested for the synthesis of aliphatic dicyclic carbonates (dicyclic carbonate #2).

I. Synthesis of dicyclic carbonate #2 from succinic acid (SA)

SA (3.14 g, 0.03 mol) was dissolved in 90 mL of dry DCM (0.33 M) before adding the GC (3 eq., 10.63 g, 0.08 mol) and DMAP (0.5 eq., 1.65 g, 0.01 mol). The DCC (3 eq., 16.71 g, 0.08 mol) in 25 mL of dry DCM (3.2 M) was added dropwise successively at 0°C for 1 h. The reaction was performed at 25°C for 24 h under argon atmosphere. The reaction mixture was filtered through a filter paper to remove DCU as a by-product. The reaction mixture was washed twice with 2 N HCl solution (2*100 mL), twice with Na_2CO_3 saturated solution (2*100 mL). The reaction mixture was dried over $MgSO_4$, filtered and evaporated to remove the solvent. The crude product was further purification by column chromatography on siliga gel (EtOAc/cyclohexane: 1:1) as described in 2.3.1.5.

II. Synthesis of dicyclic carbonate #2 from succinyl chloride

Succinyl chloride (1 eq., 1.40 g, 9.03 mmol) was dissolved in 7.5 mL of dry DCM (1.20 M) before adding glycerol carbonate (2.1 eq., 2.25 g, 0.02 mol). The reaction mixture was refluxed for 6 h under argon atmosphere. Then the reaction mixture was washed with a 1 M NaOH solution (6 mL). The crude product was obtained by filtration and the residual glycerol carbonate was removed by dissolving it in ethyl acetate. The insoluble fraction was filtered and dried under vacuum until a constant weight was obtained.

2.3.3 Synthesis of oligo(lactic acid)

Carboxylic telechelic PLA (CBPLA) and cyclic carbonate telechelic PLA (CCPLA) were an oligo(lactic acid) which it was synthesized from LA.

2.3.3.1 Synthesis of carboxylic telechelic PLA (CBPLA)

Synthesis was performed in a two-necked round bottom flask that is connected to a vacuum system via a liquid nitrogen trap as shown in Fig. 2.6. LLA (46.42 g) was heated at 110°C for 2 h before adding the $Sn(Oct)_2$ (0.5 wt%, 0.23 g, 0.20 mL). Water in LLA was removed under vacuum before prepolymerization. The prepolymerization reaction was performed at 180°C for 4 h to obtain the LLA prepolymer. The SA (5 wt%, 2.32 g) was added and reaction time was 88 h. The crude product was cool down and dissolved in the small volume of DCM before precipitating in cold hexane. The product was dried in a vacuum oven until the constant weight was obtained.

Fig. 2.6 Synthesis apparatus of CBPLA.

2.3.3.2 Synthesis of cyclic carbonate telechelic PLA (CCPLA)

CBPLA (6.30 g, $\overline{M}_{n,\,NMR}$ = 1840 g/mol, 3.42 mmol) was dissolved in 82 mL (0.042 M) of dry DCM before adding GC (5 eq., 2.02 g, 1.60 mL) and DMAP

(1.5 eq., 0.63 g, 0.01 mol). At 0°C, DCC (5 eq., 3.53 g, 0.02 mol) in 10 mL of dry DCM (1.71 M) was added dropwise successively and maintained the reaction at 0°C for 1 h. The reaction was performed at 25°C for 24 h under argon atmosphere. The reaction mixture was filtered through a filter paper to remove DCU as a by-product. The reaction mixture was washed twice with 2 N HCl solution (2*80 mL), twice with Na_2CO_3 saturated solution (2*80 mL). The reaction mixture was dried over $MgSO_4$, filtered and evaporated to remove the solvent. The crude product was further purification by column chromatography on siliga gel (EtOAc/ DCM: 0.1:1) as described in 2.3.1.5.

2.3.4 Synthesis of NIPU

Two types of NIPU were synthesized from NR and PLA. The first type was the NIPU from NR. Amino telechelic natural rubber (ATNR) and cyclic carbonate telechelic natural rubber (CCTNR) were used as a starting material for synthesis of NIPU#1 and NIPU#2, respectively. For the second type of NIPU, cyclic carbonate telechelic poly(lactic acid) (CCPLA) was used for synthesis of NIPU#3.

2.3.4.1 Synthesis of NIPU#1

NIPU#1 was synthesized in both solution (NIPU#1-1 – NIPU#1-8) and bulk reaction (NIPU#1-9 – NIPU#1-14).

For solution reaction, dicyclic carbonate#1 (8.40 mg, 0.02 mmol) was dissolved in 0.05 mL of dry dioxane (0.46 M) and ATNR1000 (2 eq., 0.05 g, 0.05 mmol) in 0.73 mL of dry dioxane (0.06 M) was added dropwise. The reaction was carried out at 100ºC for 22 h under argon atmosphere then the solvent was evaporated (NIPU#1-4). The same procedure was used to prepared both of NIPU in the absence of catalyst (NIPU#1-1 – NIPU#1-3) and presence of catalyst (NIPU#1-5 – NIPU#1-8). The other two parameters including the molecular weight of ATNR (ATNR1000 and ATNR2000) and the molar ratio of carbonate to amine (1:1 and 1:2) were studied. The reaction condition for synthesis of NIPU#1 in solution reaction are summarized in Table 2.1.

For bulk reaction, dicyclic carbonate#1 (0.20 g, 0.54 mmol) in 1.20 mL of dry dioxane (0.46 M) and ATNR1000 (1.5 eq., 0.78 g, 0.81 mmol) in 3.0 mL of dry

dioxane (0.22 M) were mixed together before pouring into a mold. The reaction was carried out at 70ºC in a vacuum oven with a pressure in the range of 1 - 10 mmHg to form the NIPU#1-10. The similar procedure was used for the preparation of NIPU#1-9 and NIPU#1-11– NIPU#1-14. All samples were characterized without purification. The reaction conditions for synthesis of NIPU#1 are summarized in Table 2.2.

Table 2.1 Reaction conditions for synthesis of NIPU#1 in solution reaction at 100ºC

Sample	Amine	C:A[a]	Catalyst
NIPU#1-1	ATNR2000	1:1	-
NIPU#1-2	ATNR2000	1:2	-
NIPU#1-3	ATNR1000	1:1	-
NIPU#1-4	ATNR1000	1:2	-
NIPU#1-5	ATNR2000	1:1	LiBr
NIPU#1-6	ATNR2000	1:2	LiBr
NIPU#1-7	ATNR1000	1:1	LiBr
NIPU#1-8	ATNR1000	1:2	LiBr

[a]Molar ratio of carbonate to amine.

Table 2.2 Reaction conditions for synthesis of NIPU#1 in bulk reaction at 70ºC

Sample	Dicyclic carbonate	Amine	C:A[a]	Time (h)
NIPU#1-9	#1	ATNR1000	1:1.2	100
NIPU#1-10	#1	ATNR1000	1:1.5	48
NIPU#1-11	#1	ATNR2000	1:1.5	100
NIPU#1-12	#2	ATNR1000	1:1.5	55
NIPU#1-13	#2	ATNR1000	1:2	50
NIPU#1-14	#2	ATNR2000	1:2	55

[a]Molar ratio of carbonate to amine.

2.3.4.2 Synthesis of NIPU#2

Linear and cross-linked NIPU#2 were performed only in the bulk reaction (Table 2.3). For linear NIPU#2, CCTNR1000 (0.23 g, 0.17 mmol) in 0.08 M of dry dioxane and EDA (1.5 eq., 0.02 g, 0.26 mmol) were mixed together before

pouring into a mold. The reaction was carried out at 70ºC for 2 h in a vacuum oven. The pressure was applied in the range of 1 - 10 mmHg to form NIPU#2-1. The NIPU#2-2 – NIPU#2-6 were similarly prepared. All samples were characterized without further purification.

The cross-linked NIPU#2 was obtained by using TAEA. 0.75 g (0.52 mmol) of CCTNR1000 in 1.90 mL of dry dioxane (0.27 M) and distilled TAEA (0.7 eq., 0.05 g, 0.36 mmol) were mixed together before pouring into a mold. The reaction was carried out at 70°C for 1 h in a vacuum oven at the pressure range of 1-10 mmHg. The obtained NIPU#2-7 was characterized without further purification. NIPU#2-8 was synthesized under the same procedure and used CCTNR2000.

Table 2.3 Reaction conditions for synthesis of NIPU#2 at 70ºC

NIPU	Amine	Cyclic carbonate	C:A[a]	Time (h)
NIPU#2-1	EDA	CCTNR1000	1:1.5	2
NIPU#2-2	EDA	CCTNR2000	1:1.5	2
NIPU#2-3	BDA	CCTNR1000	1:1.5	2
NIPU#2-4	BDA	CCTNR2000	1:1.5	2
NIPU#2-5	*p*-XDA	CCTNR1000	1:1.5	2
NIPU#2-6	*p*-XDA	CCTNR2000	1:1.5	2
NIPU#2-7	TAEA	CCTNR1000	1:0.7	1
NIPU#2-8	TAEA	CCTNR2000	1:0.7	1

[a]Molar ratio of carbonate to amine.

2.3.4.3 Synthesis of NIPU#3

All NIPU#3 (NIPU#3-1 and NIPU#3-6) were carried out in bulk reaction (Table 2.4). CCPLA1000 (0.08 g, 0.06 mmol) in 0.08 mL of dry dioxane (0.075 M) and BDA (3 eq., 0.02 g, 0.02 mmol) were mixed together before pouring into a mold. The reaction was carried out at 70°C for 24 h in a vacuum oven at the pressure ranging from 1-10 mmHg to form NIPU#3-3. The procedure was similar in NIPU#3-1 - NIPU#3-2 and NIPU#3-4 - NIPU#3-6. All the samples were characterized without further purification.

Table 2.4 Reaction conditions for synthesis of NIPU#3 at 70°C

Sample	Amine	Cyclic carbonate	C:A[a]
NIPU#3-1	EDA	CCPLA1000	1:2.2
NIPU#3-2	EDA	CCPLA2000	1:5.2
NIPU#3-3	BDA	CCPLA1000	1:3
NIPU#3-4	BDA	CCPLA2000	1:3
NIPU#3-5	*p*-XDA	CCPLA1000	1:3
NIPU#3-6	*p*-XDA	CCPLA2000	1:3

[a]Molar ratio of carbonate to amine.

2.3.5 NMR spectroscopy analysis

For one dimensional NMR spectroscopy (1D-NMR), 5-10 mg (400 MHz) and >10 mg (200 MHz) of samples were dissolved in $CDCl_3$ and DMSO-d_6 for ^{1}H-NMR and ^{13}C-NMR, respectively. For two dimensional NMR spectroscopy (2D-NMR), 60-90 mg of samples were dissolved in $CDCl_3$ and DMSO-d_6 for COSY, HSQC and HMBC, respectively.

2.3.6 FTIR spectroscopy analysis

A small amount of sample was placed on the attenuated total reflectance (ATR) crystal. The absorption bands were reported in the range of 600 – 4000 cm^{-1} with 16 scans and a resolution of 4 cm^{-1}.

2.3.7 Molecular weight analysis by SEC

10 mg of sample was dissolved in 2 mL of THF. The number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$) and dispersity (Đ) were measured on a SpectraSYSTEM® AS 1000 autosampler and a guard column (polymer laboratories, PL gel 5 lm Guard 50 X 7.5 mm) connecting to a polymer laboratories (PL) gel 5 mm MIXED-D columns at 35°C. The SpectraSYSTEM® UV2000 and SpectraSYSTEM® RI150 were used as a detector and calibrated with polystyrene standards containing molecular weight in the range from 580 g/mol to 483000 g/mol. The measurement was performed at the flow rate of 1 mL/min. The

molecular weights of oligisoprenes were corrected according to Benoit factor equal to 0.67 (Busnel, 1982).

2.3.8 Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry analysis

Matrix (dithranol in the dichloromethane) were mixed with sample (10 mg/mL) and the cationizing agent (silver trifluoroacetate, AgTFA) in the ratio of sample/matrix/salt: 5/25/1. The investigation was performed with a nitrogen laser operating a 337 nm, pulsed ion extraction source and reflection. Spectra were recorded in the reflection mode and a delay of 10 ns. A thousand single shot aquisitions were summed to give the spectra and the data were analyzed using Bruker® FlexAnalysis and Polytools softwares.

2.3.9 High-resolution mass spectra (HRMS) analysis

The investigation was performed under nitrogen atmosphere. The spectra were recorded in the range scan of 50 m/z to 1000 m/z. The source type was electrospray ionization (ESI) with the positive ion polarity.

2.3.10 Differential scanning calorimetry (DSC) analysis

5-10 mg of sample was carried out under nitrogen atmosphere. The first heating scan was from -80ºC to 250ºC at the heating rate of 10ºC/min under argon atmosphere; then the sample was cooled to -80ºC at the rate of -10ºC/min and heated again similarly to the first heating scan.

2.3.11 Thermogravimetric analysis (TGA)

5-10 mg of sample was performed under nitrogen atmosphere at a heating from 25ºC to 1000ºC at a heating rate of 10ºC/min.

2.3.12 Dynamic mechanical thermal (DMTA) analysis

The sample (12 mm x 35 mm) was investigated on a Rheometric Scientific® DMTA V under the following test condition: frequency of 1 Hz, strain

control of 0.01 % and ramp rate of 3°C/ min at the temperature from -100°C to -200°C.

2.3.13 Wettability analysis

The contact angle was determined using OCA® 15EC. The sessile method was used at the room temperature (28°C). The 3 μL of distilled water was 3 applied using a syringe. The data was evaluated using SCA software. The measurement was applied at three positions in each sample and the average contact angle value was reported.

CHAPTER 3

Results and Discussion

The results were divided into 4 main parts. The first part was described the synthesis and characterization of oligoisoprenes from NR. The second part was described the synthesis and characterization of aromatic and aliphatic dicyclic carbonates. The third part was described the synthesis and characterization of oligo(lactic acid) from lactic acid. The fourth part was described the synthesis and characterization of all NIPUs: NIPU#1, NIPU#2 and NIPU#3.

3.1 Synthesis of oligoisoprenes

Two new oligoisoprenes consisting of amino chain ends (ATNR) and cyclic carbonate chain ends (CCTNR) from carbonyl telechelic natural rubber (CTNR) are represented in Fig. 3.1. The first step was the controlled oxidative degradation of NR in order to obtain the carbonyl telechelic natural rubber (CTNR) containing aldehyde and ketone ends with the targeted chain lengths ($\overline{M}_n$) of 1000 and 2000 g/mol. This reaction was already described (Sadaka *et al*., 2012). CTNR was converted to be ATNR by a reductive amination reaction. The ^{1}H-NMR showed the disappearance of characteristic peaks at 9.77 and 2.13 ppm corresponding to the aldehydic and ketonic protons of CTNR, respectively. The new peaks were appeared at 2.57 to 2.85 ppm corresponding to the protons adjacent to amine group (NH_2) (Fig. 3.2). The FTIR spectrum showed the disappearance of the absorption band at 1721 cm^{-1} corresponding to the stretching vibration of C=O, whereas the new absorption bands were observed at 3290 and 1556 cm^{-1} assigned to NH stretching and NH bending vibrations of amine groups, respectively. (Fig. 3.3).

The cyclic carbonate telechelic natural rubber (CCTNR) was also synthesized from CTNR. The first step was the reduction of CTNR with $NaBH_4$ to obtain the oligomer containing the alcohol chain ends (hydroxy telechelic natural rubber, HTNR) (Kébir *et al*., 2005). Then HTNR was reacted with succinic anhydride in the presence of 4-(*N*,*N*-dimethylamino) pyridine (DMAP) and triethylamine (Et_3N)

to form the carboxylic ends (carboxylic telechelic natural rubber, CBTNR). The ^{1}H-NMR spectrum showed the disappearance of the peak at 3.80 and 3.65 ppm corresponding to the CH and CH_2 protons located in the α-positions of the alcohol functions, respectively. The new significant peaks at 4.92 and 4.07 ppm were assigned to the CH and CH_2 protons located in the α-positions of the oxygen (ester), respectively. In addition, the methylene protons adjacent to the carboxylic end group appeared at 2.71-2.56 ppm (Fig. 3.2). The formation of carboxylic chain ends was verified by the presence of strong absorption bands at 1737 and 1714 cm^{-1} corresponding to the C=O from ester and carboxylic groups, respectively (Fig. 3.3-3.6). Finally, the CBTNR was reacted with glycerol carbonate in Steglish conditions (dicyclohexylcarbodiimide in presence of DMAP) to produce the cyclic carbonate telechelic natural rubber (CCTNR). At the end of reaction, the dicyclohexylurea (DCU) as a by-product still presented in the sample (see more information in APPENDIX A). A normal filtration and washing process were unable to remove DCU from CCTNR. It was found that column chromatography was a very useful method for purification and giving a good yield. The new characteristic peaks of carbonate moiety were observed at 4.96-4.89, 4.55 and 4.33 ppm whereas protons at α-position of ester and methylene protons were maintained at 4.92, 4.07 and 2.72-2.58 ppm, respectively (Fig. 3.2). COSY-NMR, HSQC-NMR and HMBC-NMR spectra of CCTNR are represent in Fig 3.7-3.9, respectively. The strong absorption band of C=O stretching from carbonate was observed at 1800 cm^{-1}. (Fig. 3.3). This observation proved that the CCTNR was functionalized with cyclic carbonated chain ends. The ^{1}H-NMR chemical shifts of their oligoisoprenes are listed in Table 3.1-3.5. All oligoisoprenes were a yellowish viscous liquid except ATNR that it was a reddish viscous liquid.

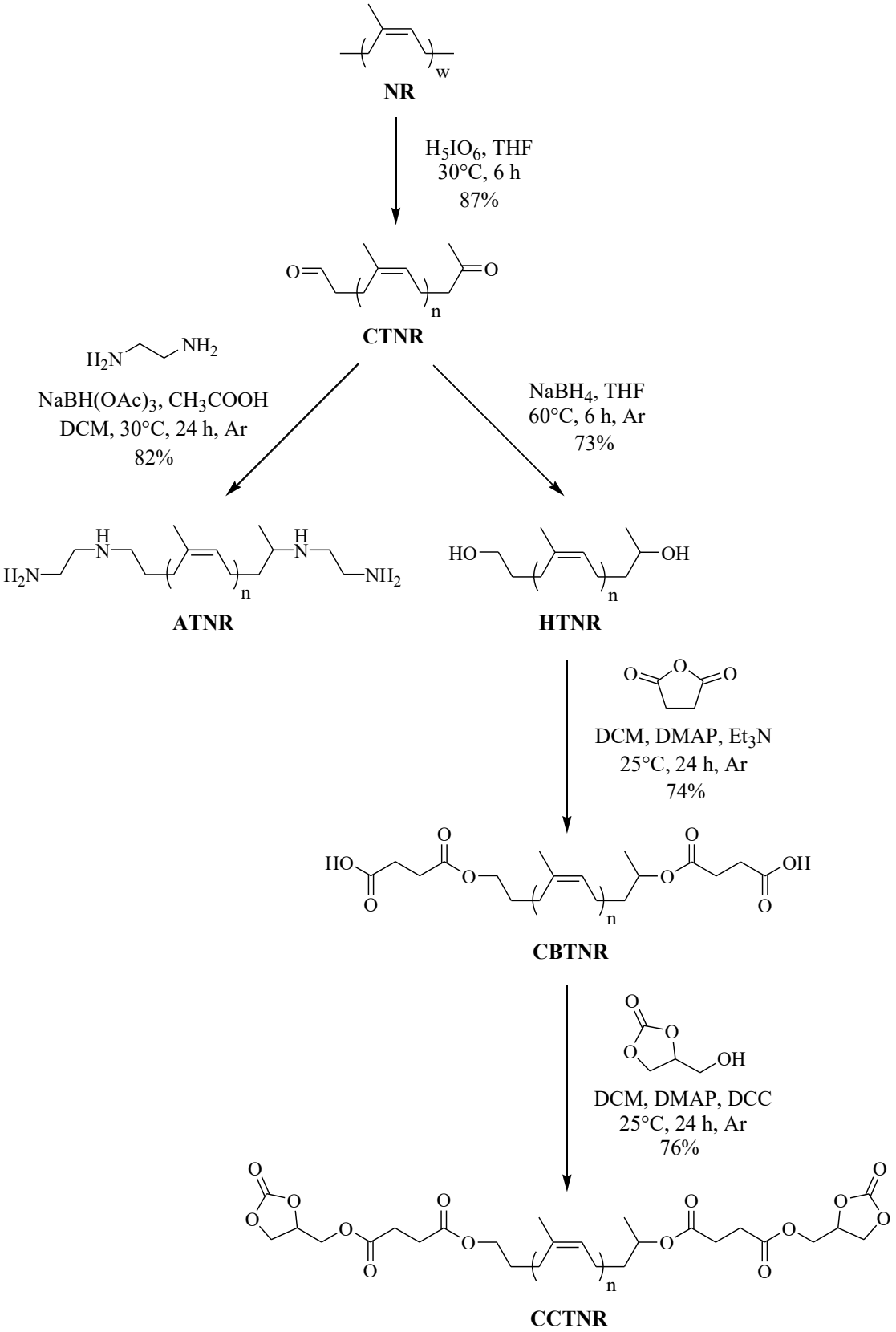

Fig. 3.1 Synthesis routes of oligoisoprenes.

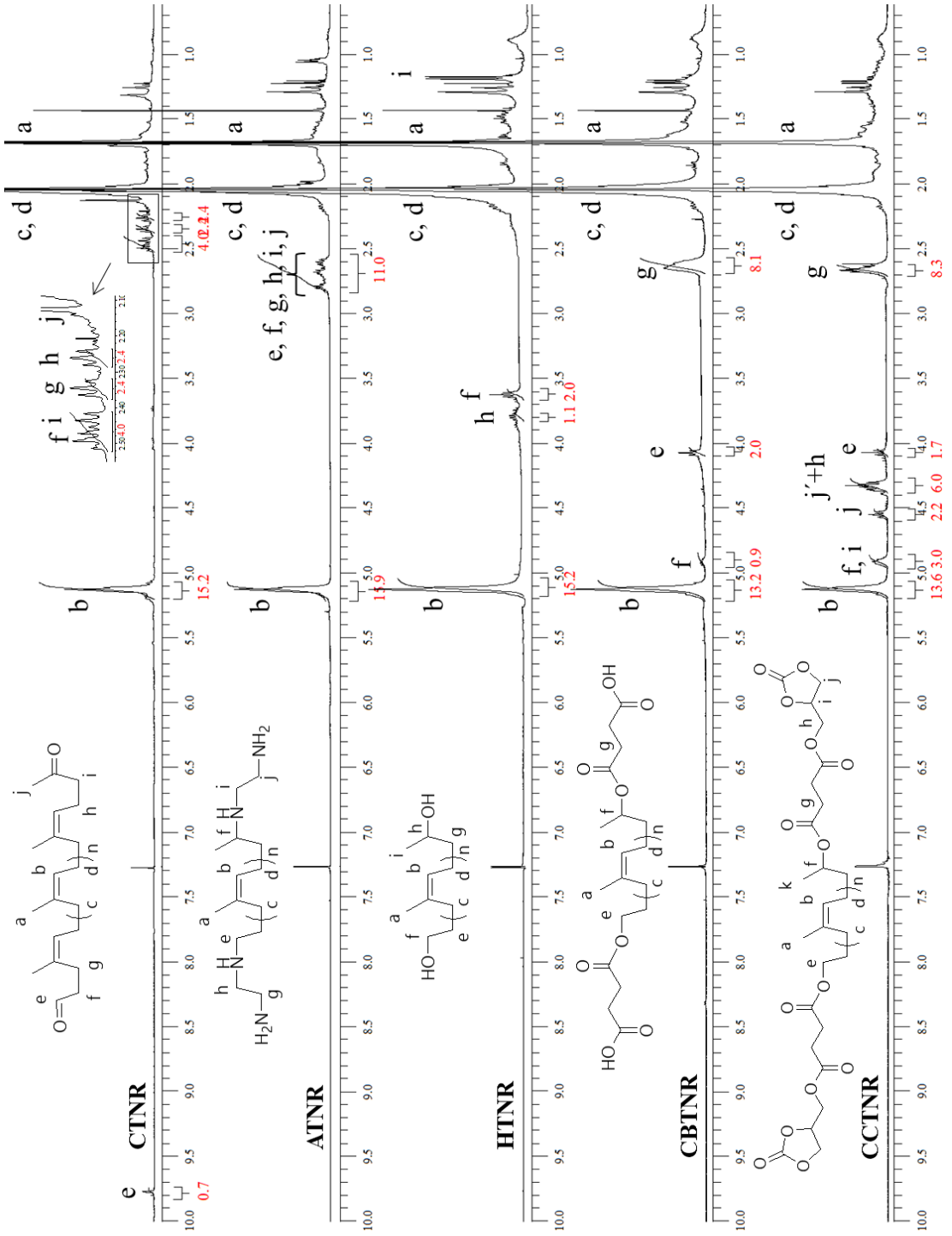

Fig. 3.2 ^{1}H-NMR spectra of oligoisoprenes

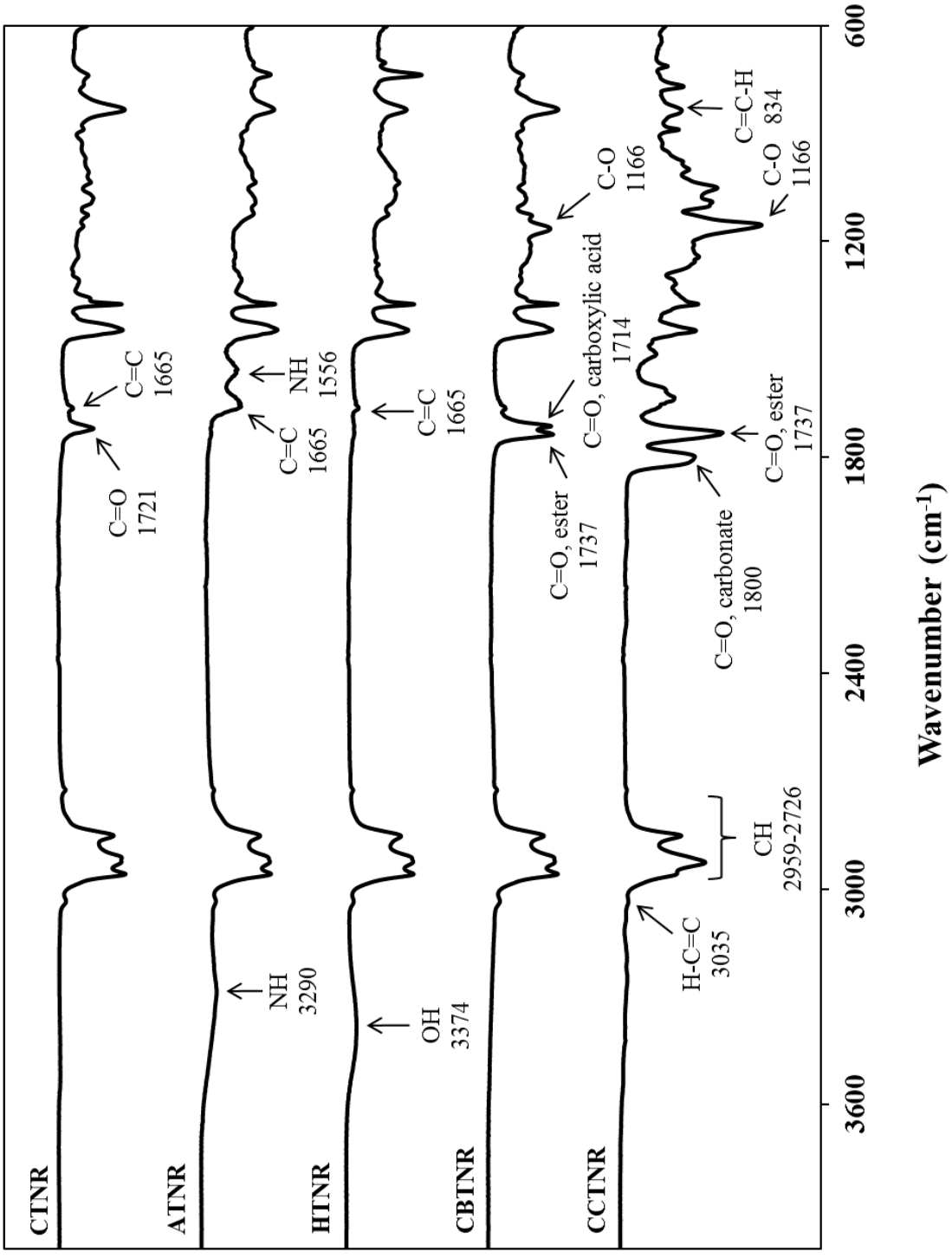

Fig. 3.3 FTIR spectra of oligoisoprenes.

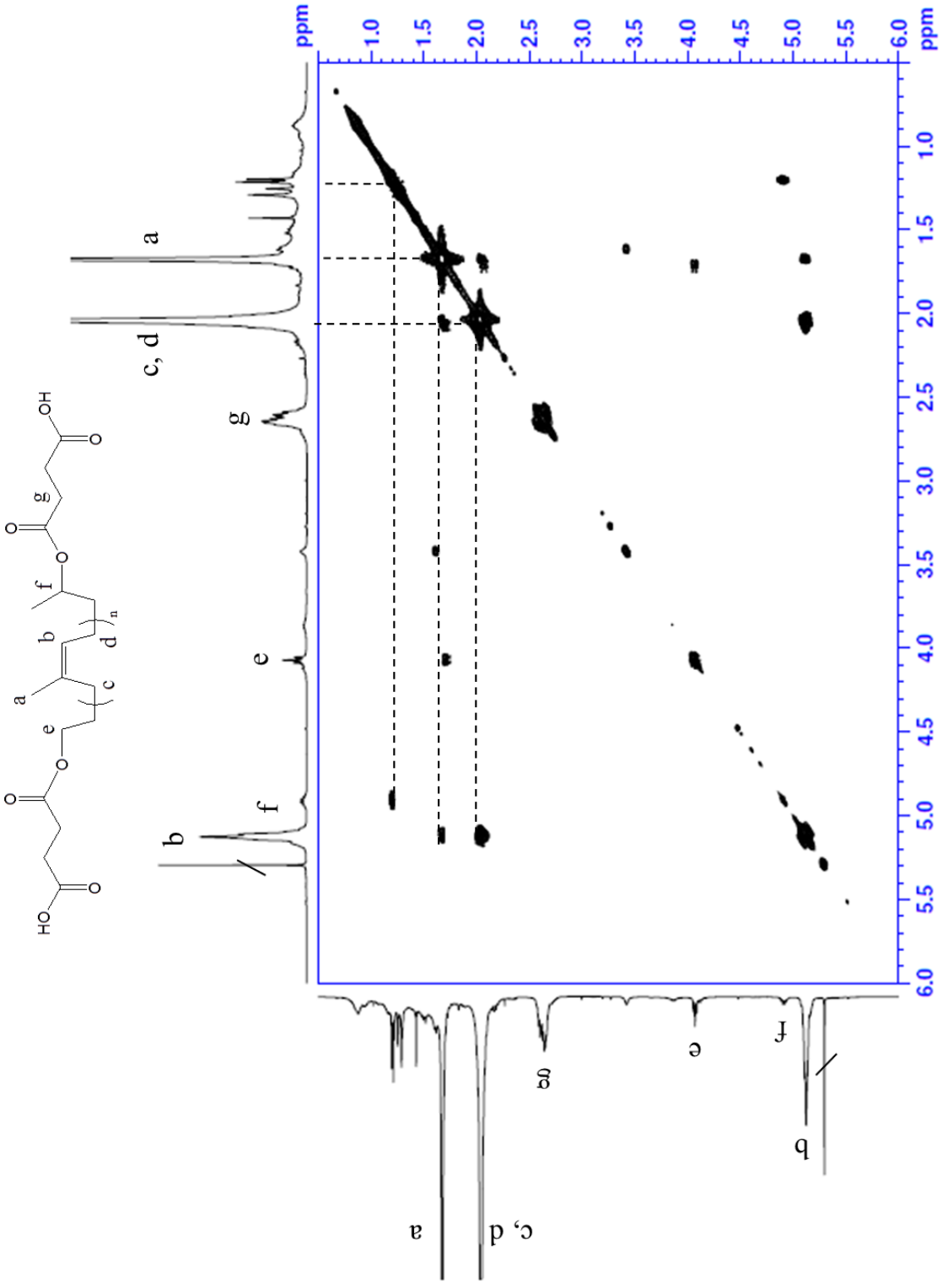

Fig. 3.4 COSY-NMR spectrum of CBTNR.

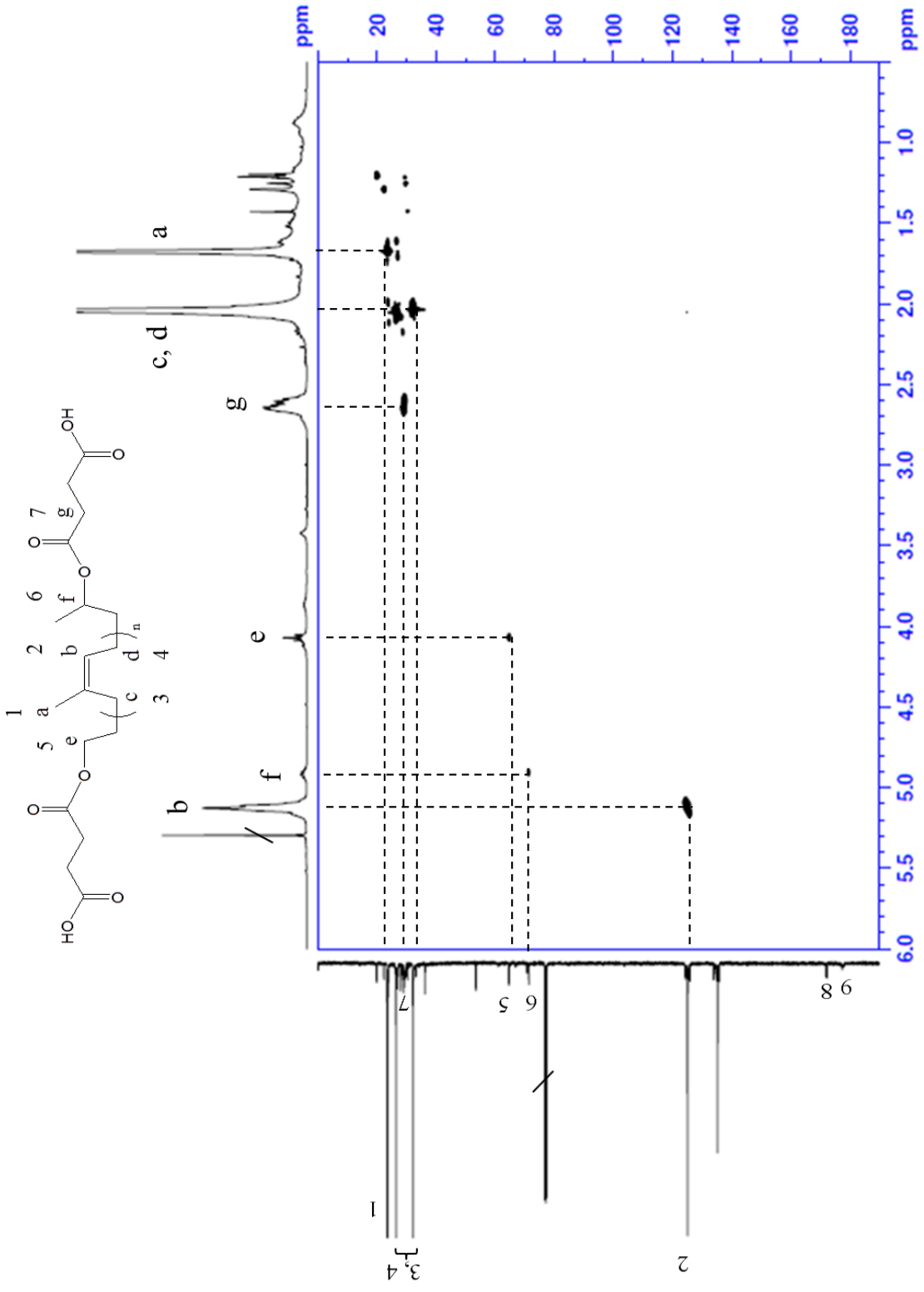

Fig. 3.5 HSQC-NMR spectrum of CBTNR.

