About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

About OMICS Group Conferences

OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Green Processes to Diisocyanates and PU Elastomers via Carbonate Raw Materials: New NPR and NIR Processes



- Green Chemistry
- NPR to MDI, DDI, HDI:DPC
- NIR to P-Urea:DPC
- NIR to PU through Cyclic Carbonate
- Other Carbonate Routes to PU and PA
- Summary

Prof. Shenghong A. Dai

National Chung-Hsin University

Taichung, Taiwan

Winterton: 12 Green Engineeing Principles

(Green Chem., 2001, 3 G73.)

1. Identify and quantify by-products. (副產物鑑定及量化)
2. Report conversions, selectivity's, and productivities. (明示程序之轉化率/產率/選擇率)
3. Establish full mass-balance for the process. (建立完整質量平衡)
4. Measure catalyst and solvent loses in air and aqueous effulent.
5. Investigate basic thermochemistry.
6. Anticipate heat and mass transfer limitations.
7. Consult a chemical or process engineer. (與化工人咨詢要點)
8. Consider the effect of overall process on choice of chemistry. (作完整化學選項之考量)
9. Help develop and apply sustainability measures.(發展永續發展之要項)
10. Quantify and minimize the use of utilities.
11. Recognize where safety and waste minimization are incompatible. (安全及減廢之考量)
12 Monitor, report, and minimize the laboratory waste emitted.

Green Chemistry– NPR, NIR Processes

- Green chemistry is a way to minimize chemical threat to human being and environment.

- **Anastas and Wnerer**: (12 principles) chemical reliability, safety, high selectivity, energy efficiency, re-usability.

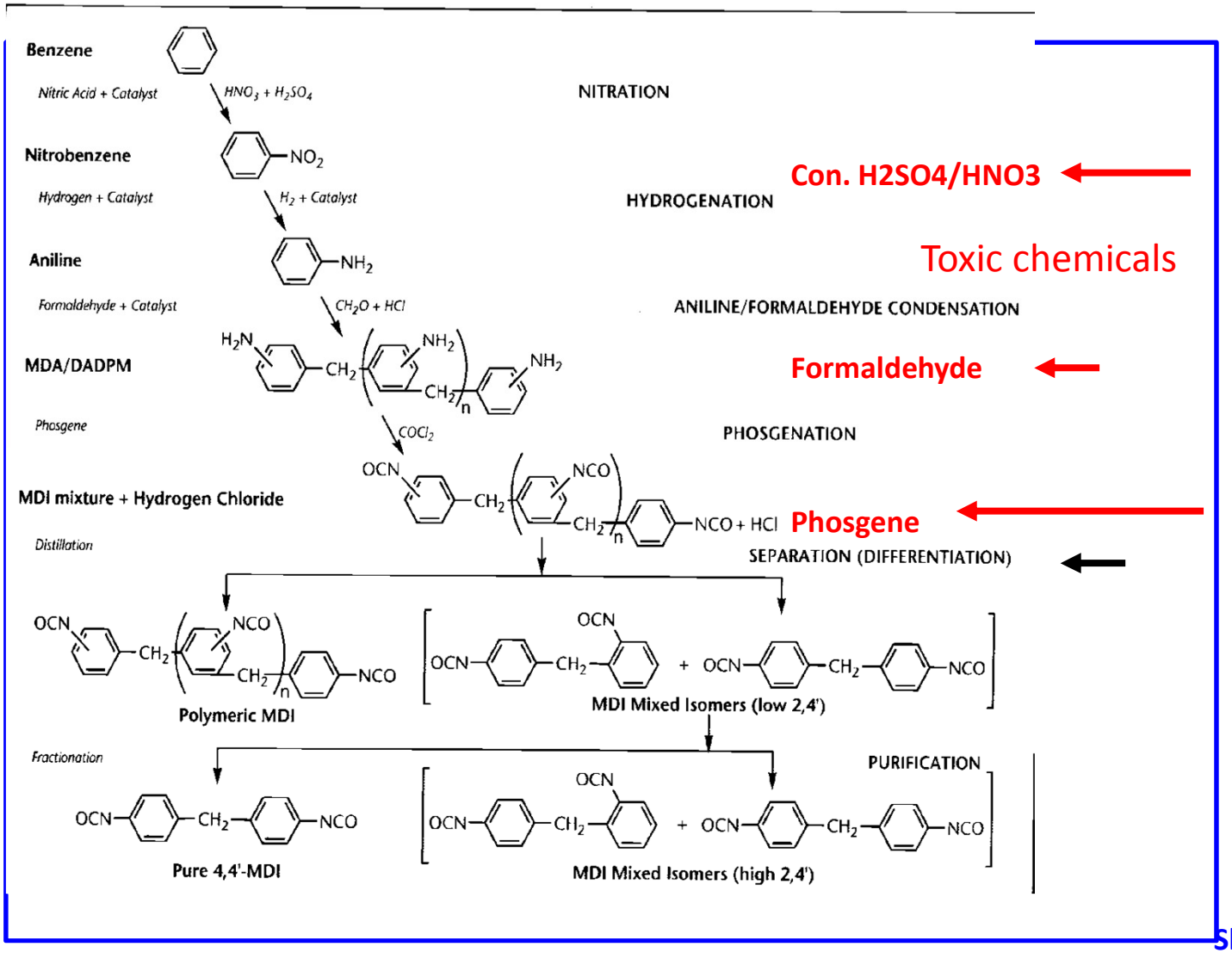
- **NPR / NIR- Our Green Research Goals:**

  - **Non-phosgene process of producing isocyanates**
  - Minimize chlorine-containing reagents and products
  - Ambient synthesis condition
  - Use low-toxic chemicals - avoid isocyanates in PU making
  - Employ sustainable low-cost raw materials

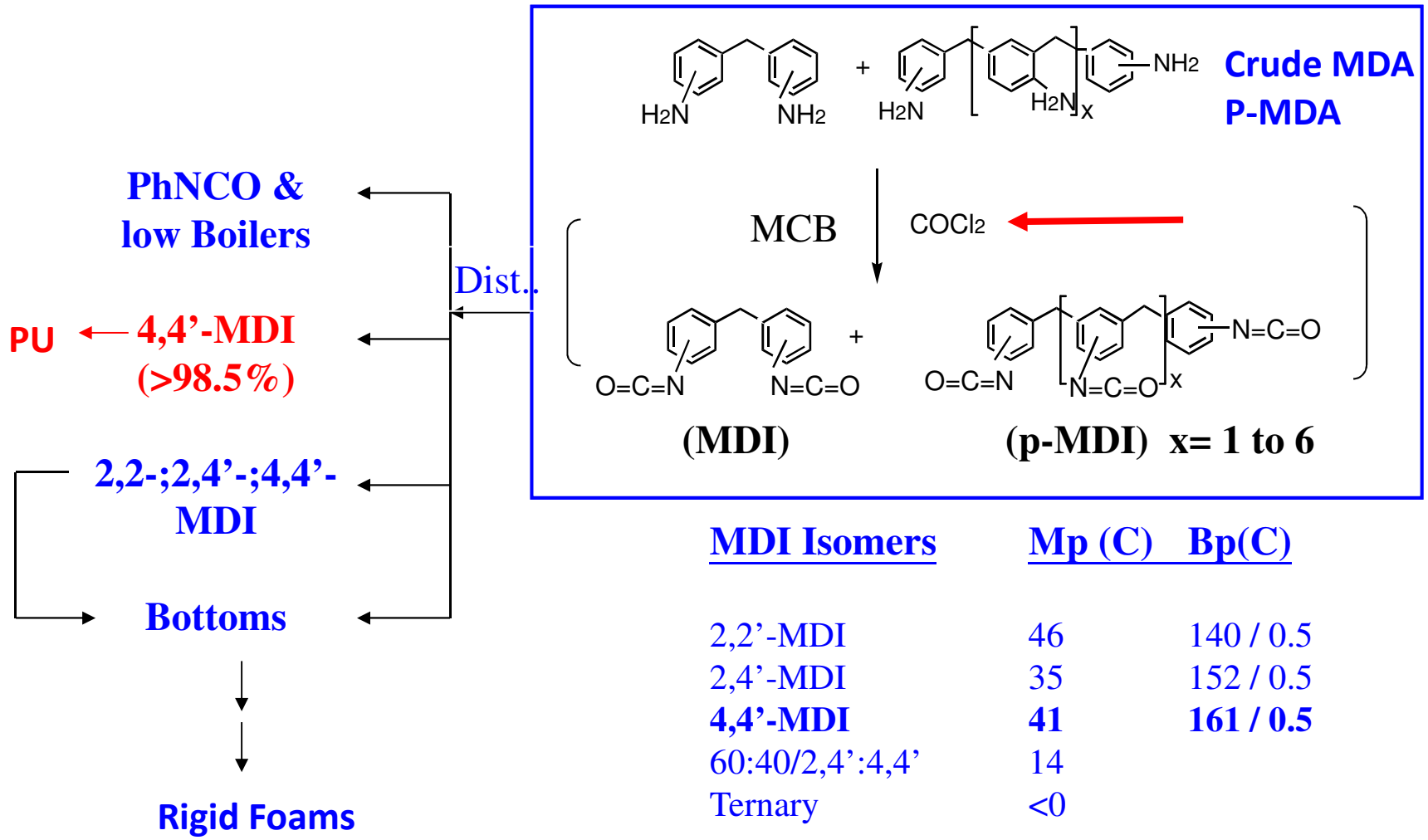
- NPR: Non-phosgene Route (非光氣製程- Isocyanates)
- NIR: Non-isocyanate Route (非異氰酸鹽製程- PU)

Phosgene Process-MDI from Benzene

(Polyurethane Handbook by Huntsman)



Phosgene Process- p-MDI from p-MDA



MDI Isomers	Mp (C)	Bp(C)
2,2'-MDI	46	140 / 0.5
2,4'-MDI	35	152 / 0.5
4,4'-MDI	**41**	**161 / 0.5**
60:40/2,4':4,4'	14	
Ternary	<0	

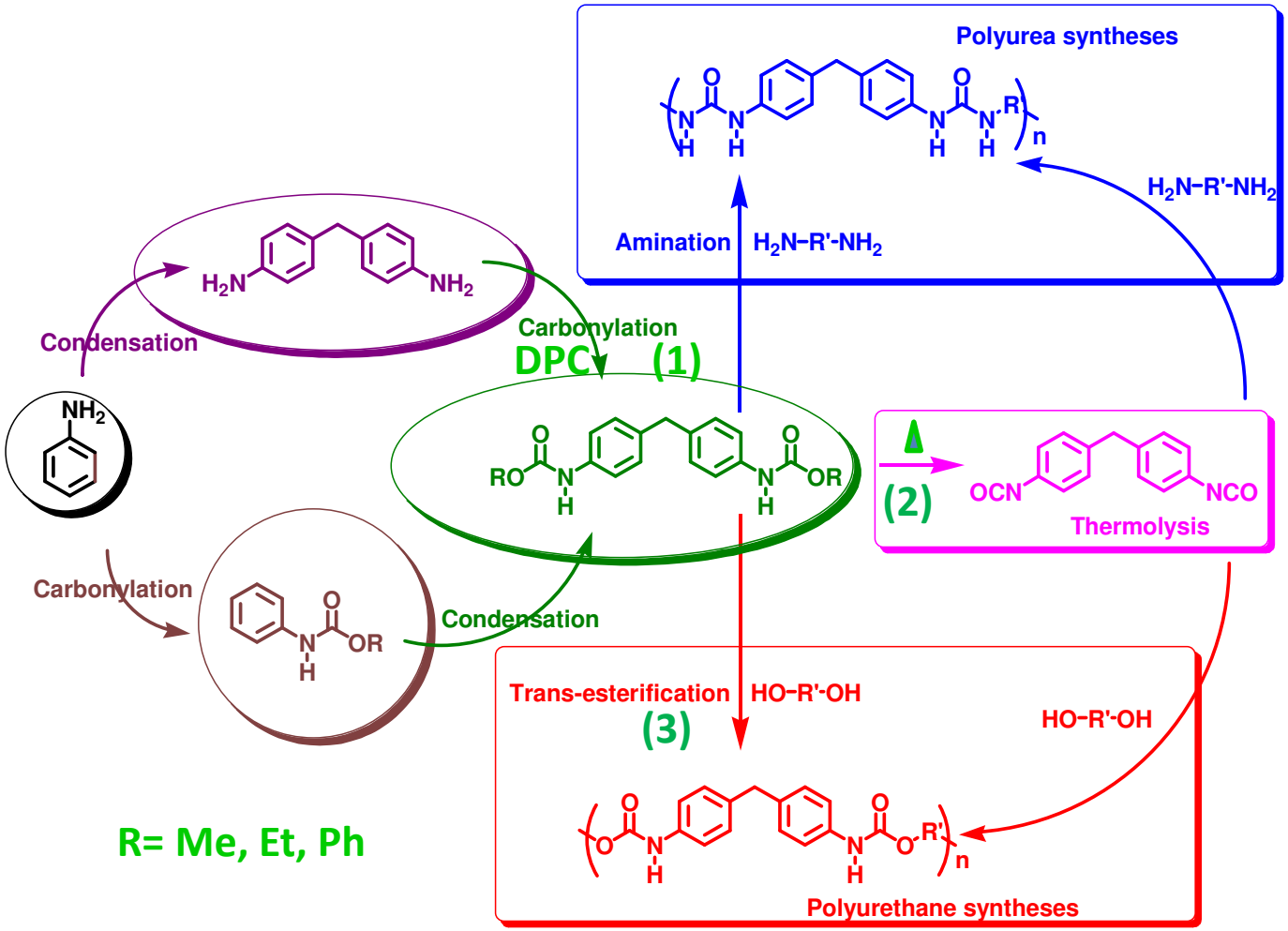
Ref: H. Ulrich in "Chemistry and Technology of Isocyanates, John Wiley, p385 (1996)

The Problems Associated with Phosgene Process

- **Safety problem: Phosgene is a highly toxic chemical with low Lethal threshold.**
- **Phosgene process generates large amount of HClg .**
- **HClg is a highly corrosive agent, and hence requires high-cost of maintenance.**
- **HClg needs to be managed into PVC or oxidized to recover as chlorine.**
- **MDI will contain hydrolyzable and non-hydrolyzable chlorides impurities.**
- **MDI process requires highly safety facilities to prevent accidents/fatality.**
- **Require large sum of initial cost for a large integration site and safety facilities.**

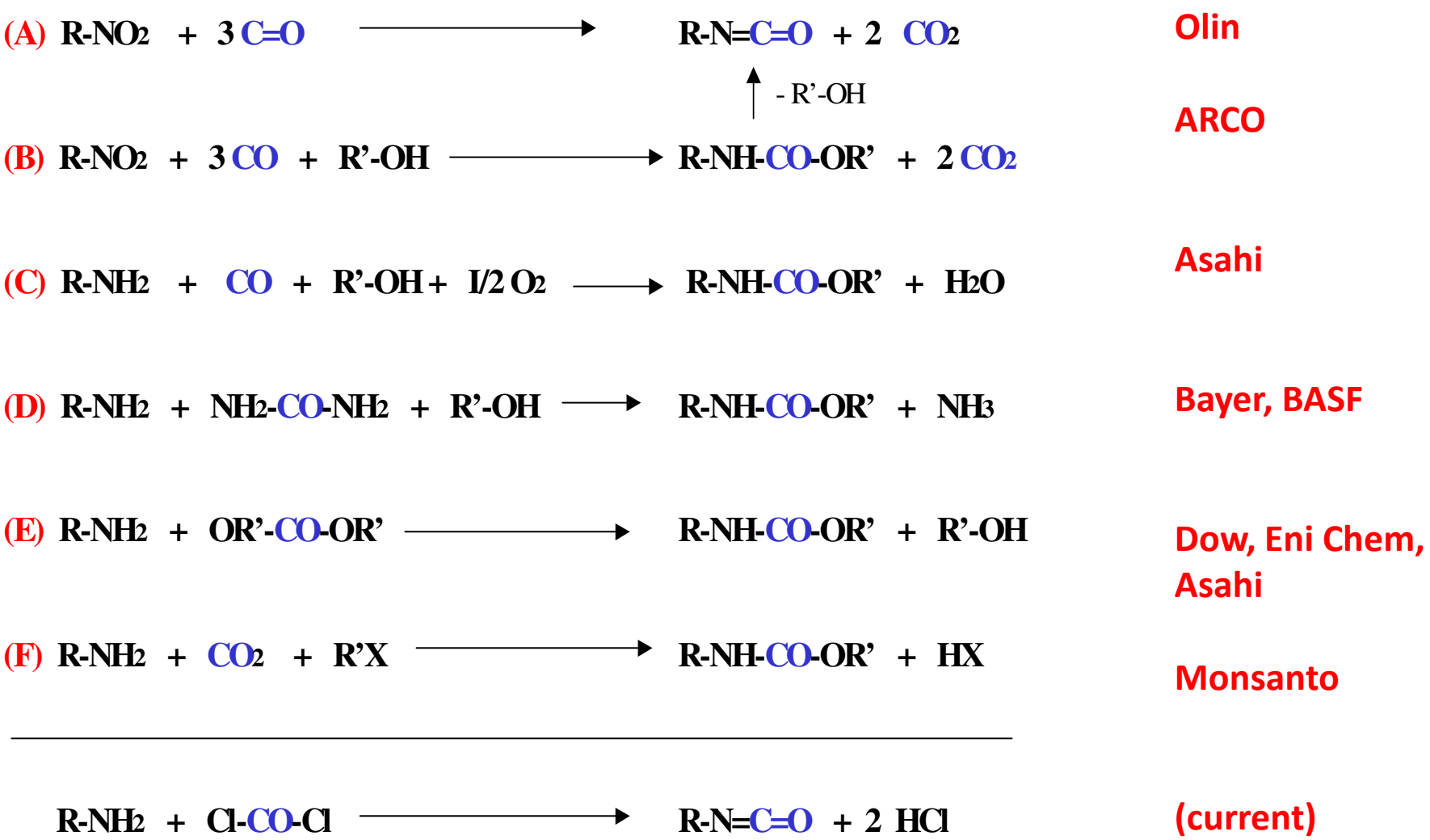
Non-phosgene Routes to MDI

- Over 40 plus years of research but with no practical process in use



Carbonylation Reagents

Phosgene still is the most efficient/cheap raw materials.



Olin

ARCO

Asahi

Bayer, BASF

Dow, Eni Chem, Asahi

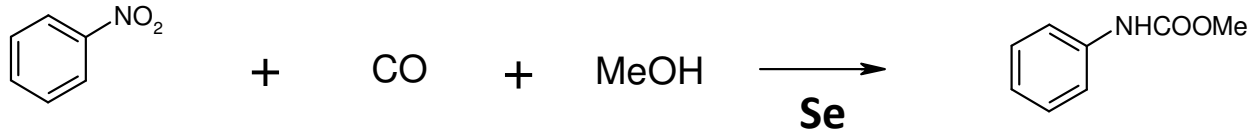
Monsanto

(current)

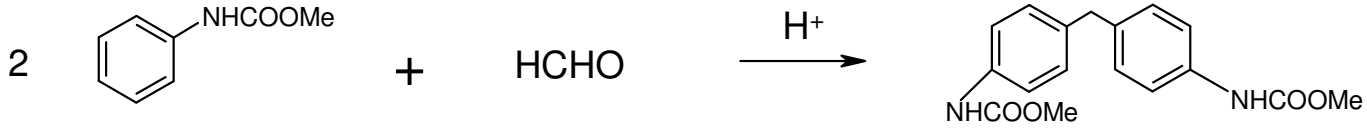
NPR to MDI – Prior Arts

ARCO : Three-Step Process from Nitrobenzene (1974)

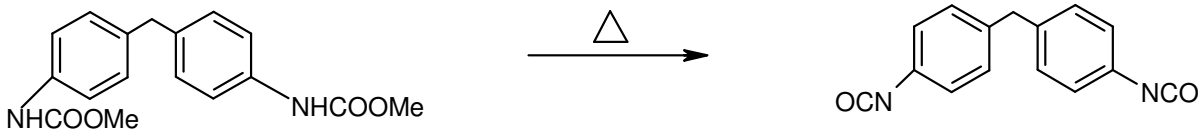
(1) Reductive Cabonylation:



(2) Condensation:



(3) Thermolysis:

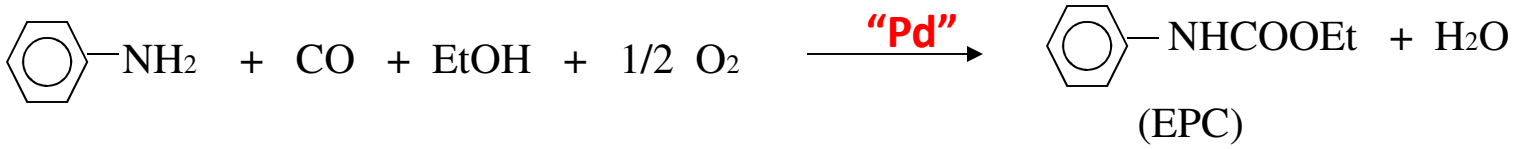


- Toxic catalyst and hart to recover [Step (1)]
- High temperature to crack carbamate [Step(3)]

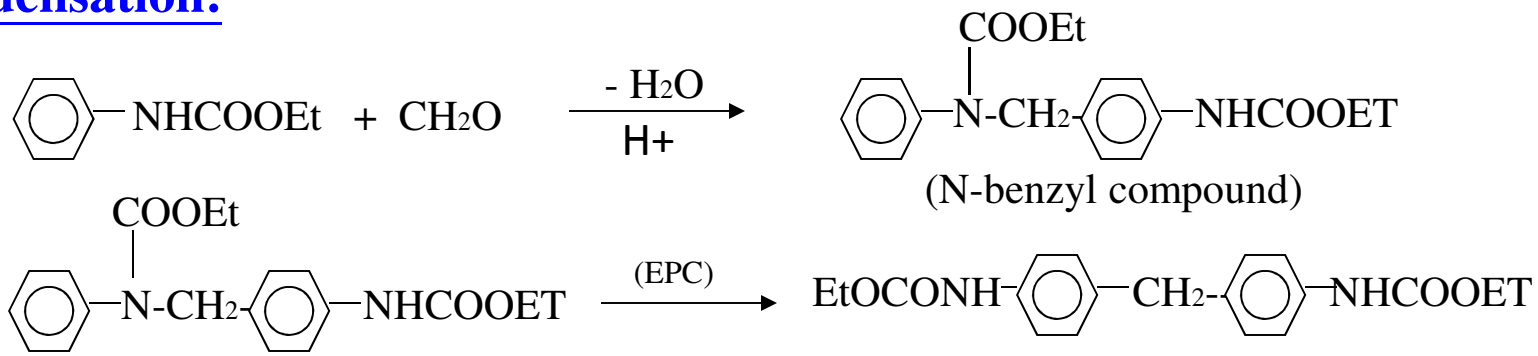
NPR to MDI – Prior Arts

Asahi : Three Step Process from Aniline (1978)

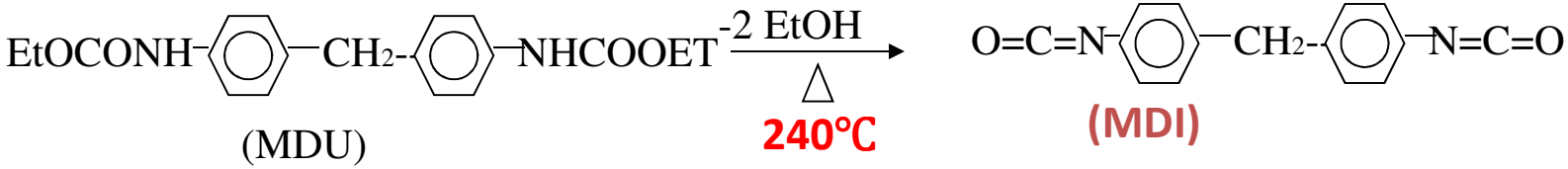
1. Oxidative Carbonylation:



2. Condensation:



3. Decomposition:

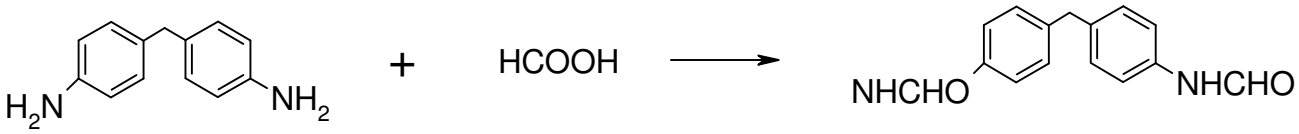


- **Similar problems to ARCO's; Being Scaled-up in pilot**

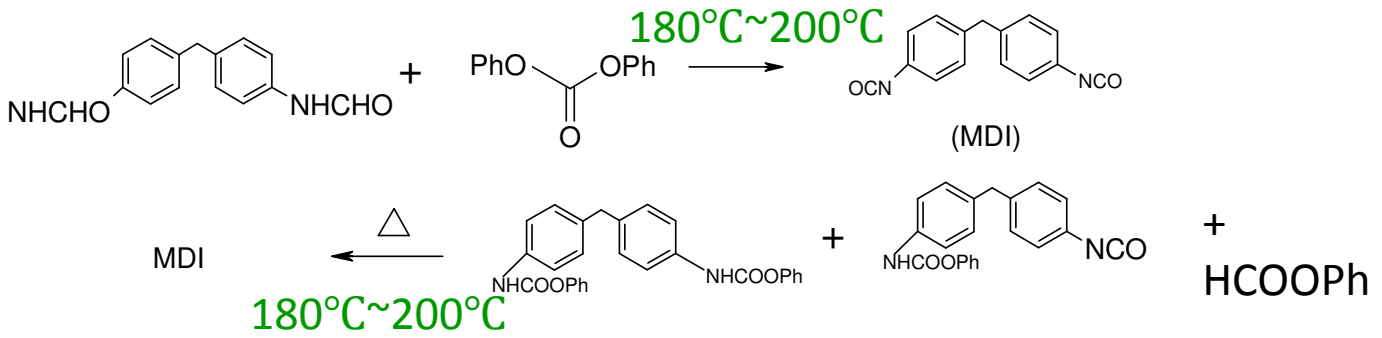
Lynodell' DPC Route to MDI

[R. W. Mason, US Patent 6,781,010 (2004)]

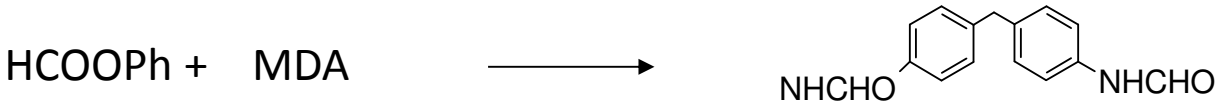
(1) MDA Condensation with Formic Acid:



(2) Carbonylation of Formamaide with DPC and Thermolysis:



(3) Trans-esterification of MDA with Phenyl Formate:



Lynodell' DPC Process to MDI

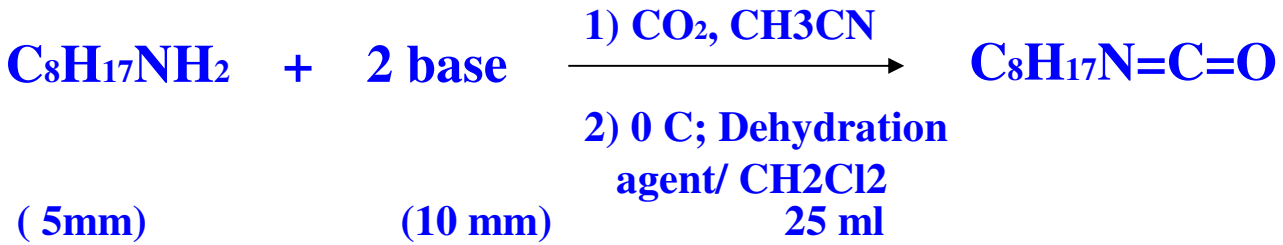
[R. W. Mason, US Patent 6,781,010 (2004)]

- Advantages:
  - Themolysis temperature of biscarbamate into MDI seems milder (<200 ℃)
  - The yields to MDA-formamaide and MDI are high.
  - Phenyl formate, the by-product, could be re-used.

- Disadvantages:
  - MDI needs to be re-distilled to separate from solvent/by-product.
  - Highly corrosive formic acid was used as the carbonylation agent.