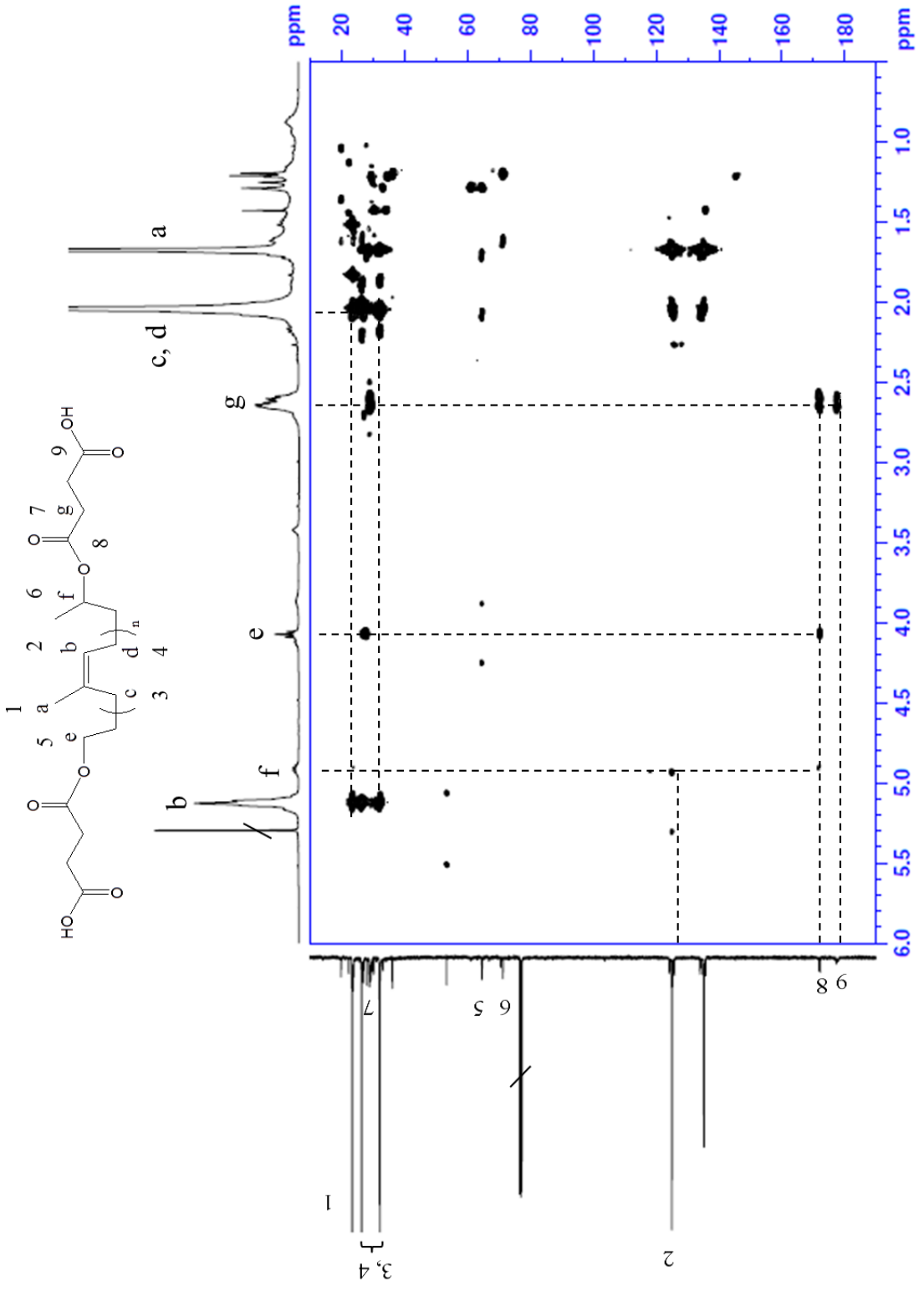

Fig. 3.6 HMBC-NMR spectrum of CBTNR.

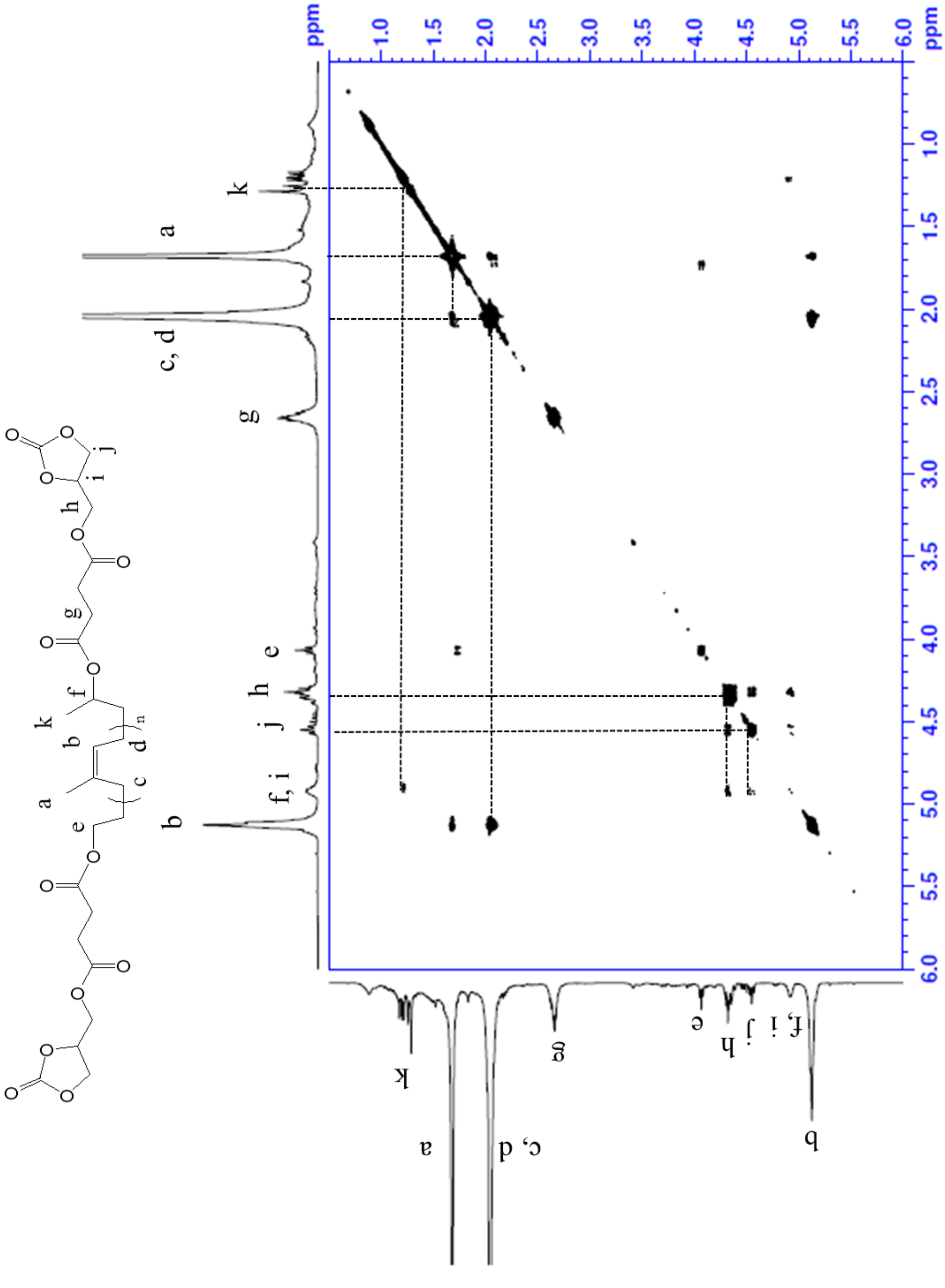

Fig. 3.7 COSY-NMR spectrum of CCTNR.

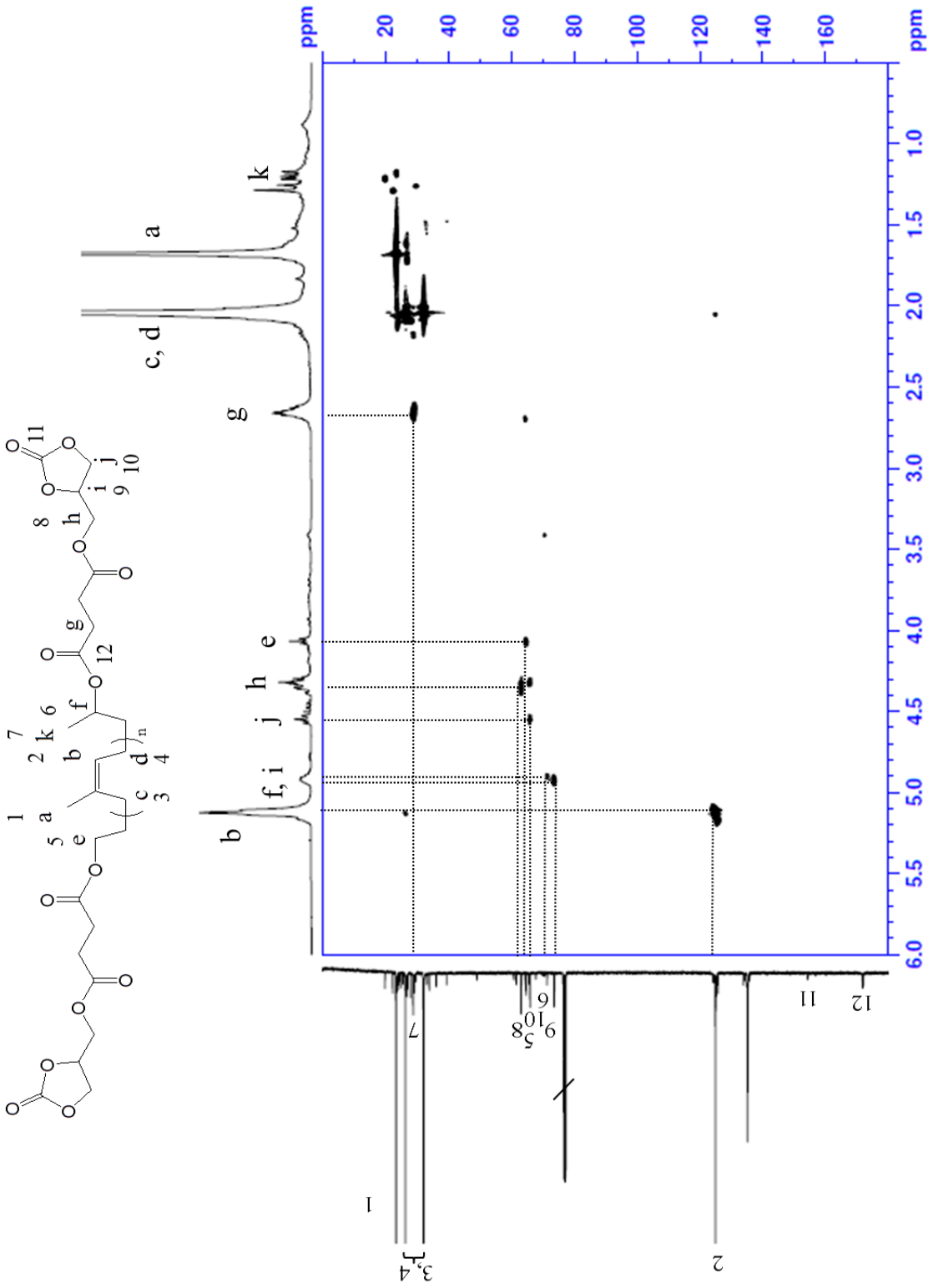

Fig. 3.8 HSQC-NMR spectrum of CCTNR.

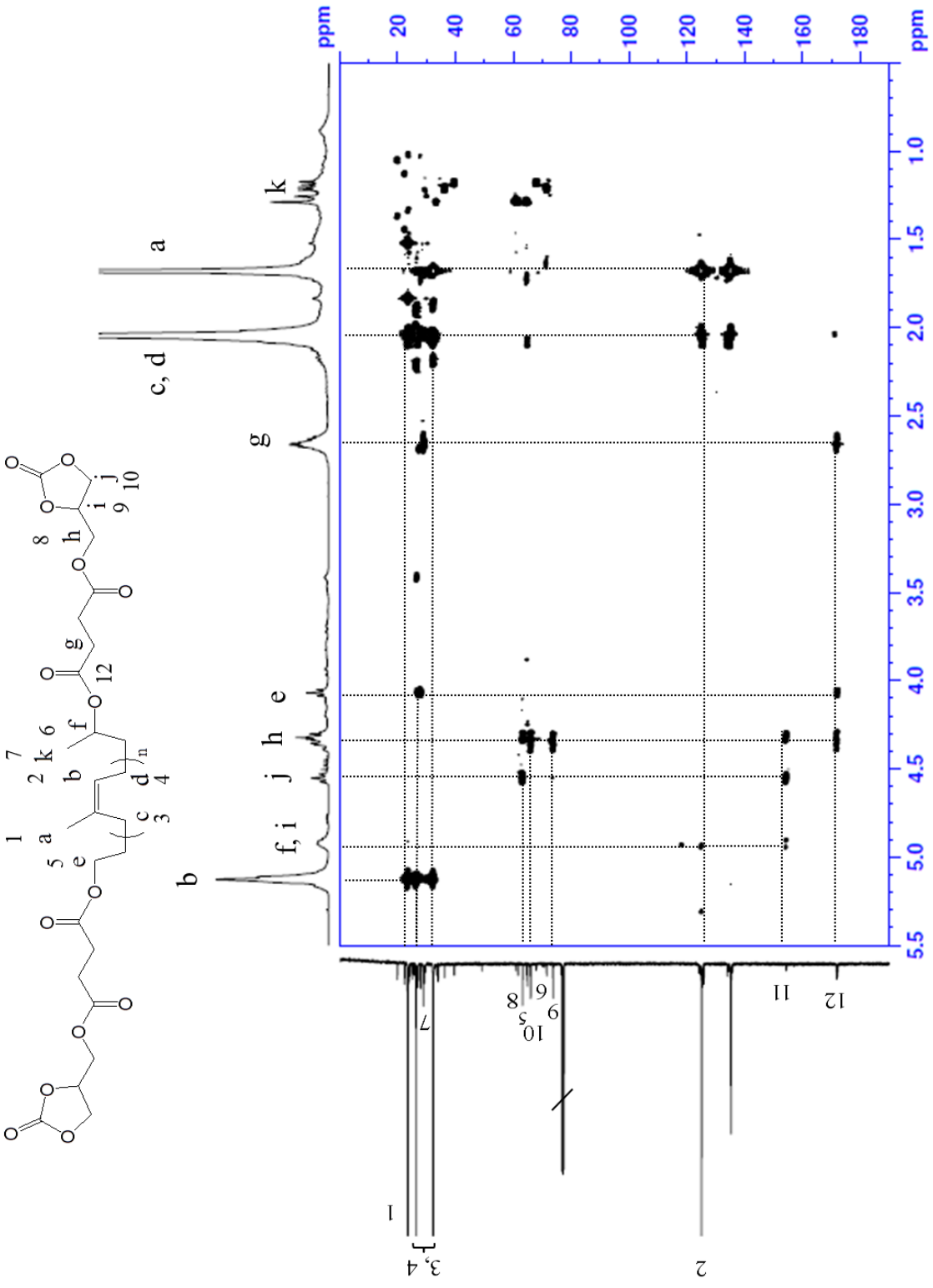

Fig. 3.9 HMBC-NMR spectrum of CCTNR.

Table 3.1 ^{1}H-NMR chemical shifts of CTNR

Type of proton	Chemical shift (ppm)
$CH_2C\boldsymbol{H}O$	9.77
$CH_3C=C\boldsymbol{H}_{\text{isoprene unit}}$	5.10
$C\boldsymbol{H_2}CHO$	2.52-2.45
$CH_3COC\boldsymbol{H_2}$	2.43
$C\boldsymbol{H_2}CH_2CHO$	2.34
$CH_3COCH_2C\boldsymbol{H_2}$	2.25
$C\boldsymbol{H_3}COCH_2$	2.13
$C\boldsymbol{H_2}$, isoprene unit	2.00-2.11
$C\boldsymbol{H_3}CCH_{\text{isoprene unit}}$	1.68

Table 3.2 ^{1}H-NMR chemical shifts of ATNR

Type of proton	Chemical shift (ppm)
$CH_3C=C\boldsymbol{H}_{\text{isoprene unit}}$	5.10
$CH_2C\boldsymbol{H_2}NH$, $CH_3C\boldsymbol{H}NH$, 2*$NHCH_2C\boldsymbol{H_2}NH_2$, 2*$NHC\boldsymbol{H}_2CH_2NH_2$	2.85-2.57
$C\boldsymbol{H_2}$, isoprene unit	2.00-2.11
$C\boldsymbol{H_3}$, isoprene unit	1.68

Table 3.3 ^{1}H-NMR chemical shifts of HTNR

Type of proton	Chemical shift (ppm)
$CH_3C=C\boldsymbol{H}_{\text{isoprene unit}}$	5.10
$C\boldsymbol{H}OH$	3.80
$C\boldsymbol{H_2}OH$	3.65
$C\boldsymbol{H_2}$, isoprene unit	2.00-2.11
$C\boldsymbol{H_3}CHOH$	1.18

Table 3.4 ^{1}H-NMR chemical shifts of CBTNR

Type of proton	Chemical shift (ppm)
$CH_3C=C\boldsymbol{H}$	5.10
$CH_3C\boldsymbol{H}OC(O)$	4.92
$C(O)OC\boldsymbol{H_2}$	4.07
$2*C\boldsymbol{H_2}CH_2C(O)OH$ and $2*CH_2C\boldsymbol{H_2}C(O)OH$	2.71-2.56
$C\boldsymbol{H_2}$, isoprene unit	2.10-2.00
$C\boldsymbol{H_3}$, isoprene unit	1.68

Table 3.5 ^{1}H-NMR chemical shifts of CCTNR

Type of proton	Chemical shift (ppm)
$CH_3C=C\boldsymbol{H}$ isoprene unit	5.10
$C(O)OC\boldsymbol{H}CH_3$ and $2*CH_2C\boldsymbol{H}CH_2OC(O)O$	4.96-4.89
$2*CH_2CHC\boldsymbol{H}\boldsymbol{H}'OC(O)O$	4.55
$2*C\boldsymbol{H_2}CHCH\boldsymbol{H}'OC(O)O$	4.33
$CH_2C\boldsymbol{H_2}OC(O)O$	4.07
$2*C\boldsymbol{H_2}CH_2C(O)O$ and $2*CH_2C\boldsymbol{H_2}C(O)O$	2.72-2.58
$C\boldsymbol{H_2}$, isoprene unit	2.15-1.95
$C\boldsymbol{H_3}$, isoprene unit	1.68

The number-average molecular weight ($\overline{M}_n$) of oligoisoprenes were determined by the integral value of the peak, isoprene repeat unit (68) and total mass of the rest of the molecule.

$\overline{M}_n$ of carbonyl telechelic natural rubber (CTNR) was calculated according to the equation (3.1), where I_b and $I_{f,i}$ were the integration value of the peak at 5.10

and 2.43-2.52 ppm, respectively. 100 was a total molar mass of the rest of the molecule (Kebir *et al*., 2005).

$$\overline{M}_n = \left[\frac{I_b}{(I_{f,i}/4)} \times 68 \right] + 100 \qquad (3.1)$$

$\overline{M}_n$ of amino telechelic natural rubber (ATNR) was calculated according to the equation (3.2), where I_b and $I_{e,f,g,h,i,j}$ were the integration values of the peaks at 5.10 and 2.85-2.57 ppm, respectively. 188 was a total molar mass of the rest of the molecule.

$$\overline{M}_n = \left[\frac{I_b}{(I_{e,f,g,h,i,j}/11)} \times 68 \right] + 188 \qquad (3.2)$$

$\overline{M}_n$ of hydroxy telechelic natural rubber (HTNR) was calculated according to the equation (3.3), where I_b and I_f were the integration values of the peaks at 5.10 and 3.65 ppm, respectively. 104 was a total molar mass of the rest of the molecule (Kebir *et al*., 2005).

$$\overline{M}_n = \left[\frac{I_b}{(I_f/2)} \times 68 \right] + 104 \qquad (3.3)$$

$\overline{M}_n$ of carboxylic telechelic natural rubber (CBTNR) was calculated according to the equation (3.4), where I_b and I_e were the integration values of the peaks at 5.10 and 4.07 ppm, respectively. 304 was a total molar mass of the rest of the molecule.

$$\overline{M}_n = \left[\frac{I_b}{(I_e/2)} \times 68 \right] + 304 \qquad (3.4)$$

$\overline{M}_n$ of cyclic carbonate telechelic natural rubber (CCTNR) was calculated according to the equation (3.5), where I_b and $I_{f,i}$ were the integration values of the peaks at 5.10 and 4.96-4.89 ppm, respectively. 504 was a total molar mass of the rest of the molecule.

$$\overline{M}_n = \left[\frac{I_b}{(I_{f,i}/3)} \times 68 \right] + 504 \qquad (3.5)$$

The targeted chain lengths of all oligoisoprenes were 1000 and 2000 g/mol. Their molecular weights are listed in Table 3.6. The number average molecular weights ($\bar{M}_n$) of CTNR determined by ^{1}H-NMR were 1134 and 2070 g/mol for the targeted chain length of 1000 and 2000 g/mol, respectively. From SEC analysis, the $\bar{M}_n$ of targeted chain length 2000 g/mol was 1800 g/mol whereas the targeted chain length of 1000 g/mol was unable to determine because the peak was partially out of the calibration curve (Fig. 3.10). The $\bar{M}_n$ of ATNR for the targeted chain lengths of 1000 and 2000 g/mol determining from ^{1}H-NMR analysis were 1270 and 2300 g/mol, respectively. For SEC analysis, ATNR have been reacted with acetic anhydride (AA) via an acylation reaction corresponding to amine derivative as referred to modified ATNR (see more information in APPENDIX B) in order to decrease the polarity of the amino group and avoid the interactions and adsorption to the SEC column leading to the low responsible intensity of the peak (Kataoka, 1996). The molecular weight distributions of ATNR and modified ATNR are shown in Fig. 3.11. It was clear that the peak intensity of modified ATNR was higher than unmodified ATNR. $\bar{M}_n$ of ATNR with the targeted chain length of 1000 g/mol could not be determined due to peak was partially out of the calibration curve as similar reason to the CTNR. $\bar{M}_n$ of ATNR with the targeted chain length 2000 g/mol was 2200 g/mol by SEC analysis.

Table 3.6 Molecular weights of oligoisoprenes

Sample	$\bar{M}_n$(g/mol)[a]	$\bar{M}_n$(g/mol)[b]	$\bar{M}_w$(g/mol)[b]	Đ[b]
CTNR	1134	NA	NA	NA
ATNR	1270	NA	NA	NA
HTNR	1138	NA	NA	NA
CBTNR	1200	NA	NA	NA
CCTNR	1430	1800	3200	1.80
CTNR	2070	1800	3900	2.15
ATNR	2300	2200[c]	4900[c]	1.69[c]
HTNR	2130	2400	5000	2.09
CBTNR	2200	2600	5500	2.13
CCTNR	2270	2800	6200	2.21

[a]Determined by ^{1}H-NMR.

[b]Determined by SEC and corrected by Benoit factor for polyisoprene (0.67).

[c]Determined by SEC after modification with acetic anhydride.

NA: Not applicable because part of peak was out of the calibration curve.

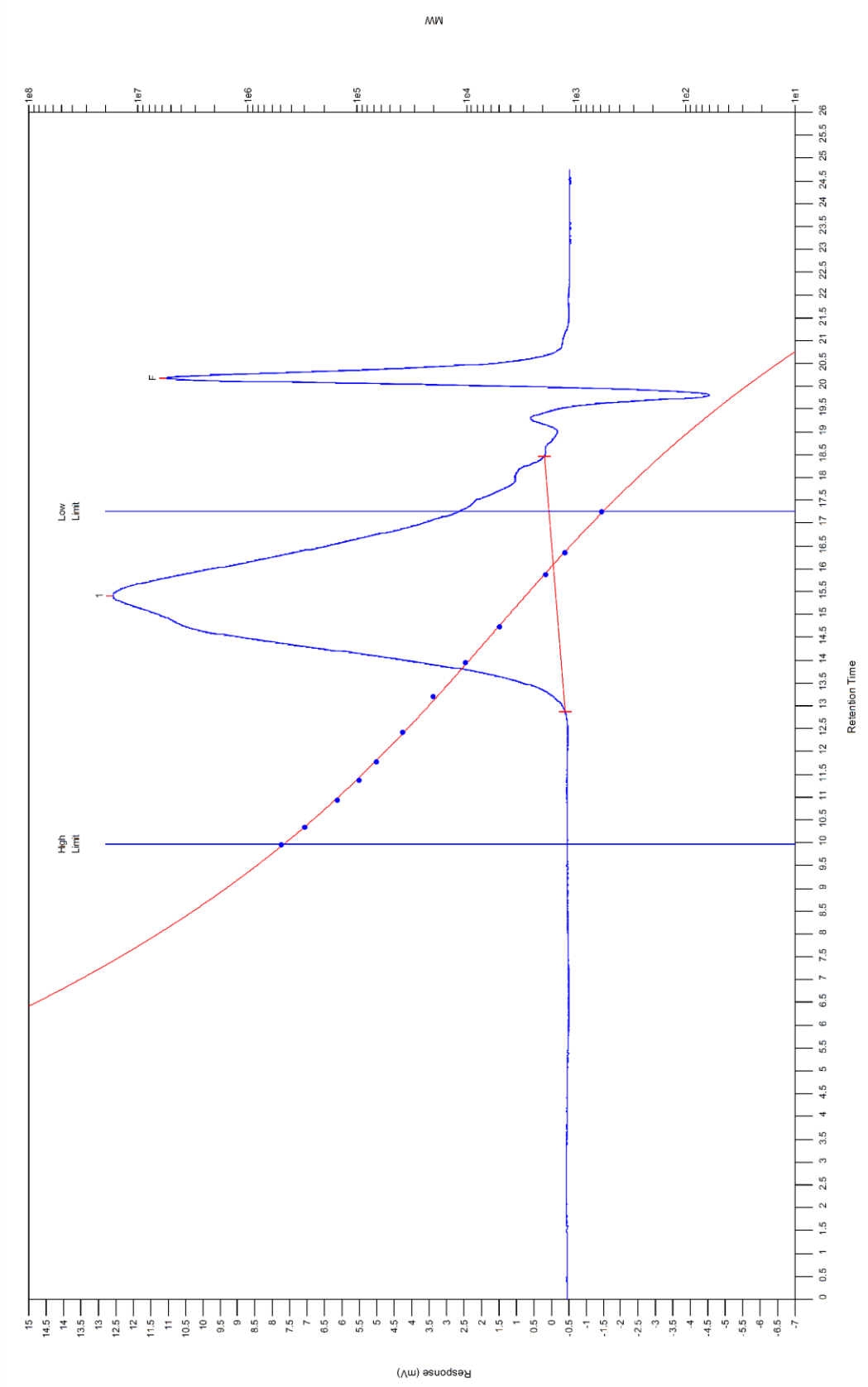

Fig. 3.10 Size exclusion chromatography of CTNR with targeted chain length of 1000 g/mol from SEC analysis.

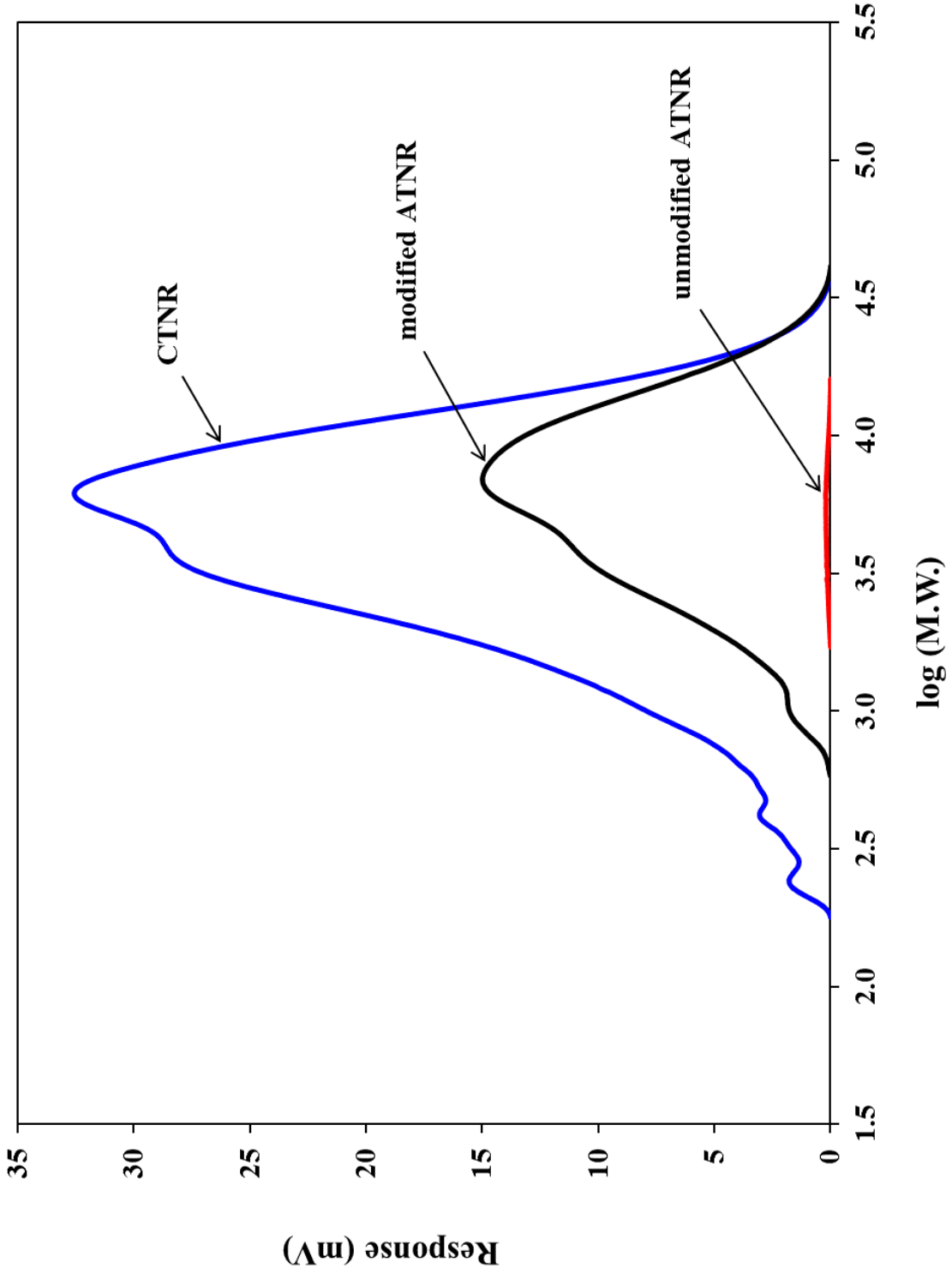

Fig. 3.11 Molecular weight distributions of CTNR, unmodified and modified ATNR (targeted chain length of 2000 g/mol) from SEC analysis.

The molecular weights of HTNR, CBTNR and CCTNR were slightly higher than the expected one for both targeted chain lengths of 1000 and 2000 g/mol. For SEC data, $\bar{M}_n$ of HTNR and CBTNR for the targeted chain lengths 1000 g/mol were out of the calibration range. $\bar{M}_n$ of CCTNR with the targeted chain lengths of 1000 and 2000 g/mol were 1800 and 2800 g/mol, respectively. The dispersity for all oligoisoprenes were roughly around 2. The molecular weight distributions of all oligoisoprenes with targeted chain lengths of 2000 g/mol are presented in Fig. 3.12.

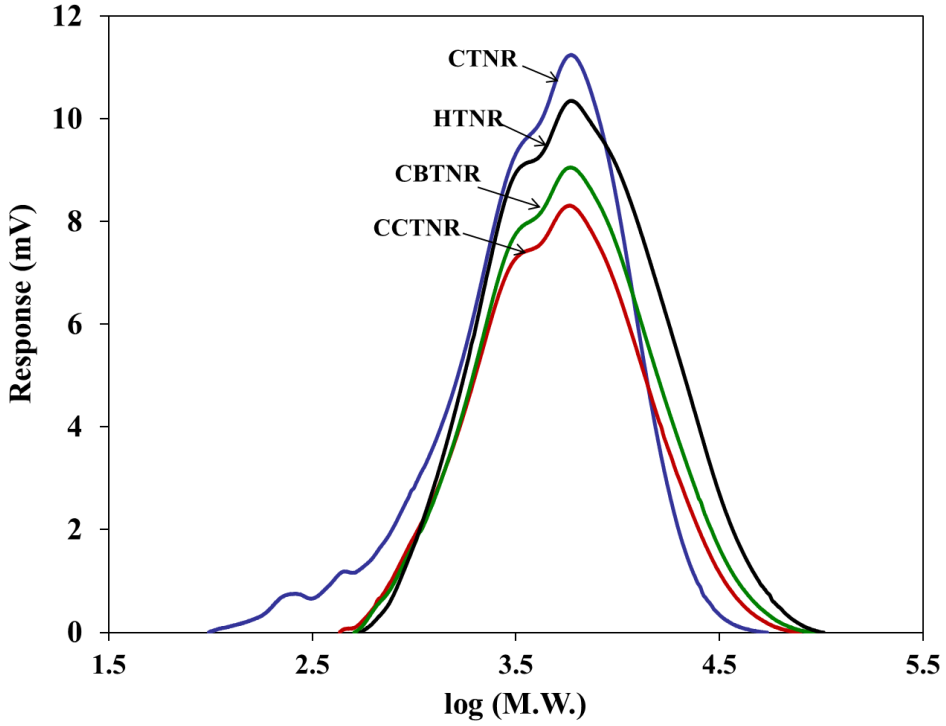

Fig. 3.12 Molecular weight distributions of CTNR, HTNR, CBTNR and CCTNR with the targeted chain lengths of 2000 g/mol from SEC analysis.

MALDI-TOF was a useful method to verify the structure of CCTNR and the presence of cyclic carbonate at both chain ends. The MALDI-TOF spectrum of CCTNR (targeted chain lengths of 1000 g/mol) is displayed in Fig. 3.13. Two distribution modes were observed. In the first one was the most intense with a constant mass difference of 68 corresponding to the repeating unit of polyisoprene (calculated value = 68.063 g/mol). One of the most intense peaks located at m/z

[M+Ag$^+$] = 1223.497 (calculated value for $C_{66}H_{100}AgO_{14}$ [M+Ag$^+$] = 1223.616) was attributed to a CCTNR oilgoisoprene with nine units. The second population also presented a constant mass difference of 68 attributed to the repeating unit of polyisoprene. The intense peak located at m/z [M+Ag$^+$] = 1443.649 (calculated value for $C_{81}H_{124}AgO_{15}$ [M+Ag$^+$] = 1443.799) was attributed to the chains of CCTNR oligoisoprene with eleven units and an epoxide group on one unit of polyisoprene coming from the incomplete oxidative degradation of CTNR. This phenomenon has already been reported (Kébir *et al*., 2005).

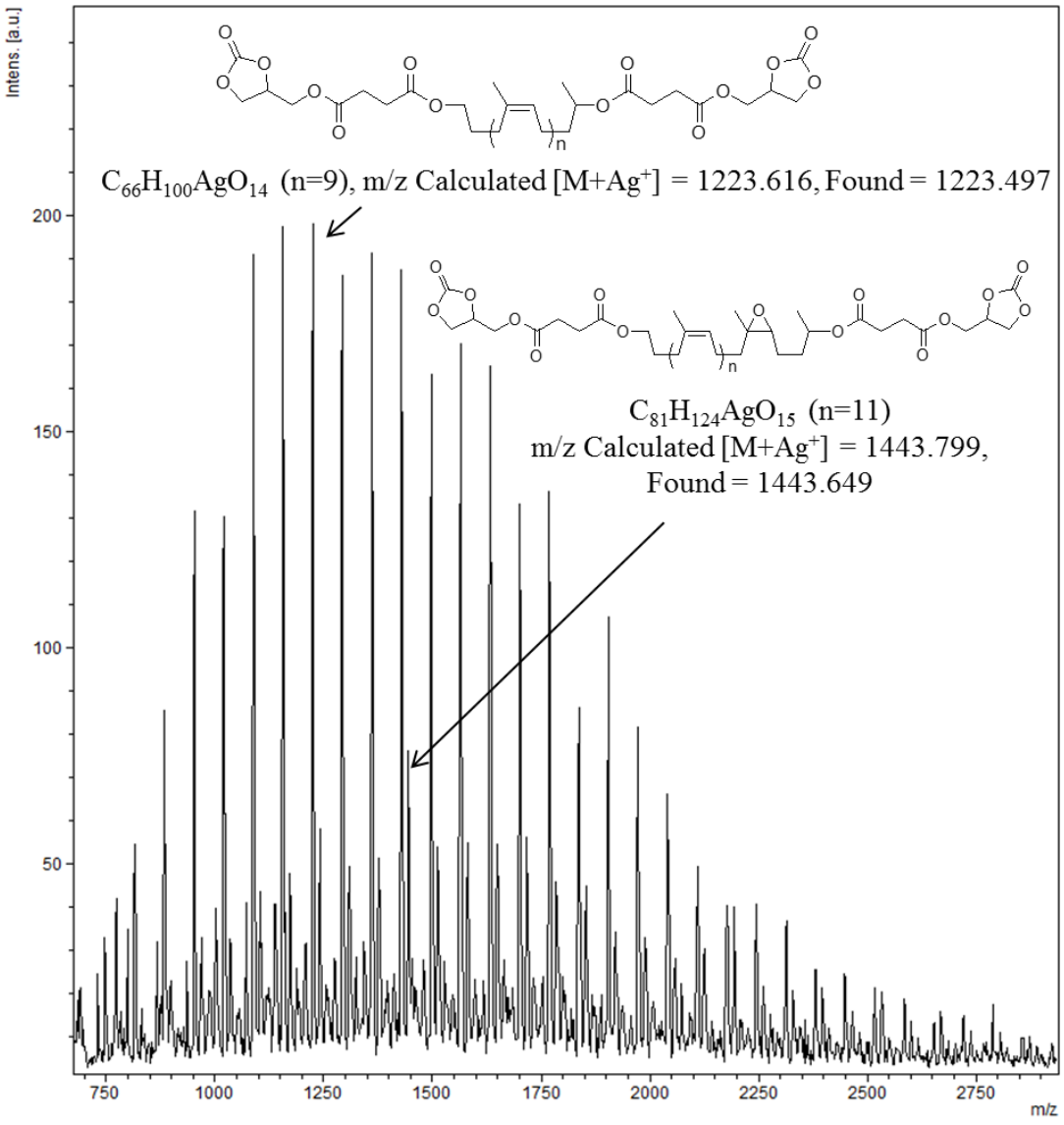

Fig. 3.13 MALDI-TOF spectrum of CCTNR with targeted chain lengths of 1000 g/mol.

3.2 Synthesis of dicyclic carbonates

The reaction conditions for synthesis of aromatic and aliphatic dicyclic carbonates are summarized in Table 3.7. The synthetic routes of diyclic carbonates are shown in Fig. 3.14. For aromatic dicyclic carbonate (dicyclic carbonate #1), the terephthalic acid was used in the preliminary study and the product was obtained with only 10% of yield. By using the terephthaloyl chloride, high yield (90%) was obtained. For aliphatic dicyclic carbonate (dicyclic carbonate #2), the Steglish coupling showed a modest yield of 28% yield whereas the method using succinyl chloride and glycerol carbonate allowed the synthesis in a yield of 80%.

Table 3.7 Reaction conditions for synthesis of dicyclic carbonates

Dicyclic carbonate	Reactant	R	Catalyst	t (◦C)	T (h)	Yield (%)
Aromatic	Terephthalic acid	OH	DMAP/DCC	25	24	10
	terephthaloyl chloride	Cl	-	reflux	3	90
Aliphatic	Succinic acid	OH	DMAP/DCC	30	24	28
	Succinyl chloride	Cl	-	reflux	6	80

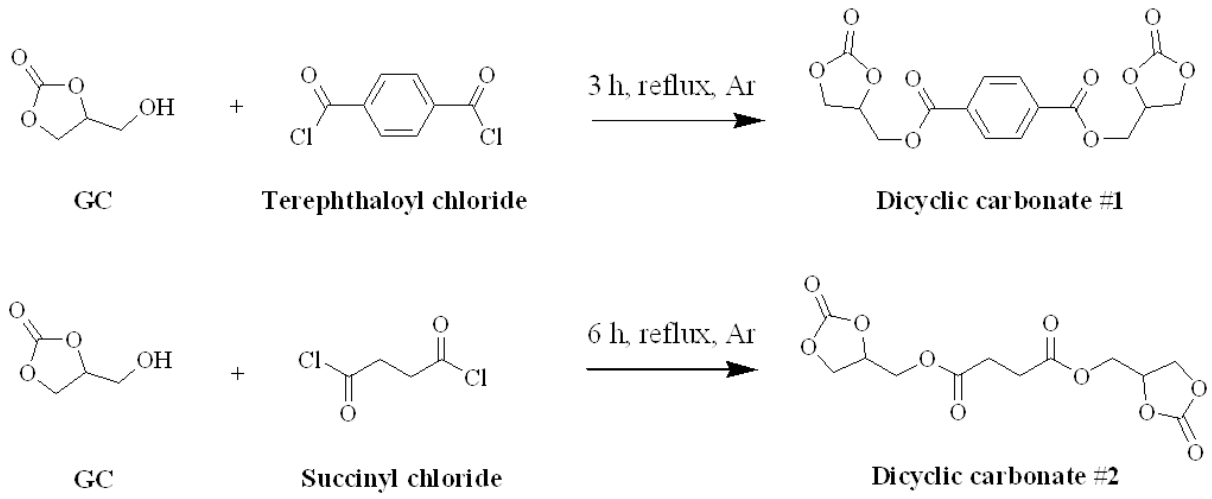

Fig. 3.14 Synthesis routes of dicyclic carbonates.

The ^{1}H-NMR spectra of dicyclic carbonates represent in Fig. 3.15. The aromatic dicyclic carbonate showed the characteristic peaks at 8.11, 5.20-5.25 and 4.66-4.52 ppm corresponding to aromatic ring and the carbonate moiety. COSY-NMR, HSQC-NMR and HMBC-NMR spectra of dicyclic carbonate #1 are shown in Fig. 3.16-3.18, respectively.

The aliphatic dicyclic carbonate showed the significant peak at 2.62 ppm corresponding to the methylene proton and the characteristic protons from the carbonate part were located at 5.07-5.00, 4.57 and 4.28 ppm (Fig. 3.15, Fig. 3.19-3.21).

The FTIR spectrum of dicyclic carbonate #1 showed the strong absorption bands at 1780 and 1721 cm^{-1} assigning to C=O from carbonate and ester, respectively (Fig. 3.22). For cyclic carbonate #2, the absorption bands of C=O from carbonate and ester were observed at 1780 and 1732 cm^{-1}.

The HRMS analysis was used to identify the structure and the presence of cyclic carbonate chain ends for dicyclic carbonates. The HRMS mass spectra of aromatic and aliphatic dicyclic carbonates were demonstrated in Fig. 3.23. The HRMS mass spectrum of dicyclic carbonate #1 showed the intense peak located at m/z $[M+Na^{+}]$ = 389.0478 (calculated value for $C_{16}H_{14}NaO_{10}$ $[M+Na^{+}]$ = 389.0485) corresponding to a cyclic carbonate #1. For dicyclic carbonate #2, the intense peak was observed at m/z $[M+Na^{+}]$ = 341.0480 (calculated value for $C_{12}H_{14}NaO_{10}$ $[M+Na^{+}]$ = 341.0485) corresponding to a dicyclic carbonate #2. All results proved the presence of cyclic carbonate at both chain ends.

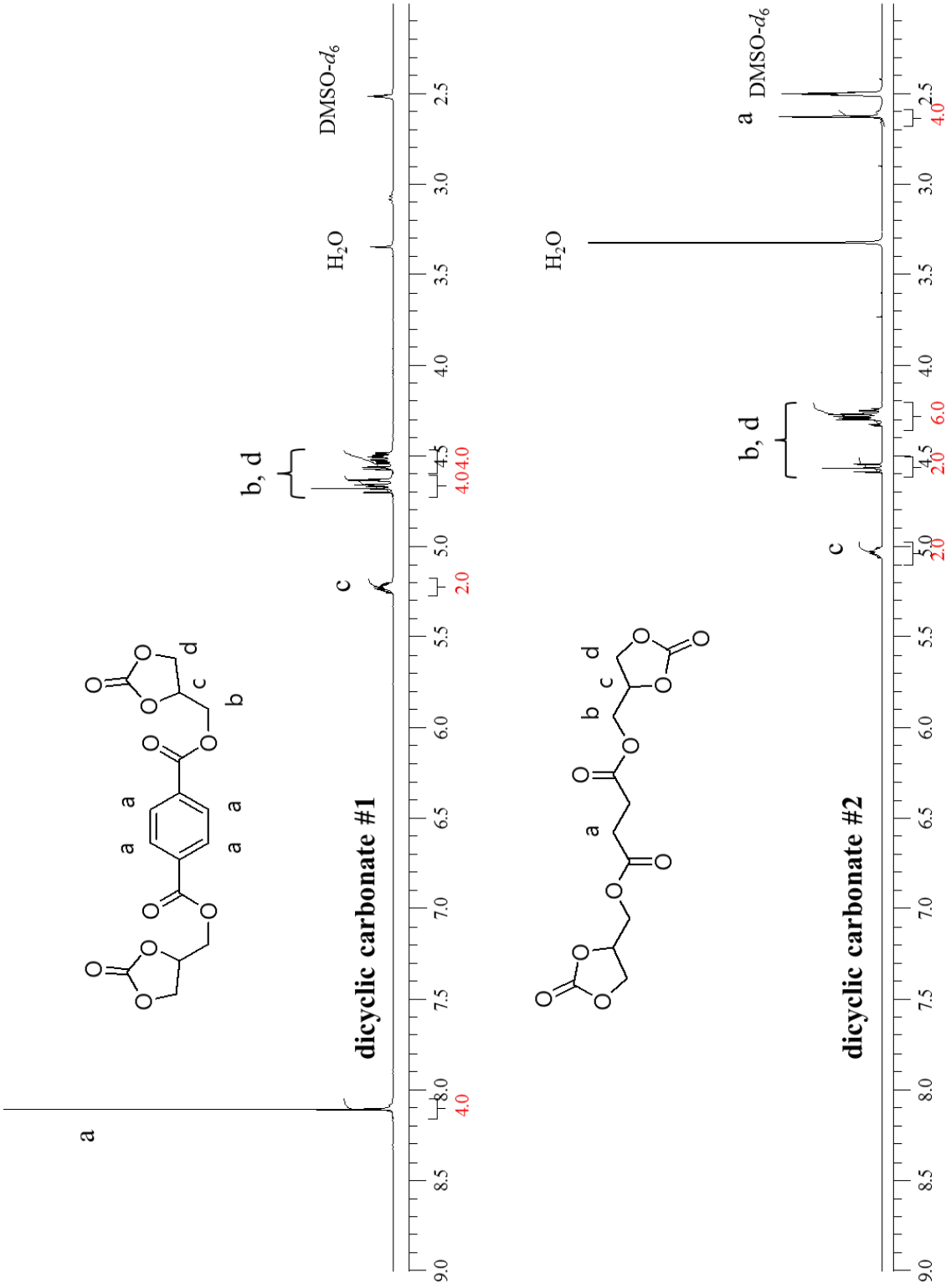

Fig. 3.15 ^{1}H-NMR spectra of dicyclic carbonate #1 and dicyclic carbonate #2 (DMSO-d_6, 200 MHz).

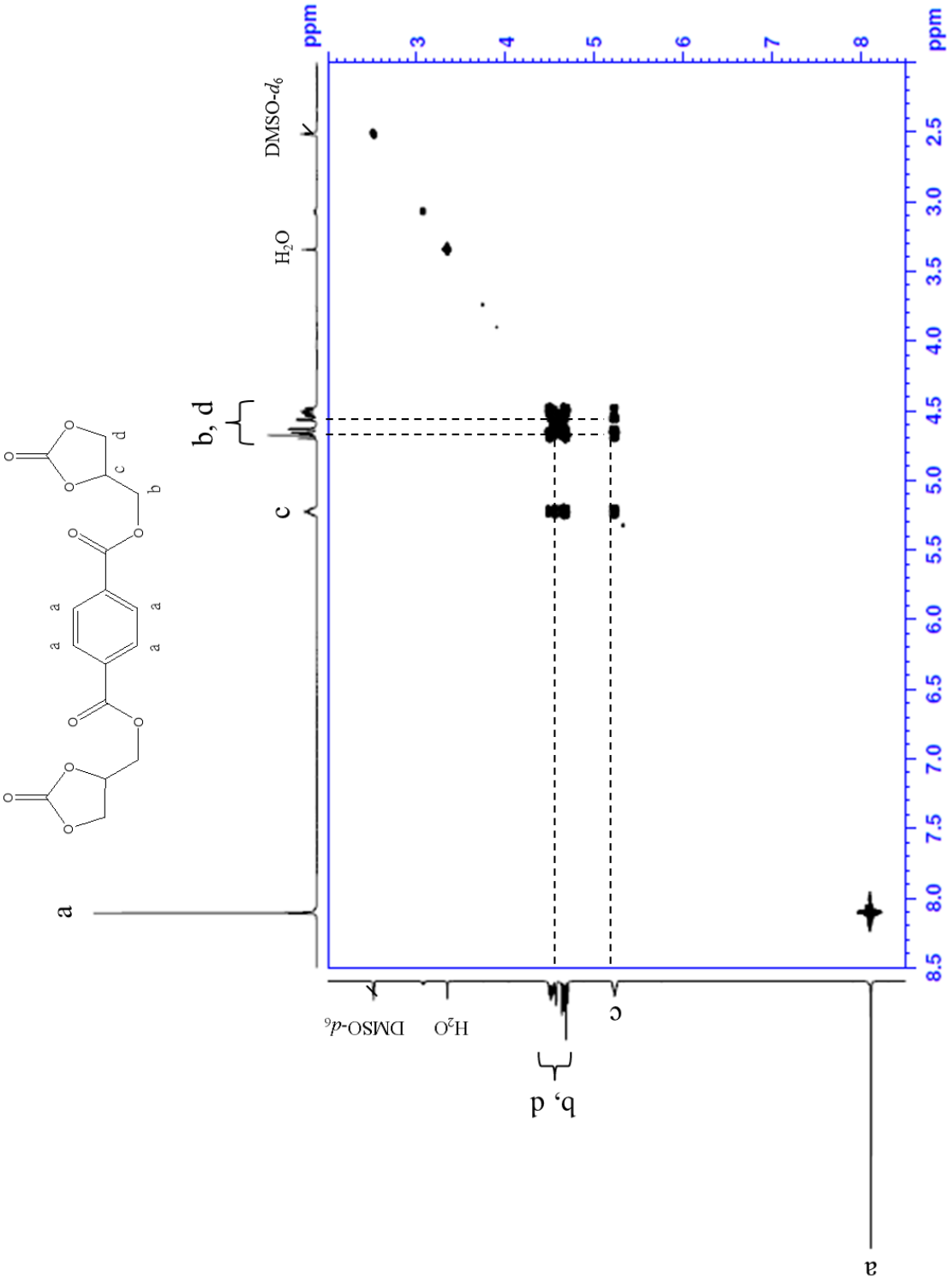

Fig. 3.16 COSY-NMR spectrum of dicyclic carbonate #1 (DMSO-d_6, 400 MHz).

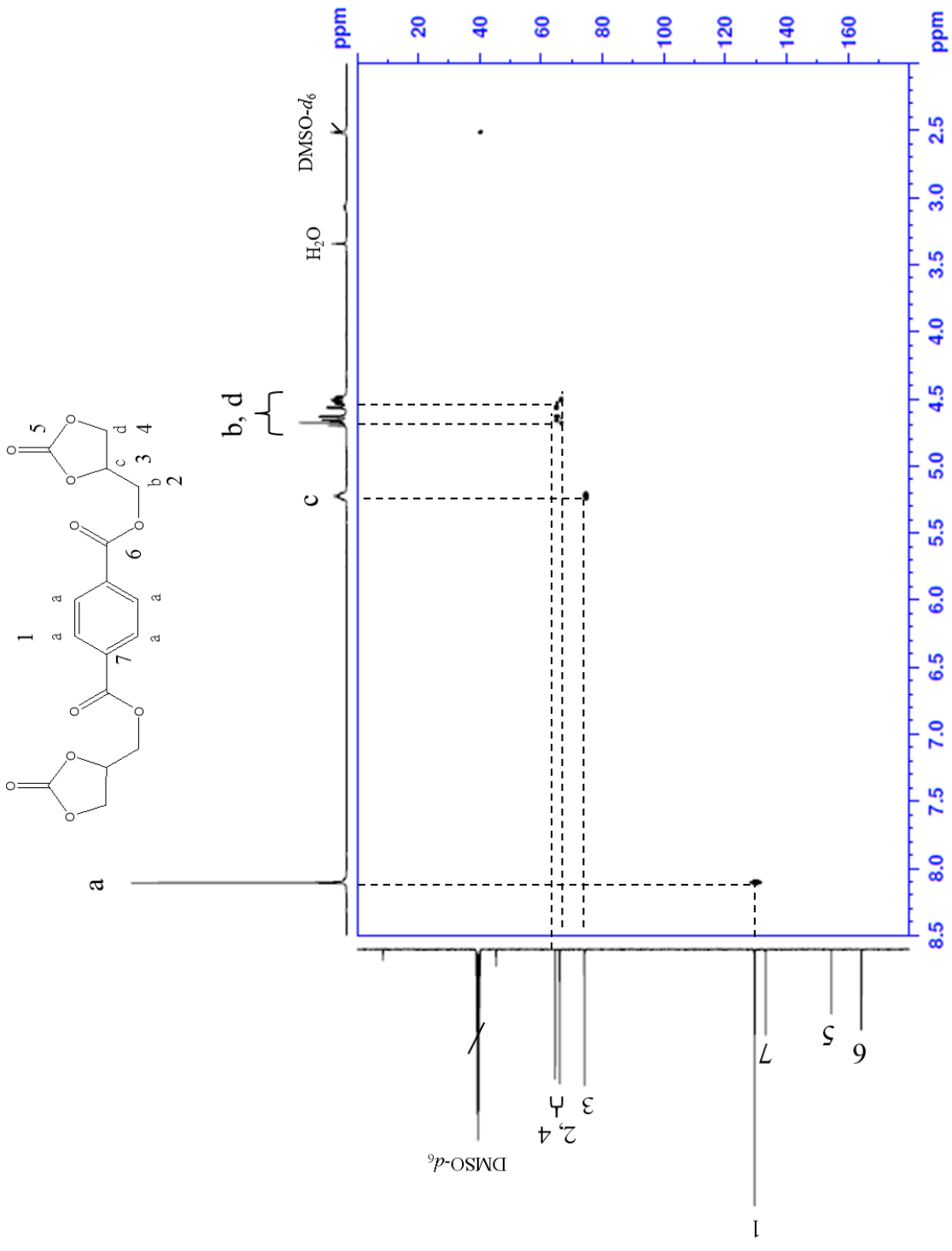

Fig. 3.17 HSQC-NMR spectrum of dicyclic carbonate #1 (DMSO-d_6, 400 MHz).

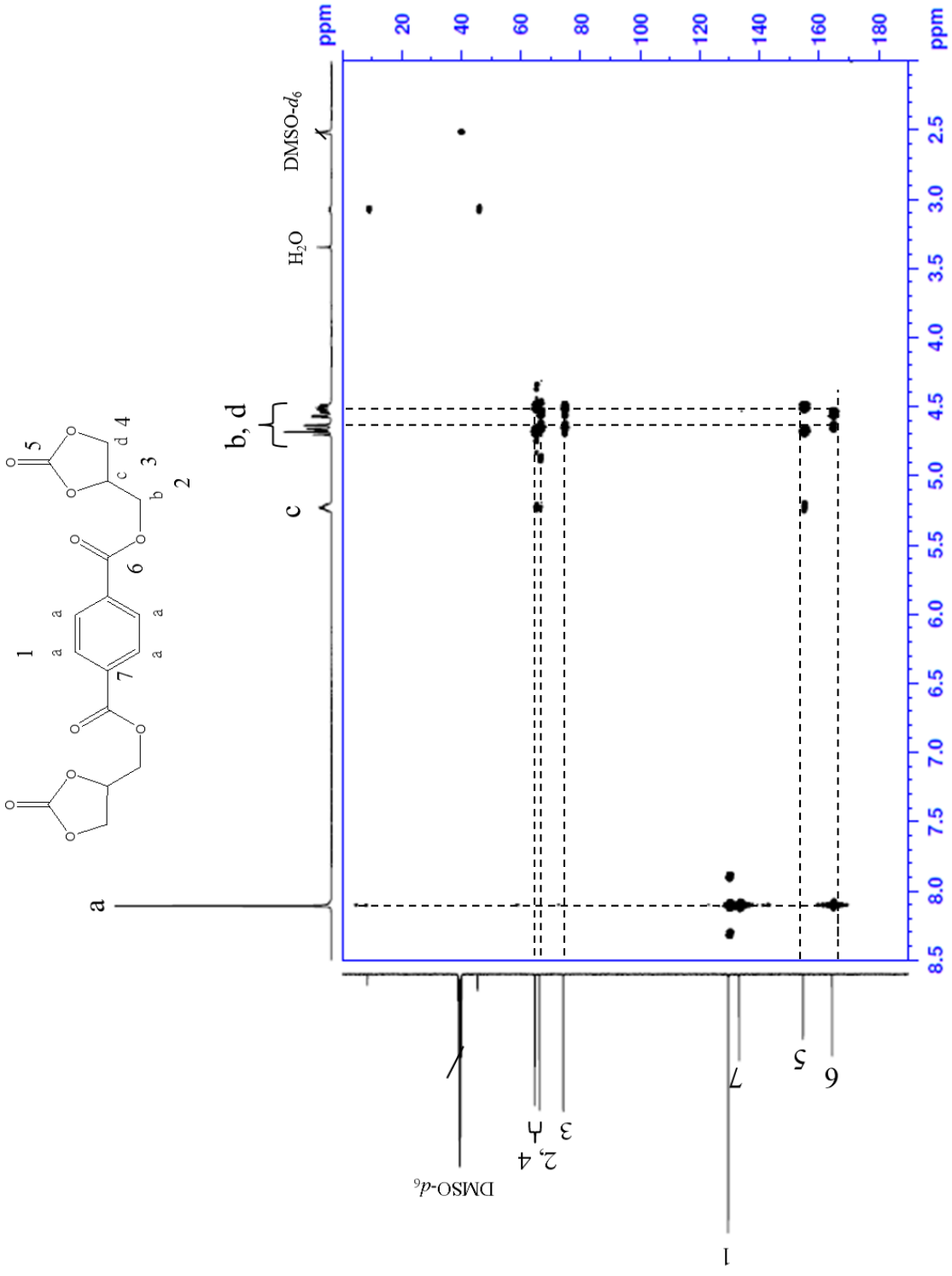

Fig. 3.18 HMBC-NMR spectrum of dicyclic carbonate #1 (DMSO-d_6, 400 MHz).

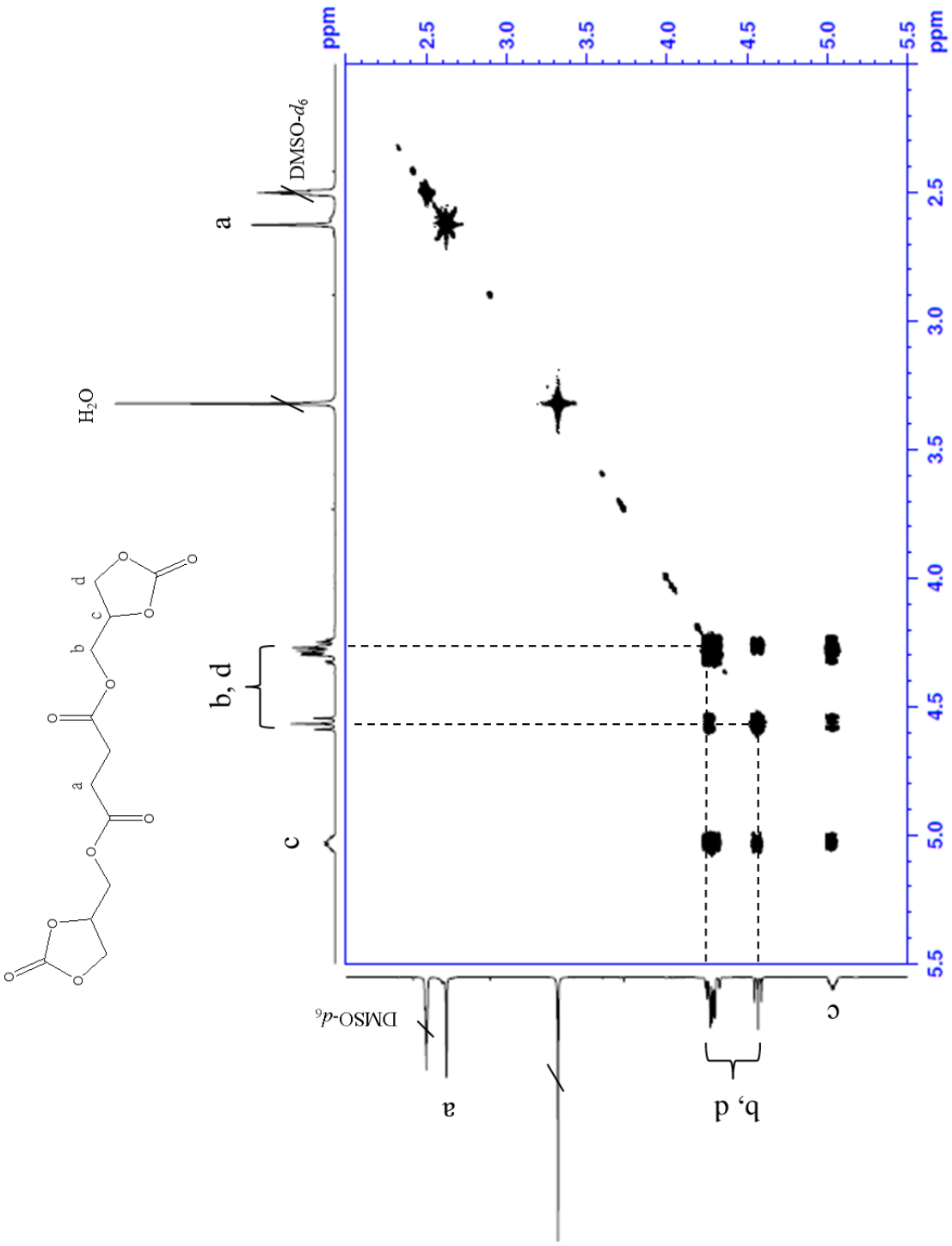

Fig. 3.19 COSY-NMR spectrum of dicyclic carbonate #2 (DMSO-d_6, 400 MHz).

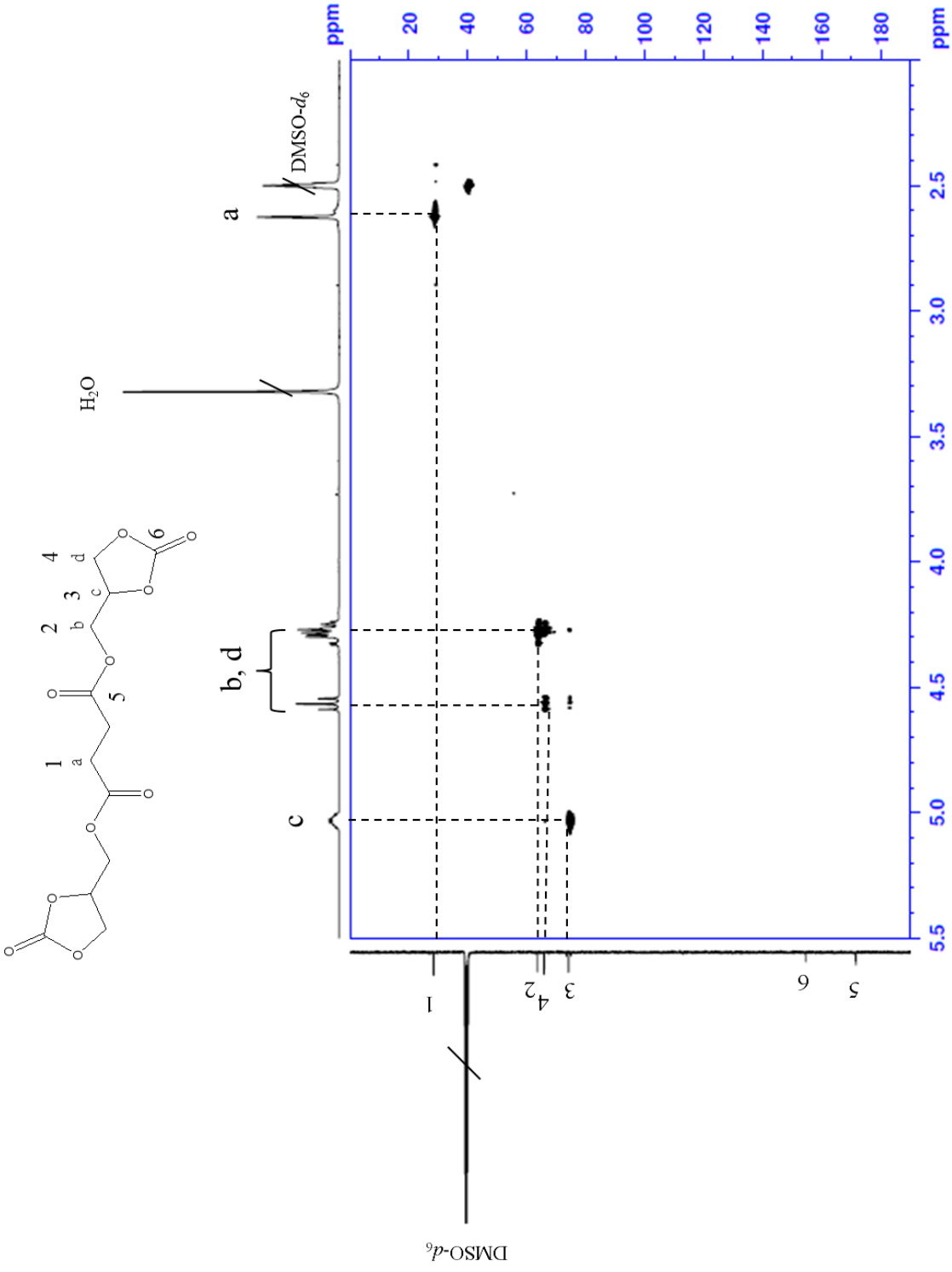

Fig. 3.20 HSQC-NMR spectrum of dicyclic carbonate #2 (DMSO-d_6, 400 MHz).

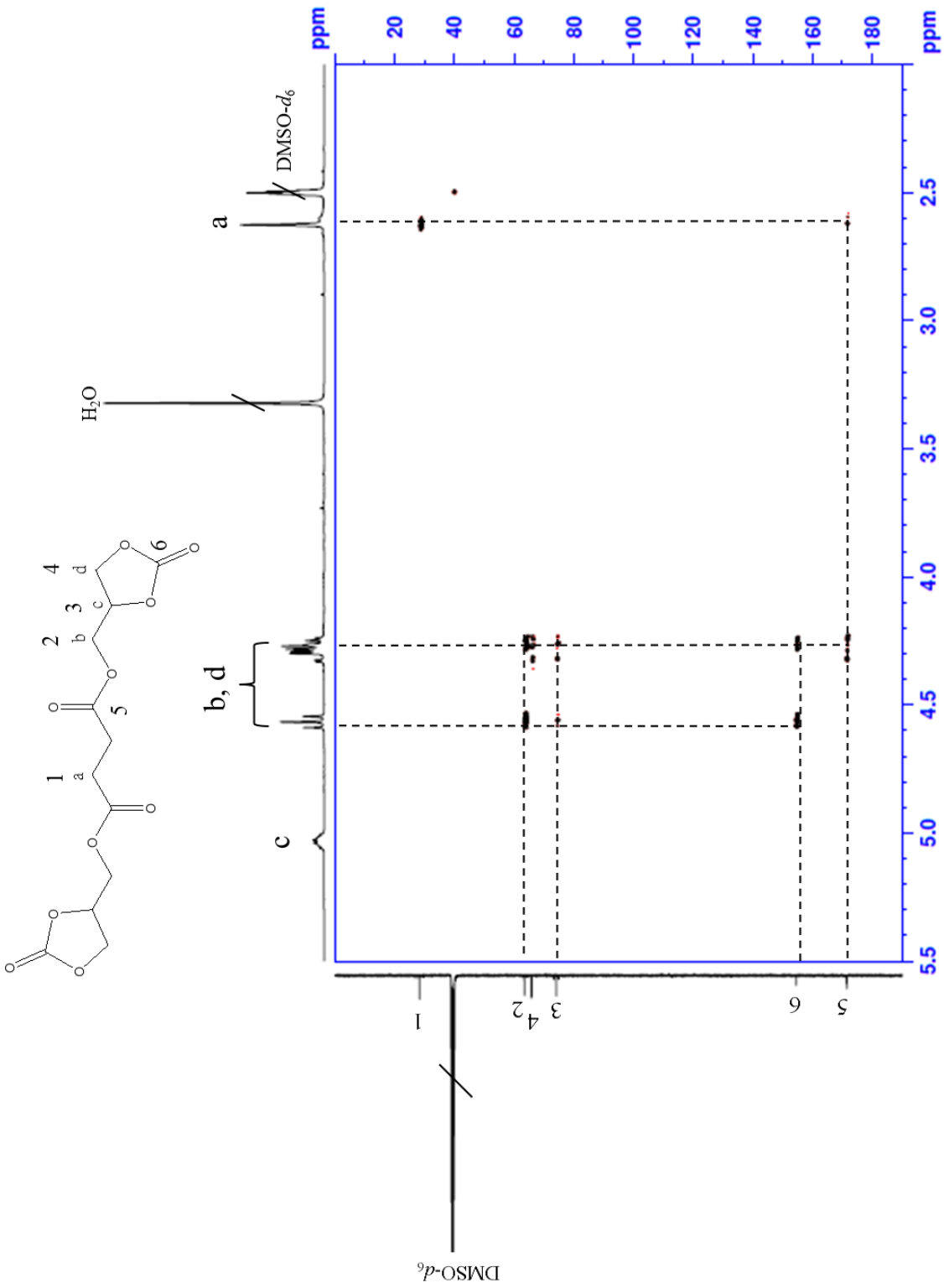

Fig. 3.21 HMBC-NMR spectrum of dicyclic carbonate #2 (DMSO-d_6, 400 MHz).

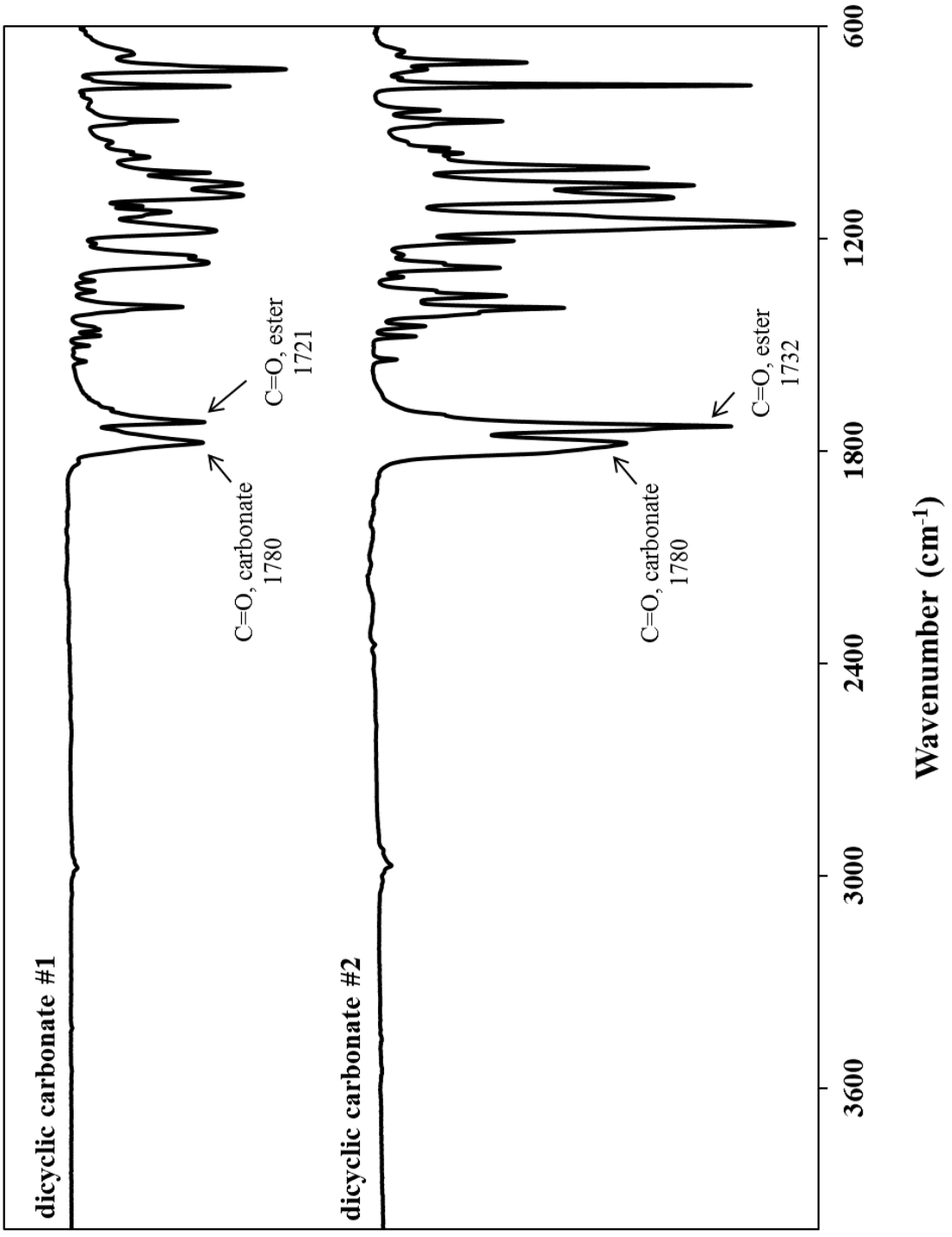

Fig. 3.22 FTIR spectra of dicyclic carbonate #1 and dicyclic carbonate #2.