NPR to Aliphatic Diisocyanates

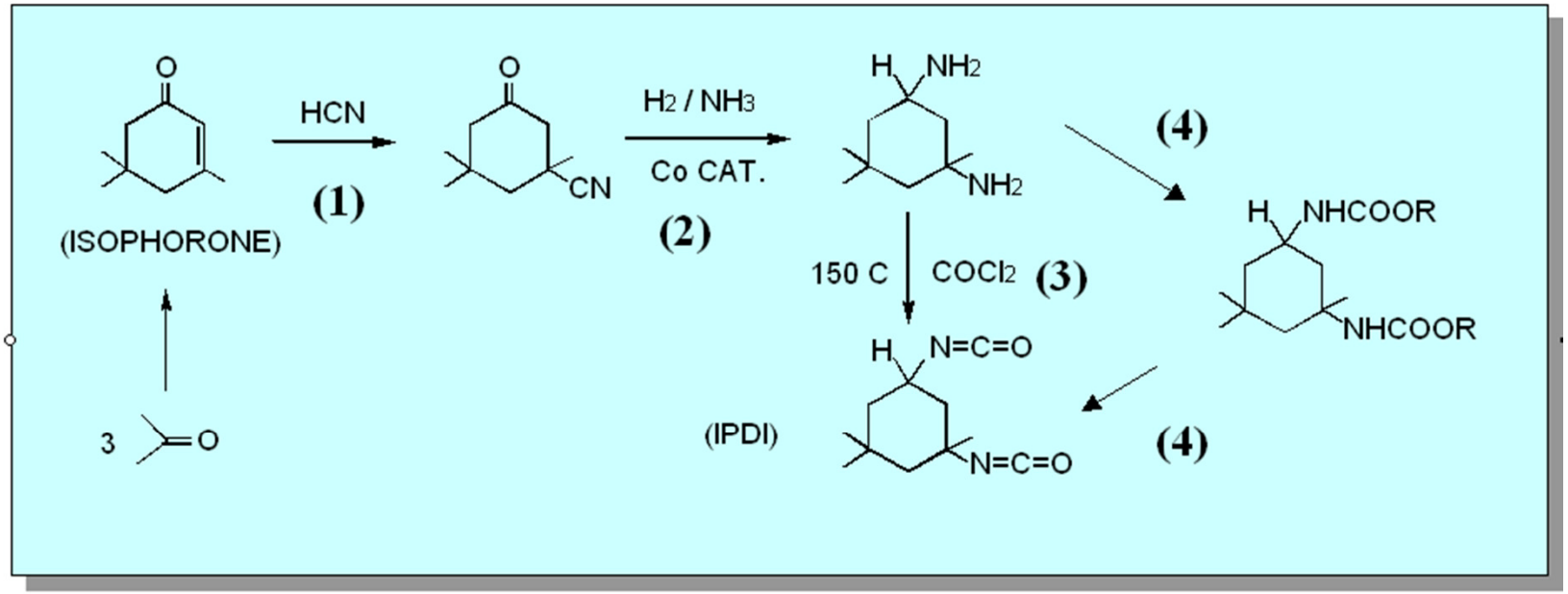
Monsanto: CO_2 Carbonylation-Dehydration Process



BASE	PRESSURE CO_2	DEHYD. AGENT	% YIELD
NEt_3	1 ATM	$POCl_3$	98%
NEt_3	1 ATM	PCl_3	96%
NEt_3	1 ATM	SO_3	99%
CyTEG	80 PSI	$(CF_3CO)_2O$	91%
CyTEP	80 PSI	$SOCl_2$	70%

- Applicable only to aliphatic diamines
- Require strong tertiary amine to stabilize the initial carbamic acid

NPR to IPDI : Urea Route

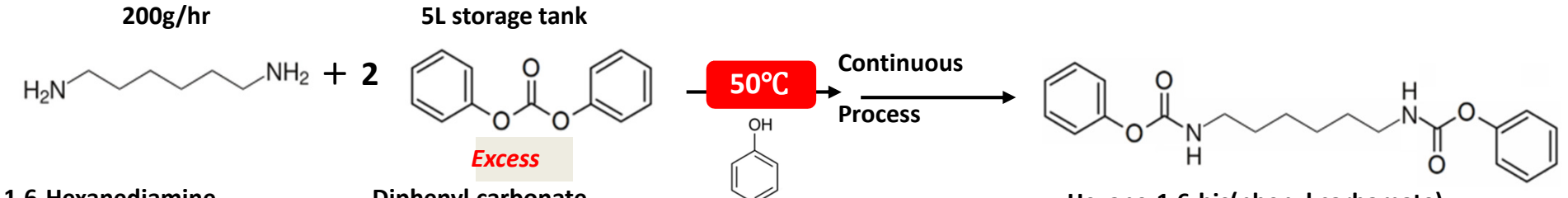


Ref: ***(1)*** *Scholven, Br. Patent, 1,047,920 (1966)*
(2) *Hibernia, Br, Patent, 972,010 (1964)*
(3) *K. Schimitt, et. al., German Patent 1,202,785 (1965)*
(4) BASF, DE 3,314,790 (1983); Hul; DE 4,231,417 (1992)

- **Applicable only to aliphatic diamine. (Bayer, Huls, BASF)**

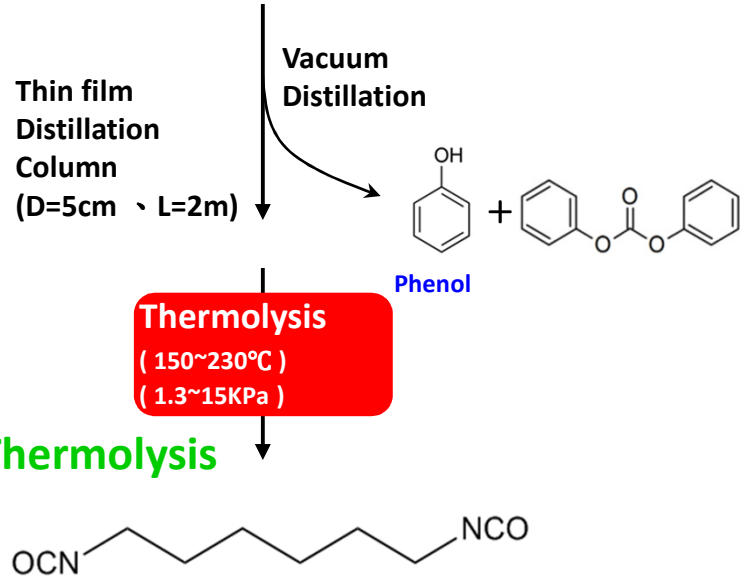
Franz M, USP 4,596,678(1986)

NPR to Aliphatic Diisocyanates : Review of Prior Arts



(4) Carbonylation

- *Total operation time= 10 day*
- *Hexane-1,6-bis(phenyl carbamate) Yield= 99.5%*
- DPC recycling rates= 99.9% (232℃、15KPa、119g/hr)
- Phenol recycling rates= 99.9% (230℃、1atm、200g/hr)
- *HDI Yield= 95.3%* (150℃、1.5KPa、140g/hr)
- HDI Purity= 99.8% (L.C)



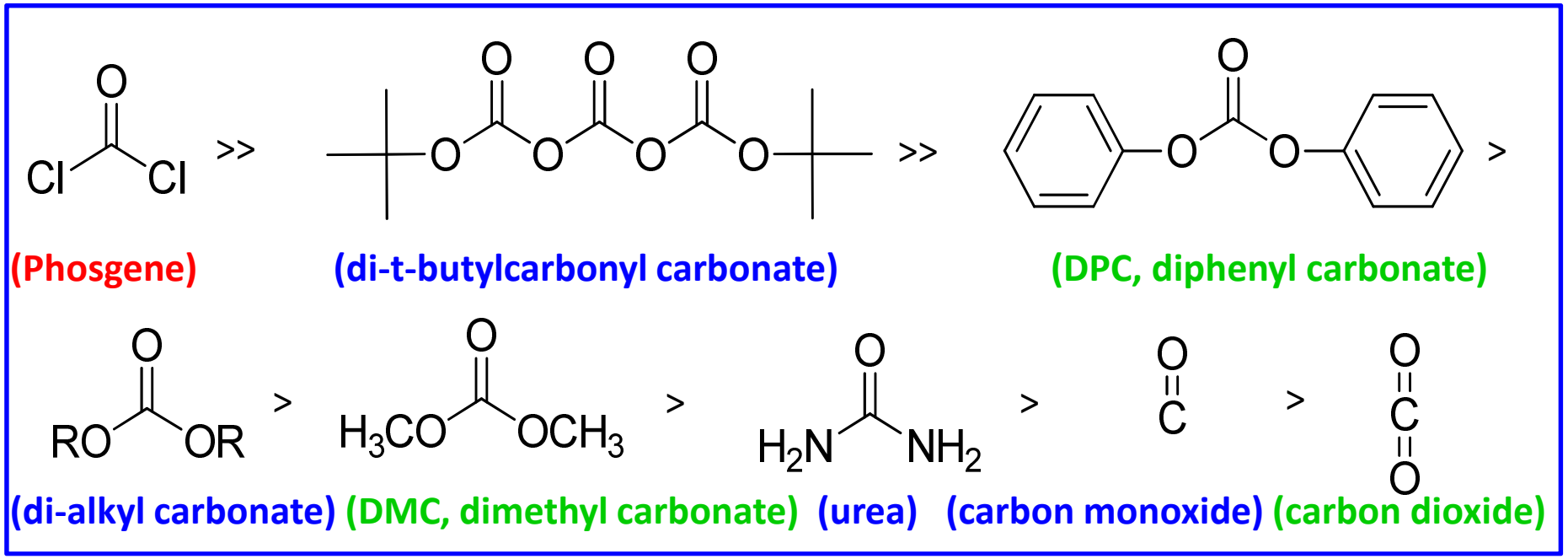
(5) Thermolysis

Hexamethylene-1,6-diisocyanate

- Phenol as solvent and DPC as carbonylation agent
- Most similar to our approach for aliphatic iso
- Slow processing speed

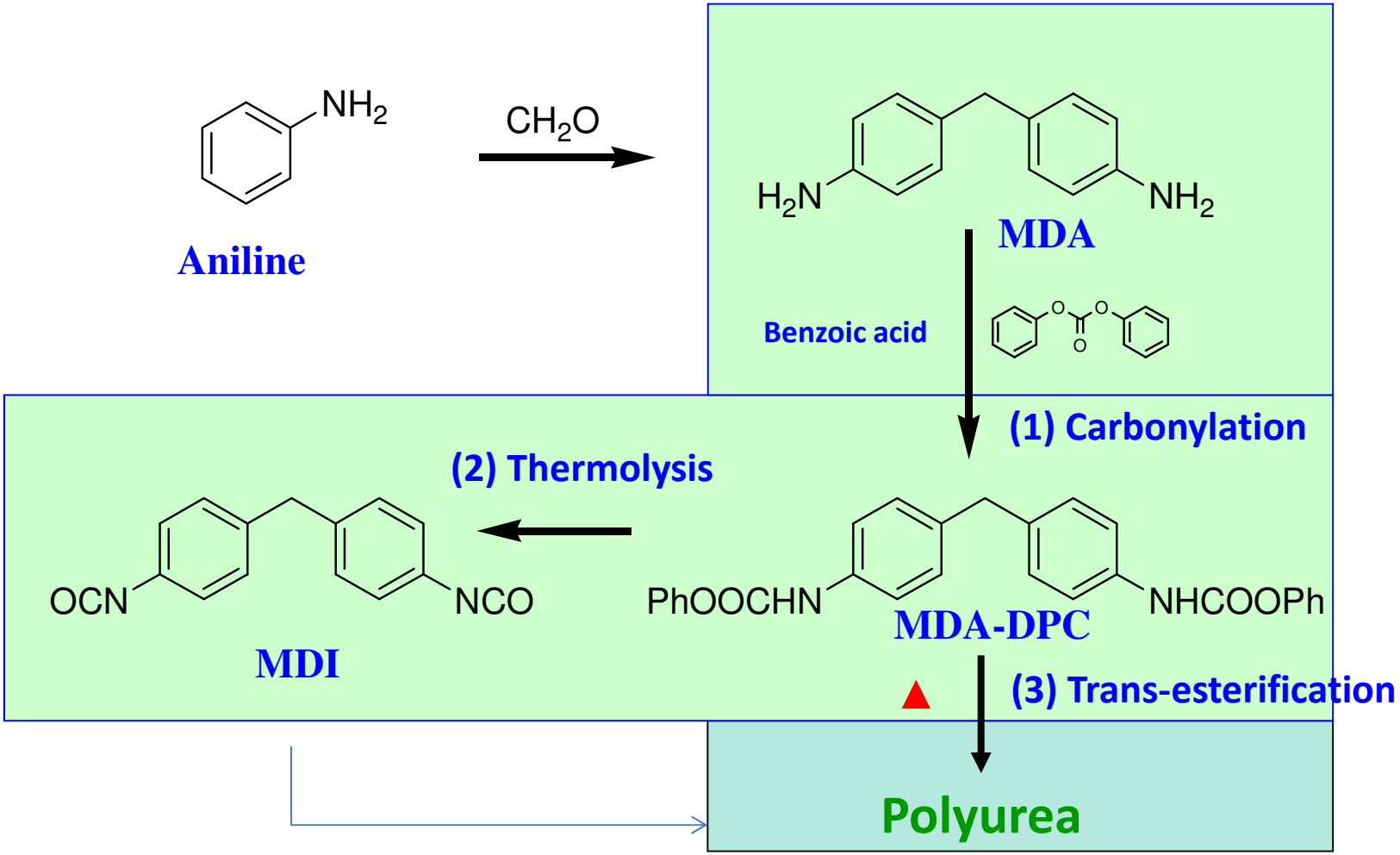
[24] M. Shinohata, N. Miyake, EP 2275405(2011) to Asahi

Principal Carbonylation Agents

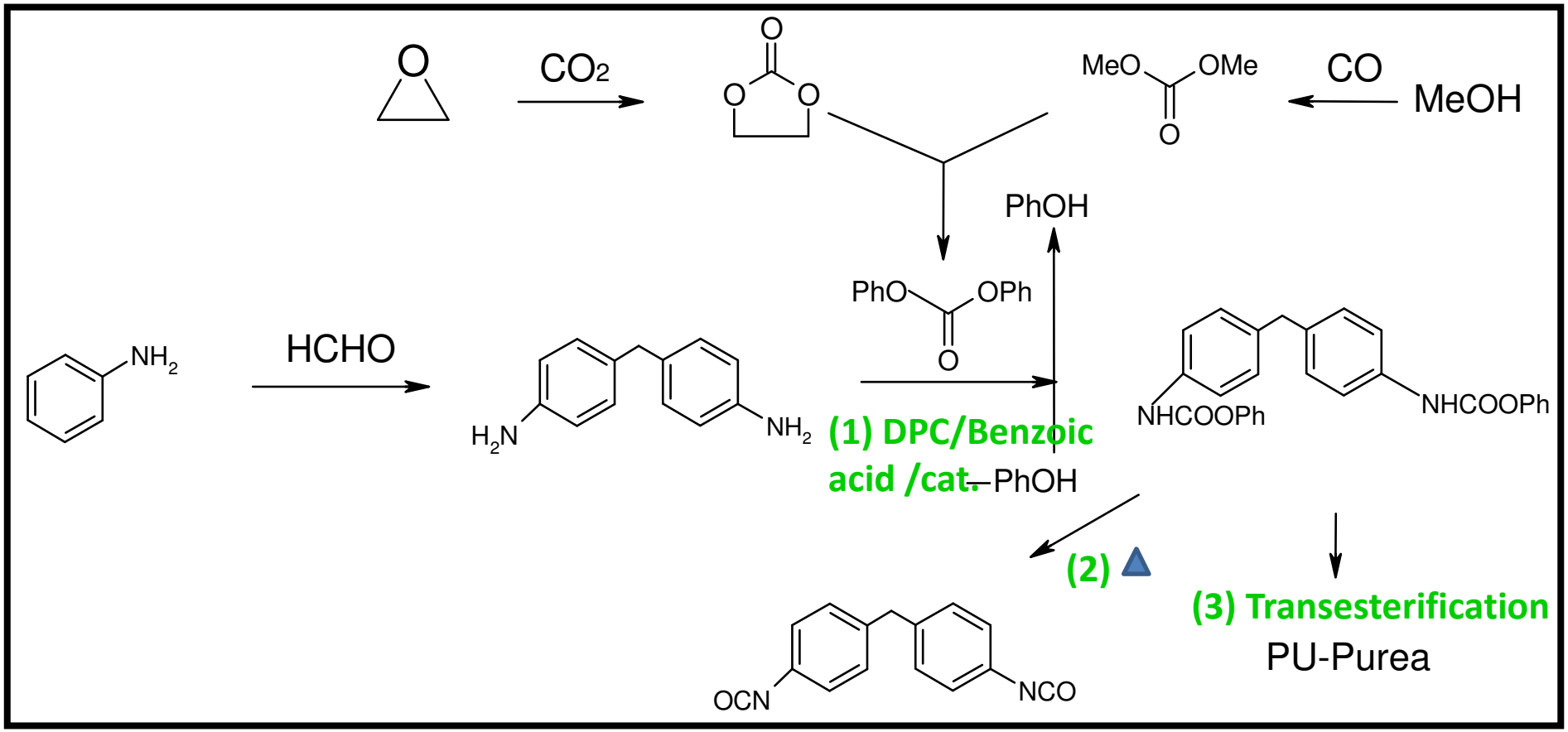


Dai's Group - 4,4'-MDI and P-urea Processes

(1) DPC carbonylation of MDA (2) Thermolysis to make MDI (3) NIR to Polyurea



Potential Sources of DPG for NPR to MDI



NPR- Our Optimization of 4,4'-DP-MDC Synthesis

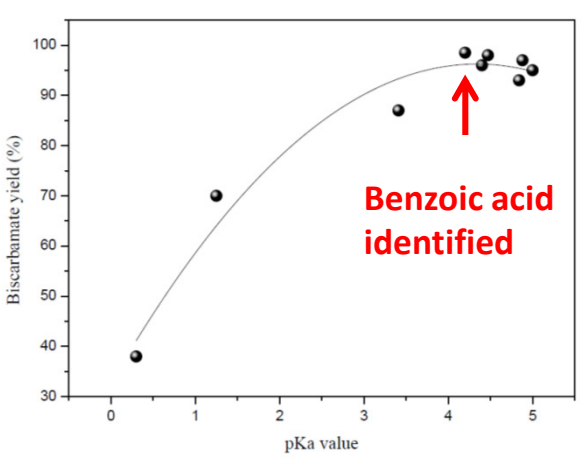


Fig 1. Effect of **carboxylic acids** of different pKas on 4,4'-DP-MDC yields.

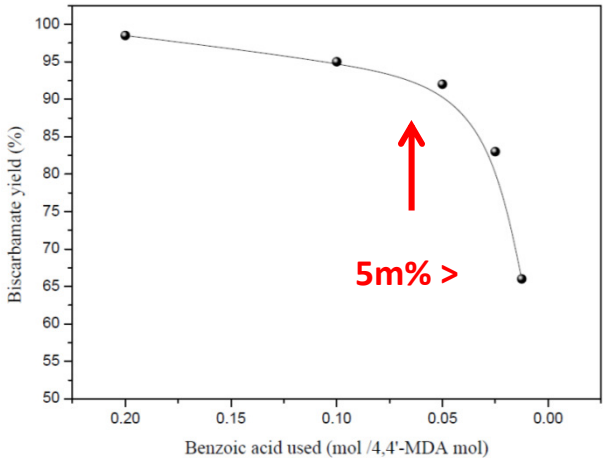


Fig 2. Effect of different **benzoic acid amounts** on 4,4'-DP-MDC yields.

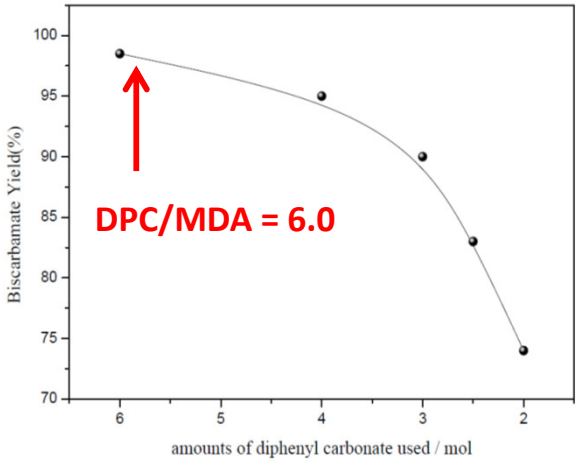


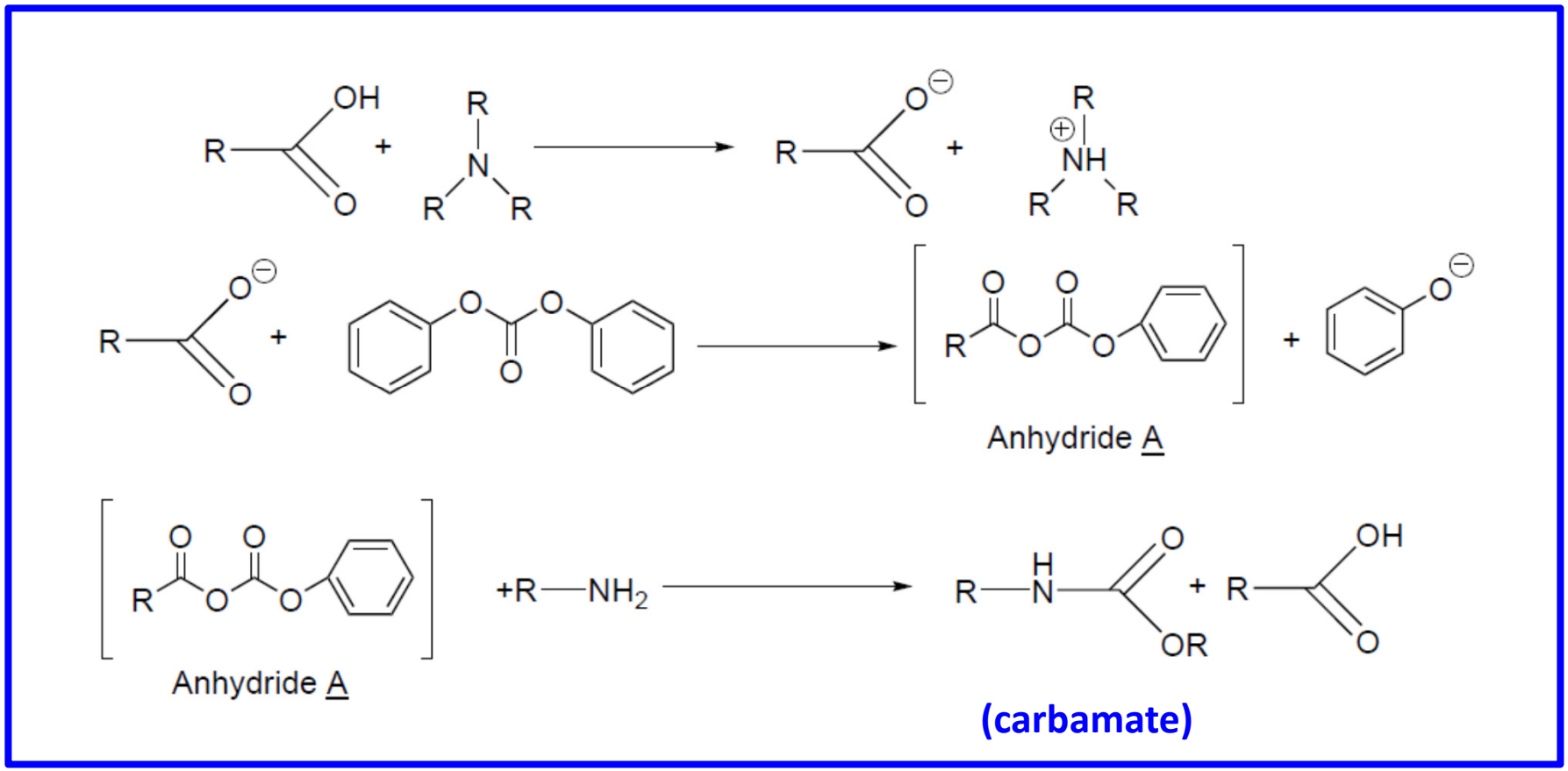
Fig 3. Effect of diphenyl carbonate concentrations on 4,4'-DP-MDC yields.

Composition[a]	Biscarbamate Yield (%)	Urea Yield(%)[b]
4,4'-MDA/DPC/Benzoic acid(1/6/0.2/0)	65	1.06
4,4'-MDA/DPC/Benzoic acid/Pyridine(1/6/0.2/0.009)	97	0.15
4,4'-MDA/DPC/Benzoic acid/TEDA(1/6/0.2/0.009)	**99**	0.15

[a]Molar ratio. **At 40 C ~60 C**
[b]Calculated by ^{1}H-NMR analysis.

- **Catalyzed by pyridine or TEDA.**

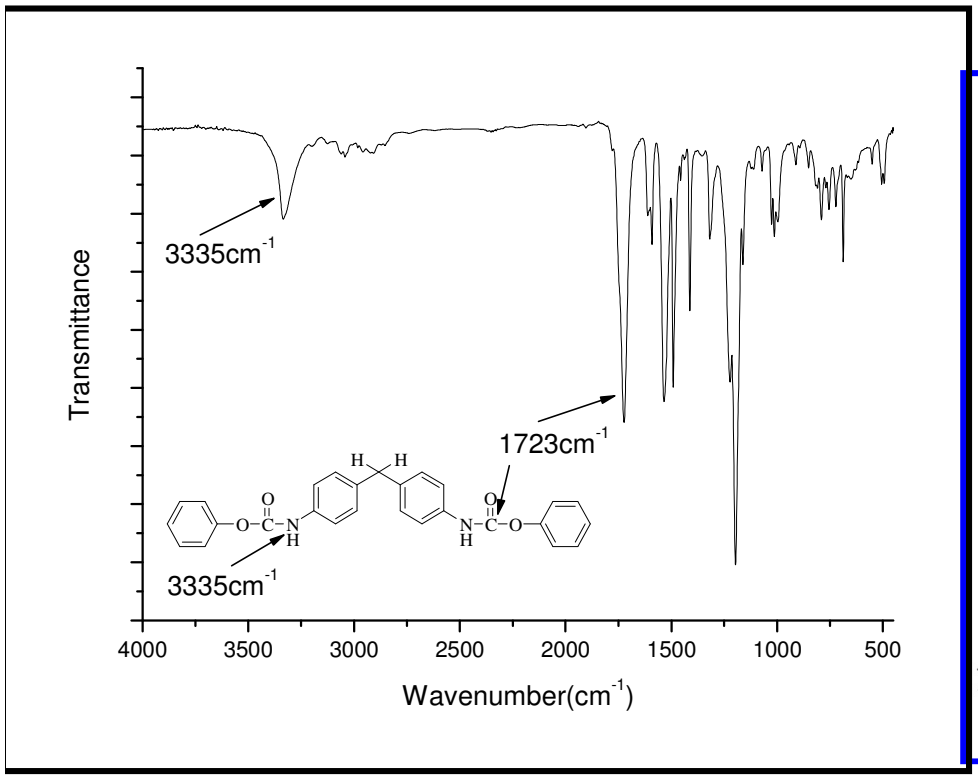
NPR-Mechanism of Carbonylation: Co-catalyzed by benzoic acid/tertiary amine



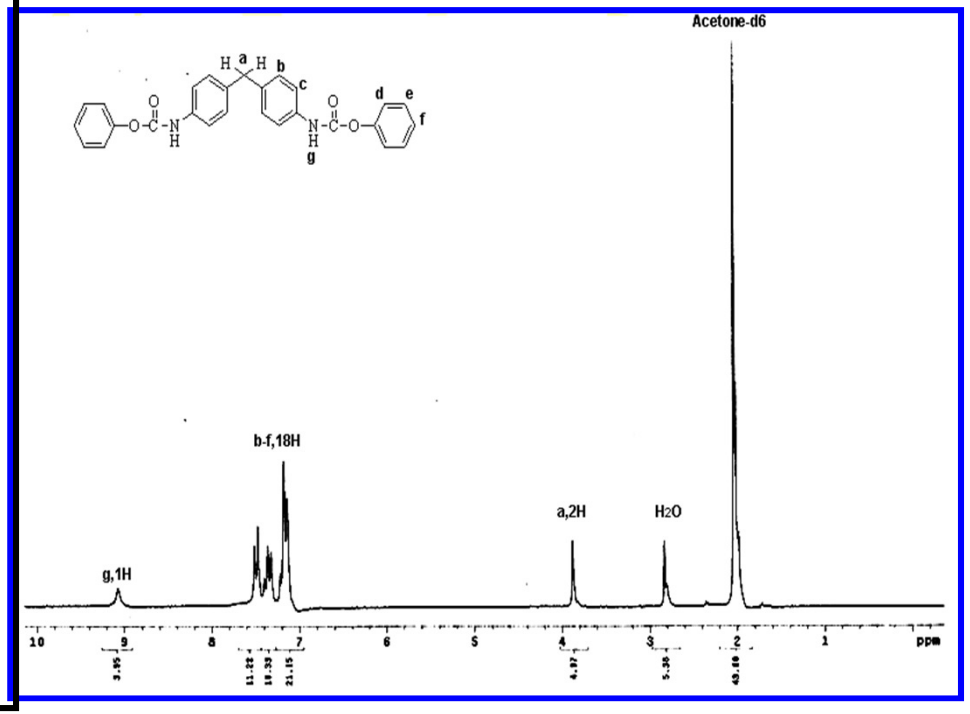
- Key active intermediate anhydride A in carbonylation of amine

NPR- MDA Carbonylation with DPC

(IR and ^{1}H-NMR of the MDA-DPC; mp 194 ℃)