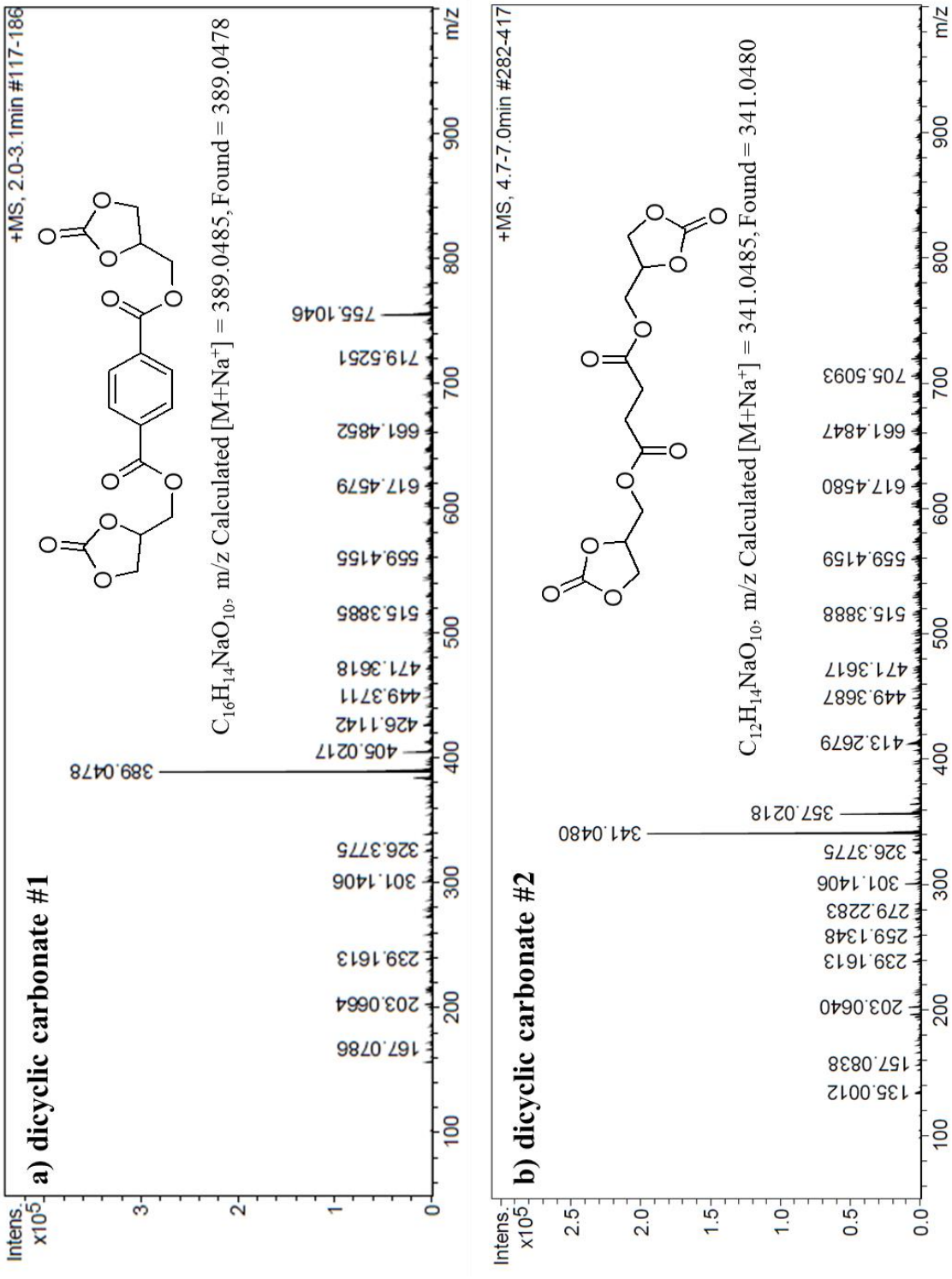

Fig. 3.23 HRMS spectra of dicyclic carbonates: (a) dicyclic carbonate #1 and (b) dicyclic carbonate #2.

3.3 Synthesis of cyclic carbonate telechelic poly(lactic acid) (CCPLA)

The synthetic method of CCPLA consisted of two steps (Fig. 3.24). The first step was the synthesis of PLLA containing the carboxylic acid chain ends (carboxylic telechelic poly(lactic acid), CBPLA) in the presence of stannous octoate ($Sn(Oct)_2$) and succinic acid (SA) via a melt condensation. The content of $Sn(Oct)_2$ acted as a catalyst was maintained at 0.5 wt% while the content of SA was varied from 5 to 15 wt%. The effect of SA content on the reaction time and molecular weights was investigated.

^{1}H-NMR spectrum of CBPLA presents the disappearance of methine proton at 4.37 ppm which adjacent to the OH chain ends while the methylene proton from the SA showed at 2.73 ppm (Fig. 3.25). The ^{1}H-NMR chemical shifts of CBPLA are listed in Table 3.8. The strong absorption band of C=O was observed at 1748 cm^{-1} (Fig. 3.26).

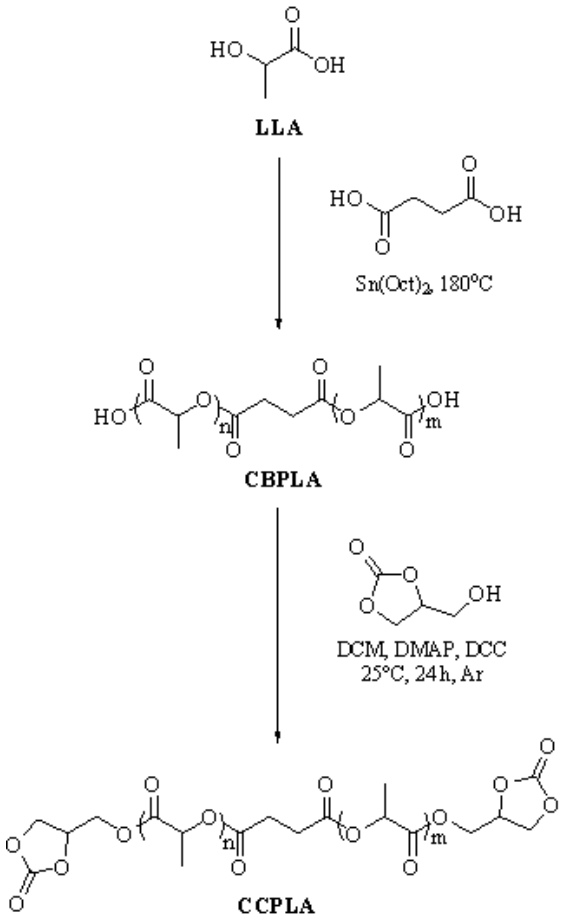

Fig. 3.24 Synthetic route of CCPLA.

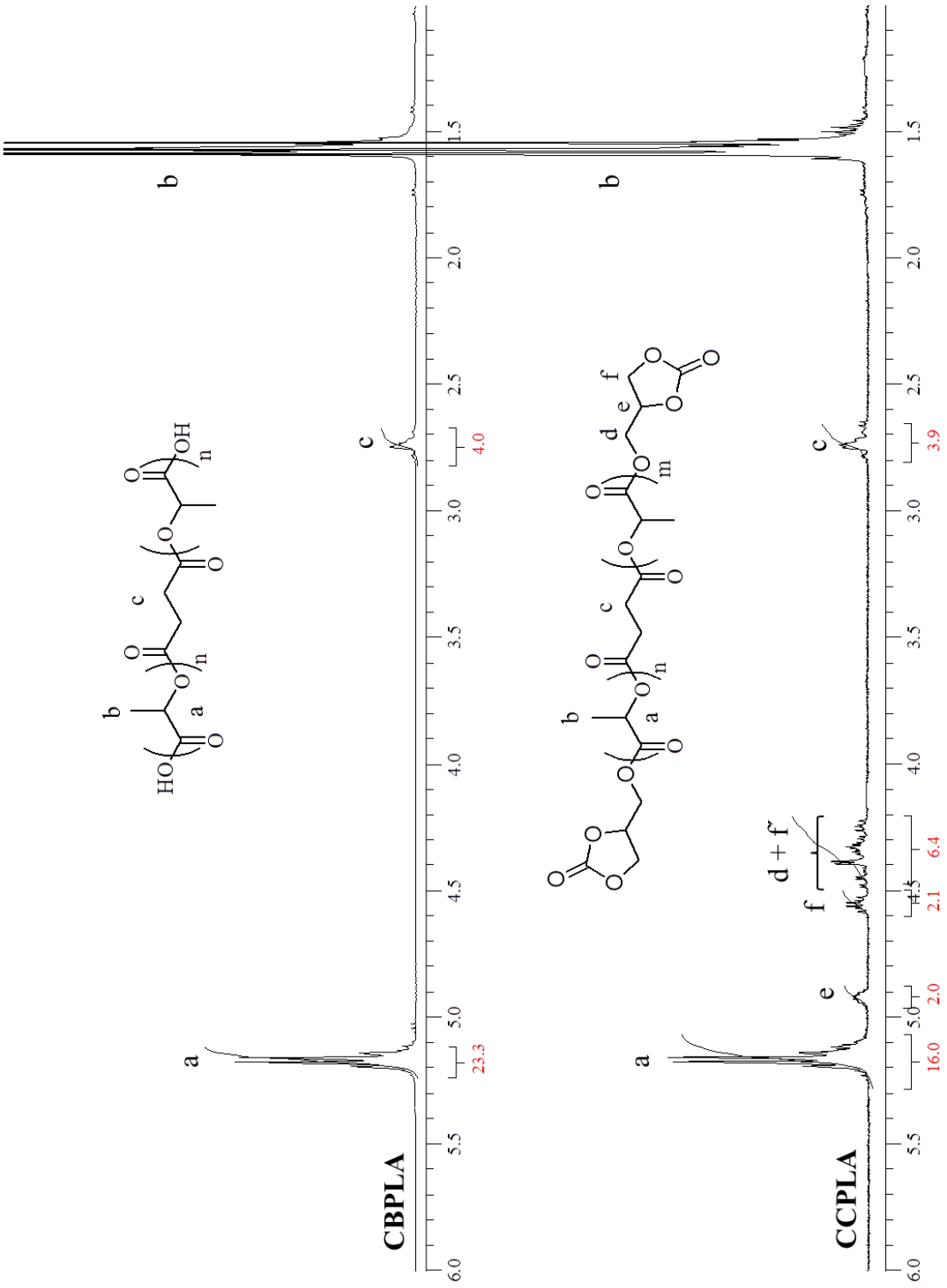

Fig. 3.25 ^{1}H-NMR spectra of CBPLA and CCPLA.

Table 3.8 ^{1}H-NMR chemical shifts of CBPLA

Type of proton	Chemical shift (ppm)
$CH_3C\boldsymbol{H}O_{repeating\ unit}$	5.17
$CH_3C\boldsymbol{H}O_{end\ unit}$	5.05
$2*C\boldsymbol{H_2}CH_2C(O)O$ and $2*CH_2C\boldsymbol{H_2}C(O)O$	2.73
$C\boldsymbol{H}_3CHO_{repeating\ unit}$	1.56

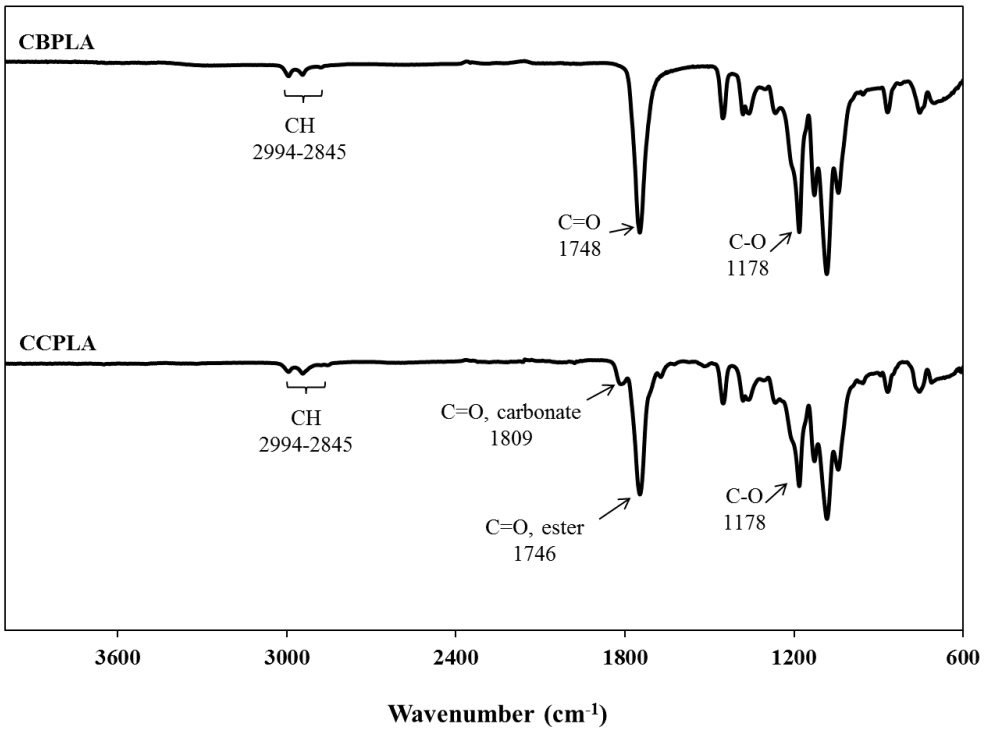

Fig. 3.26 FTIR spectra of CBPLA and CCPLA.

The COOH end group conversion was determined by ^{1}H-NMR according to the equation (3.6) (Huh and Bae, 1999), where I_d and I_c were the integration value of the peaks 5.05 and 4.36 ppm, respectively.

$$COOH\ end\ \ group\ conversion = \frac{I_d}{(I_d + I_c)} \times 100 \qquad (3.6)$$

The residual lactide and residual monomer conversion of CBPLA were according to the equation (3.7) and (3.8), respectively (Yoo and Kim, 2005). I_e, I_a, I_d, I_f, I_g and I_h were the integration value of the peaks of 5.36, 5.17, 5.05, 4.98, 4.36 and 4.36 ppm, respectively.

$$\text{Residual lactide conversion} = \frac{I_e}{\left(I_e + I_a + I_d + I_f + I_g + I_h\right)} \times 100 \qquad (3.7)$$

$$\text{Residual monomer conversion} = \frac{I_h}{\left(I_e + I_a + I_d + I_f + I_g + I_h\right)} \times 100 \qquad (3.8)$$

The COOH end group conversion of all samples were approximately 94% (Table 3.9). The residual of lactide was not observed in all samples except in CBPLA1 and no observation of residual monomer for all ones. The yield of CBPLA was in the range of 58-63%. All samples were solid. The color of sample was changed to beige and brown when increasing the amount of SA. The color change probably caused from the side reactions that are the discoloration and racemization (Moon *et al*., 2000).

Table 3.9 Conversions of COOH end group, lactide, yield and appearances of CBPLA

Sample	$\bar{M}_n$ (g/mol)[a]	$\bar{M}_n$ (g/mol)[b]	$\bar{M}_w$ (g/mol)[b]	Đ[b]
CBPLA1	1840	2980	4700	1.58
CBPLA2	1630	2600	4000	1.53
CBPLA3	1040	1600	2400	1.50

[a]Determined by ^{1}H-NMR.

$\bar{M}_n$ of carboxylic telechelic PLA (CBPLA) was calculated according to the equation (3.9), where I_a and I_c were the integration value of the peaks of 5.17 and 2.73 ppm, respectively. 72 and 118 were a molar mass of lactic acid (repeating unit) and a total molar mass of the rest of the molecule, respectively.

$$\overline{M}_n = \left[\frac{I_a}{(I_c/4)} \times 72 \right] + 118 \qquad (3.9)$$

$\bar{M}_n$ from ^{1}H-NMR analysis of CBPLA1, CBPLA2 and CBPLA3 were 1039, 1627 and 1840 g/ mol, respectively. For SEC analysis, $\bar{M}_n$ of CBPLA1, CBPLA2 and CBPLA3 were 1600, 2600 and 2980 g/mol, respectively. The dispersity was approximately 1.5 (Table 3.10). The content of SA played a role on both reaction time and molecular weight. The molecular weights and reaction time were decreased with increasing the content of SA (Fig. 3.27).

Table 3.10 Molecular weights of CBPLA

Sample	SA (wt%)	Time (h)	COOH[a] (%)	lactide[a] (%)	Yield (%)	Appearances
CBPLA1	5	88	94.51	1.43	63.54	White solid
CBPLA2	10	60	94.27	-	58.74	Beige solid
CBPLA3	15	35	95.72	-	60.12	Brown solid

[a]Determined by ^{1}H-NMR.
[b]Determined by SEC.

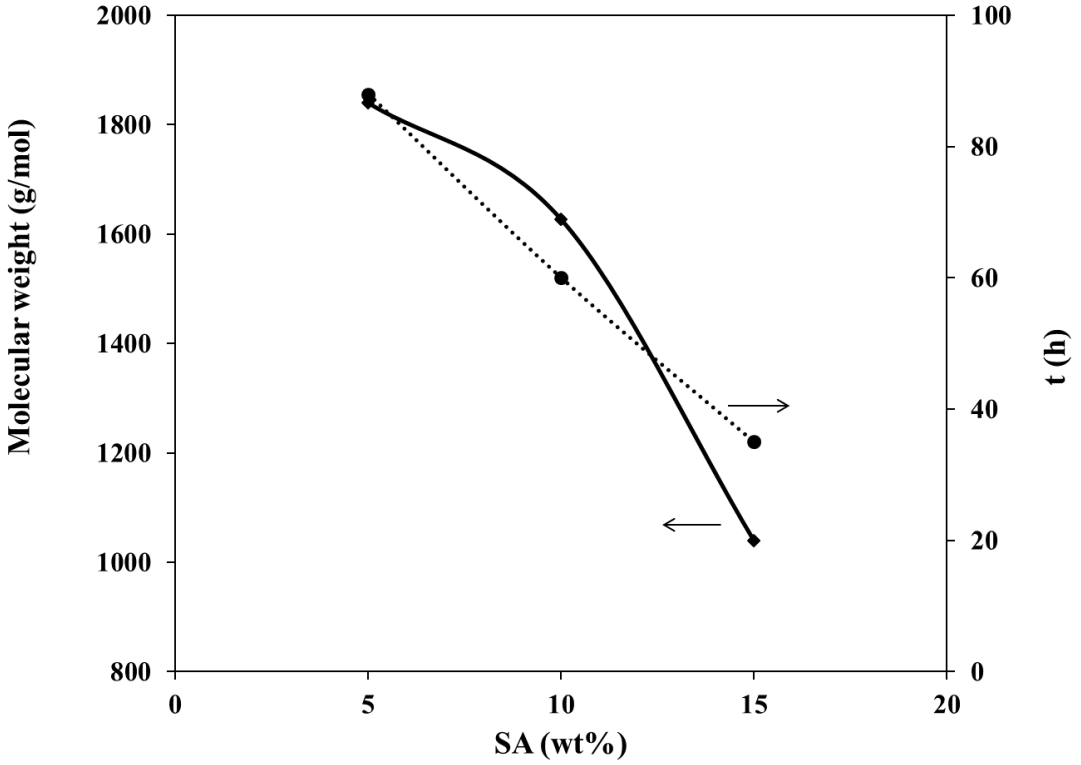

Fig. 3.27 Effect of SA contents on the reaction time and number average molecular weight ($\bar{M}_n$) of CBPLA.

In the final step, CBPLA1 and CBPLA3 were chosen to react with glycerol carbonate in the presence of DMAP and DCC corresponding cyclic carbonate chain ends (cyclic carbonate telechelic poly(lactic acid), CCPLA). The characteristic protons of carbonate moiety appeared at 4.95 and 4.22-4.60 ppm while the methylene proton from the SA still maintained at 2.73 ppm (Fig. 3.25, Fig. 3.28-3.30). The ^{1}H-NMR chemical shifts of CCPLA are listed in Table 3.11. The FTIR spectrum showed the new significant absorption band of C=O stretching from carbonate at 1809 cm^{-1} (Fig. 3.26).

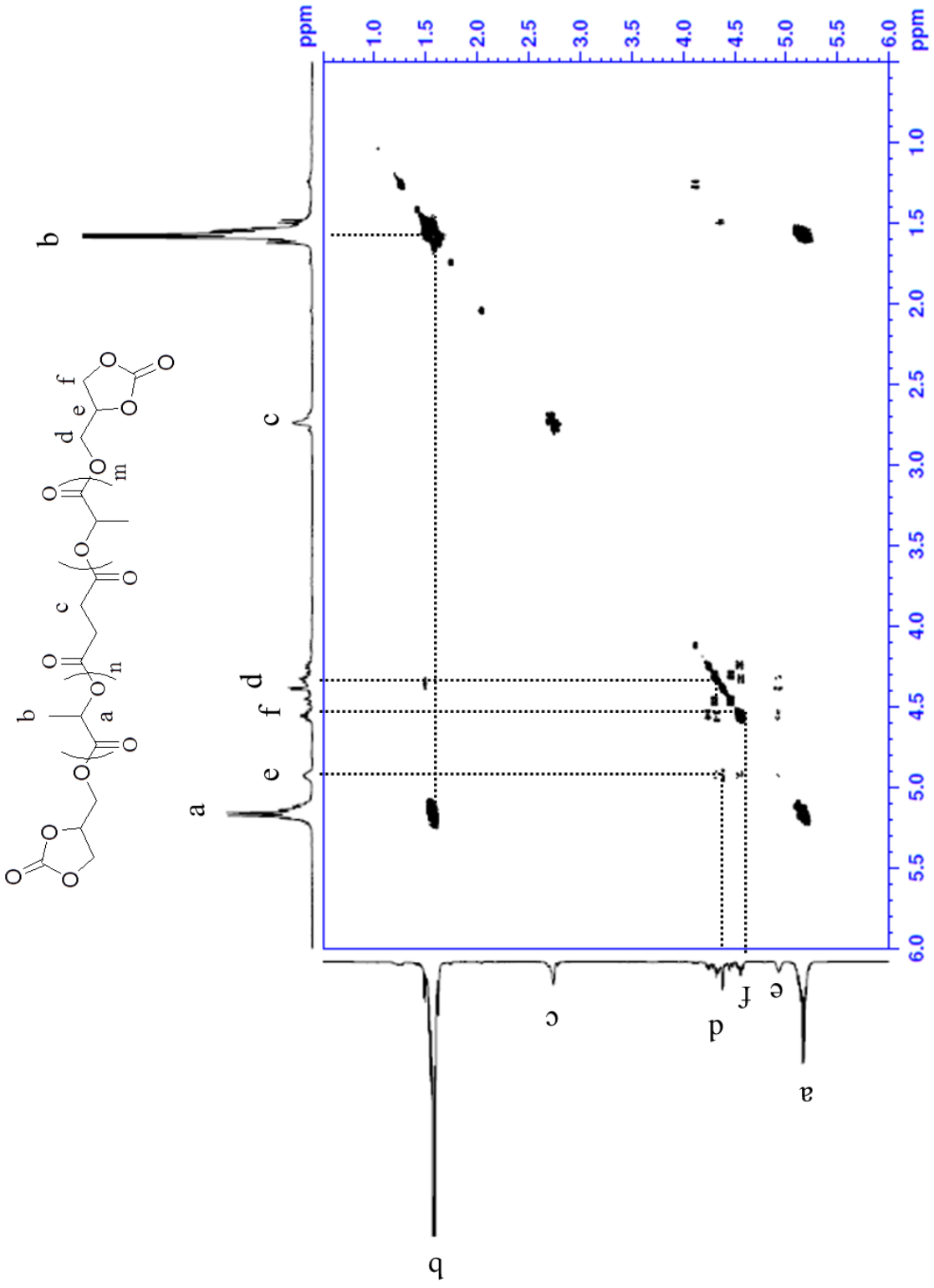

Fig. 3.28 COSY-NMR spectrum of CCPLA.

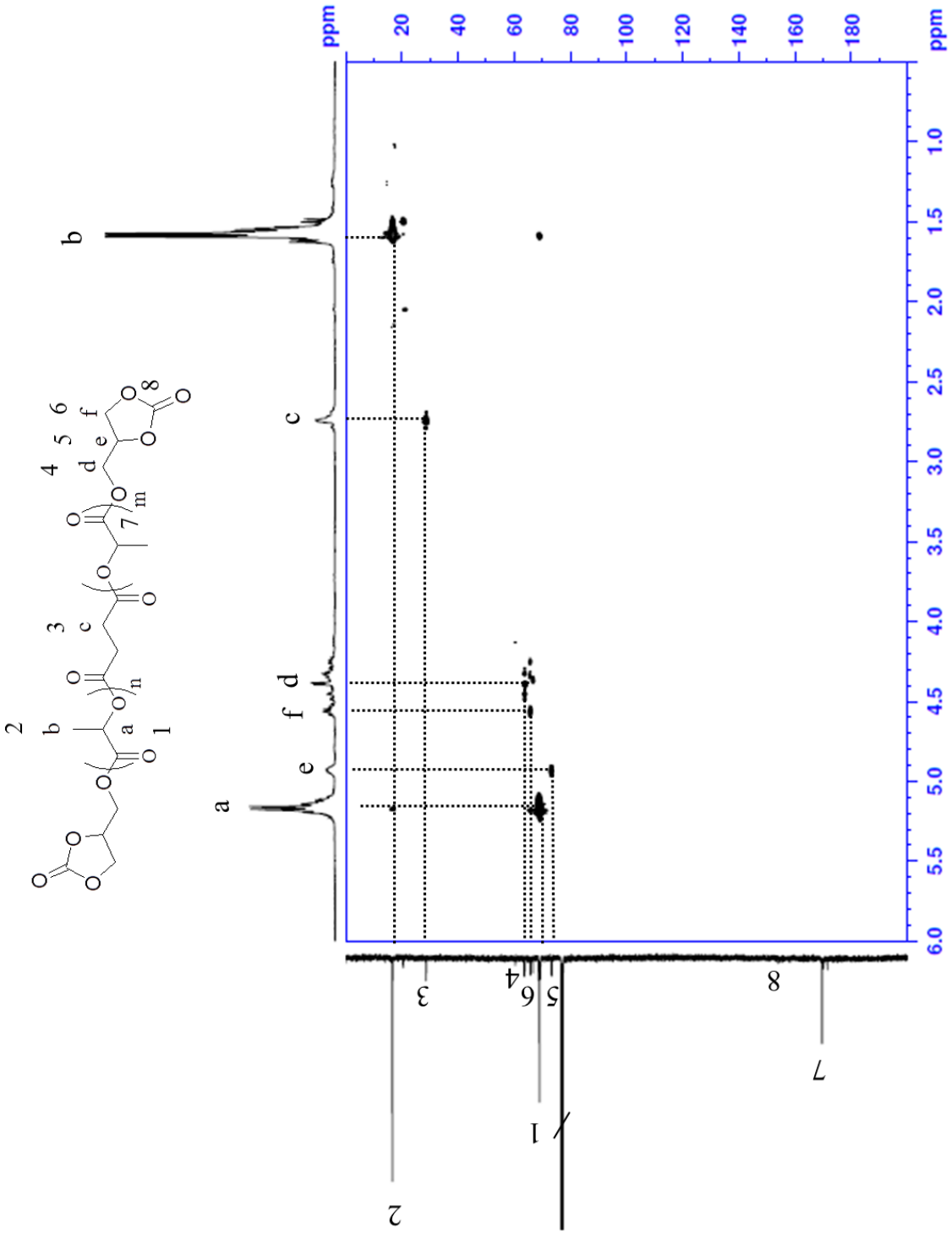

Fig. 3.29 HSQC-NMR spectrum of CCPLA.

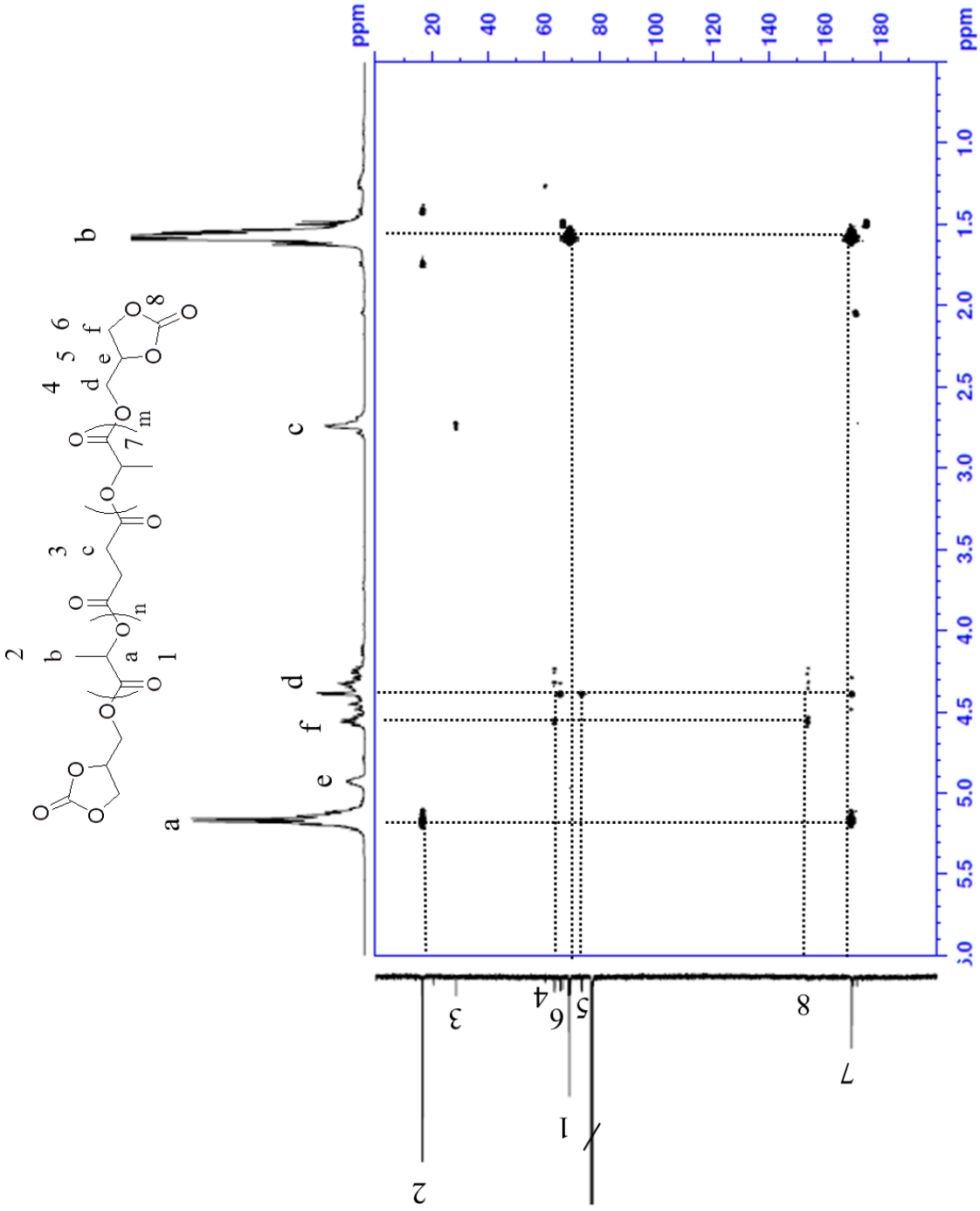

Fig. 3.30 HMBC-NMR spectrum of CCPLA.

Table 3.11 ^{1}H-NMR chemical shifts of CCPLA

Type of proton	Chemical shift (ppm)
$CH_3C\boldsymbol{H}O_{repeating\ unit}$	5.17
2*$CH_2CHC\boldsymbol{H}H'OC(O)O$	4.95
2*$C\boldsymbol{H_2}CHCH\boldsymbol{H'}OC(O)O$	4.22-4.60
2*$C\boldsymbol{H_2}CH_2C(O)O$ and 2*$CH_2C\boldsymbol{H_2}C(O)O$	2.73
$C\boldsymbol{H}_3CHO_{repeating\ unit}$	1.56

$\overline{M}_n$ of cyclic carbonate telechelic PLA (CCPLA) was determined by ^{1}H-NMR according to the equation (3.10), where I_a and I_c were the integration value of the peaks of 5.17 and 2.73 ppm, respectively. 72 and 318 were a molar mass of lactic acid (repeating unit) and a total molar mass of the rest of the molecule, respectively.

$$\overline{M}_n = \left[\frac{I_a}{(I_c/4)} \times 72 \right] + 318 \qquad (3.10)$$

The molecular weights are summarized in Table 3.12. For ^{1}H-NMR, $\bar{M}_n$ of CCPLA1 and CCPLA2 were 2100 and 1200 g/mol, respectively. For SEC analysis, $\bar{M}_n$ of CCPLA1 was 2900 g/mol. $\bar{M}_n$ of CCPLA2 was unable to determine because the peak was partially out of the calibration curve. Both CCPLA1 and CCPLA2 were solid with a good yield in the range of 70 to 90 %.

Table 3.12 Molecular weights, yields and appearances of CCPLA

Sample	$\bar{M}_n$ of CBPLA[a]	$\bar{M}_n$ (g/mol)[b]	$\bar{M}_n$ (g/mol)[c]	$\overline{M}_w$ (g/mol)[c]	Đ[c]	Yield (%)	Appearances
CCPLA1	1840	2100	2900	4500	1.51	92.07	White solid
CCPLA2	1040	1200	NA	NA	NA	73.38	Biege solid

[a]Molecular weight of CBPLA dertermining by ^{1}H-NMR
[b]Determined by ^{1}H-NMR.
[c]Determined by SEC.
NA: Not applicable because the peak was out of the calibration curve.

The presence of cyclic carbonate at both chain ends were identified by MALDI-TOF. The MALDI-TOF spectrum of CCPLA2 is presented in Fig. 3.31. One population was detected. A constant mass difference of 72 was observed assigning to the repeating unit of PLA. The most intense peak located at m/z [M+K^+] = 1437.399 (calculated value for $C_{57}H_{74}KO_{40}$ [M+K^+] = 1437.339) corresponding to a CCPLA with fifteen units.