IR

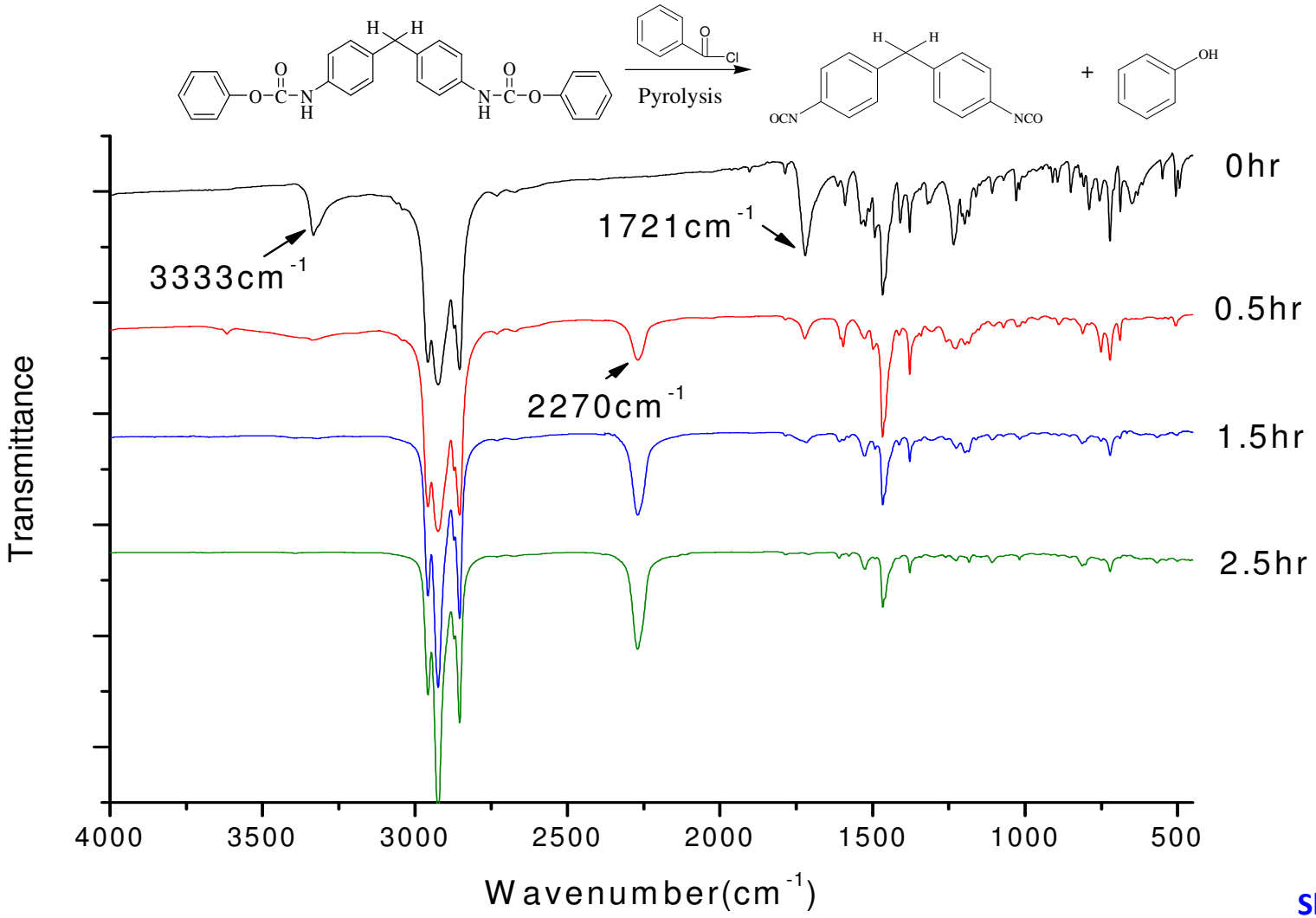


^{1}H-NMR

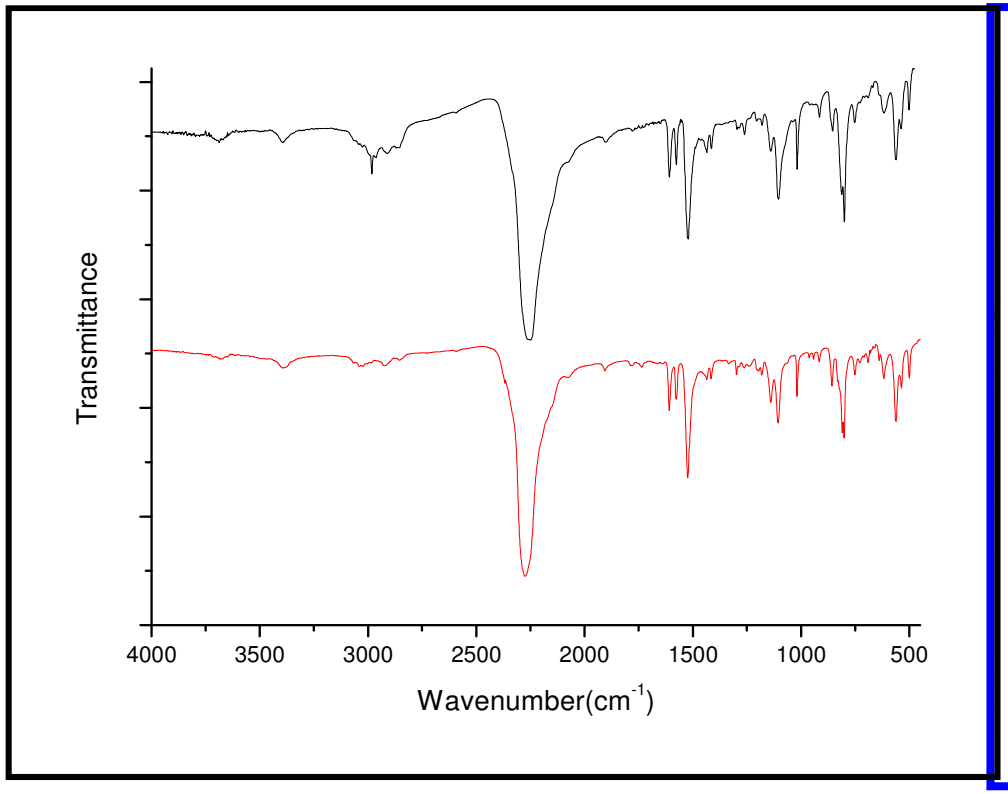
- MDA-DPC/dodecane: No detection of diphenyl urea formation

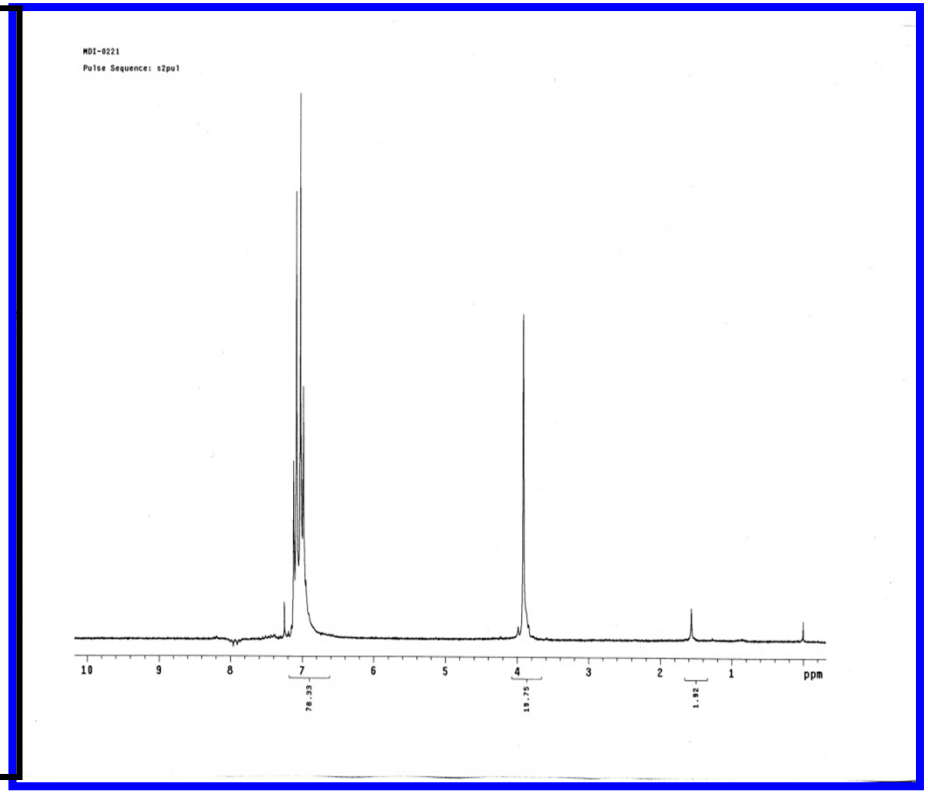
NPR-Thermolysis of MDI-DPC into MDI (a)

(Monitoring Thermolysis of MDA-DPC 200°Cin Dodecane)



NPR- Thermolysis of MDA-DPC into MDI





- Isolated MDI (76%) after fractionation

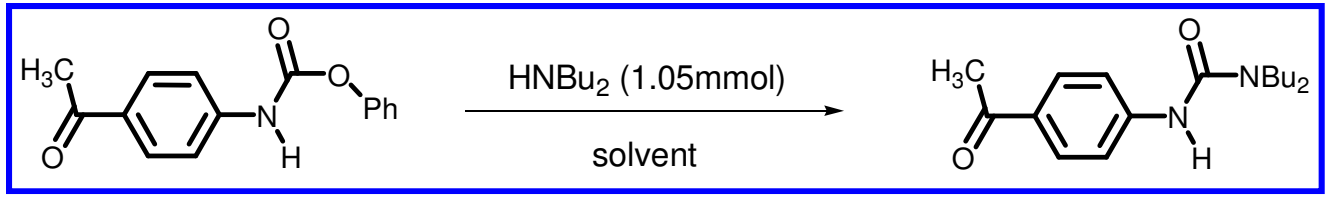
NPR- Thermolysis of MDA-DPC into MDI (b)

Summary of Lab-scale MDI Synthesis

- Carried out in dodecane (bp:216℃) at boiling temperature
- MDA-DPC conversion rate at 100%
- MDI crude yield >95%; Purified after distillation >76 %
- Recovered solvent and phenol >95%
- Little (CDI) by-product formation in the heating
- No chlorine content in the product
- The use of polar solvent resulted in complicated products.

Trans-amination of Ph-carbamate in Different Solvents

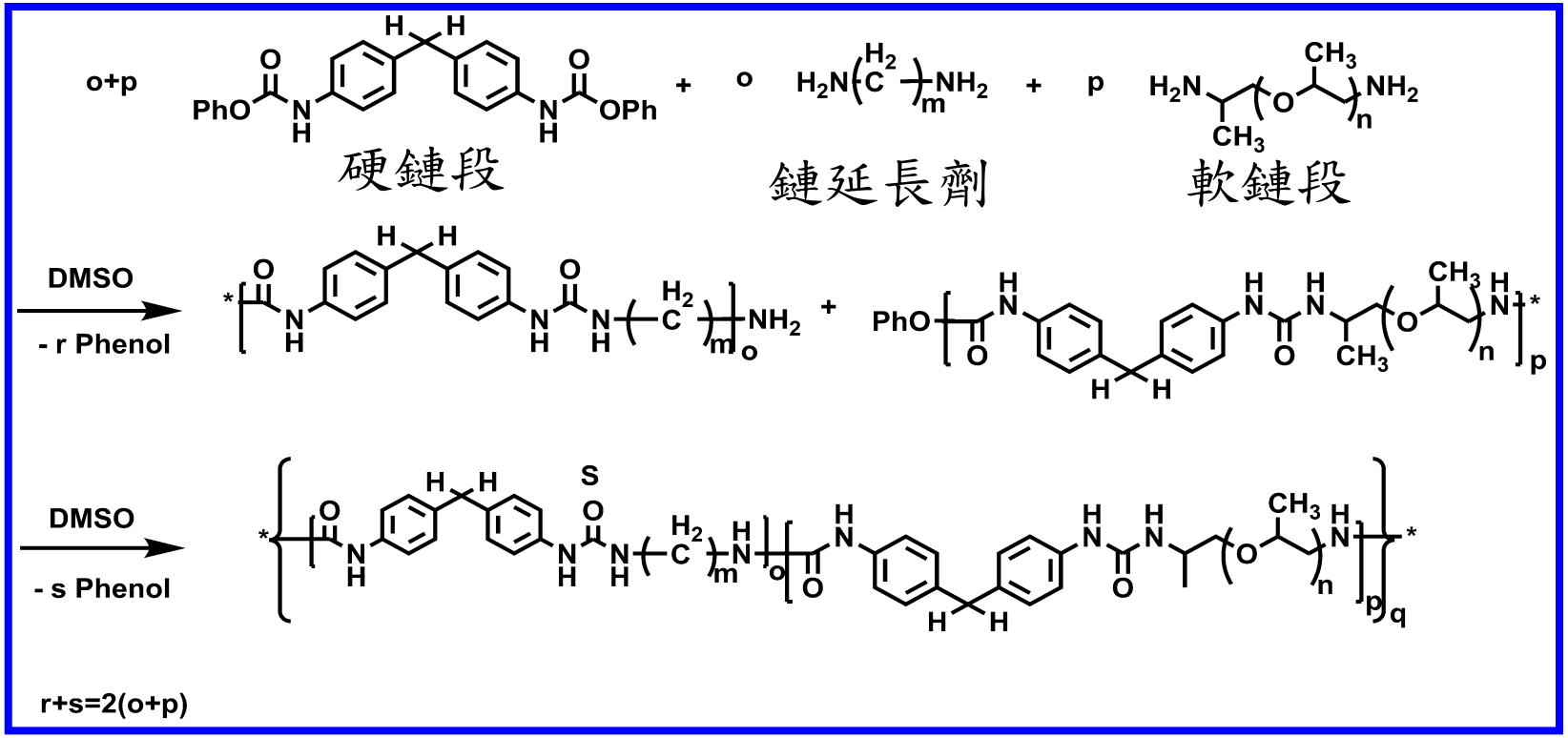
(B. Thavonekham, Synthesis, 1997, 1189-1194)



Solvent	DMSO	DMF	THF	MeCN	Dioxane	DME	$CHCl_3$	MeOH	Pyr	TMS
結構式										
Bp(℃)	189	153	65	81	100	64	60	65	115	285
Relative Polarity (water=1)	0.444	0.404	0.207	0.46	0.164	-	0.259	0.762	0.3	0.41
Condition	rt	rt	reflux	rt	reflux	rt	rt	rt	rt	70
Time	15min	15min	5h	1h	5h	24h	24h	24h	2.5h	2h
Yield(%)	96	74	92	79	65	92	90	74	85	89

NIR-MDA-DPC and Diamines into Polyurea
NIR to P-urea

MDA-DPC Short Chain Extender Long Chain Diamine



Polyurea Elastomers

NIR: Polyurea from MDA-DPC and Diamines

Solvent	Diamines	Extender	Hard Segment%	Mol. Wt
DMSO	Jeffamine-2000	1,6-HAD	57	54,400
DMSO	Jeffamine-2000	PPG-230	61	71,000
DMSO	Jeffamine-2000	1,8-diamino-3,6-dioxetane	58	131,000
TMS	Jeffamine-2000	1,6-HAD	46	79,000a (59,676)b
TMS	Jeffamine-2000	H12-MDA	40	84,269a (68,000)b
TMS	Jeffamine-2000	IPDA	40	61,338a (57,170)b

- Run at 60~100℃ in DMSO as the solvent. (Hard to separate with PhOH)
- Run at 60~140℃ in TMS with recovering of phenol/TMS

a. Distilled phenol+ TMS b. just distill phenol after the reaction

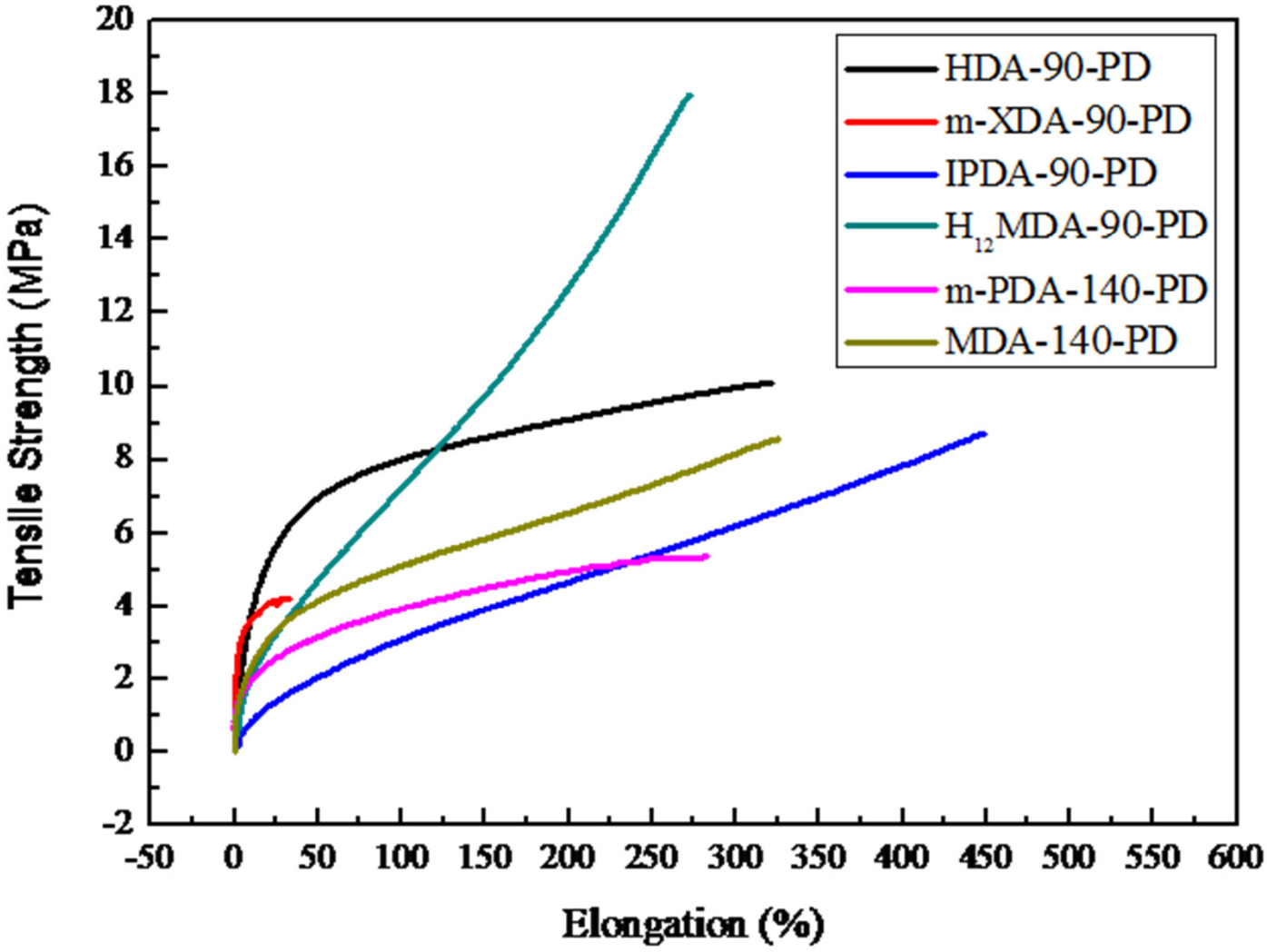
NIR- Polyurea Prepared in TMS

Run No.	Polyurea	Td[a] (℃)	Tg (℃)	Yield (%)	Tensile Strength (MPa)	Elongation (%)	η_{inh}	TMS Recovery (%)	Phenol Recovery (%)
9	H_{12}MDA-90-DB[a]	**290**	-56.9	97	**25.5**	425.4	**0.71**	95	88
12	HDA-90-DB	287	-59.3	86	10.4	547.8	0.42	92	79
14	m-XDA-90-DB	280	-58.4	98	3.6	186.1	0.35	94	87
15	IPDA-90-DB	282	-57.3	100	16.9	**1003.4**	0.46	95	91

[a] 5% weight loss.

[B] Distillation (140℃, 7×10^{-3} mmHg, 1h).

NIR-MDA-DPC Polyurea Prepared in TMS

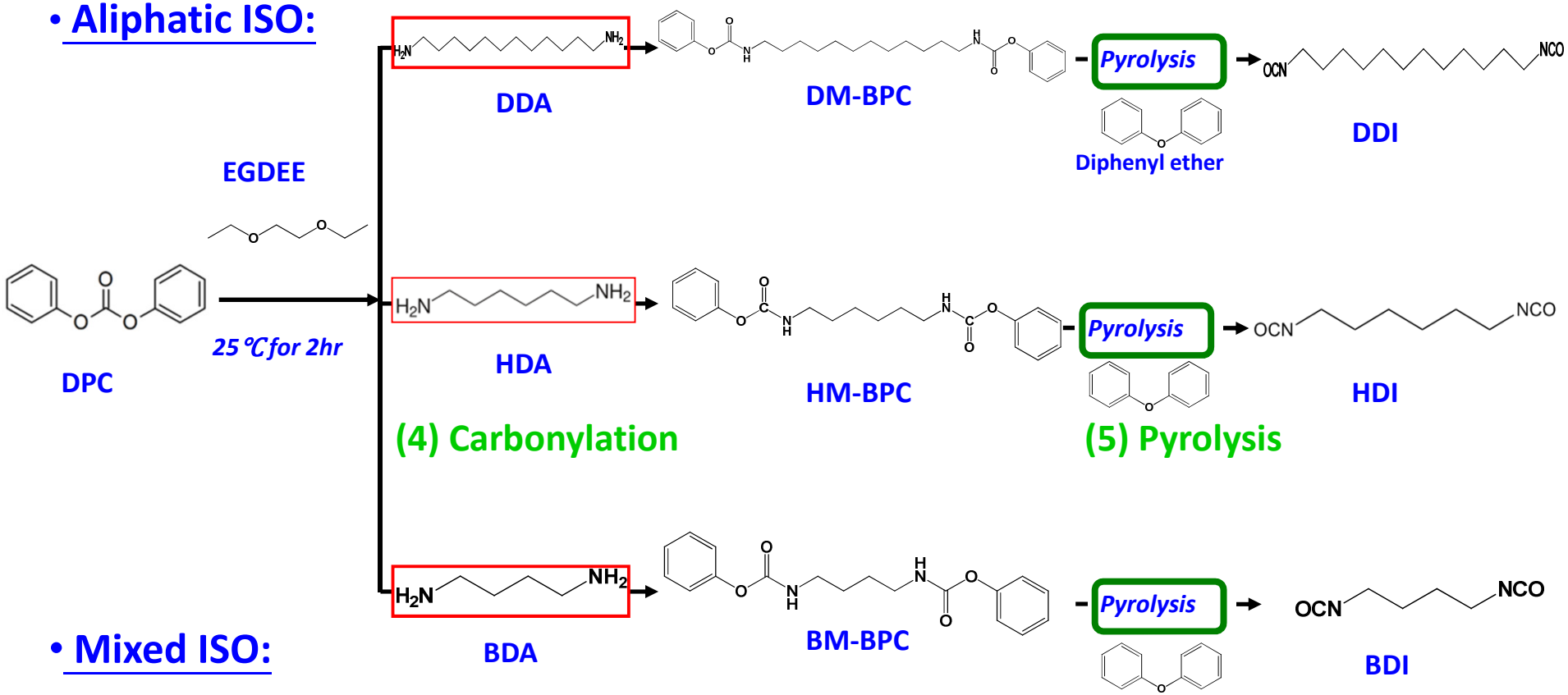


NPR to Aliphatic Diisocyanates

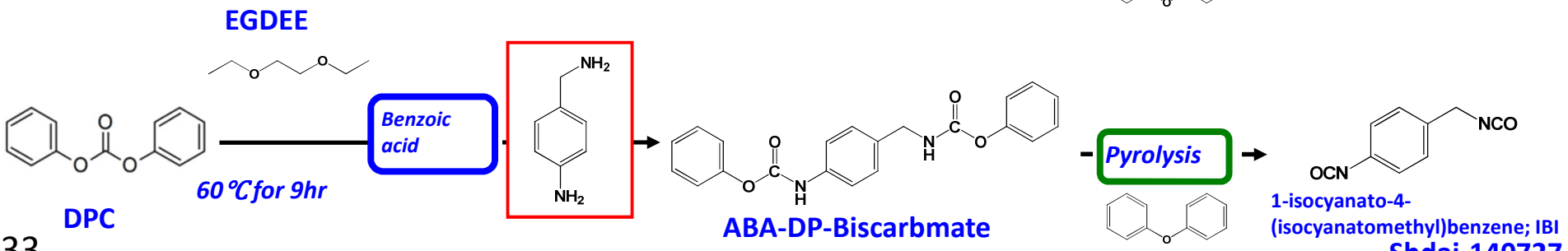
Wei-Hsing Lin (Lin, W-S; Ph. D Candidate; NCHU)

Our Overall 2-Step NPR Scheme: HDI, DDI, BDI, IBI (4) (5)

- **Advantages:** a. Reactivity DPC>> DMC; b. Lower temperature for isocyanate generation
- **Aliphatic ISO:**



- **Mixed ISO:**



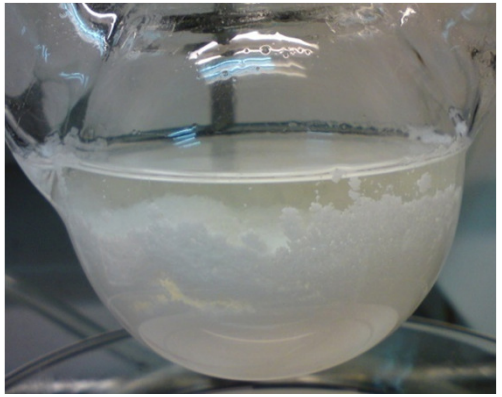
Shdai-140727

(4) NPR First Step: Carbonylation of *1,12-dodecane Diamine*

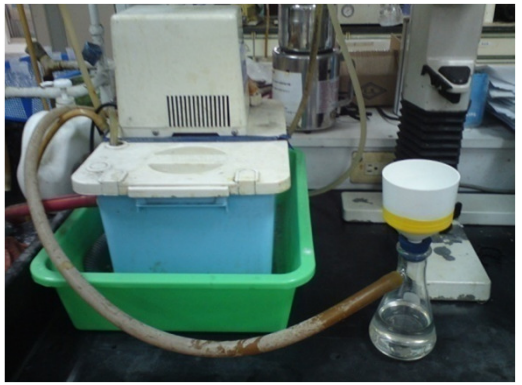


25℃、2hr → 75℃、20min → Overnight (RT)

EGDEE; Recrystallization



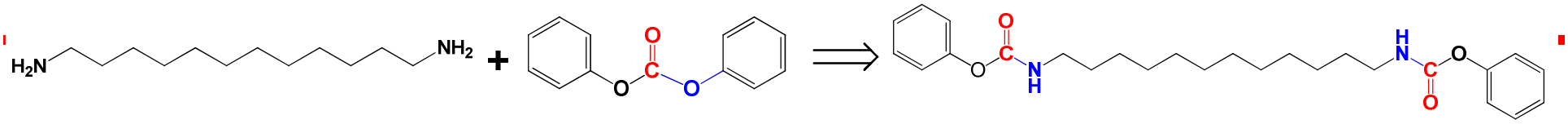
Filtration

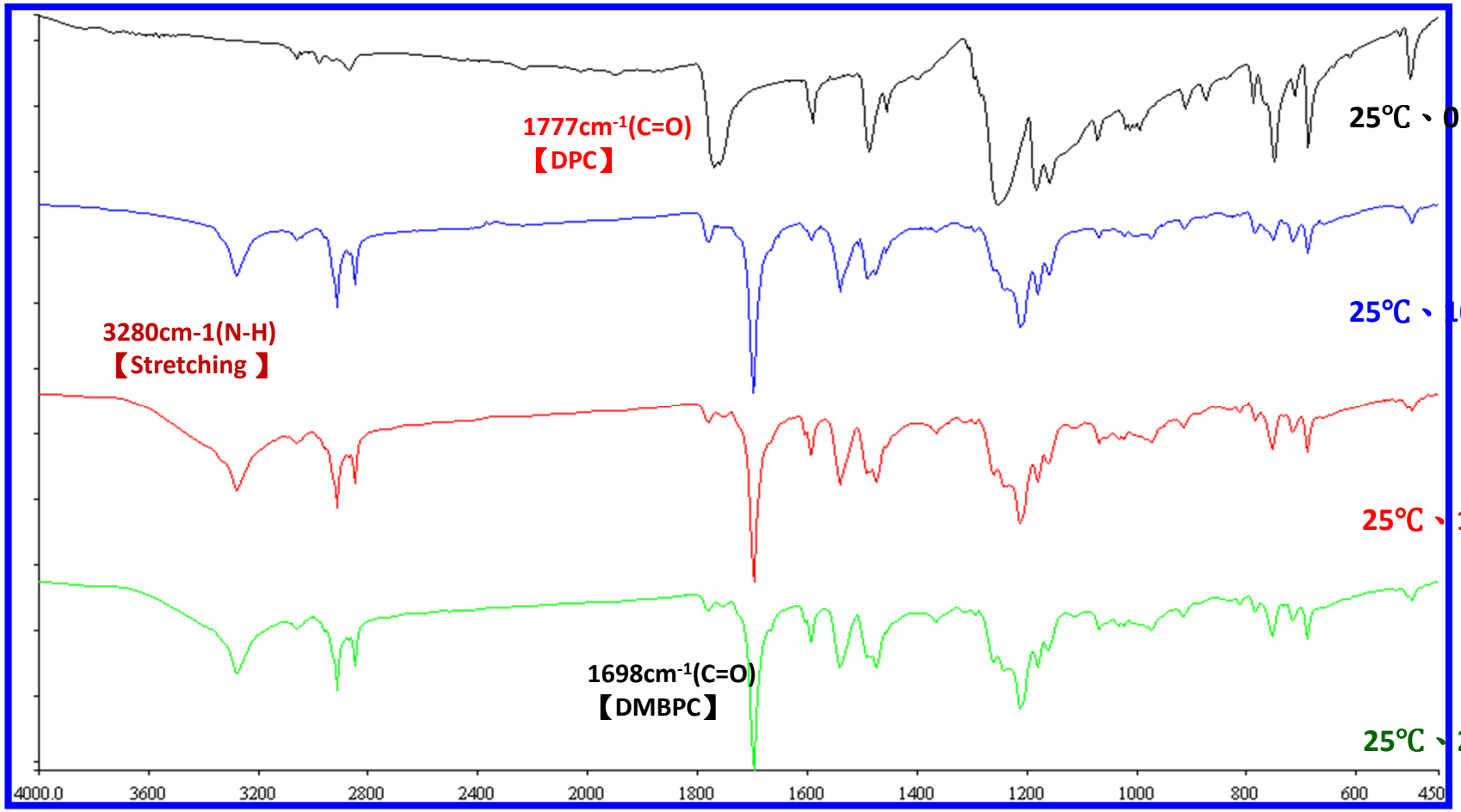


65℃、2hr (Vacuum)