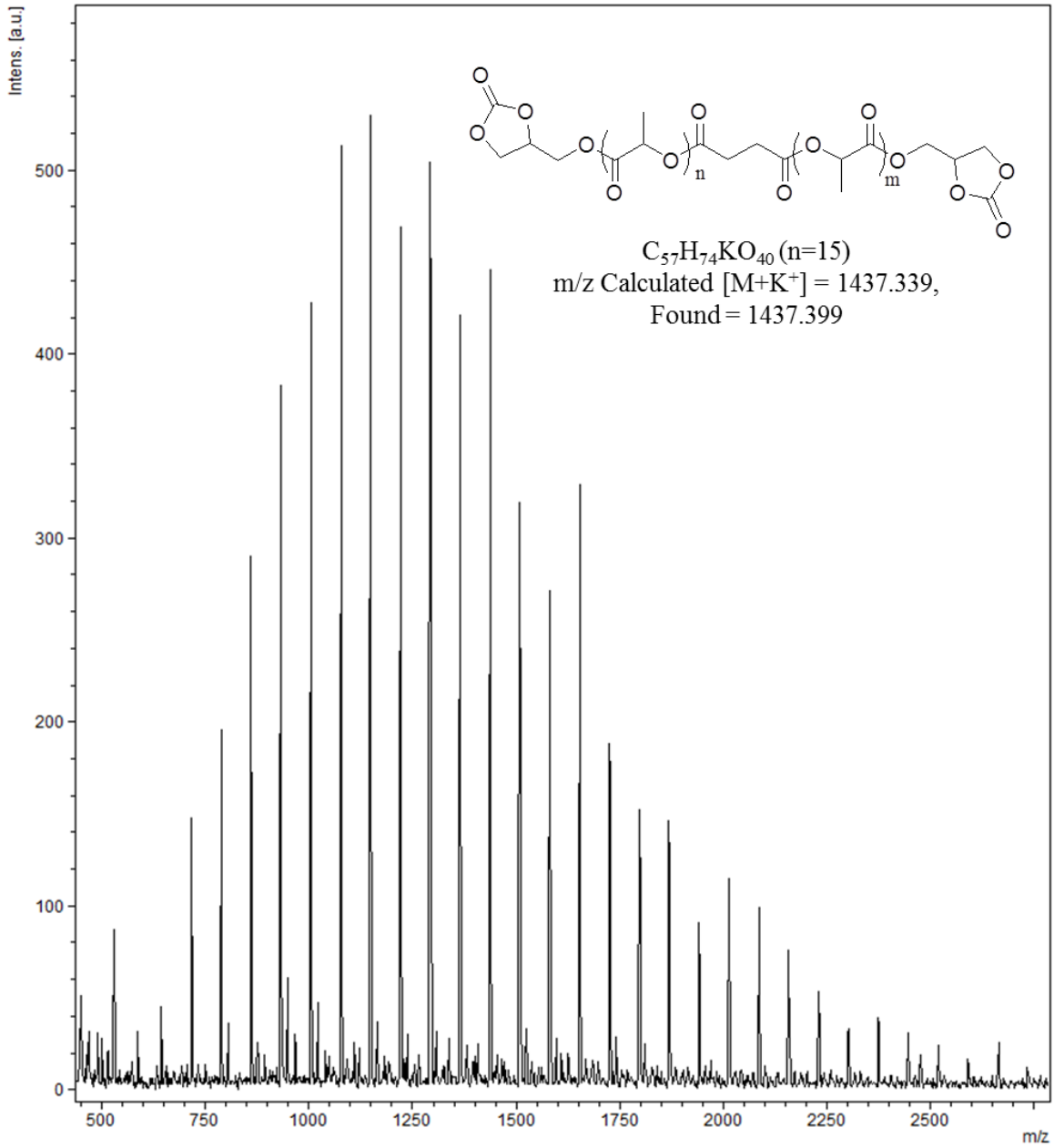

Fig. 3.31 MALDI-TOF spectrum of CCPLA with molecular weight of 1000 g/mol.

3.4 Synthesis of NIPUs

In this section, three strategies for the synthesis of NIPUs were described from two oligoisoprenes (ATNR and CCTNR) and oligo(lactic acid) (CCPLA). The first pathway was the reaction of ATNR and dicyclic carbonate (dicyclic carbonate #1 and dicyclic carbonate #2) as refered to NIPU#1. The second pathway was the reaction of CCTNR and various amines (di- and triamine) as refered to NIPU#2. The third pathway was the reaction of CCPLA and various diamines as refered to NIPU#3.

3.4.1 Synthesis of NIPU from ATNR and dicyclic carbonates (NIPU#1)

3.4.1.1 NIPU#1 characterization

The first approach was the synthetic method to produce NIPU#1 from the reaction of ATNR and dicyclic carbonate #1 (Fig. 3.32). The reaction was firstly performed in solution. The reaction was monitored by FTIR until no carbonate band or no change in FTIR spectrum. No reaction was found when the reaction was performed at 40°C for 22 h in THF. The urethane formation was observed when the reaction was performed at 100°C for 22 h in dioxane. The effect of molecular weight (1270 and 2300 g/ mol, named ATNR1000 and ATNR2000, respectively) and the molar ratio between carbonate to amine of 1:1 and 1:2 were studied. FTIR spectrum of all NIPU#1 and standing materials is shown in Fig. 3.33. The decreasing of carbonate band at 1780 cm^{-1} which indicated the urethane formation was found in NIPU#1-2, NIPU#1-3 and NIPU#1-4 while no reaction was found in NIPU#1-1. The disappearance of carbonate band indicating the complete reaction was found in NIPU#1-4. The absorption band of C=O from the urethane linkage was found and overlapped to the C=O from the ester at 1721 cm^{-1}. The bending vibration of NH appeared at 1556 cm^{-1}. These observations suggested that ATNR with lower molecular weight (1000 g/mol) was more reactive than the higher one and an excess amine was required. It has been already reported that using the excess of amine to produce the NIPU (Helou *et al*., 2011).

It has reported that LiBr (5 mol%) was efficient catalyst for synthesis of NIPU (Annunziata *et al*., 2014). Therefore, the preliminary study was performed under a similar condition with 5 mol% of LiBr (NIPU#1-5-NIPU#1-8). It was found

that the reaction was not complete because the carbonate band still presented as shown in Fig. 3.34.

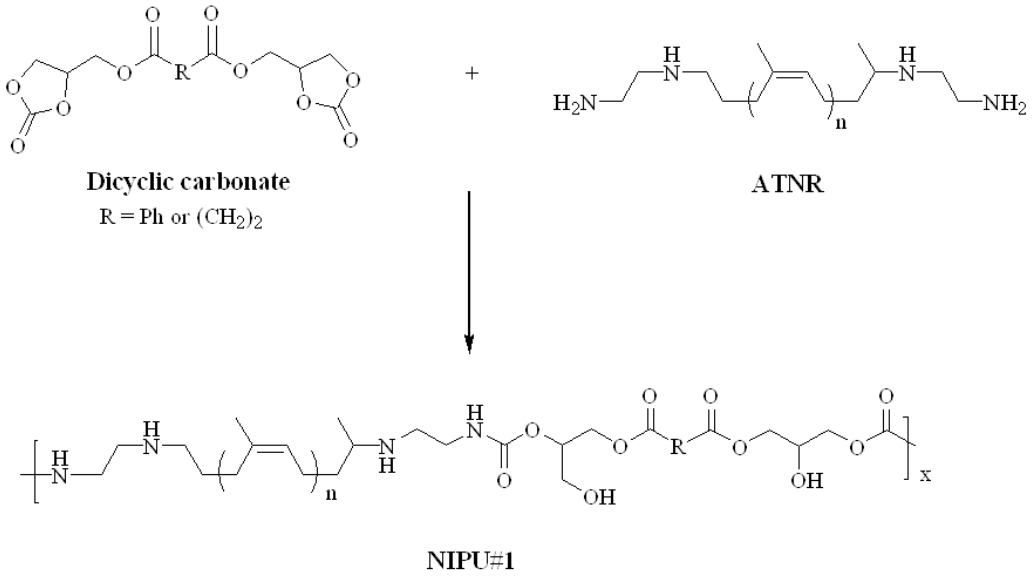

Fig. 3.32 Synthesis route of NIPU#1.

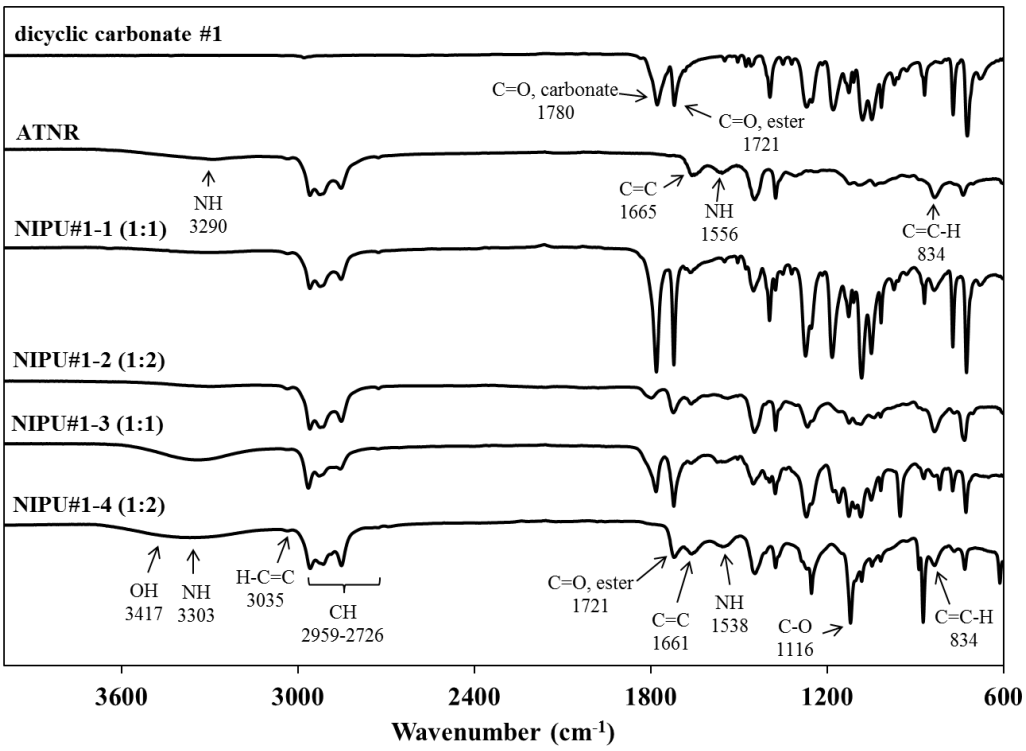

Fig. 3.33 FTIR spectra of NIPU#1.

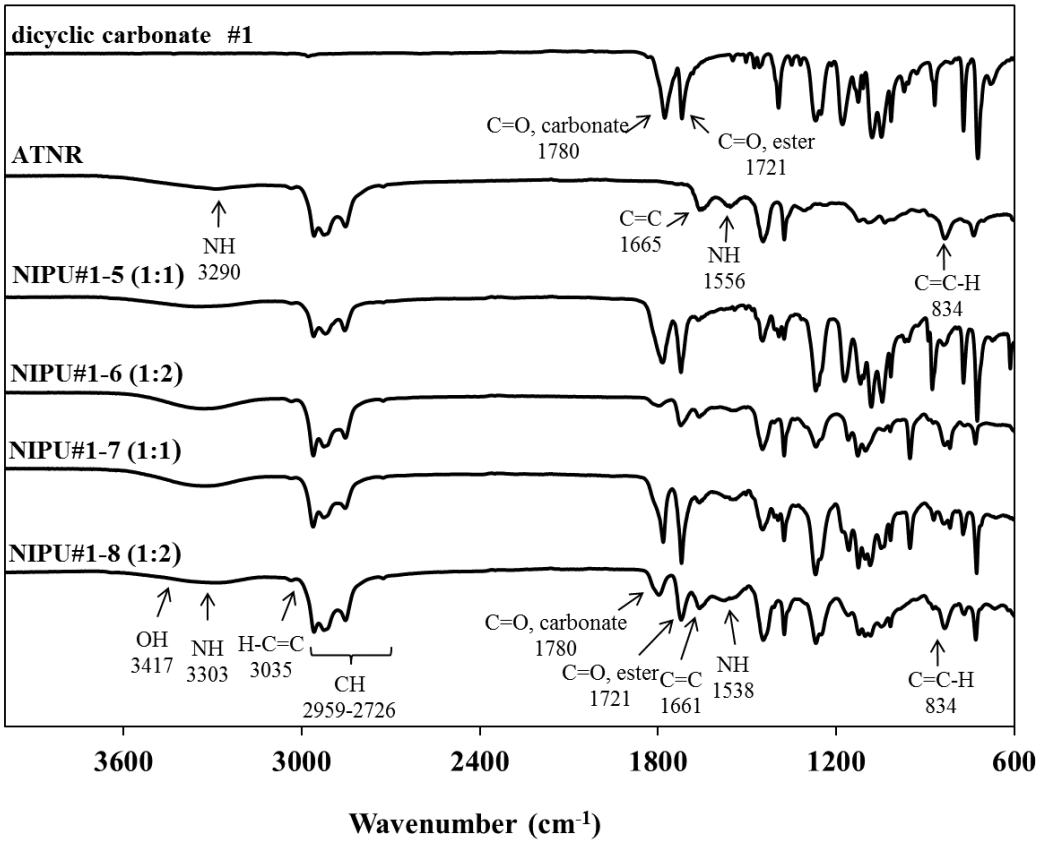

Fig. 3.34 FTIR spectra of NIPU#1 in the presence of catalyst.

Due to the high functional group concentration in bulk reaction, the second approach was performed without any solvent. The reaction was carried out at 70°C under vacuum. The molecular weight and the carbonate to amine ratio were determined. In the first type of experiment, dicyclic carbonate #1 was reacted with ATNR corresponding to NIPU#1-9-NIPU#1-11 (Fig. 3.35). The disappearance of carbonate band at 1721 cm^{-1} was found when the molar ratio of carbonate to amine rose to 1:1.5 (NIPU#1-10). It was found that the reaction time of NIPU#1-10 (48 h) with low molecular weight of ATNR (ATNR1000) was shorter than that NIPU#1-11 (100 h) with high molecular weight (ATNR2000). The characteristic bands of OH stretching, NH stretching and NH bending vibration of urethane linkage appeared at 3417, 3303 and 1538 cm^{-1}, respectively. The C=O stretching assigning to urethane linkage was overlapped with C=O from ester at 1721 cm^{-1}.

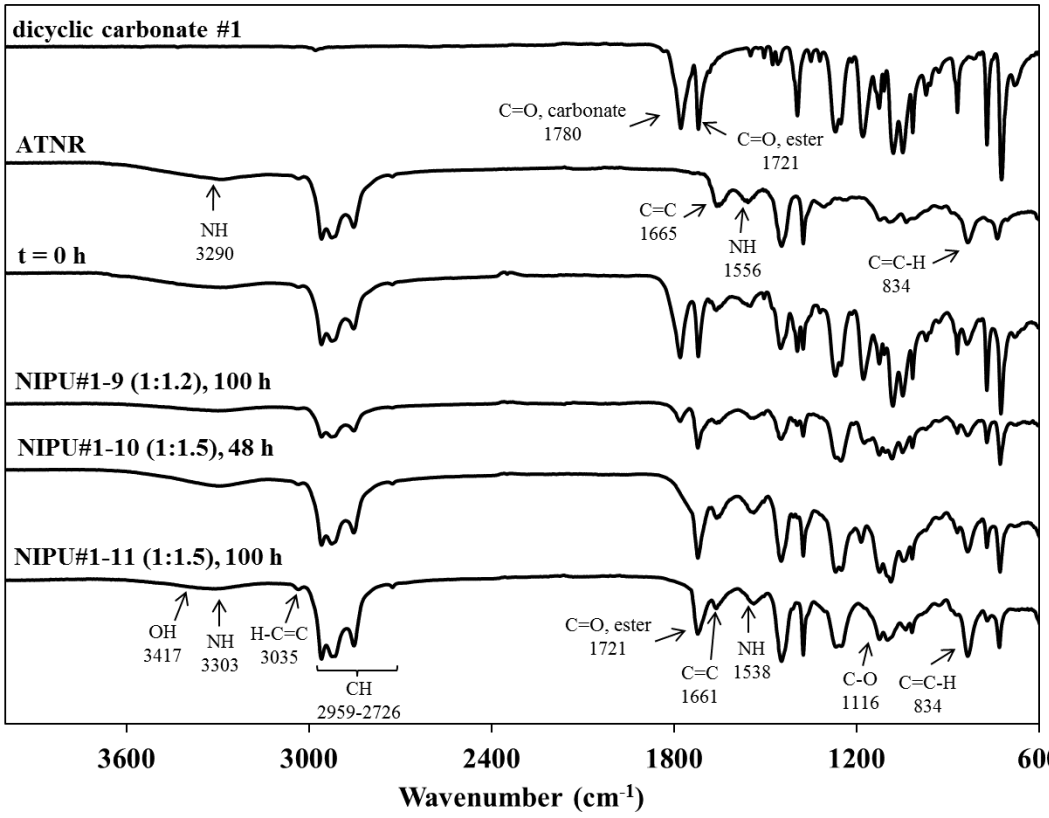

Fig. 3.35 FTIR spectra of NIPU#1 from the ATNR and dicyclic carbonate#1 in bulk reaction.

In the second one of experiment, dicyclic carbonate #2 was reacted with ATNR to afford NIPU#1-12-NIPU#1-14. At the carbonate to amine ratio of 1:1.5 (NIPU#1-12), the incomplete reaction was observed because the presence of carbonate band at 1780 cm^{-1} (Fig. 3.36). The carbonate band was not noticeable when the carbonate to amine ratio was rose to 1:2 (NIPU#1-13 (ATNR1000) and NIPU#1-14 (ATNR2000)). The complete reaction showed the characteristic bands of urethane linkage at 3417, 3303, 1711 and 1538 cm^{-1} corresponding to OH stretching, NH stretching, C=O stretching and NH bending, respectively. The peak at 1650 cm^{-1} assigning to amide formation was not observed indicating that no side reaction between amine and ester linkage (Javni *et al*., 2008).

All sample showed the similar appearance as reddish brown and opaque. The molecular weight of NIPU#1-10 was determined by SEC. It was partially soluble in THF because hydrogen bonding caused the solubility or insolubility in

common solvent. The $\overline{M}_n$, $\overline{M}_w$ and dispersity from the partially soluble fraction were 3000 g/mol, 4100 g/mol and 1.39, respectively. The molecular weight distribution of NIPU#1-10 is shown in Fig. 3.37. The soluble fraction was identified the chemical structure by ^{1}H-NMR by dissolving in $CDCl_3$ (50°C). ^{1}H-NMR spectrum is shown in Fig 3.38. The characteristic protons of urethane formation were observed between 4.17 and 4.56 ppm assigning to alpha protons adjacent to urethane linkage.

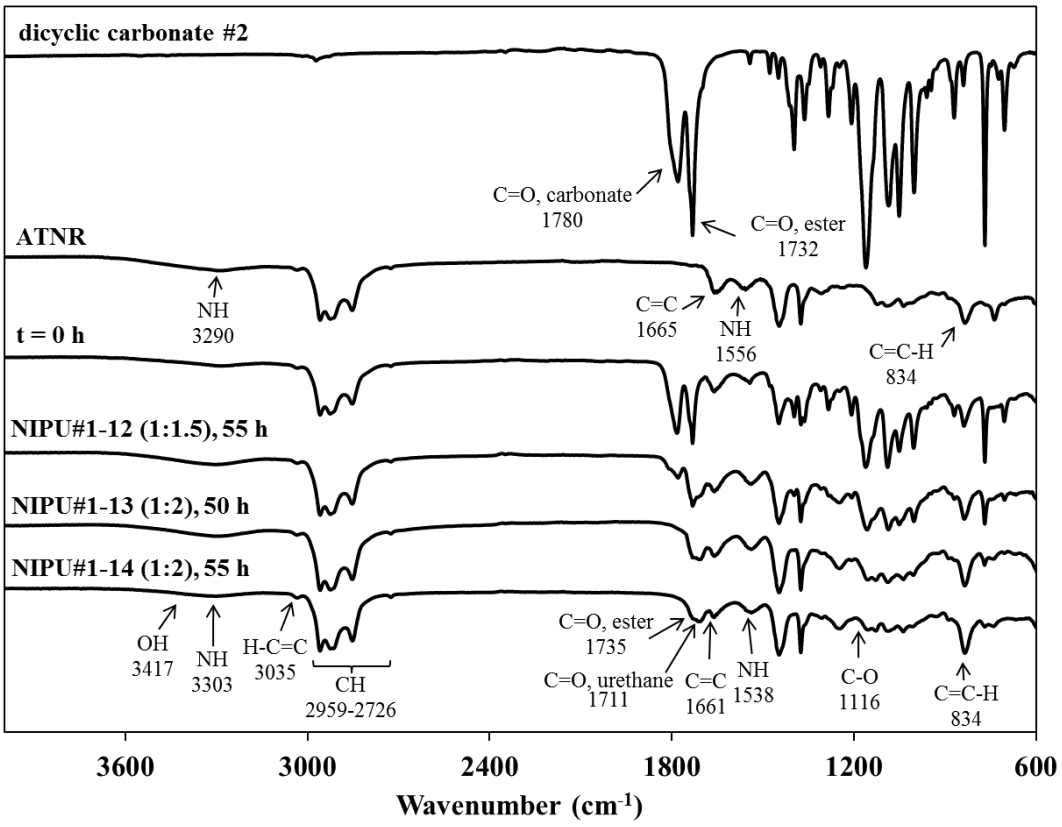

Fig. 3.36 FTIR spectra of NIPU#1 from the ATNR and dicyclic carbonate#2 in bulk reaction.

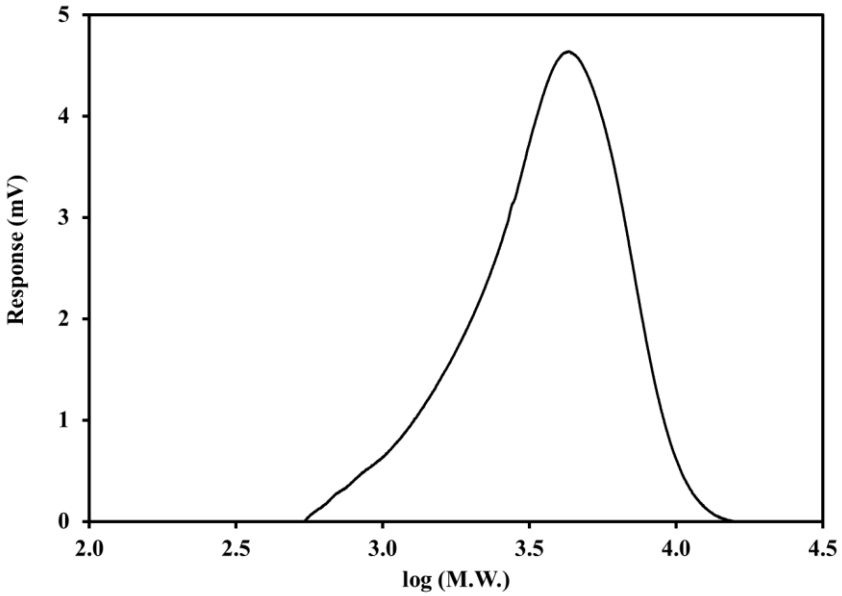

Fig. 3.37 Molecular weight distribution of NIPU#1-10 from a partially soluble fraction.

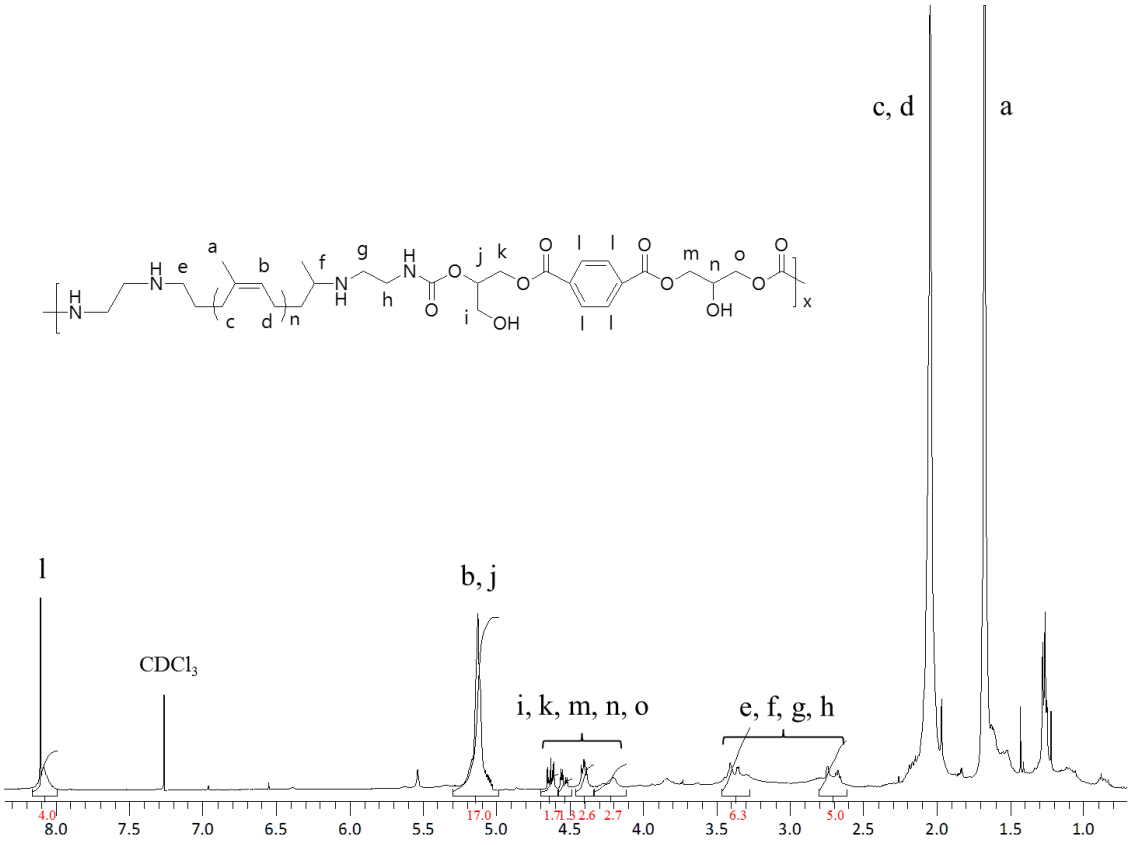

Fig. 3.38 ^{1}H-NMR spectrum of NIPU#1-10 from partially soluble fraction in $CDCl_3$.

3.4.1.2 Thermal properties of NIPU#1

The thermal properties of the NIPU#1 were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC thermograms of NR and ATNR from the second heating scan (2H) are displayed in Fig. 3.39. The glass transition temperature (T_g) of NR**,** ATNR2000 and ATNR1000 were -63.2, -58.1 and -39.7°C, respectively. It was found that T_g decreased when increasing the molecular weight because of the highly chain flexibility. This observation was implied that the $\overline{M}_n$ played an important role in the T_g value.

The DSC thermograms of NIPU#1 from the first heating scan and second heating scan are shown in Fig. 3.40. The thermal transition temperatures of NIPU#1 are listed in Table 3.13. All samples showed the melting temperature (T_m) in the first heating scan (Fig. 3.40a) but was not observed in the second heating scan (Fig. 3.40b) because of the lower crystallization rate. The similar phenomenon has been reported that the T_m showed only in the first heating scan (Velthoven *et al***.,** 2015). No significant difference between T_g from the first and second heating scans were observed. The T_g from the first and heating scans of all samples closed to the T_g of ATNR indicating that the molecular weight of ATNR has an influence on T_g of NIPU#1.

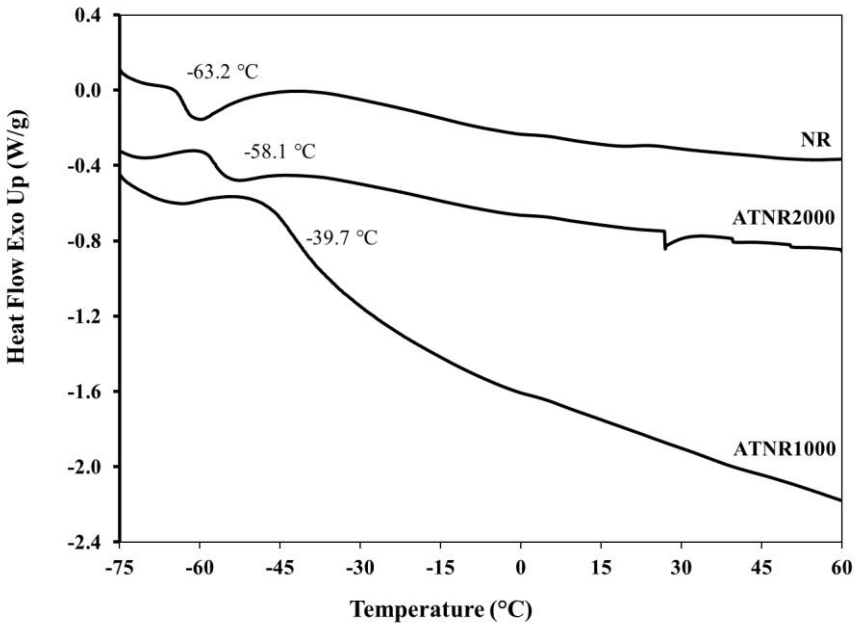

Fig. 3.39 DSC thermograms of NR, ATNR2000 and ATNR1000 from second heating scan.

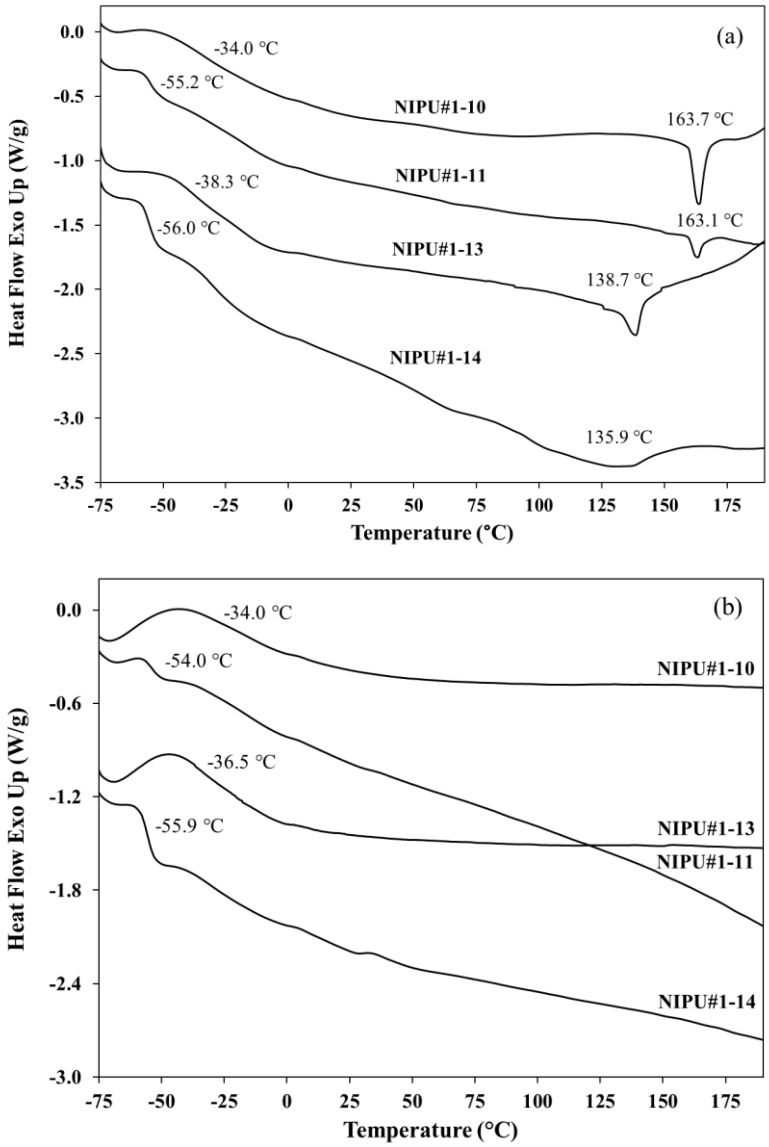

Fig. 3.40 DSC thermograms of NIPU#1: (a) 1H-NIPU#1 and (b) 2H-NIPU#1.

Table 3.13 Glass transition and thermal degradation temperature of NIPU#1

Sample	1H[a]		2H[b]	T_d[c]	
	T_g (°C)	T_m (°C)	T_g (°C)	T_{10} (°C)	T_{max} (°C)
NIPU#1-10	-34.0	163.7	-34.0	200	339
NIPU#1-11	-55.2	163.1	-54.0	204	341
NIPU#1-13	-38.3	138.7	-36.5	191	340
NIPU#1-14	-56.0	135.9	-55.9	193	345

[a]Determined by DSC from the first heating scan (1H).
[b]Determined by DSC from the second heating scan (2H).
[c]Determined by TGA.

The decomposition temperature (T_d) was evaluated and classified into two temperatures as T_{10} and T_{max}. T_{10} was the temperature at 10% weight loss and derived from the TGA curve. T_{max} was the maximum weight loss temperature derived from the maximum peak of the DTG curve. All samples showed the similar decomposition step (Fig. 3.41). The general decomposition steps of NIPUs have been described (Carré *et al*., 2014; Nanclare et al., 2015; Duval *et al*., 2016). The first decomposition step at the lower temperature was assigned to the rupture of the urethane linkage leading to evaporation of small molecules. The next decomposition step at the higher temperature was attributed to the hydrocarbon chain or soft segment degradation. T_{10} and T_{max} of NIPU#1 are summarized in Table 3.13. T_{10} was not significant difference and approximately at 190-200°C. T_{max} was also not significant difference around at 339 to 345°C.

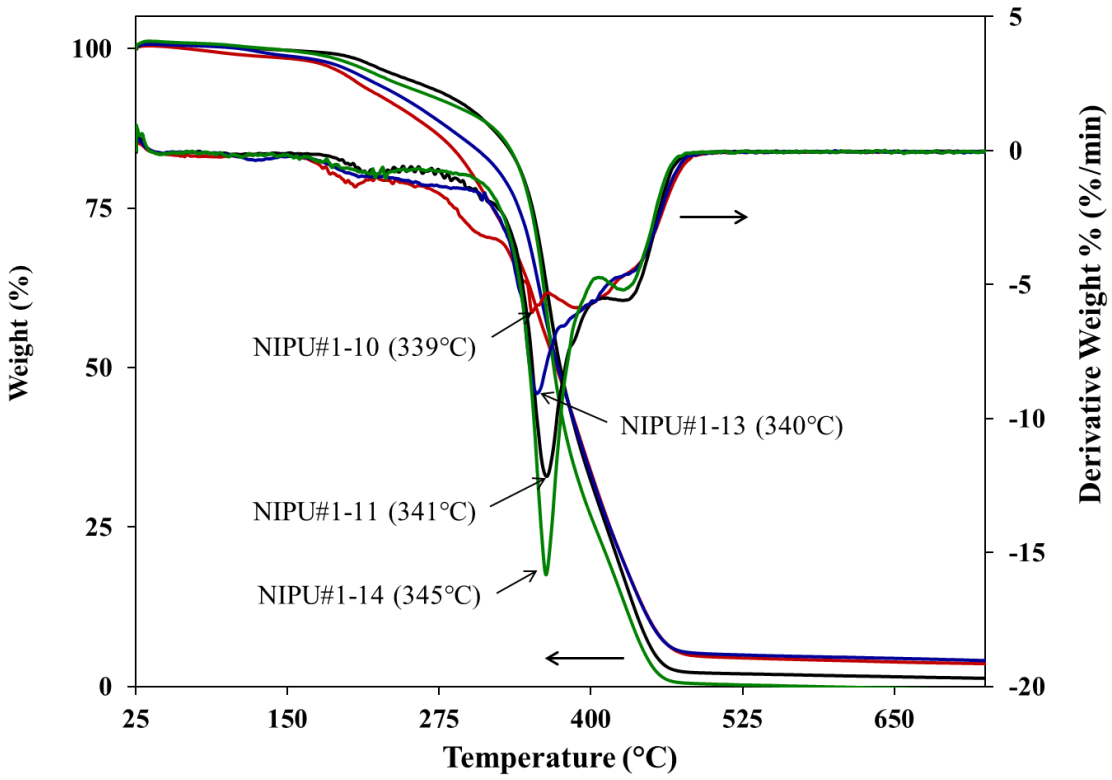

Fig. 3.41 TGA and DTG curves of NIPU#1.

3.4.2 Synthesis of NIPU#2

3.4.2.1 NIPUs characterization

The reaction of CCTNR with two molecular weights ($\bar{M}_n$ = 1430 and 2270 g/mol, named CCTNR1000 and CCTNR2000, respectively) and various amines (1,2-diamine (EDA), butane-1,2-diamine (BDA), *p*-xylylenediamine (*p*-XDA) and tris(2-aminoethyl)amine (TAEA)) corresponding linear and cross-linked NIPU#2 are shown in Fig. 3.42. The reaction was performed at 70°C in bulk reaction under vacuum. The linear and cross-linked structure of NIPU#2 were controlled by type of amine.

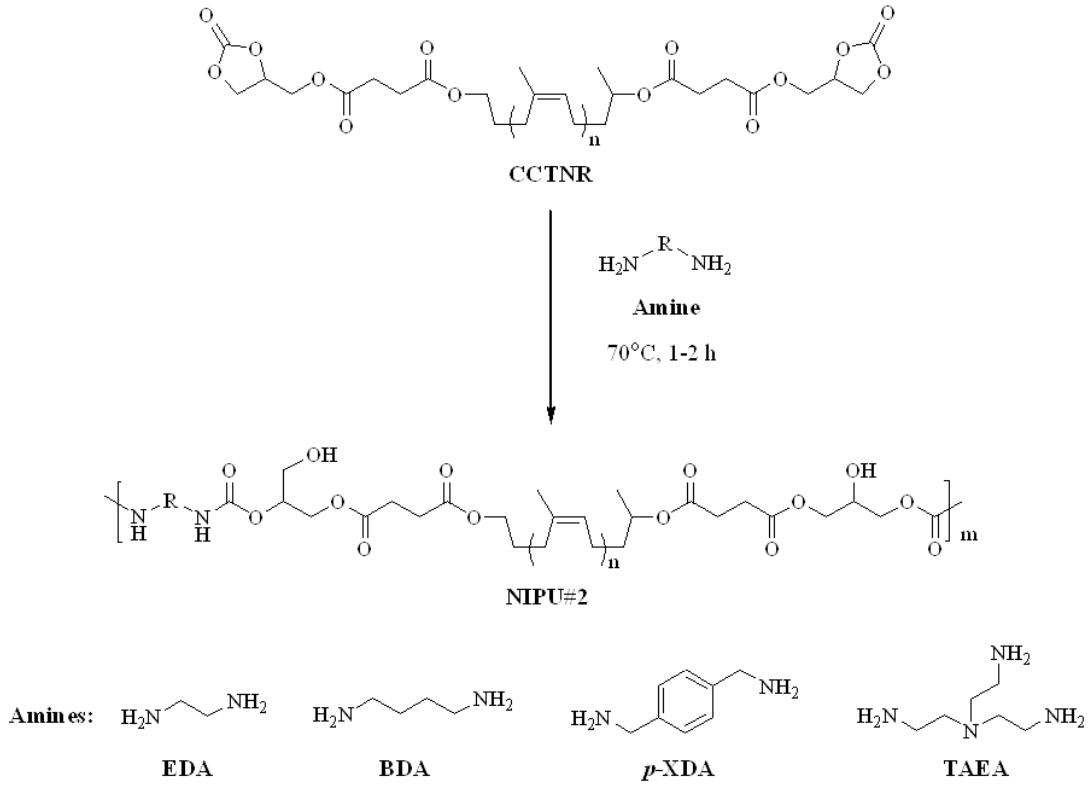

Fig. 3.42 Synthesis route of NIPU#2.

The linear NIPU#2 was synthesized by using diamines (EDA, BDA and *p*-XDA) as referred to NIPU#2-1 – NIPU#2-6. The carbonate to amine ratio was 1:1.5 in all reactions. Fig. 3.43 represents the FTIR spectra of linear NIPU#2. All samples showed the disappearance of the carbonate band at 1800 cm^{-1} indicating a complete

reaction. The characteristic absorption bands were observed at 3417, 3322, 1704 and 1538 cm^{-1} corresponding to the OH stretching, NH stretching, C=O stretching and NH bending vibrations of urethane, respectively.

CCTNR2000 was reacted with diamines as the same carbonate to amine ratio in order to study the influence of molecular weight of CCTNR. The similar bands were observed in Fig. 3.44. The disappearance of carbonate band suggested a complete reaction. Therefore, the molecular weight had no influence in this case. The amide absorption band at 1650 cm^{-1} was not observed in all spectra indicating that the side reaction did not occur.

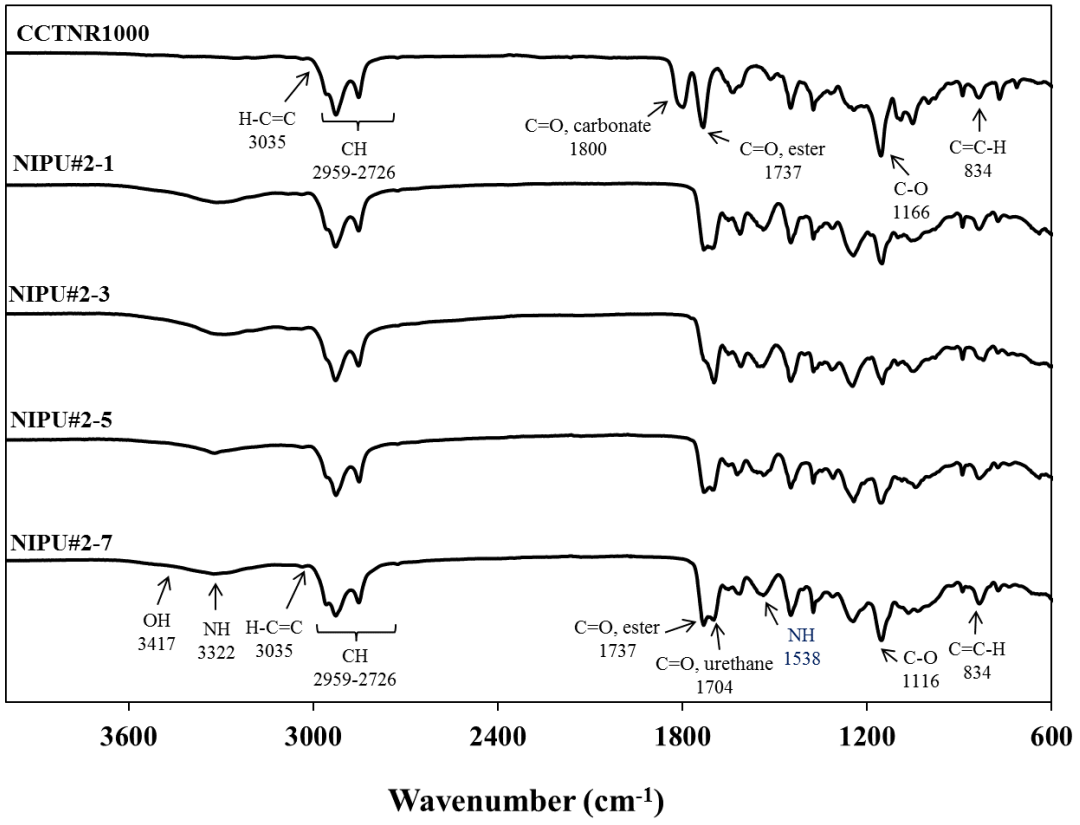

Fig. 3.43 FTIR spectra of NIPU#2 prepared from the CCTNR1000 and various diamines.

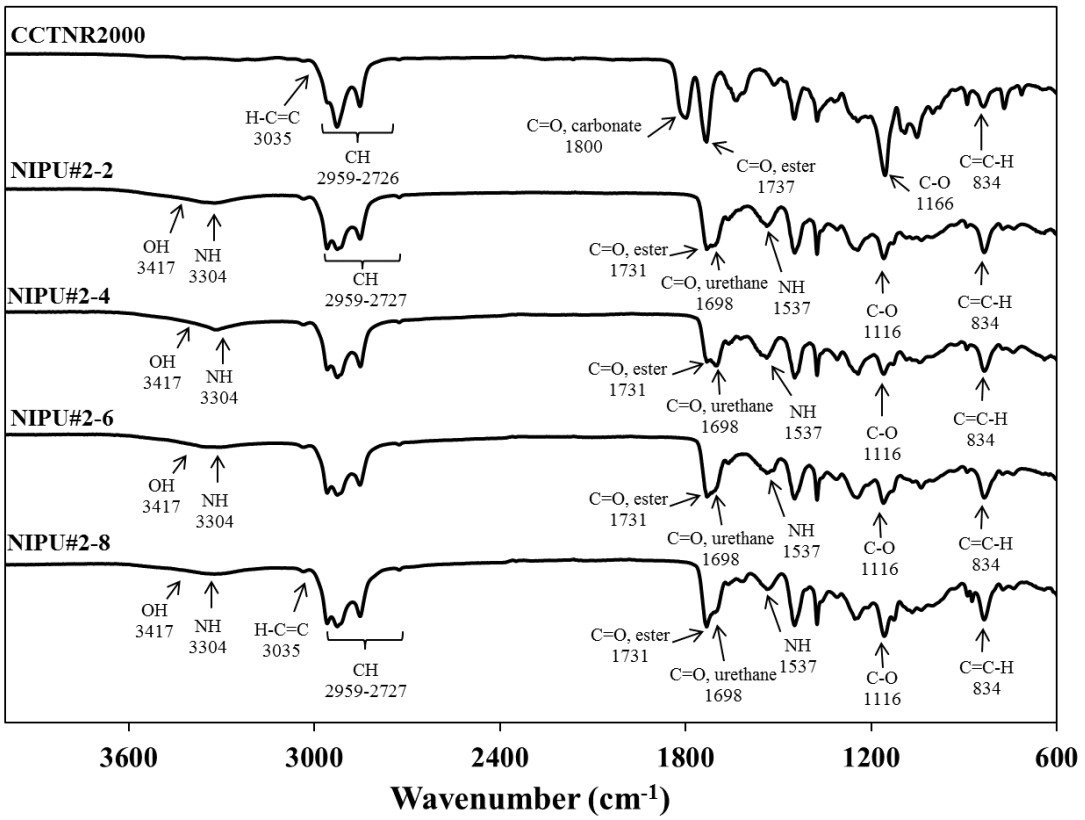

Fig. 3.44 FTIR spectra of NIPU#2 prepared from the CCTNR2000 and various diamines.

The cross-linked NIPU#2 (NIPU#2-7 and NIPU#2-8) was carried out from the reaction of CCTNR (CCTNR1000 and CCTNR2000) and triamine (TAEA) (Fig. 3.42). The reaction was performed at 70°C under vacuum. As the carbonate to amine ratio of 1:0.7, the disappearance of carbonate band at 1800 cm^{-1} were observed in both NIPU#2-7 and NIPU#2-8 indicating a complete reaction (Fig. 3.43 and Fig. 3.44). The characteristic absorption bands showed at 3417, 3322, 1704 and 1538 cm^{-1} assigning to OH stretching, NH stretching, C=O stretching and NH bending vibrations of urethane linkage, respectively. No influence of molecular weight was observed. The absence of amide band indicated that the undesirable aminolysis from amine and ester linkage did not occur.

In order to evaluate the $\overline{M}_n$ of all NIPU#2 by SEC, the samples were dissolved in THF and DMF. The linear NIPU#2 (NIPU#2-1 – NIPU#2-6) were insoluble in

DMF but partially soluble in THF. Therefore, THF was chosen as a solvent. The molecular weights of samples from the partially soluble fraction are listed in Table 3.14. The $\overline{M}_n$ of soluble linear NIPU#2 was in the range of 3300 to 6200 g/mol. The $\overline{M}_w$ was in the range between 4700 and 13600 g/mol. The dispersity was roughly around 2. The molecular weight distributions of linear NIPU#2 from the partially soluble fraction are presented in Fig 3.45. As expected, the cross-linked NIPU#2-7 and NIPU#2-8 were not unable to determine the molecular weight because the samples were insoluble. The homogeneous films could be able to prepare only in cross-linked samples. The yellowish and transparent films of NIPU#2-7 and NIPU#2-8 were presented in Fig. 3.46. It has also described in the literature that the hydrogen bonds caused the partially soluble or insoluble in common solvent (Duval *et al*., 2016). They have reported the $\overline{M}_n$ was approximately 5000 g/mol from a partially soluble part. Similarly, Carré *et al*. (2014) have also reported the $\overline{M}_n$ from the soluble (6000 and 9000 g/mol) and partially soluble part (7000 g/mol).

Table 3.14 Molecular weight of different NIPU#2

NIPU	$\overline{M}_n$(g/mol^{-1})[a]	$\overline{M}_w$(g/mol^{-1})[a]	Đ[a]
NIPU#2-1	3400	4700	1.40
NIPU#2-2	3700	9600	2.58
NIPU#2-3	3300	5400	1.64
NIPU#2-4	4200	8300	1.99
NIPU#2-5	4700	9000	1.92
NIPU#2-6	6200	13600	2.20
NIPU#2-7	Insoluble		
NIPU#2-8	Insoluble		

[a]Determined by SEC from the partially soluble fraction.

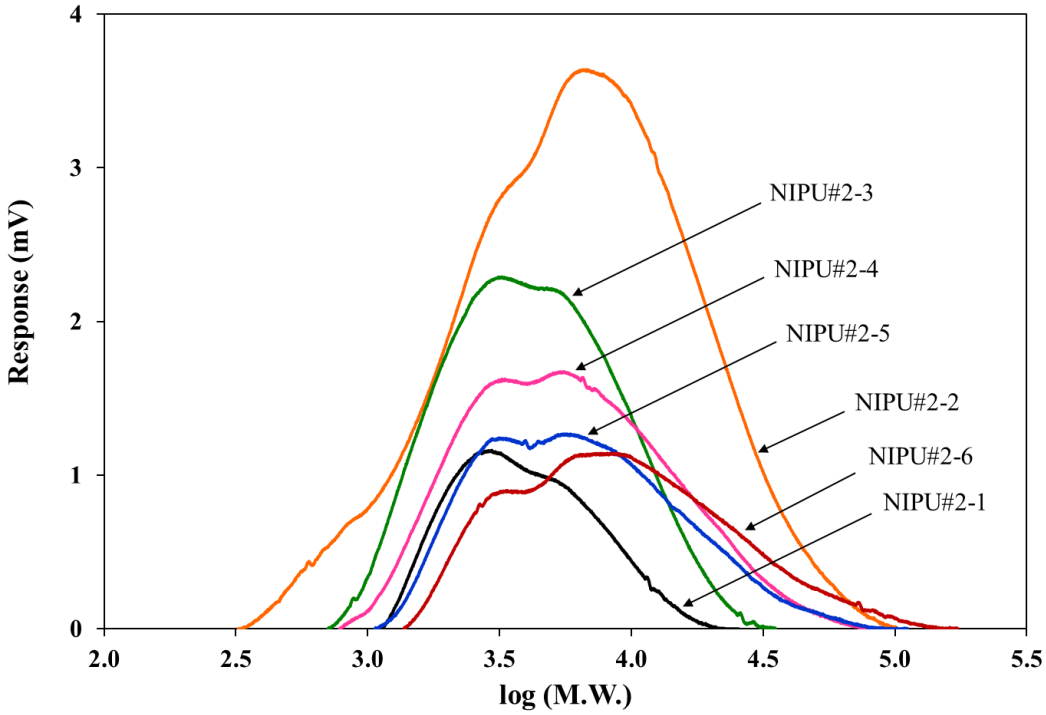

Fig. 3.45 SEC molecular weight distributions of linear NIPU#2 from partially soluble fraction.

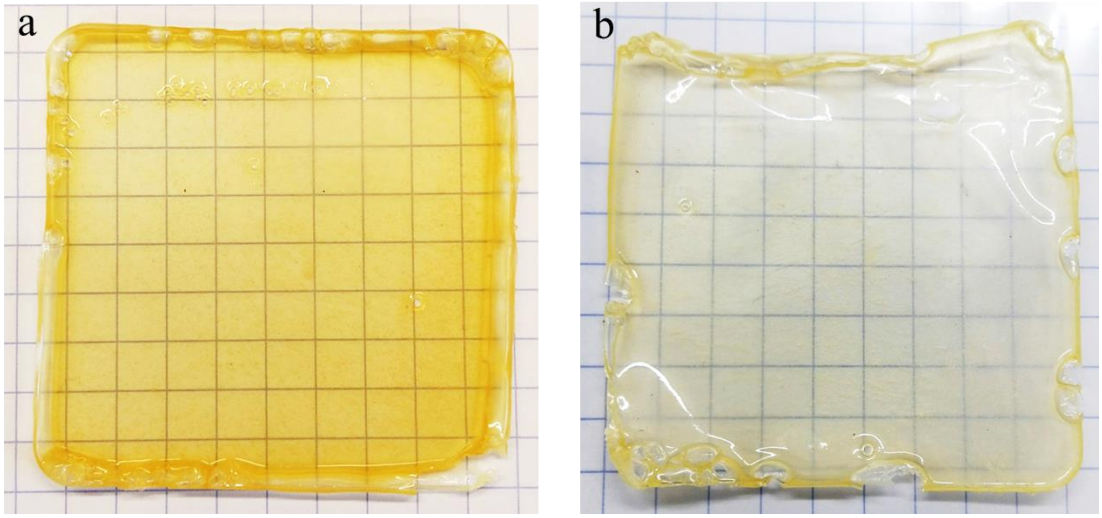

Fig. 3.46 Photographs of cross-linked NIPU#2 films: (a) NIPU#2-7 and (b) NIPU#2-8.

The chemical structure of NIPU#2-1 was attempted to identify by ^{1}H-NMR in $CDCl_3$ (t=50°C). The soluble fraction was analyzed. The disappearance of carbonate peaks at 4.55 and 4.33 ppm indicated the opening of carbonate ring corresponding the urethane formation (Fig. 3.47). The significant protons which were the α-protons adjacent to ester and protons adjacent to the alcohol were observed between 4.00 and 4.22 ppm. The methylene protons and protons at α-position of ester were observed at 2.56 to 2.86 ppm.

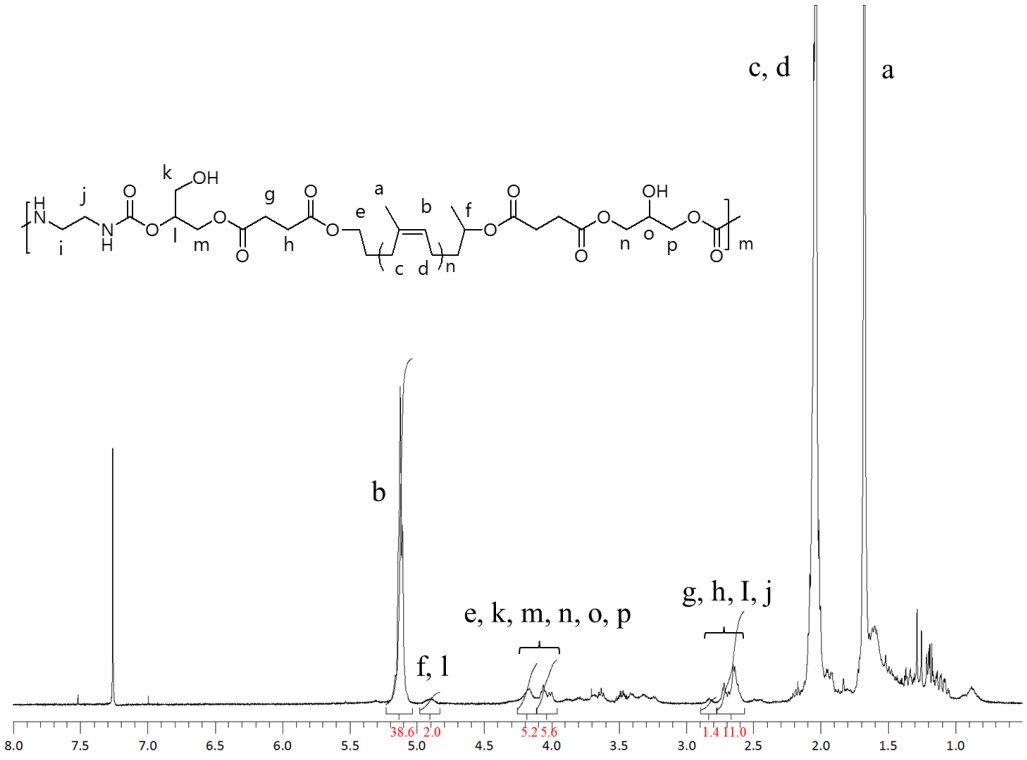

Fig. 3.47 ^{1}H-NMR spectrum of NIPU#2-1 from the partially soluble fraction in $CDCl_3$.

3.4.2.2 Thermal properties of NIPU#2

Fig. 3.48 presents the T_g from the second heating scan of NR, CCTNR2000 and CCTNR1000 at -63.2, -53.9 and -38.6°C, respectively. The CCTNR2000 showed the lower T_g than that CCTNR1000 due to the higher flexibility of chain as a similar reason to ATNR.

No observation of melting peak in all samples suggested that all samples were amorphous (Fig. 3.49 and Table 3.15). The linear NIPU#2 preparing from CCTNR1000 (NIPU#2-1, NIPU#2-3 and NIPU#2-5) showed the T_g which was in the range of -34.5 to -32.7°C. It was found that the T_g of sample closed to the CCTNR1000 (-38.6°C). While the similar observation was found in sample preparing from CCTNR2000 (NIPU#2-2, NIPU#2-4 and NIPU#2-6) which has the T_g ranging from -53.9 to -51.8°C. These observations suggested the type of amine did not effect T_g. The cross-linked NIPU#2 (NIPU#2-7 and NIPU#2-8) showed slightly higher T_g than that linear NIPU#2 because of the presence of hydrogen bonding leading to reducing the chain mobility of sample (Wang *et al*., 2013). The molecular weight of CCTNR has strong influence on T_g both linear and cross-linked NIPU#2.

The TGA and DTC thermograms of NIPU#2 are shown in Fig. 3.50 and Table 3.15. T_{10} and T_{max} of linear NIPU#2 was in the range of 170-214°C and 311-342°C (Fig. 3.44a). As expected, the cross-linked NIPU#2 showed higher T_{10} and T_{max} than the linear ones (Fig. 3.44b). The decomposition step of this sample was similar to that of NIPU#1 which the first and second steps were the decomposition of urethane linkage and hydrocarbon chain or soft segment.

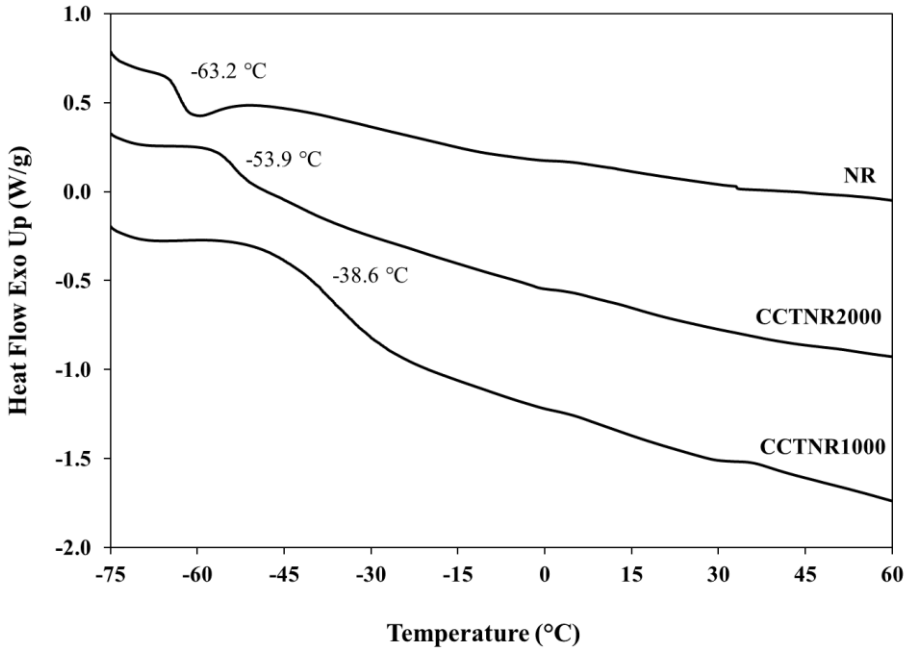

Fig. 3.48 DSC thermograms of NR and CCTNR from the second heating scan**.**

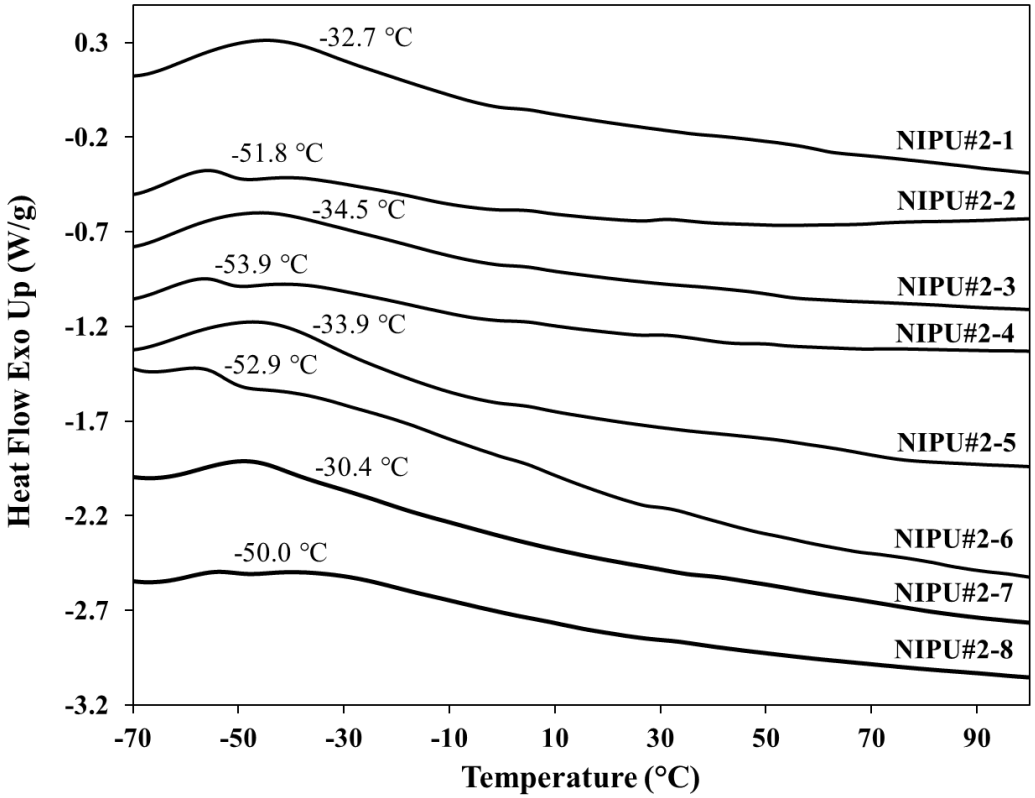

Fig. 3.49 DSC thermograms of NIPU#2 from second heating scan.

Table 3.15 Glass transition and thermal degradation temperature of NIPU#2

Sample	T_g (°C)[a]	T_d[b]	
		T_{10} (°C)	T_{max} (°C)
NIPU#2-1	-32.7	172	329
NIPU#2-2	-51.8	170	311
NIPU#2-3	-34.5	175	338
NIPU#2-4	-53.9	185	342
NIPU#2-5	-33.9	214	324
NIPU#2-6	-52.9	214	341
NIPU#2-7	-30.4	280	360
NIPU#2-8	-50.0	285	370

[a]Determined by DSC from the second heating scan.
[b]Determined by TGA.

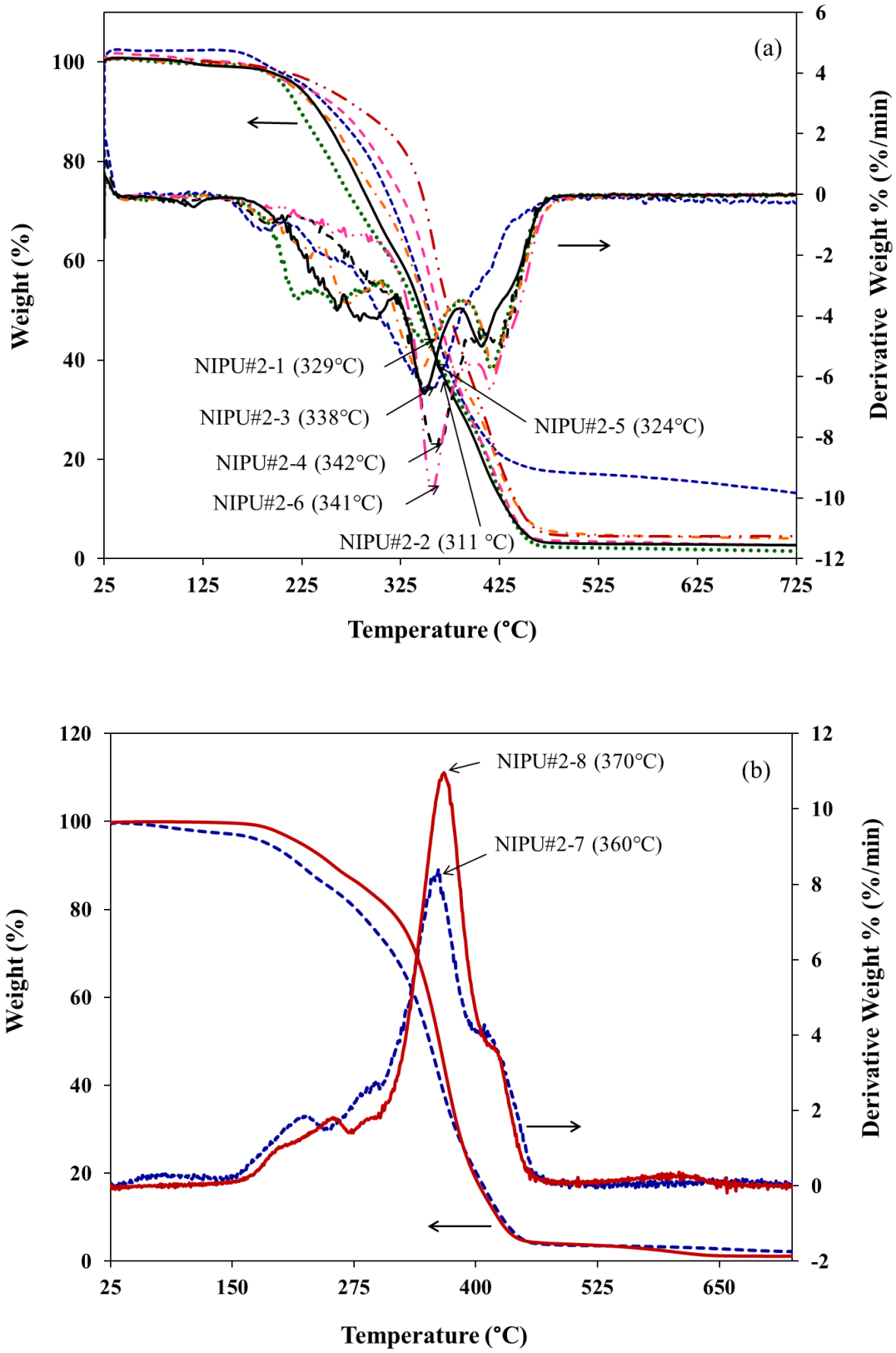

Fig. 3.50 TGA and DTC curves of NIPU#2; (a) linear NIPU#2 and cross-linked NIPU#2 from second heating scan.

3.4.2.3 Dynamic mechanical analysis of cross-linked NIPU#2

The cross-linked samples (NIPU#2-7 and NIPU#2-8) were chosen to study the thermal behavior. The storage modulus (E'), loss modulus (E") and loss tangent (tan delta) as a function of temperature are shown in Fig. 3.51. The E' was usually associated with the stiffness and related to the Young's modulus. At the glassy state, < -50°C, NIPU#2-8 showed higher modulus than NIPU#2-7 because of the higher molecular weight of CCTNR2000. At the glass transition state, -50°C to -10°C, a gradually drop of the modulus occurred in NIPU#2-7 and NIPU#2-8 (Fig. 3.51a). NIPU#2-7 showed higher modulus than that NIPU#2-8 probably due to the more flexible chains of NIPU#2-8. Similarly, the E" decreased in both NIPU#2-7 and NIPU#2-8 after glassy state. (Fig. 3.51b)**.** The α transition temperature was associated to T_g. One α transition temperature was observed in NIPU#2-7 and NIPU#2-8 at -29.5 and -40.6°C, respectively ((Fig. 3.51c)**.** Tan delta of NIPU#2-7 was higher than that NIPU#2-8. This might be the shorter chain length of CCTNR1000 providing a cross-linking density and/or more hydrogen bonding.

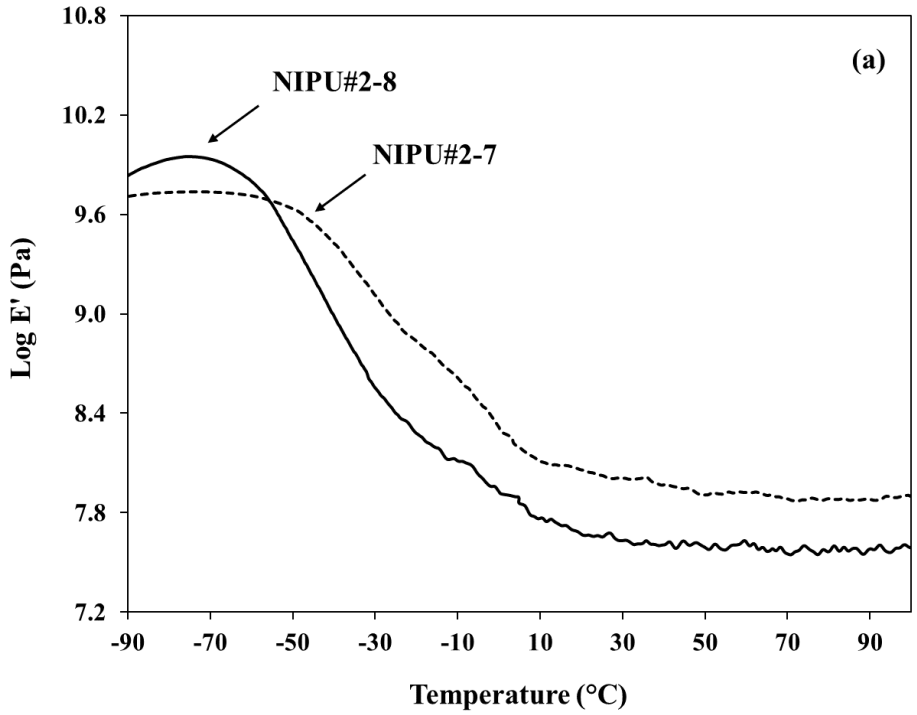

Fig. 3.51 Dynamic mechanical curves versus temperature of NIPU#2-7 and NIPU#2-8: (a) storage modulus, (b) loss modulus and (c) tan delta**.**

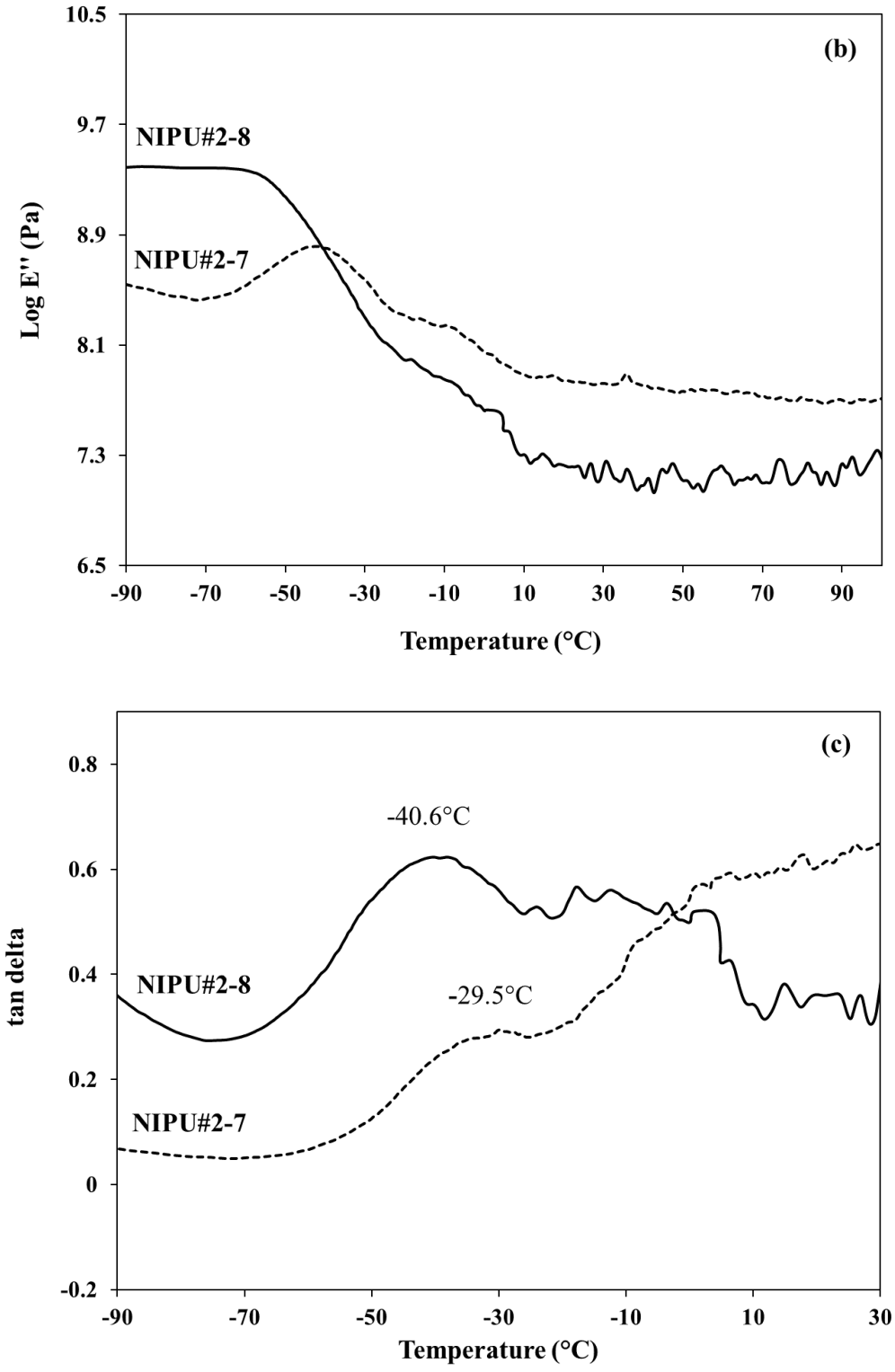

Fig. 3.51 Dynamic mechanical curves versus temperature of NIPU#2-7 and NIPU#2-8: (a) storage modulus, (b) loss modulus and (c) tan delta**.**

3.4.2.4 Contact angle measurement

The wettability of cross-linked NIPU#2-7 and NIPU#2-8 were determined by measurement of the contact angle. No significant difference in contact angle was observed in both NIPU#2-7 (112°) and NIPU#2-8 (110°) (Fig. 3.52). Generally, a small contact angle (<90°) indicates a high wettability (hydrophilic materials). In this case, the hydrophobic nature of NR should remain in the CCTNR and NIPU resulting to the high contact angle.