NPR- Monitoring of Carbonylation by IR: C12 Diamine

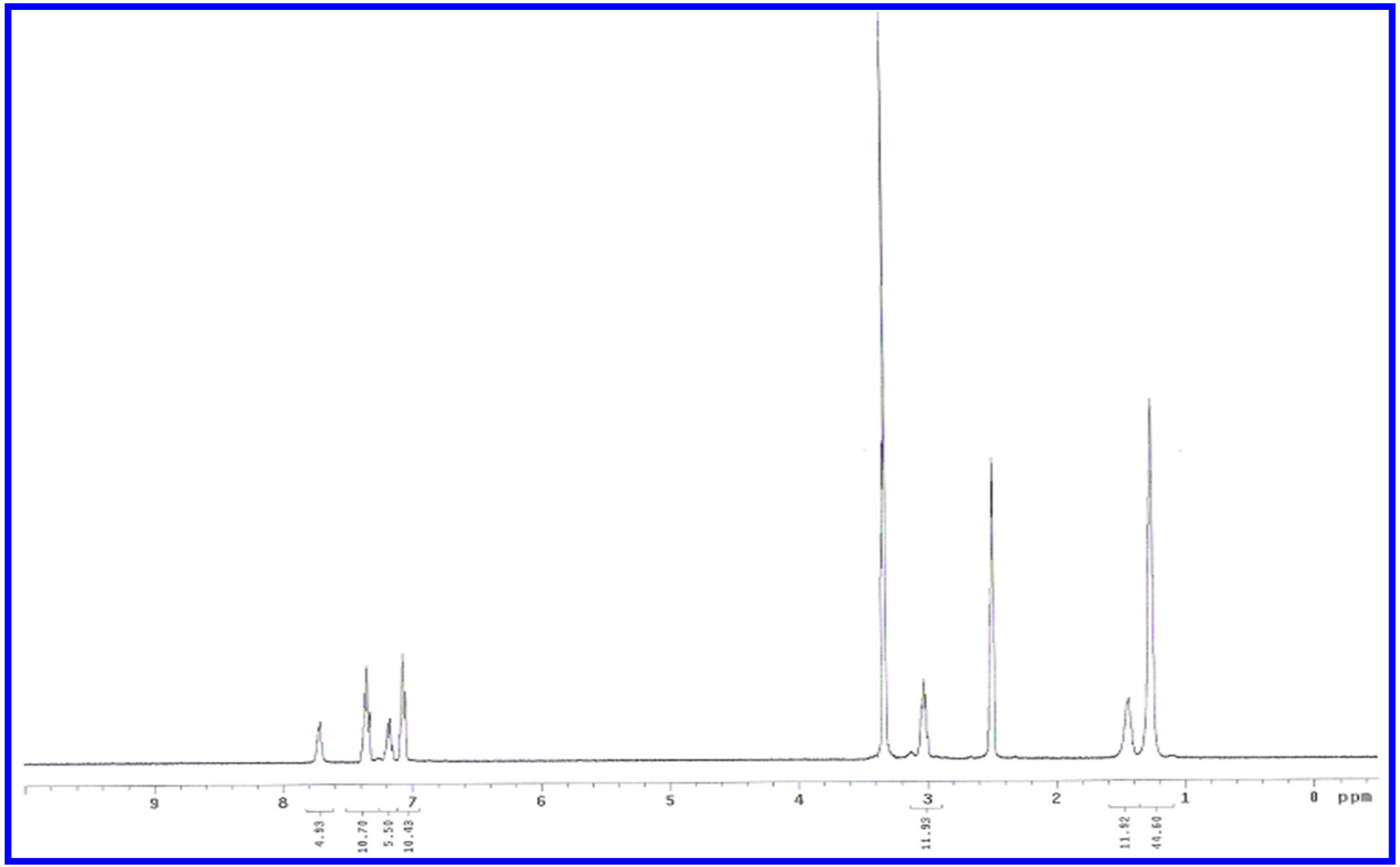




NPR First Step: Carbonylation Data of *1,12-dodecane Diamine*

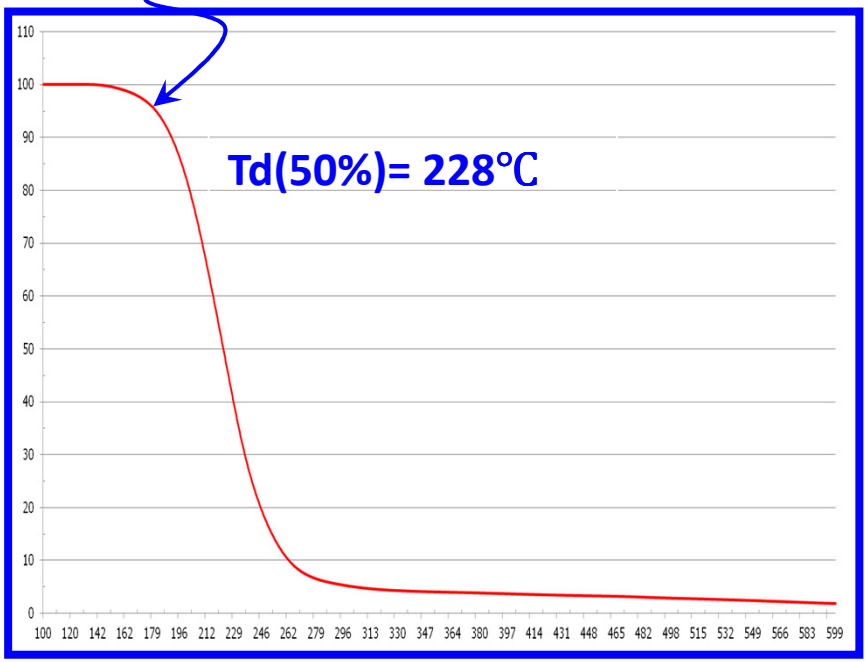
	C-12 –biscarbamate preparation
Molar ratio	DDA：DPC＝ 1：*2.05*
Weight ratio	DDA：DPC＝ *5* g：*10.96* g
Catalyst	*Catalyst-free*
Nitrogen flux	N_2 =0.3L/min
Reaction solvent	*EGDEE＝ 48* g （S.C=25% ）
Reaction Temp.	*25℃*
Reaction time	*2hr*
DMBPC Yield	*98%*
Urea yield	Non
Melting point	*121.5℃ ~ 122.4℃*

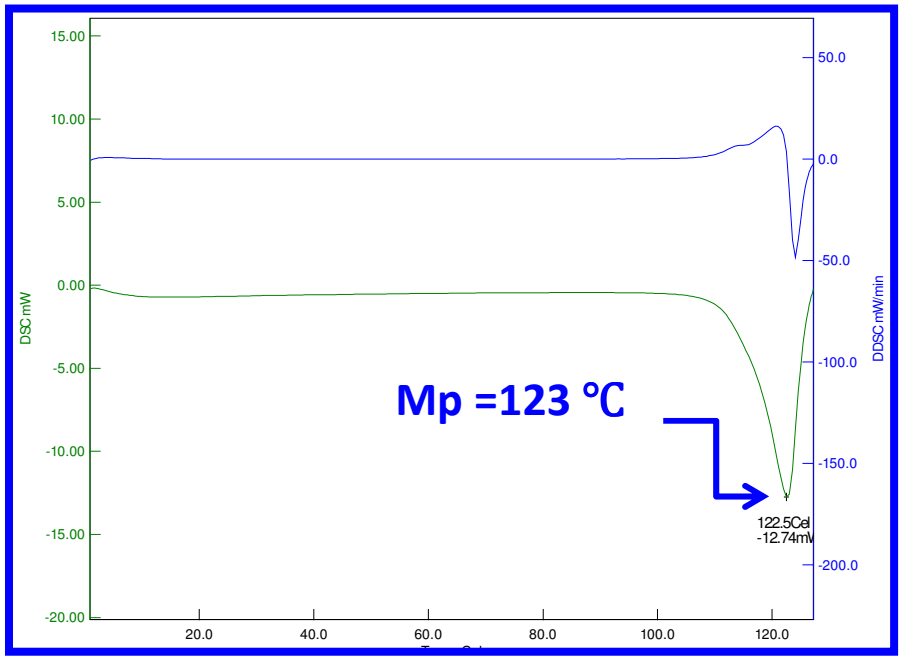
NPR- NMR of 1,12-Dodecamethylene-Bis-phenyl carbamate



Thermo-Data of 1,12-Dodecamethylene-Bisphenyl carbamate

Td(5%)= 181.6℃

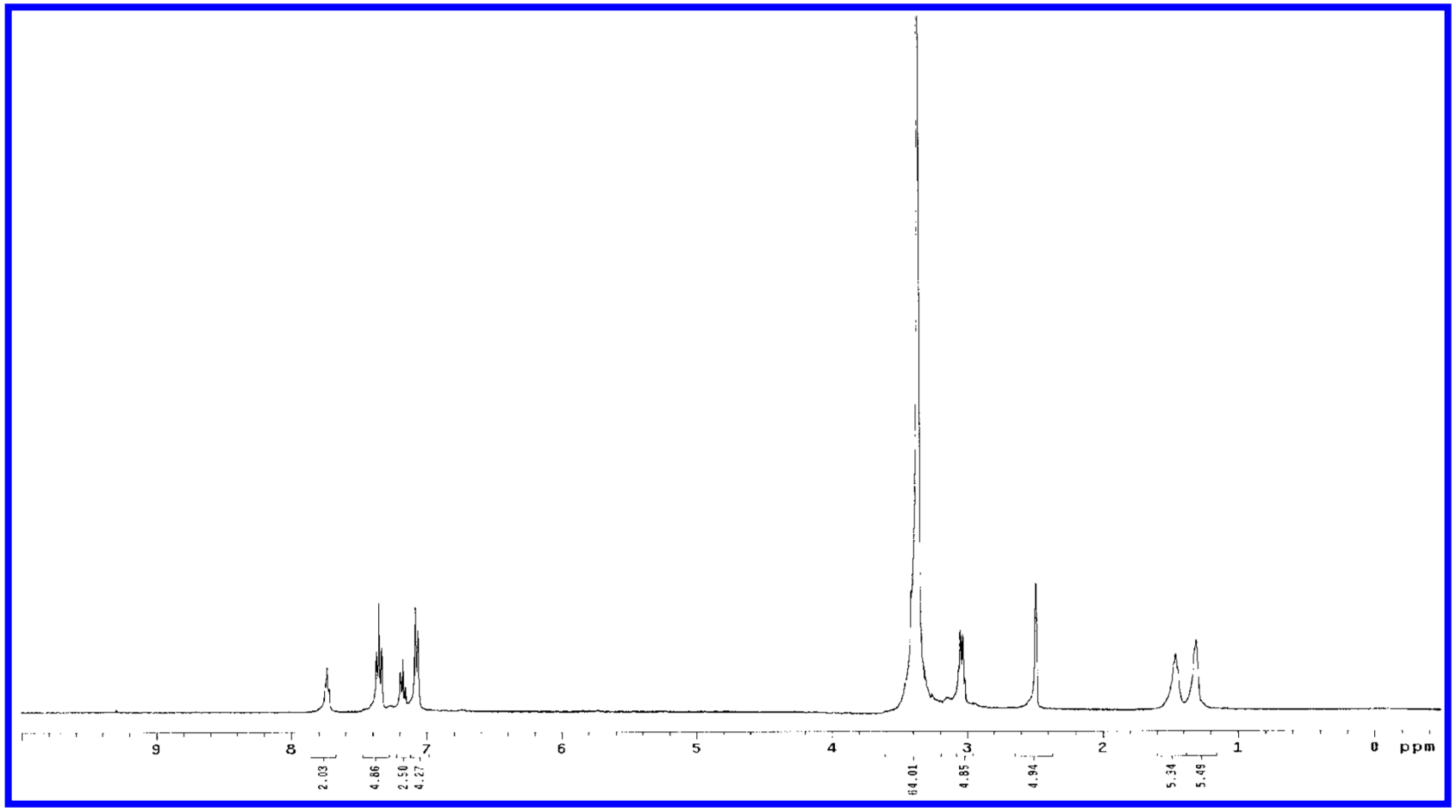




NPR to 1,6-hexamethylene-bis(phenyl carbamate)

	C-6-biscarbamate preparation
Molar ratio	HDA：DPC＝ 1：*2.05*
Weight ratio	HDA：DPC＝ *215* g：*813* g
Catalyst	*Catalyst-free*
Nitrogen flux	N_2 =0.3L/min
Agitation speed	200rpm
Reaction solvent	*EGDEE＝ 2500* ml
Reaction Temp.	*25℃*
Reaction time	*2hr*
HMBPC Yield	*95%*
Urea yield	Non
Melting point	*127℃ ~ 128.2℃*

NPR- NMR of 1,6-Hexamethylene-Bis(phenyl carbamate)



[27] Luc Ubaghs, Isocyanate-free Synthesis of（Functional）Polyureas, Polyurethanes, and Urethane-containing Copolymers , 2005, P.49

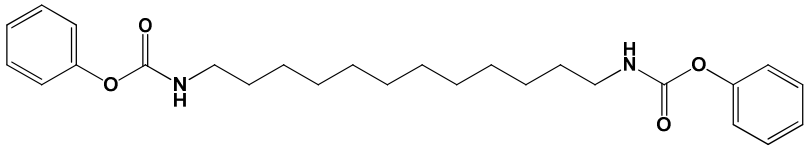
(4) Summary : Bis-Carbamate Preparations

Biscarbamates	DDI (C12)	HDI (C6)	BDI (C4)	1-isocyanato-4-(isocyanatomethyl)benzene
Biscarbmate Yield	DMBPC 98%	HMBPC 98%	BMBPC 89%	*ABA-DP-Biscarbamate* 85%
Melting point (DSC)	*122.5* ℃	*126.6* ℃	*162*℃	*175.8* ℃
Td (TGA; 5%)	*181.6* ℃	*147.4* ℃	*167.7* ℃	*167.7* ℃

Aliphatic Bis-carbamates → Mixed

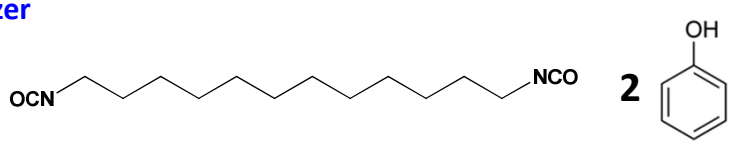
- Excellent yield of biscarbamates could be prepared from C12, C6 and C4 diamine/+DPC.
- C4-biscarbamate crystal was contaminated ~ 6% of phenol that could not be separated.
- Preparation of ABA-biscarbamate is best done in two step.