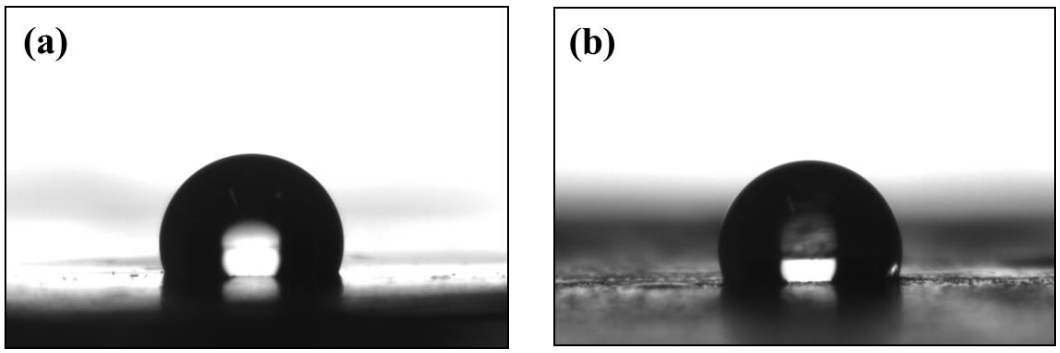

Fig. 3.52 Water drop contact angle on NIPU#2: (a) NIPU#2-7 and (b) NIPU#2-8.

3.4.3 Synthesis of NIPU#3

NIPU#3 was prepared from the reaction of CCPLA and various diamines (EDA, BDA and *p*-XDA) in bulk reaction (Fig. 3.53). The reaction was carried out at 70°C for 24 h under vacuum. Two different molecular weight of CCPLA ($\bar{M}_n$ = 1200 and 2100 g/ mol, named CCPLA1000 and CCPLA2000, respectively) were used. The carbonate band at 1809 cm^{-1} disappeared indicating that a complete reaction (Fig. 3.54 and Fig. 3.55). The characteristic bands of urethane were observed at 3417, 3338 and 1538 cm^{-1} corresponding to the OH stretching, NH stretching and NH bending, respectively. The C=O stretching of urethane was overlapped with C=O stretching of ester at 1746 cm^{-1}. This result confirmed the urethane formation; however, the strong C=O absorption band from amide formation was also noticed at 1638 cm^{-1}. The side reaction occurred because there were C=O of ester group along the chain much more than C=O of carbonate at the chain ends; therefore, amines have attached C=O of ester group instead of C=O of carbonate. It

has been reported that the urethane and amide formation occurred simultaneously (Javni *et al*., 2008). The influence of $\overline{M}_n$ was also investigated. It seems no influence of $\overline{M}_n$ (CCPLA2000) and the carbonate to amine ratio on the reaction except in NIPU#3-2. The equivalent of EDA was rose to 5.2 in order to obtain a complete reaction. All these observations implied that the aminolysis of amine and ester linkage could not prevent from the reaction of CCPLA and amine. It has been reported that the side reaction was a main drawback to reach the high molecular weight of NIPU due to the scission of polymer chains (Besse *et al*., 2015). SEC analysis of NIPU#3-3-NIPU#3-6 were clear to confirm the low molecular weight (Fig. 3.56-3.59).

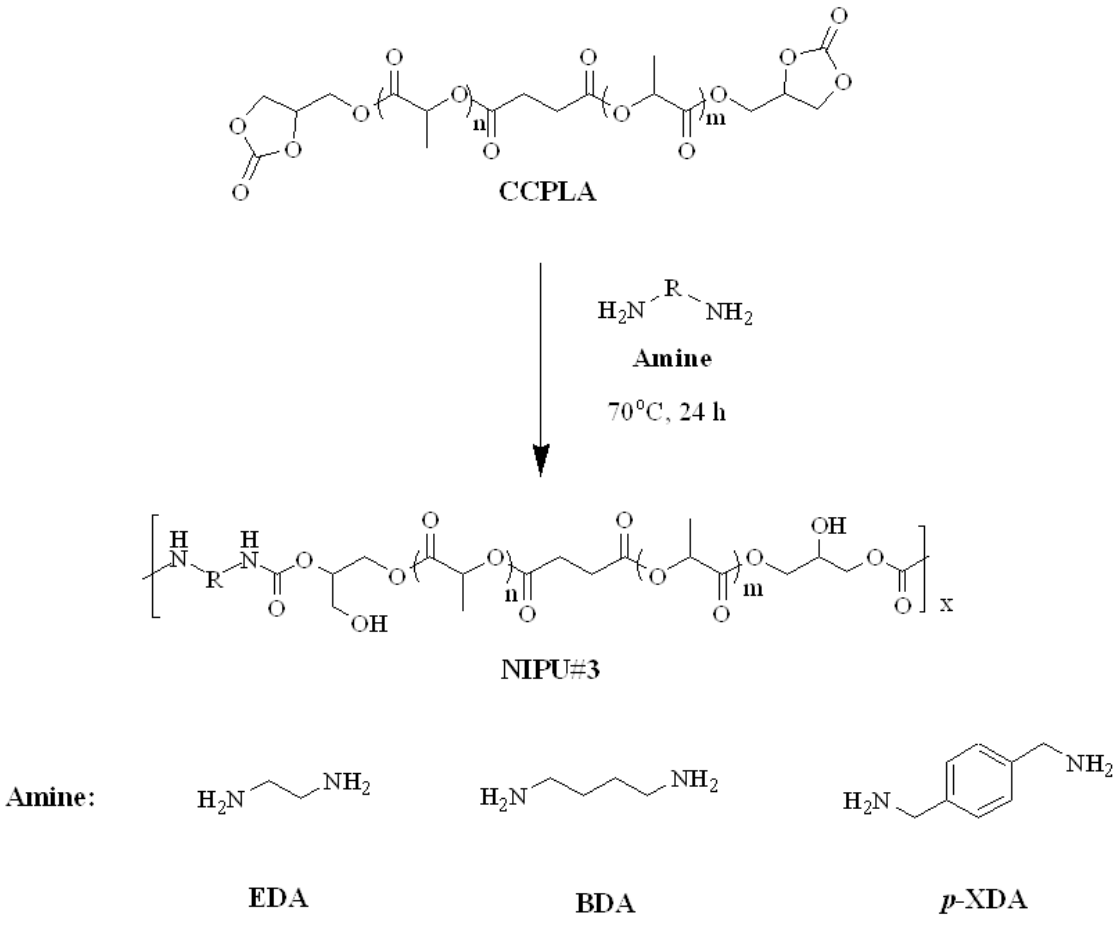

Fig. 3.53 Synthetic route of NIPU#3.

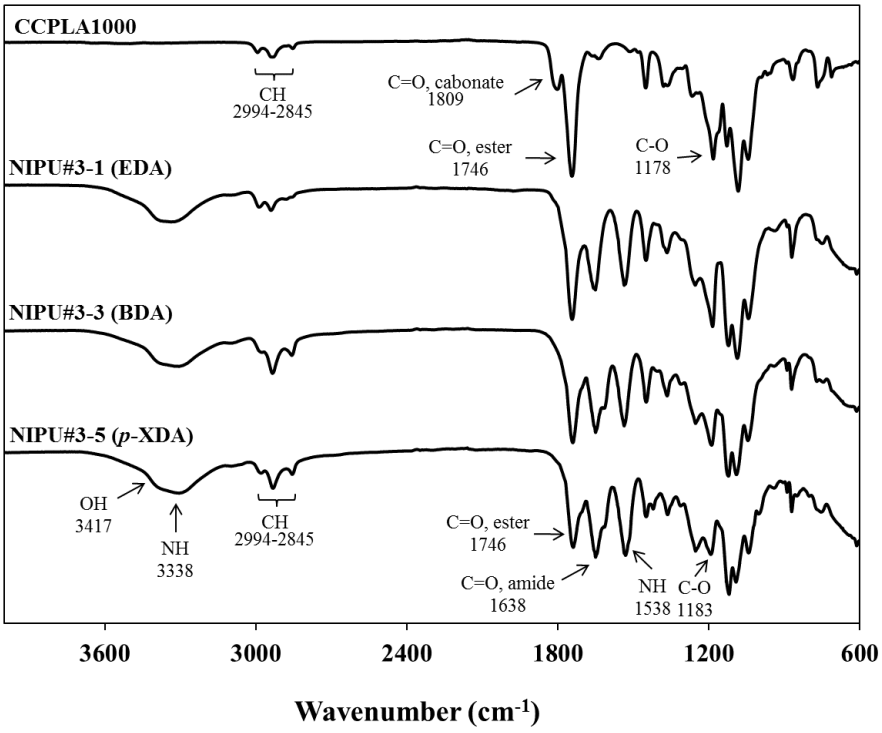

Fig. 3.54 FTIR spectra of NIPU#3 prepared from CCPLA1000 and various diamines.

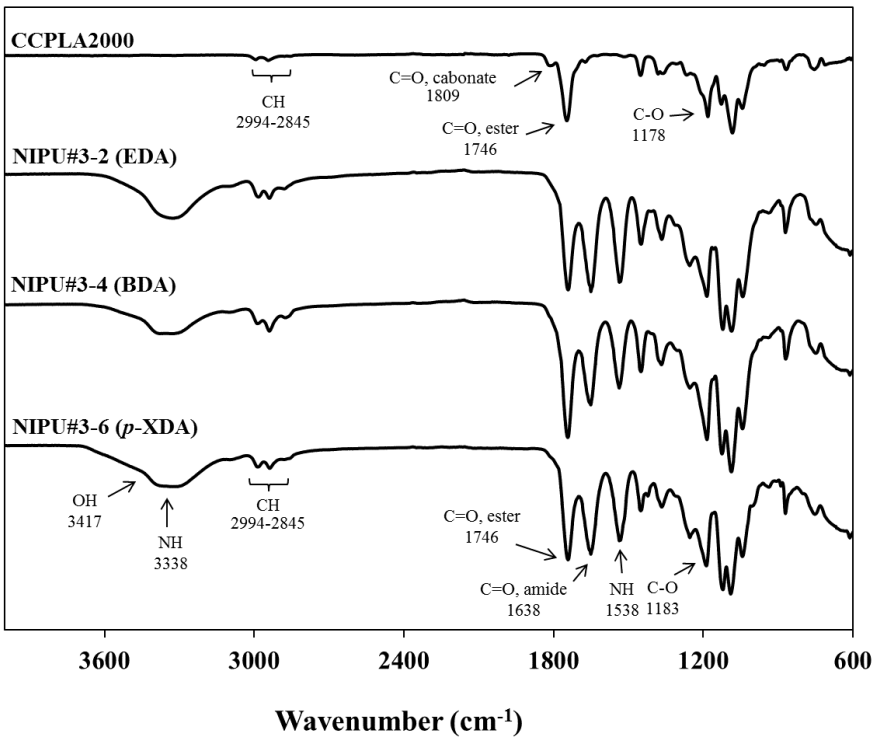

Fig. 3.55 FTIR spectra of NIPU#3 prepared from CCPLA2000 and various diamines.

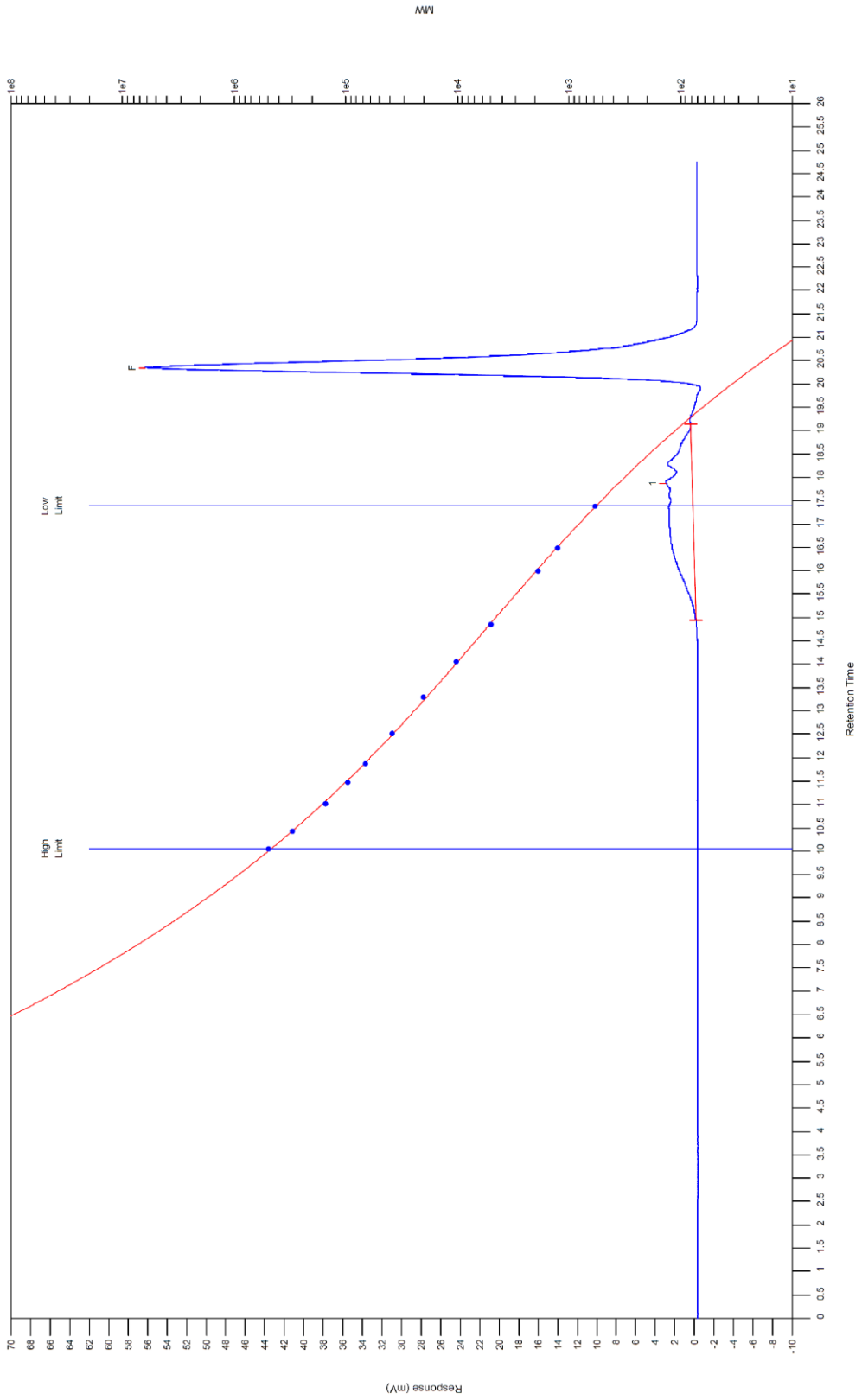

Fig. 3.56 SEC trace of NIPU#3-3 from the reaction of CCPLA1000 and BDA.

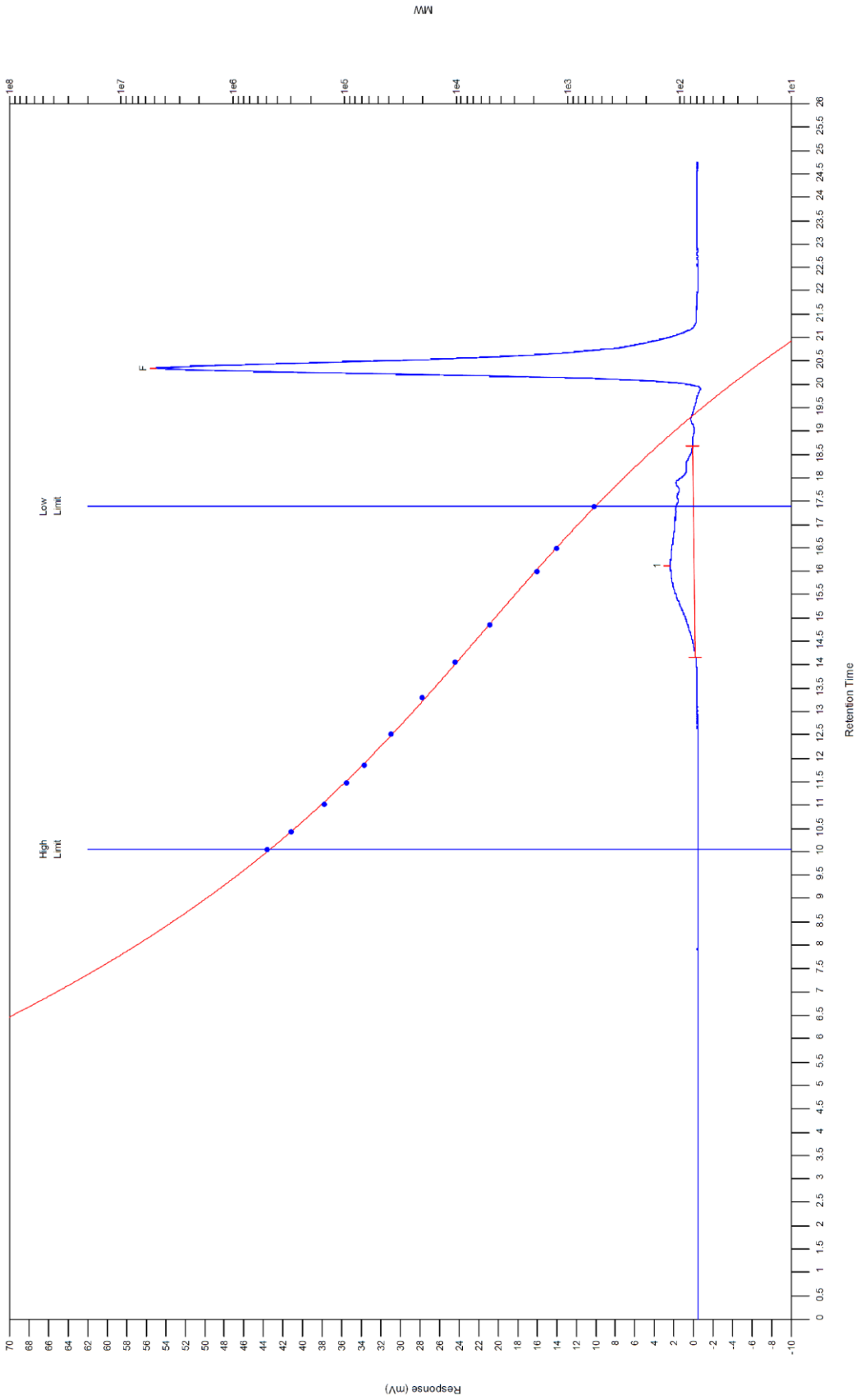

Fig. 3.57 SEC trace of NIPU#3-4 from the reaction of CCPLA2000 and BDA.

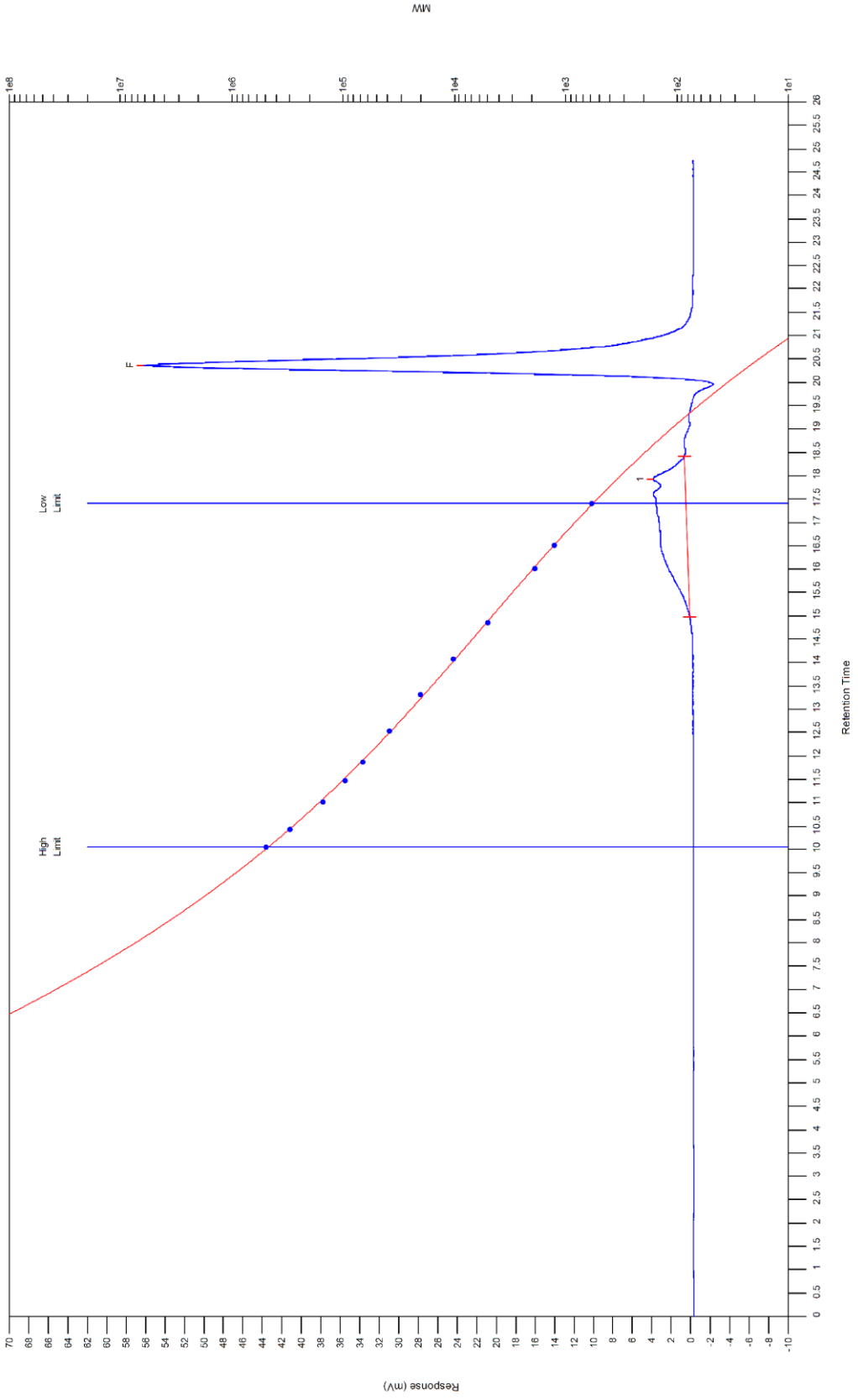

Fig. 3.58 SEC trace of NIPU#3-5 from the reaction of CCPLA1000 and *p*-XDA.

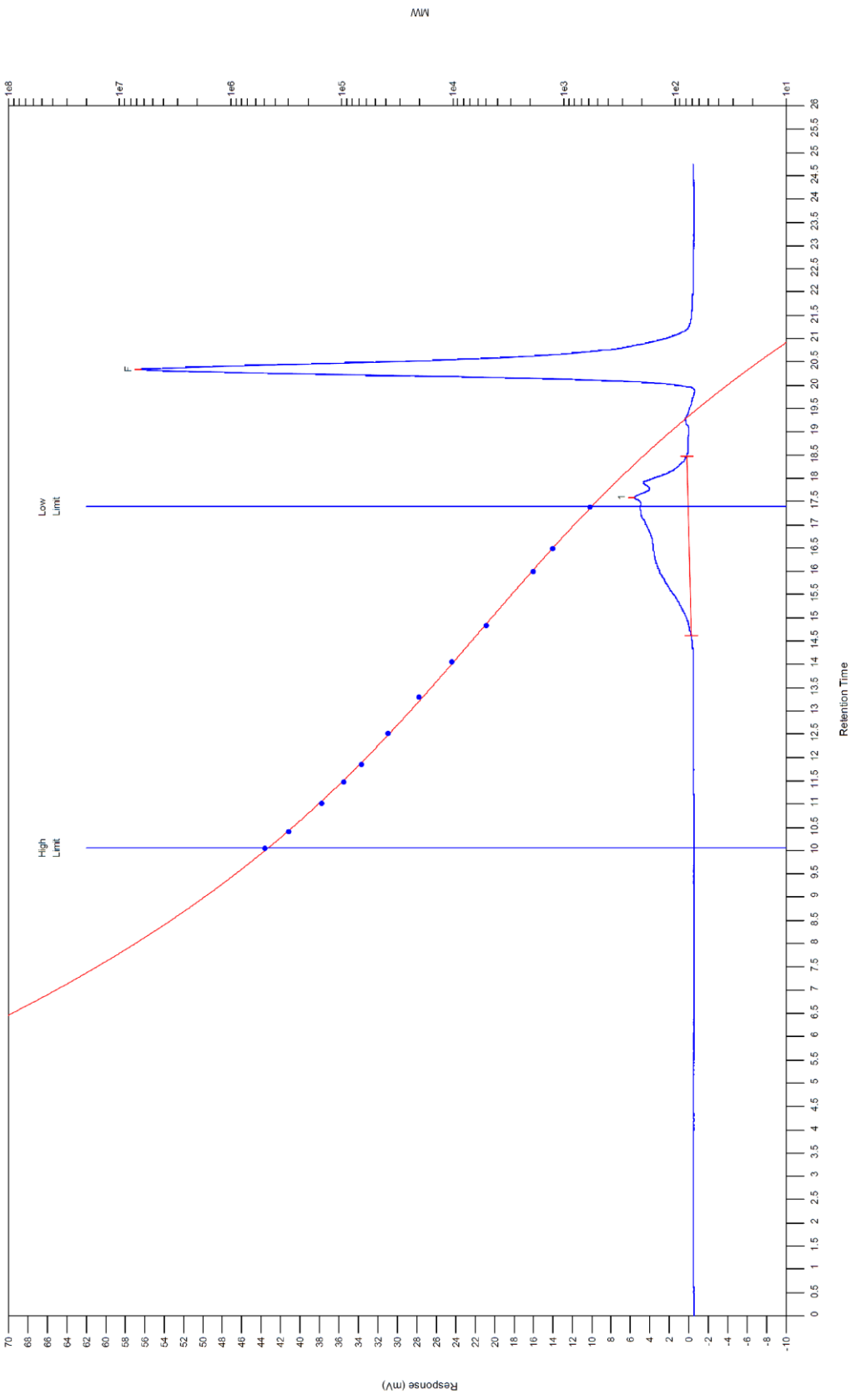

Fig. 3.59 SEC trace of NIPU#3-6 from the reaction of CCPLA2000 and *p*-XDA.

CHAPTER 4

Conclusions

4.1 Synthesis of oligoisoprenes

Both amino telechelic natural rubber (ATNR) and cyclic carbonate telechelic natural rubber (CCTNR) have been successfully synthesized from carbonyl telechelic natural rubber (CTNR) by the controlled oxidative degradation of natural rubber with the targeted chain lengths of 1000 and 2000 g/mol. The ^{1}H-NMR and FTIR analyses proved the chemical structure of all oligoisoprenes. The presence of cyclic carbonate at both chain ends of CCTNR was also characterized by MALDI-TOF analysis. The glass transition temperature (T_g) of ATNR and CCTNR depended on the molecular weight of their oligoisoprenes.

4.2 Synthesis of dicyclic carbonates

The aromatic dicyclic carbonate (dicyclic carbonate #1) has been synthesized from the reaction of terephthaloyl chloride and glycerol carbonate and high yield (90%) was obtained. The reaction of succinyl chloride and glycerol carbonate allowed to form the aliphatic dicyclic carbonate (dicyclic carbonate #2) with 80% of yield. The structures of dicyclic carbonates were confirmed by ^{1}H-NMR, FTIR and HRMS.

4.3 Synthesis of oligo(lactic acid)

Two oligo(lactic acid) (CBPLA and CCPLA) have been synthesized from lactic acid (LA). Carboxylic telechelic PLA (CBPLA) was synthesized by melt condensation in the presence of catalyst and succinic acid. The reaction time and molecular weight of CBPLA were decreased with increasing the content of SA. The content of COOH end groups were approximately 94%. The $\bar{M}_n$ of CBPLA was in the range from 1000 to 2000 g/mol. The CBPLA was reacted with glycerol carbonate in the Steglish esterification to form CCPLA. The chemical structures of both oligomers were

characterized by ^{1}H-NMR and FTIR analyses. The MALDI-TOF spectrum proved the presence of cyclic carbonate at both chain ends.

4.4 Synthesis of NIPUs

4.4.1 Synthesis of NIPU#1

NIPU#1 has been synthesized from the reaction of amino telechelic natural rubber (ATNR) and aromatic or aliphatic dicylic carbonates. The solution reaction was not suitable for the synthesis of NIPU#1 because the reaction temperature was too high (100°C) and lower functional group concentration. LiBr was not an effective catalyst in this reaction. Due to a high functional group concentration in bulk reaction, a complete reaction was obtained. The ATNR with lower molecular weight (1000 g/mol) was more reactive than the higher one (2000g/ mol) and the excess ATNR was required. The urethane formation was verified by FTIR analysis. No amide formation was observed in a complete reaction. The melting temperature (T_m) was found in NIPU#1 from DSC traces in the first heating scan. No significant difference of T_g was noticed. The type of amines did not affect T_g value. The molecular weight of ATNR controlled the T_g. Two decomposition steps were found in all samples. The first and second steps were the rupture of urethane linkage and hydrocarbon chain, respectively.

4.4.2 Synthesis of NIPU#2

NIPU#2 has been synthesized from the reaction of cyclic carbonate telechelic natural rubber (CCTNR) and di- or tri- amines in bulk reaction. The linear and cross-linked NIPUs were controlled by the structure of amines. The linear NIPU#2 was synthesized from the reaction of CCTNR and various diamines (EDA, BDA and *p*-XDA) while the cross-linked one used the triamine (TAEA). A slight excess of amine was required in linear NIPU#2. The molecular weight of CCTNR (1000 and 2000 g/mol) was not influence in this reaction. The continuous films were found only in the cross-linked NIPU#2. The urethane formation was found in all samples without aminolysis occurrence. The $\overline{M}_n$ from the partially soluble fraction of linear NIPU#2 were between 3300 and 6200 g/mol. The cross-linked NIPU#2 were insoluble in THF and DMF as an eluent for SEC analysis. All NIPU#2 were amorphous structure. Type of amines did not affect T_g of linear NIPU#2. The cross-linked NIPU#2 showed the slightly higher T_g than

the linear one. The molecular weight of CCTNR showed the influence on T_g of the linear and cross-linked NIPU#2. The decomposition steps were similar to those of NIPU#1. The cross-linked NIPU#2 showed the higher thermal stability than the linear one. A cross-linked NIPU#2 with higher molecular weight showed the higher modulus than the lower one at the glassy state. At the glass transition state, the cross-linked NIPU#2 with lower molecular weight showed the higher modulus than that the higher one due to the more flexible chain. One α transition temperature was found in all samples which belonged to NR. No significant difference of contact angle was observed in cross-linked NIPU#2.

4.4.3 Synthesis of NIPU#3

NIPU#3 has been synthesized from the reaction of cyclic telechelic PLA (CCPLA) in bulk reaction. The complete reaction was found in all samples. The urethane and amide formation occurred simultaneously.

4.5 Suggestion

The mechanical properties such as tensile, tear strength and hardness tests of cross-linked NIPU#2 should test further in the future in order to compare with the classical PU from NR.

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APPENDIX

APPENDIX A

Column chromatography

Dicyclohexylurea (DCU) is an organic compound (Fig. A.1). It is a by-product from the reaction of dicyclohexylcarbodiimide and amine or alcohol. In the final step to obtain a purified CCTNR, a filtration and normal washing process were not able to remove all DCU. The residual DCU in CCTNR was confirmed by ^{1}H-NMR (Fig. A.2). The peaks at 1.9 and 3.2 ppm assigning to proton from DCU did not observe after purification by column chromatography (CCTNR-CC). The disappearance band of DCU was observed in FTIR spectra of CCTNR-CC after purification (Fig. A. 3).

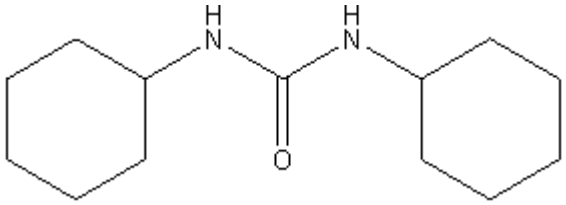

Fig. A.1 Chemical structure of DCU.

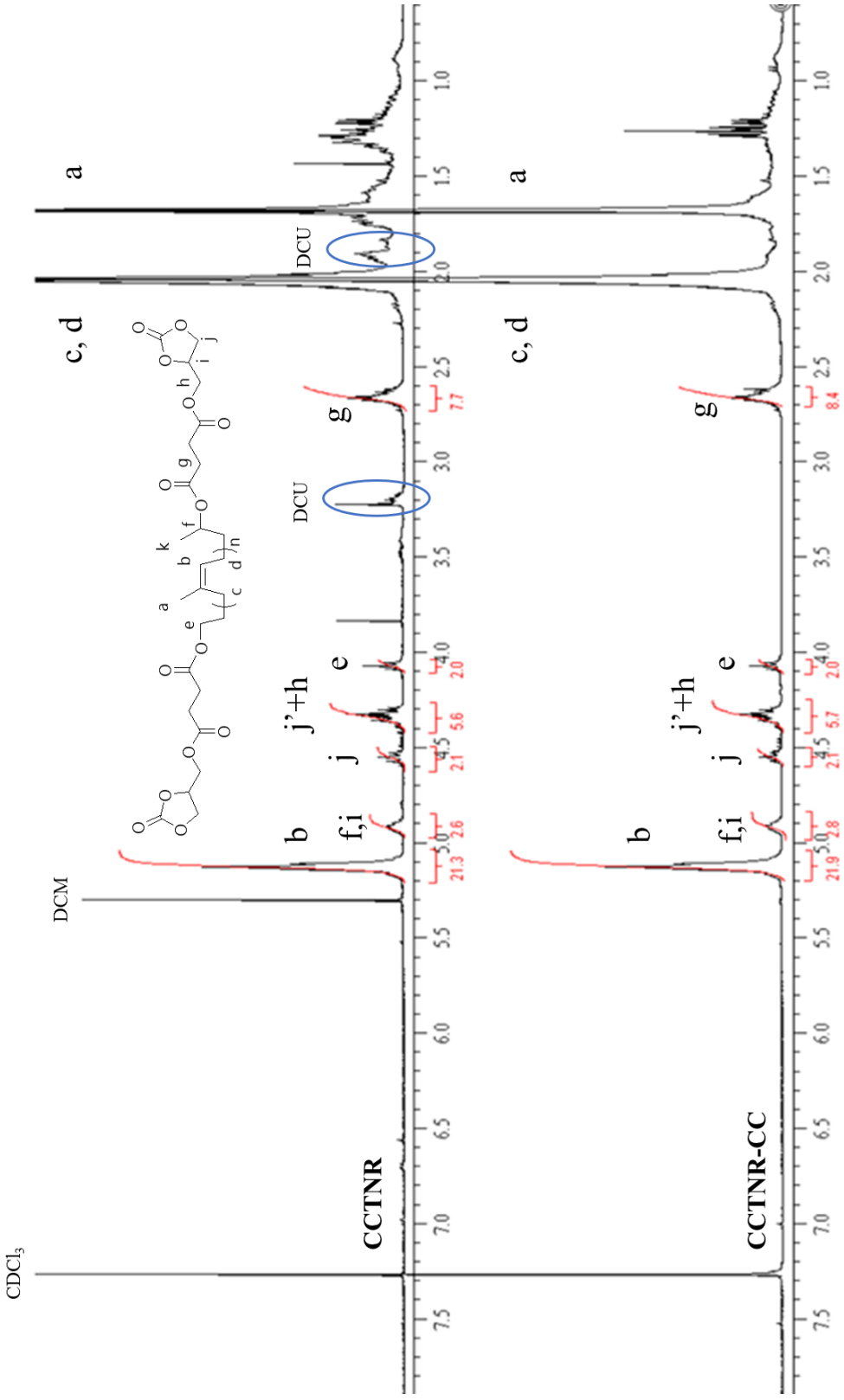

Fig. A.2 ^{1}H-NMR spectra of CCTNR and CCTNR-CC.

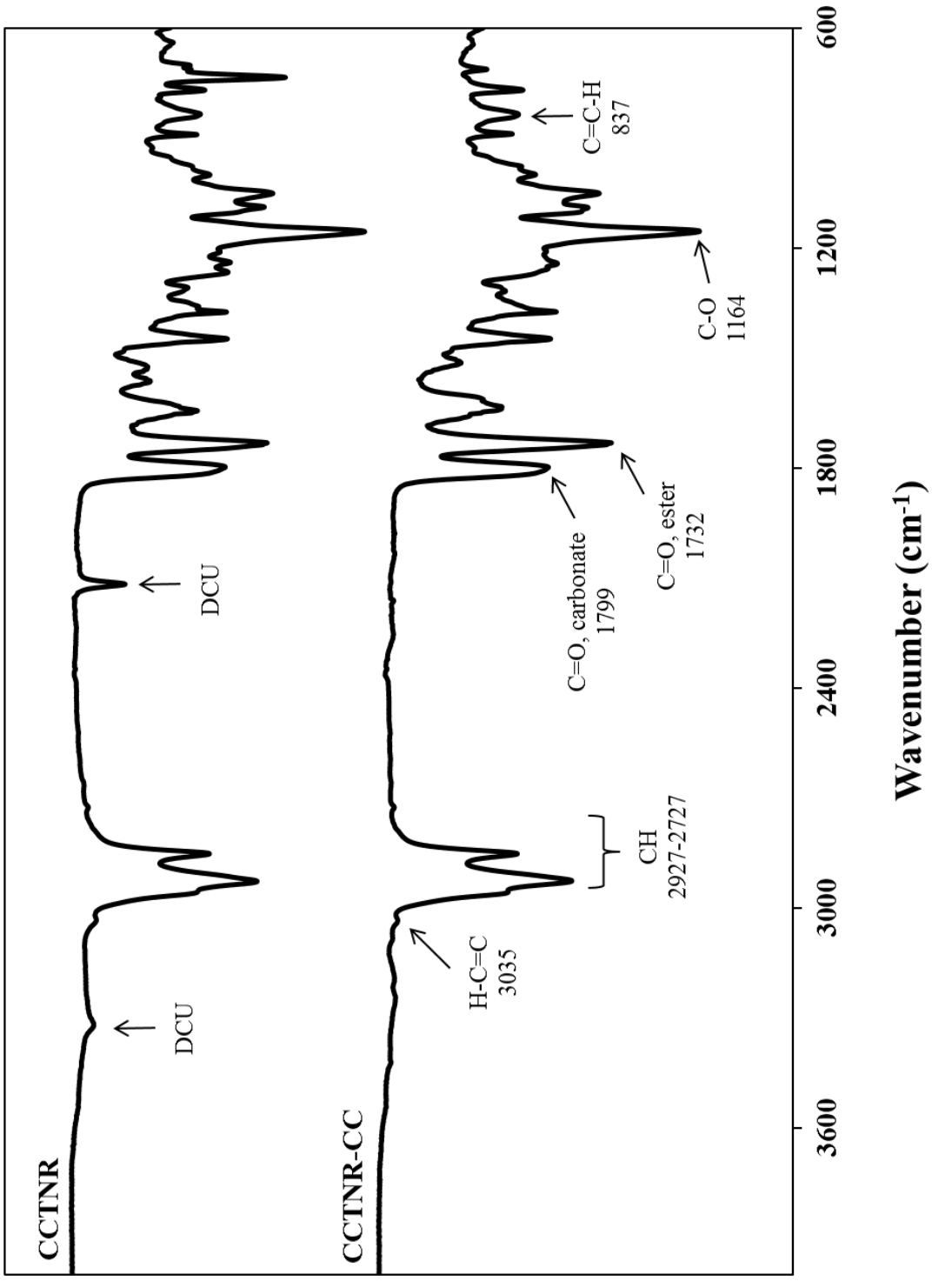

Fig. A.3 FTIR spectra of CCTNR and CCTNR-CC.

APPENDIX B

Acylation reaction

Acylation reaction is one of the derivatization reactions for primary and secondary amines. Acid anhydride, acyl chlorides, acylimidazoles and acylamides were used as an acylating reagents (Kataoka, 1996). It reacted with the amino group (NH_2) to form an amine derivative and by-product acid.

Procedure

ATNR (0.41 g, $\overline{M}_{n,\ NMR}$ = 1134 g/mol, 0.36 mmol) was dissolved in 5 mL (0.072 M) of dry DCM in a reactor. Acetic anhydride (AA) (10 eq., 0.38 g, 3.60 mmol) was added dropwise using a dropping funnel. The reaction was performed at 25 °C for 24 h under Ar atmosphere. The mixture was washed twice with 1 N NaOH solution (2*4 mL) and dried over $MgSO_4$ for 1 h. Then it was filtered using a filter paper, evaporated to eliminate the DCM using a rotary evaporator and dried in a vacuum oven until a constant weight was obtained.

Results and discussion

ATNR was reacted with acetic anhydride (AA) as an acylating reagent under a mild reaction. The AA reacted with amino end groups to form the amine derivative (named as modified ATNR) and acetic acid as a by-product (Fig. B.1). The chemical structure of modified ATNR was characterized by ^{1}H-NMR and FTIR analyses. The characteristic protons adjacent to the amine groups appeared between 2.57 to 2.85 ppm (Fig. B.2). The significant absorption bands presented at 1715 and 1622 cm^{-1} associated to the stretching vibration of C=O from carbonyl and amide groups, respectively (Fig. B.3).

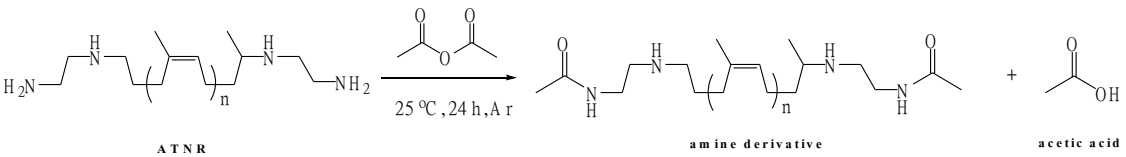

Fig. B.1 Acylation reaction of ATNR.

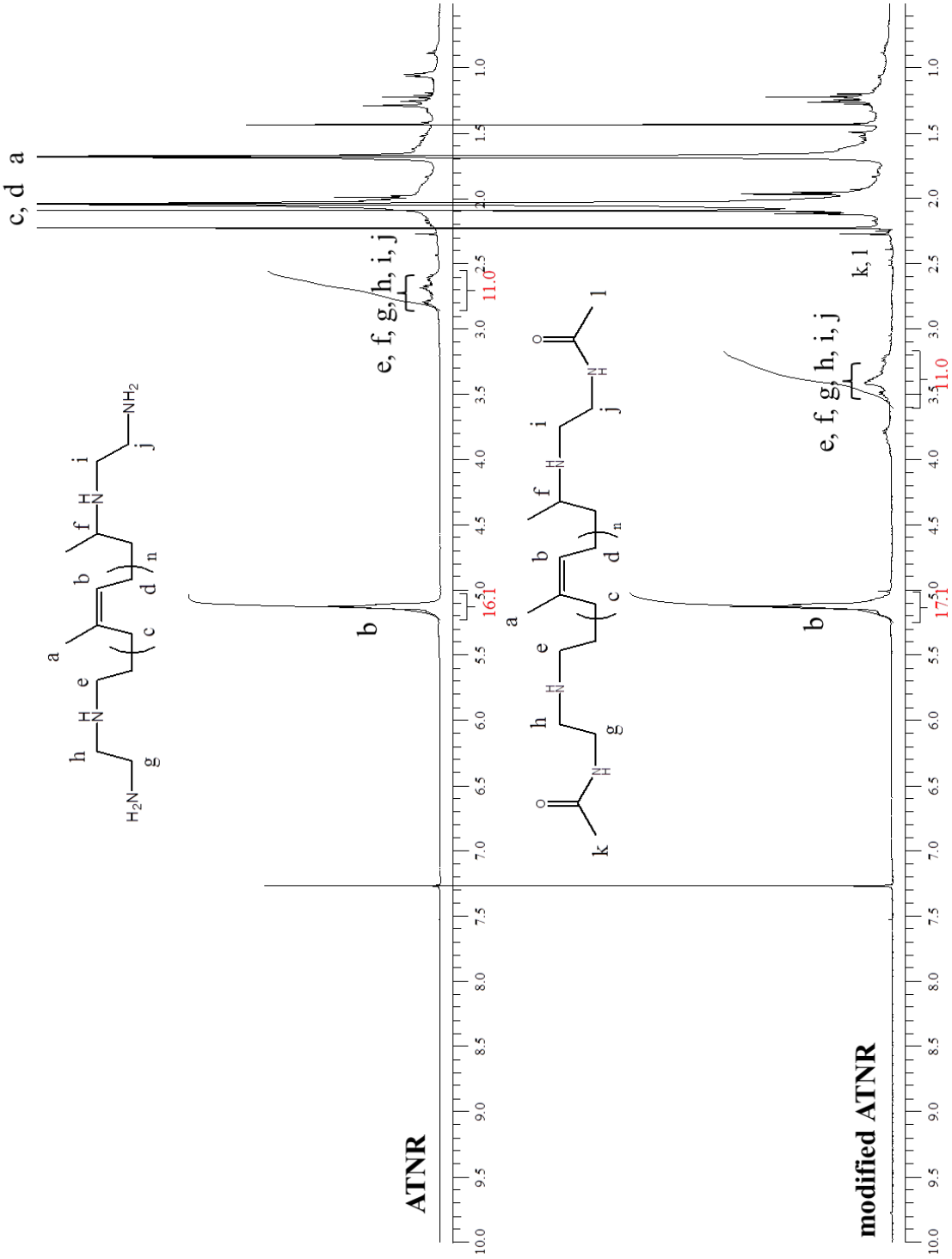

Fig. B.2 ^{1}H-NMR spectra of ATNR and modified ATNR.

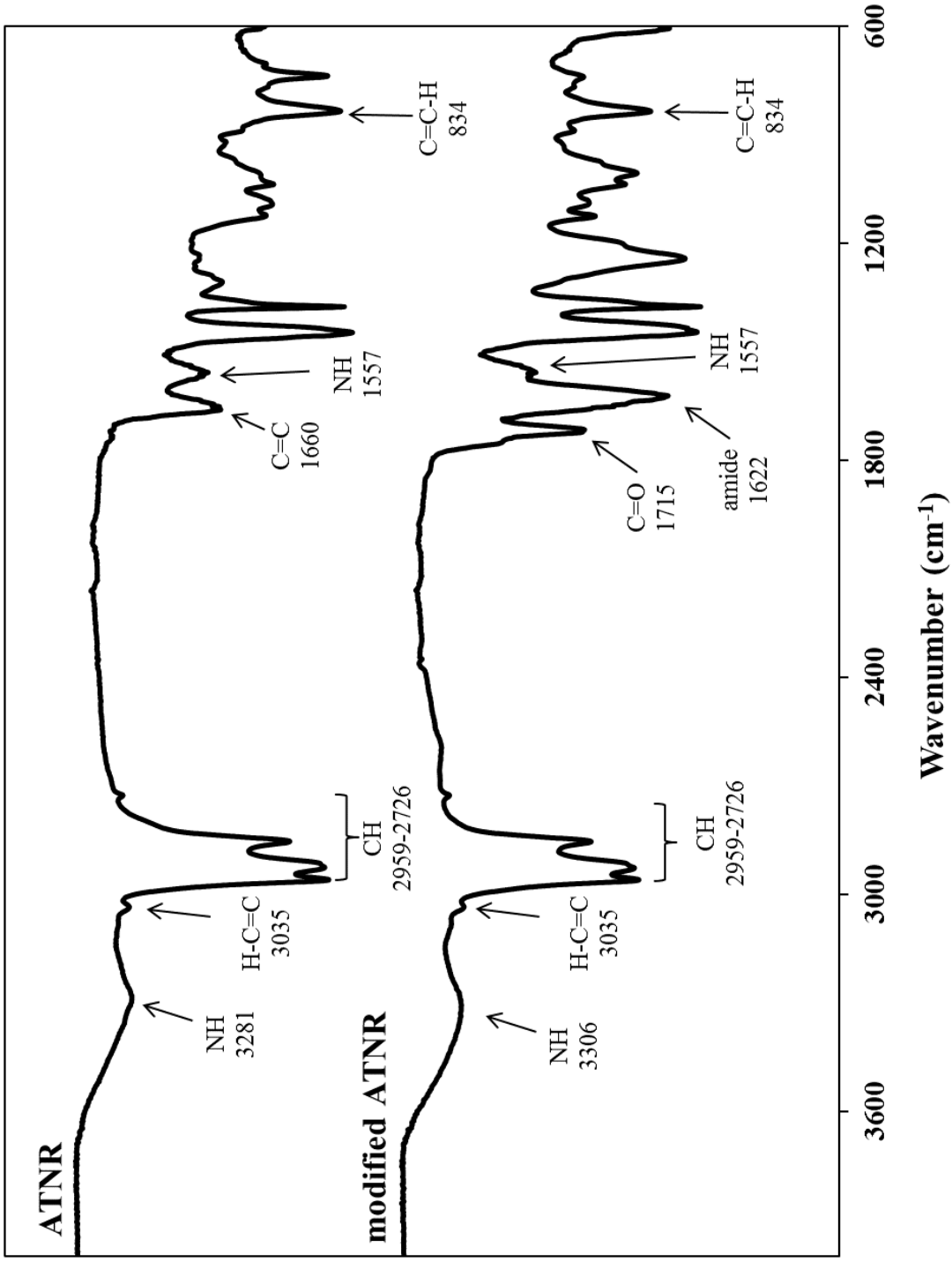

Fig. B.3 FTIR spectra of ATNR and modified ATNR.

APPENDIX C

Functionalization of HTNR

Procedure

HTNR (0.23 g, $\overline{M}_{n,\,NMR}$ = 2100 g/mol, 0.11 mmol) was dissolved in 1.8 mL (0.06 M) of dry DCM. DMAP (1 eq., 0.013 g, 0.11 mmol) and SAH (3 eq., 0.03 g, 0.32 mmol) were added. The reaction was performed at room temperature for 24 h under argon atmosphere. The mixture was washed twice with $NaHCO_3$ saturated solution and NaCl saturated solution. Then the organic phase was dried over $MgSO_4$ for 1 h, and after filtration the organic solution was evaporated in a rotary evaporator and dried in a vacuum oven until a constant weight was obtained.

Results and discussion

Fig. C.1 represents the synthesis route of functionalized HTNR. The chemical structure was identified by ^{1}H-NMR (Fig. C.2). The new peak appeared at 4.07 and 2.60 ppm corresponding to CH_2 proton in the α-position of oxygen (ester) and CH_2 adjacent to carboxylic end group, respectively.

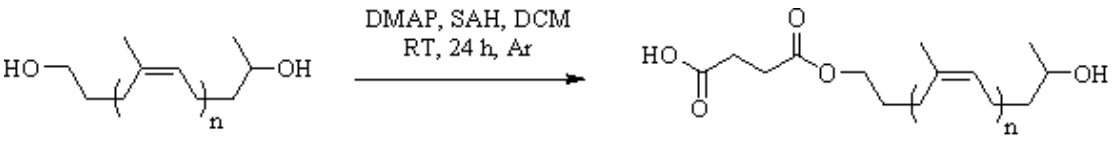

Fig. C.1 Synthesis route of functionalized HTNR.

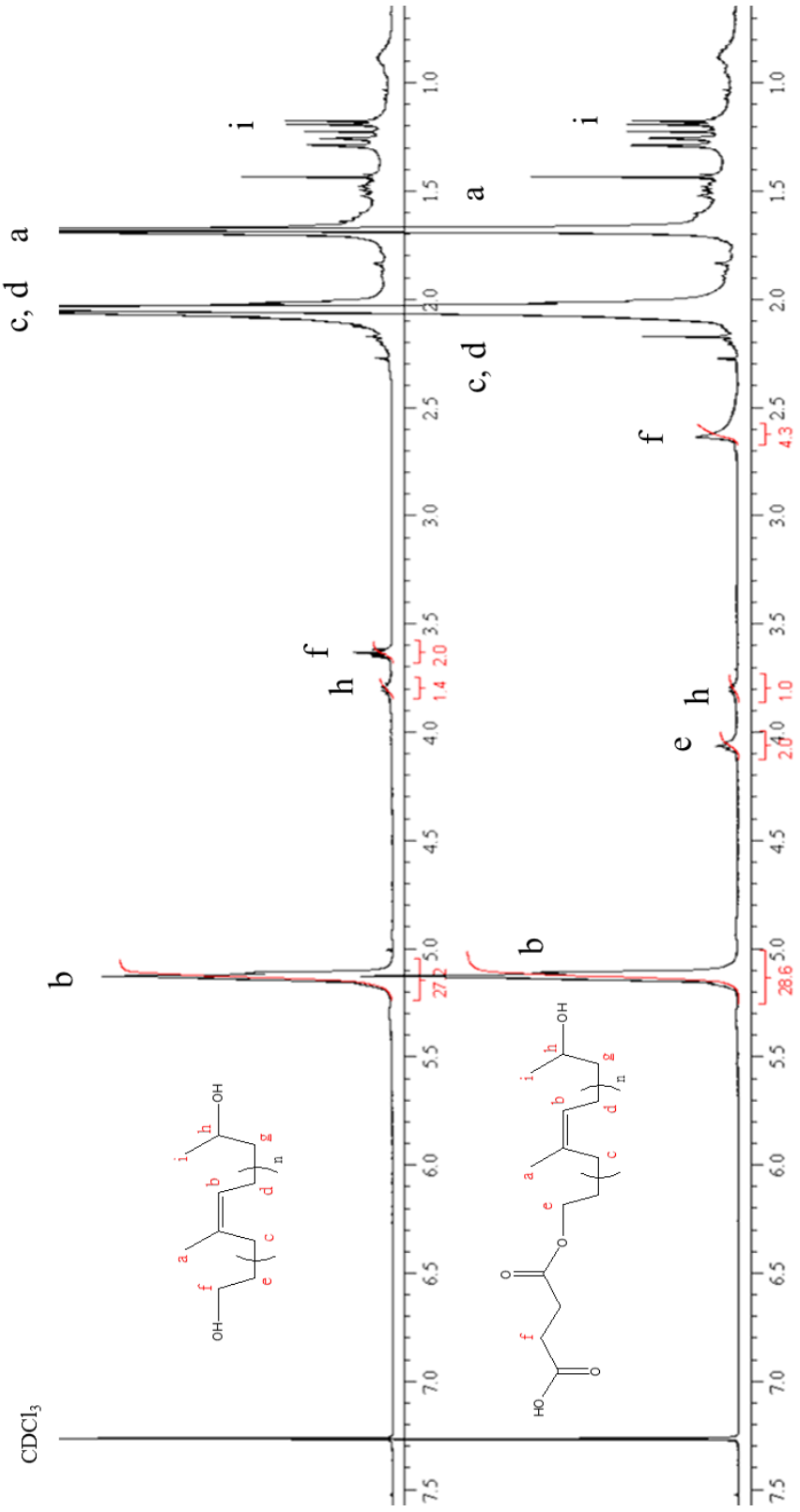

Fig. C.2 ^{1}H-NMR spectra of HTNR and functionalized HTNR.

APPENDIX D

List of Proceedings

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1030

Synthesis of bio-based, non-isocyanate polyurethane from poly(lactic acid) and natural rubber

Ruedee Jaratrotkamjorn[1], Jean-François Pilard[2], Chuanpit Khaokong[1], Varaporn Tanrattanakul[1]*

[1]*Department of Materials Science and Technology Faculty of Science, Prince of Songkla University, Songkla 90112, Thailand*
[2]*Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Université du Maine, 72085, Le Mans Cedex, France*
Phone 0-7428-8362, Fax 0-7444-6925, E-Mail: varaporn.t@psu.ac.th

Introduction

Polyurethane (PU) is widely used in various fields, such as foams, adhesives, paints, and fibers [1]. The conventional PU is polymerized by the polyaddition of diol/polyols and diisocyanates/polyisocyanates, and it is referred to as an isocyanate PU. The disadvantages of the isocyanate PU are the toxicity of phosgene and the free isocyanate residue in the PU products. Phosgene is a starting material for producing isocynates and it is an insidious poison as the odor may not be noticed and symptoms may be slow to appear. In severe situation only 0.4 ppm of phosgene in the environment causes suffocation. Additionally, isocyanates can result in health effects, such as skin irritation, eye irritation and asthma [2]. Therefore, there is an attempt to synthesize PU without the isocynate and this PU is referred to as a non-isocyanate polyurethane (NIPU) [3-12]. The urethane linkage in the NIPU has been formed by a reaction between a cyclic carbonates and an amine end-group. This reaction produces not only a urethane linkage but also hydroxyl groups; as a result, this NIPU may be named as a polyhydroxyurethane.

Natural rubber (NR) is an unsaturated rubber that consists of cis-1, 4-polyisoprene. A telechelic natural rubber (TNR) is a chemically modified NR containing a functional group, particularly the reactive endgroups. TNR is generally used as a precursor or a starting material in polymer synthesis. Periodic acid (H_5IO_6) is an effective scission agent for the synthesis of TNR such as a carbonyl telechelic natural rubber (CTNR) [13-16]. In order to obtain an amine telechelic natural rubber (ATNR), a direct reductive amination of CTNR has been carried out [17, 18].

Poly(lactic acid) or polylactide (PLA) is a biodegradable, aliphatic polyester derived from polymerization of lactic acid or lactide. PLA is claimed as a bio-based polymer because its monomer is from renewable resources. The low molecular weight PLA which has reactive functional groups such as hydroxyl [19] and carboxyl group [20-23] at both sides can be synthesized by a direct melt condensation. Recently, our group reported the novel PU synthesized from poly(lactic acid) and hydroxyl telechelic natural rubber (HTNR) [24]. This PU is the bio-based polymer which has a potential to be a biodegradable PU. We already found the selected microorganisms for biodegradation of NR and the study of biodegradation of this PU by the selected microorganisms is in the process.

As stated earlier, the new trend of PU products in the future is the NIPU. Thus, it is interesting to develop the bio-based NIPU from PLA and NR. This work was a preliminary study of a synthesis of the NIPU from PLA and TNR. Based on our knowledge, there has been no publication of this NIPU.

Experimental

Materials

Natural rubber (NR STR5LCV60) was produced by Jana Concentrated Latex Co., Songkla, Thailand. All chemicals were reagent grade and used as received. Periodic acid (H_5IO_6) was produced from Himedia laboratories Pvt. Ltd. Tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), chloroform (CH_3Cl), hydrochloric acid (HCl) and methanol (MeOH) were produced from Lab-scan Asia Co., Ltd. Sodium hydrogen carbonate (Na_3HCO_3) was produced from Fisher Scientific UK Limited.

Sodium thiosulfate ($Na_2S_2O_3$) was produced from Loba Chemie Pvt. Ltd. Magnesium sulfate anhydrous (Mg_2SO_4) was produced from Panreac Química S.L.U.. D,L-lactic acid, stannous octoate ($Sn(Oct_2)$), p-toluenesulfonic acid monohydrate (TSA), 4-(hydroxymethyl)-1,3-dioxolan-2-one ($DMCCH_2OH$), N,N-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), sodium triacetoxyborohydride ($NaBH(Oac)_3$), succinic acid (SA) and deuterated chloroform (d-$CDCl_3$) were produced from Sigma-Aldrich Co. Ammonium acetate (NH_4OAc) was produced from Merck KGaA. and sodium hydroxide (NaOH) was produced from Ajax Finechem Pty. Ltd.

Synthesis of dicarboxylic poly(lactic acid) (diCOOH-PLA)

Lactic acid was added into a three-necked round bottom flask connected to a vacuum line and heated to 110°C at 0 bar for 4 h to remove water. The temperature was increased at 180°C, then the catalyst ($Sn(Oct_2)$) and the co-catalyst (TSA) were added. The pressure was gradually reduced from 0.4 to 0 bar. The polymerization reaction was maintained for 12 h before adding SA. The reaction time was 12 h at the pressure of 0 bar.

Synthesis of dicyclic poly(lactic acid) (dicyclic-PLA)

The diCOOH-PLA, CH_2Cl_2, $DMCCH_2OH$, DCC and DMAP were added into a reactor. The reaction was carried out at room temperature (25-27°C) for 24 h under a nitrogen atmosphere. The residual DMAP in the final product was removed by adding 0.01 M HCl and the product was precipitated in a cold MeOH, filtered and dried in a vacuum oven at 40°C for 6 h.

Synthesis of carbonyl telechelic natural rubber (CTNR)

NR was dissolved in 0.6 M of THF at room temperature (25-27°C) for 24 h under continuous stirring. The H_5IO_6 in 0.4 M of THF was added dropwise to the NR solution. The reaction condition was 30°C for 6 h. The product was filtered and evaporated to remove THF. Purification of the product was performed by washing the CTNR solution with the saturated aqueous Na_3HCO_3, $Na_2S_2O_3$ and NaCl, respectively. The CTNR was dried with Mg_2SO_4, filtered and evaporated to remove CH_2Cl_2.

Synthesis of α-amino, ω-carbonyl natural rubber (ACNR)

ACNR was synthesized according to Kebir et al [17]. $NaBH(Oac)_3$ that dissolved with CH_2Cl_2 was mixed with CTNR solution. The NH_4OAc and CH_3COOH were added under the nitrogen atmosphere at room temperature (25-27°C). After 24 h the reaction mixture was washed with 1 N NaOH solution and the product was extracted with Et_2O. The product was dried with Mg_2SO_4, filtered and evaporated to remove CH_2Cl_2.

Synthesis of non-isocyanate polyurethane (NIPU)

ACNR was dissolved in THF before adding DMAP and dicyclic-PLA. The reaction condition was 40°C for 24 h under the nitrogen atmosphere. The mole ratio of dicyclic-PLA and ACNR was 1:2.

Characterization

The chemical structure of materials were characterized by a proton nuclear magnetic resonance (^{1}H-NMR, Varian® INOVA, 500 Hz) using a deuterated chloroform as a solvent. The molecular weight of NIPU was determined by a gel permeation chromatography (GPC, SHIMADZU LC-20AD-230V) using THF as an eluent. The measured temperature was 40°C and THF was an eluent.

Results and Discussion

The chemical structures of NR and modified NR are shown in Figure 1. The ^{1}H-NMR spectrum of ACNR (Figure 2) showed the amine terminated chain end at 2.68 ppm (position f) and the carbonyl terminated chain end at 2.2 (position i) and 2.5 ppm (position h). ACNR had only one amine end-group which occurred at the chain end that had no a methyl group. This methyl group caused the steric hindrance of the double bond of the isoprene unit. The ^{1}H-NMR spectrum of dicyclic-PLA (Figure 3) showed the characteristic cyclic carbonate protons of the dicyclic-PLA at 4.35 (position f), 4.58 (position d) and 4.95 ppm (position e).

Figure 4 shows a ^{1}H-NMR spectrum of NIPU which consisted of the primary and secondary hydroxyl groups. The characteristic protons of the PLA backbone were indicated at the following chemical shifts: 1.5 (position b), 2.75 (position c) and 5.25 ppm (position a). The NH proton of the urethane linkage was presented at 5.00 ppm. The obtained NIPU film was a soft material and had dark brown color due to the natural color of NR. The NIPU slightly dissolved in tetrahydrofuran (THF) and the soluble part showed the number averaged molecular weight of ~11,000 g/mol. The non-soluble part became a gel. It is believed that the intramolecular and intermolecular hydrogen bonding were formed among hydroxyl groups and the carbonyl groups of the NIPU leading to improve the resistance in the organic solvents [25]. As a result, NIPU was not completely dissolved in THF which was an organic solvent [26].

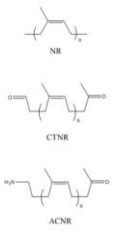

Figure 1. Chemical structures of NR, CTNR and ACNR.

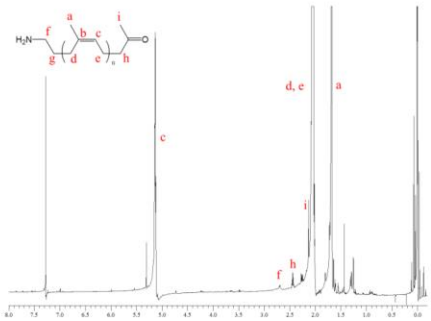

Figure 2. ^{1}H-NMR spectrum of ACNR.

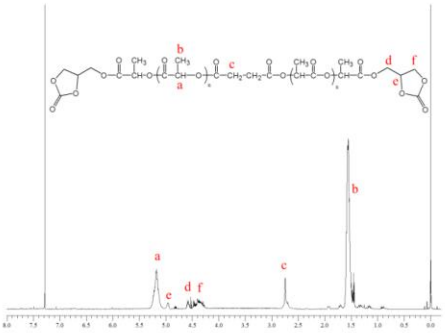

Figure 3. ^{1}H-NMR spectrum of dicyclic-PLA.

Conclusions

The bio-based non-isocyanate polyurethane was successfully prepared from modified poly(lactic acid) and modified natural rubber. The starting materials were functional oligomers: dicyclic poly(lactic acid) and amino carbonyl telechelic natural rubber. The chemical structure of the starting materials and NIPU was verified by the ^{1}H-NMR spectra. The new urethane linkage was found in the NIPU. THF was the eluent for GPC analysis and it was unable to dissolve the NIPU due to the strong hydrogen bonding between THF and NIPU. Therefore, its true molecular weight was unable to evaluate in the present analysis.

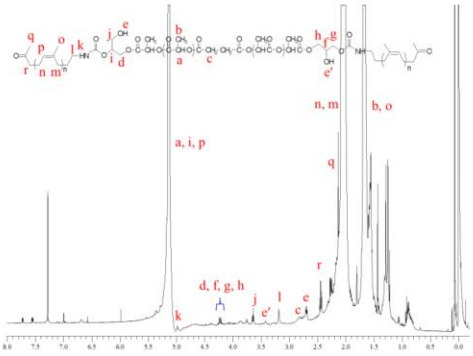

Figure 4. ^{1}H-NMR spectrum of NIPU.

Acknowledgement

This project is supported by Thailand Research Fund (Grant no. 5650089) and Prince of Songkla University.

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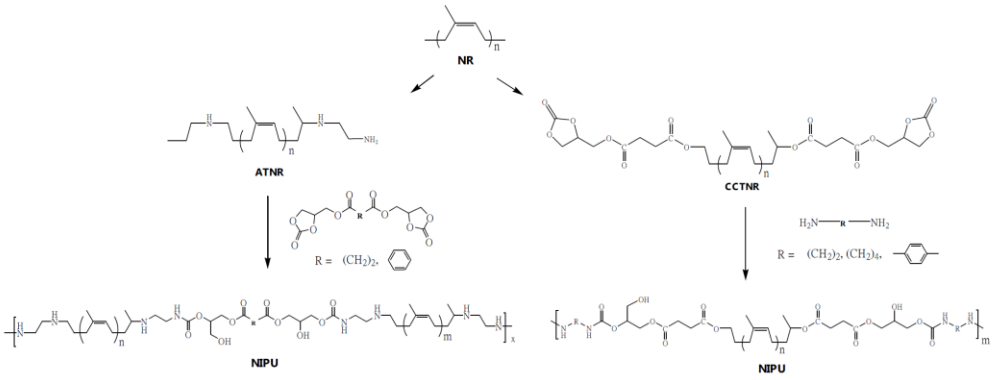
O05- SYNTHESIS OF BIO-BASED, NON-ISOCYANATE POLYURETHANE FROM NATURAL RUBBER

Ruedee Jaratrotkamjorn[a], Arnaud Nourry[b], Pamela Pasetto[b], Jean-François Pilard[b*], Varaporn Tanrattanakul[a*]

[a]*Bioplastic Research Unit, Department of Materials Science and Technology Faculty of Science, Prince of Songkla University, Songkhla 90112, Thailand*
[b]*Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Université du Maine, 72085, Le Mans Cedex, France*
Phone +33243833540, Fax +33243833754, E-mail: jean-francois.pilard@univ-lemans.fr
Phone +6674288362, Fax +6674446925, E-mail: varaporn.t@psu.ac.th

NIPUs (Non Isocyanate PolyUrethanes) are prepared from the reaction of cyclic carbonates and amines without using toxic isocyanates and catalysts. This research work deals with the synthesis and characterization of NIPUs from Natural Rubber (NR). Two approaches have been investigated and developed (scheme 1). The first one is based on the reaction between Amino Telechelic Natural Rubber (ATNR) and aliphatic or aromatic molecules of dicyclocarbonates, whereas the second one is relied on the reaction of diCycloCarbonates Natural Rubber (CCTNR) and aliphatic or aromatic diamines. Oligomers ATNR and CCTNR were obtained by controlled and oxidative degradation of NR then by functionalization of the chain ends. The molecular weights (M_n) of these oligomers were included between 1000 and 2000 g/mol and their dispersities roughly equal to 2. The different steps for the syntheses of these oligomers and corresponding NIPUs will be presented as well as their thermal properties.



Scheme 1 Synthesis of NIPU.

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14P-S7-051a

Synthesis and Characterization of Cyclic Carbonate Telechelic Poly(lactic acid)

[1,2]R. Jaratrotkamjorn, [2]A. Nourry, [2]P. Pasetto, [1]V. Tanrattanakul, and [2]J.-F. Pilard

[1]Department of Materials Science and Technology, Faculty of Science,
Prince of Songkla University

[2]LUNAM Université, Institut des Molécules et Matériaux du Mans,
UMR CNRS 6283, Université du Maine

[1]Hatyai, Songkhla, 90112, Thailand

[2]Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France

[1]Phone: +66-74-288-362; Fax: +66-74-446-925; varaporn.t@psu.ac.th

[2]Phone: +33-24-383-3540; Fax: +33-24-383-3754; jean-francois.pilard@univ-lemans.fr

Introduction

The cyclic carbonate telechelic poly(lactic acid) (CCPLA) was synthesized by two steps. The first step was the synthesis of carboxylic telechelic poly(lactic acid) (CBPLA) in the presence of stannous octoate ($Sn(Oct)_2$) and succinic acid (SA) via a melt condensation. The second step, the CBPLA was reacted with the glycerol carbonate in the Steglish esterification to form the CCPLA. The chemical structure of CBPLA and CCPLA were characterized by NMR, FTIR and MALDI-TOF. The molecular weights of obtained materials were also determined by using a ^{1}H-NMR and SEC.

Results and Discussion

Scheme 1 represents a synthesis route of CBPLA and CCPLA. The amount of SA was varied from 5 to 15 wt%. The contents of COOH end groups in CBPLA were higher than 94%. Their molecular weights decreased with increasing the amount of SA and decreasing the reaction time. Then, CBPLA was reacted with the glycerol carbonate in the presence of *N*,*N*-dicyclohexylcarbodiimide (DCC) and *N*,*N*-dimethyl-4-aminopyridine (DMAP). The characteristic protons of carbonate moiety appeared at 4.10-4.60 and 4.92 ppm (Figure 1). The molecular weights of CCPLA were in the range from 1000 to 2000 g/mol. The dispersity was approximately 2.

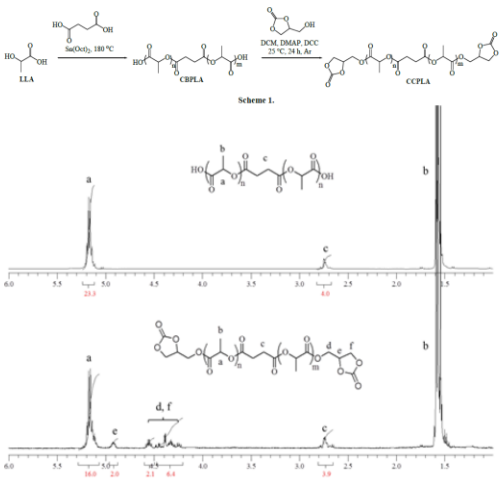

Figure 1. ^{1}H-NMR spectra of CBPLA and CCPLA.

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VITAE

Name Miss Ruedee Jaratrotkamjorn

Student ID 5510230010

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor Degree in Chemistry	Prince of Songkla University	2007
Master Degree in Polymer Science and Technology	Prince of Songkla University	2012

Scholarship during Enrolment

PSU Ph.D. Scholarship, Prince of Songkla University, Thailand

List of Proceeding

1. Ruedee Jaratrotkamjorn, Arnaud Nourry, Pamela Pasetto, Varaporn Tanrattanakul and Jean-François Pilard. “Synthesis and Characterization of Cyclic Carbonate Telechelic Poly(lactic acid)”, the 11th SPSJ International Polymer Conference (IPC 2016), Fukuoka International Congress Center, Fukuoka, Japan, 13-16 December 2016 (334).
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