Typical Set-up for Thermolysis of Biscarbamates



1,12-dodecamethylene-bis(phenyl carbamate)

Benzoyl chloride as stabilizer



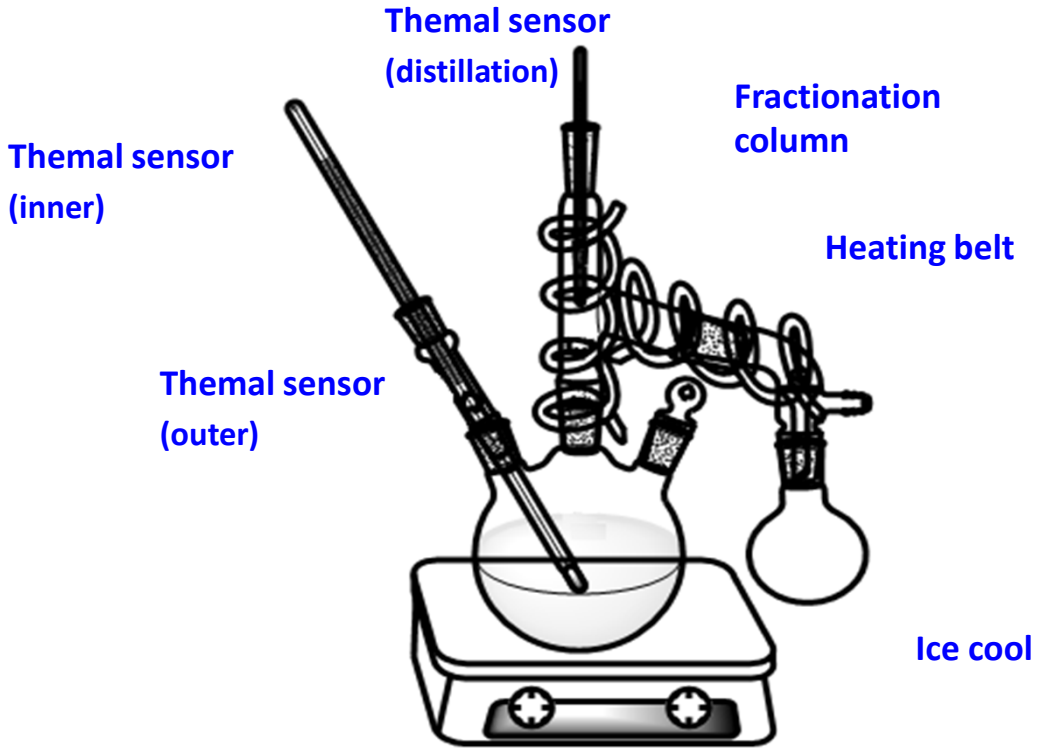
Dodecamethylene-1,12-diisocyanate

(bp = 168℃ at 3mmHg)

Diphenyl ether

(bp = 82℃ at 3mmHg or

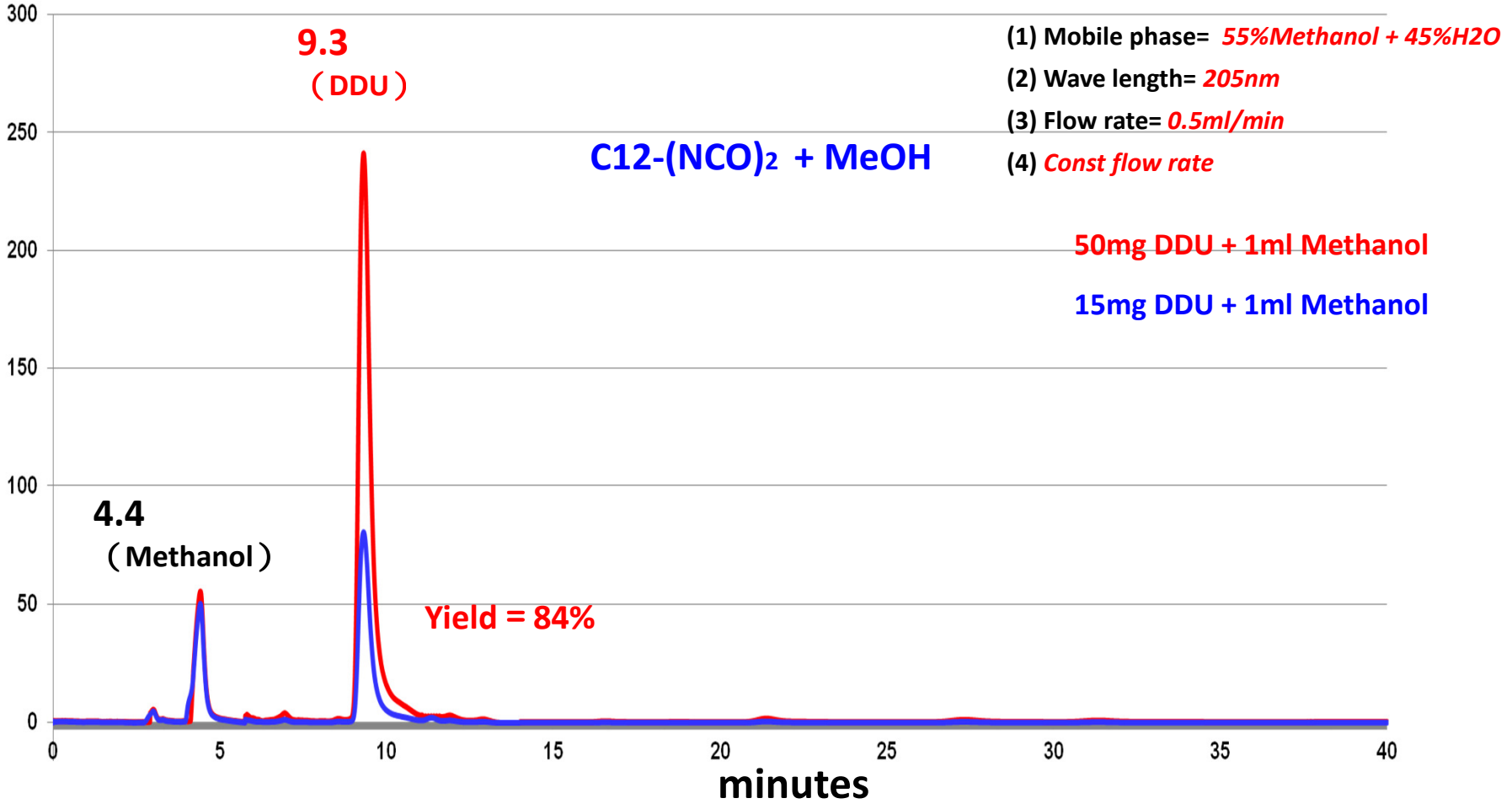
250 ℃ at atm pressure)



NPR- (5) Data on Isolation C-12 -Diisocyanate

		CG1020317
Weight		DMBPC＝ *5* g
Catalyst		*Benzoyl chloride＝ 0.013* g
Nitrogen flux		Non
Solvent		*Diphenyl ether＝ 45* g （S.C=10% ）
Pyrolysis	Initial NCO	*180℃*
	Maximum NCO	*254℃*（ HMBPC disappeared after 0.5hr at 240 ℃ ）
	Final	All NCO peaks disappear
Reactor byproduct		*No yellow coking by-products*
Flask (Ice cool)	Initial product	*240℃*（ Phenol appeared for 0hr at 240 ℃ ）
	Final product	*254℃*（ Phenol appeared for 0.5hr at 240 ℃ ）
1,12-diisocyanatododecane Yield		*84%*
Phenol recycling rate		*100%*

Quantitative Analyses of C12-$(NCO)_2$ by Quenching (by HPLC)

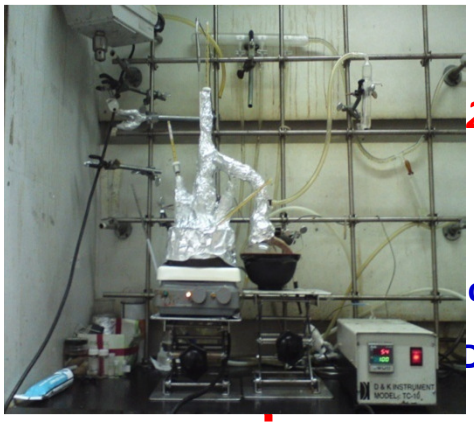


Experiment (3) – One-pot two-stage NPR process

DMBPC → DDI

SC = 18%

Pyrolysis



240℃、0.5hr

onitoring

DI by IR

Separated by DDI and

Diphenyl Ether (Vacuum)





Pure Diphenyl Ether

(99%)

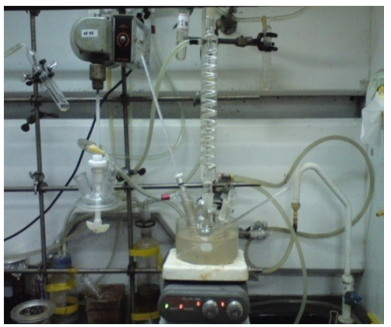
Pure DDI

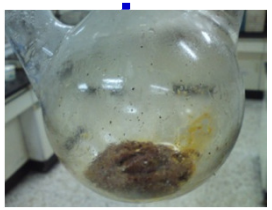
(80%)



Capped by 10X MEOH

(90 ℃1hr)



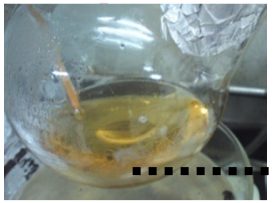


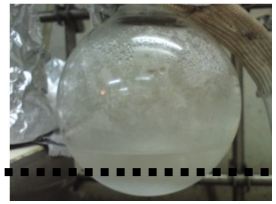
Reactor

Quantitative analyses of

DDU by HPLC







Reactor

Flask (100%phenol)

(1) Mobile phase= *55%Methanol+ 40%H2O*

(2) Wave length= *205nm*

(3) Flow rate= *0.5ml/min*



Experiment (3) – One-pot two-stage NPR process

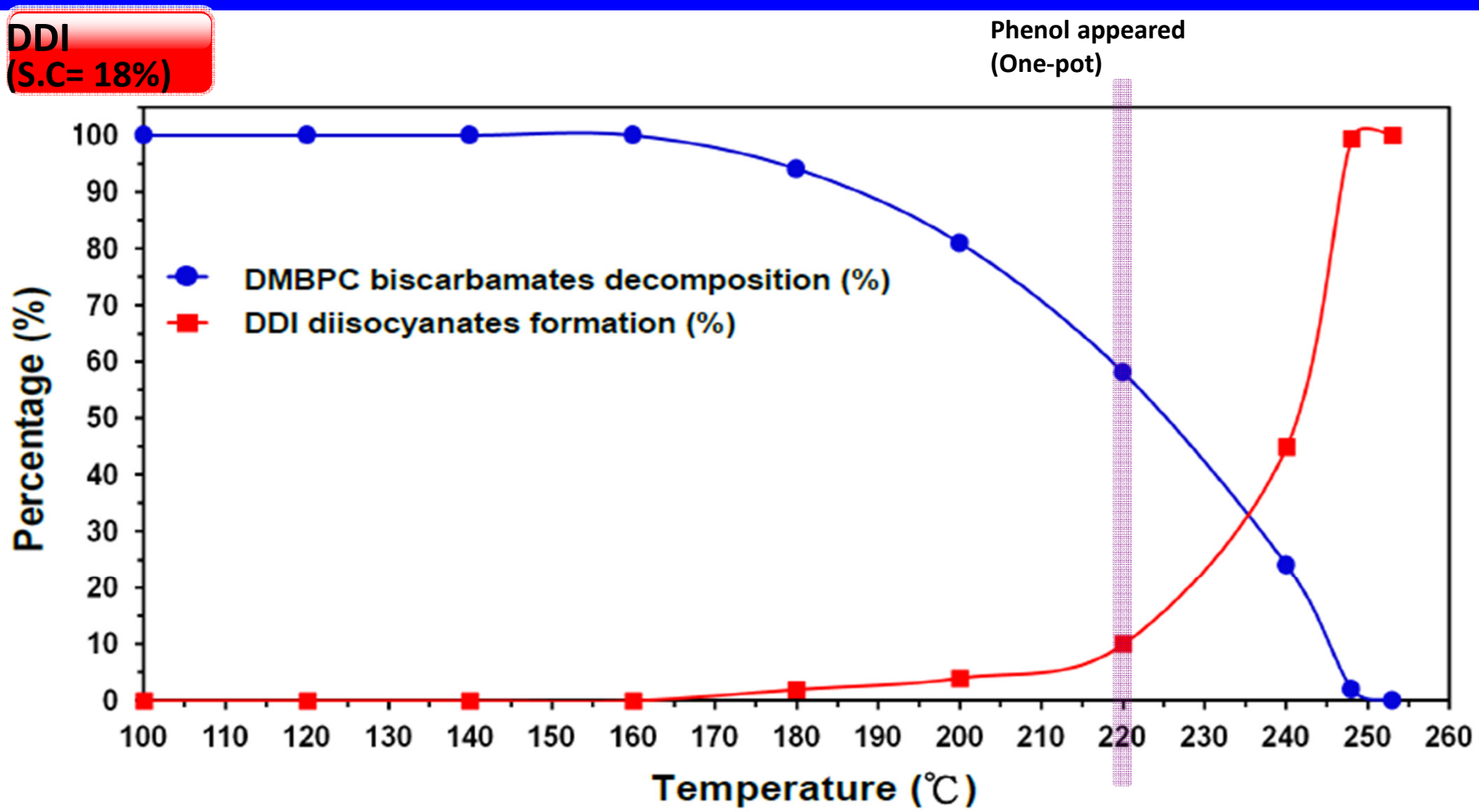


Figure 12. DMBPC biscarbamates decrease (%) and DDI diisocyanates formation (%) in the pyrolysis in one-pot two stage NPR process under 18% solid content in Diphenyl Ether at (a) 100℃, (b) 120℃, (c) 140℃, (d) 160℃, (e) 180℃, (f) 200℃, (g) 220℃ (phenol was collected in the flask), (h) 240℃, (i) 240℃-0.5 hr, (j) 240℃-1 hr.

Experiment (3) – One-pot two-stage NPR process

DMBPC → DDI	**CG1030203**
Molar ratio	**DDA：DPC＝ 1：*2.05***
Weight ratio	**DDA：DPC＝ *10* g：*21.9* g (SC=25%)**
Catalyst	***Catalyst-free***
Nitrogen flux	**N_2 =0.3L/min**
Agitation speed	**200rpm**
Carbonylation solvent	***Diphenyl Ether (DPE)＝ 96 g***
Carbonylation Conditions	**60℃、2hr**
DMBPC Yield (HPLC)	***100%***
Pyrolysis solvent	***Diphenyl Ether (DPE) as pyrolysis solvent* (SC=18%)**
Stabilizer (Benzoyl chloride)	**None**
Pyrolysis Conditions	**240℃、0.5hr (220℃→NCO, 220℃→Phenol)**
Recycling rate	**Phenol =*100%*、Diphenyl Ether =*99%***
Isocyanate Yield (HPLC)	***Pure DDI=80%、Trimer=20%***

Summary : One-pot two-stage NPR process

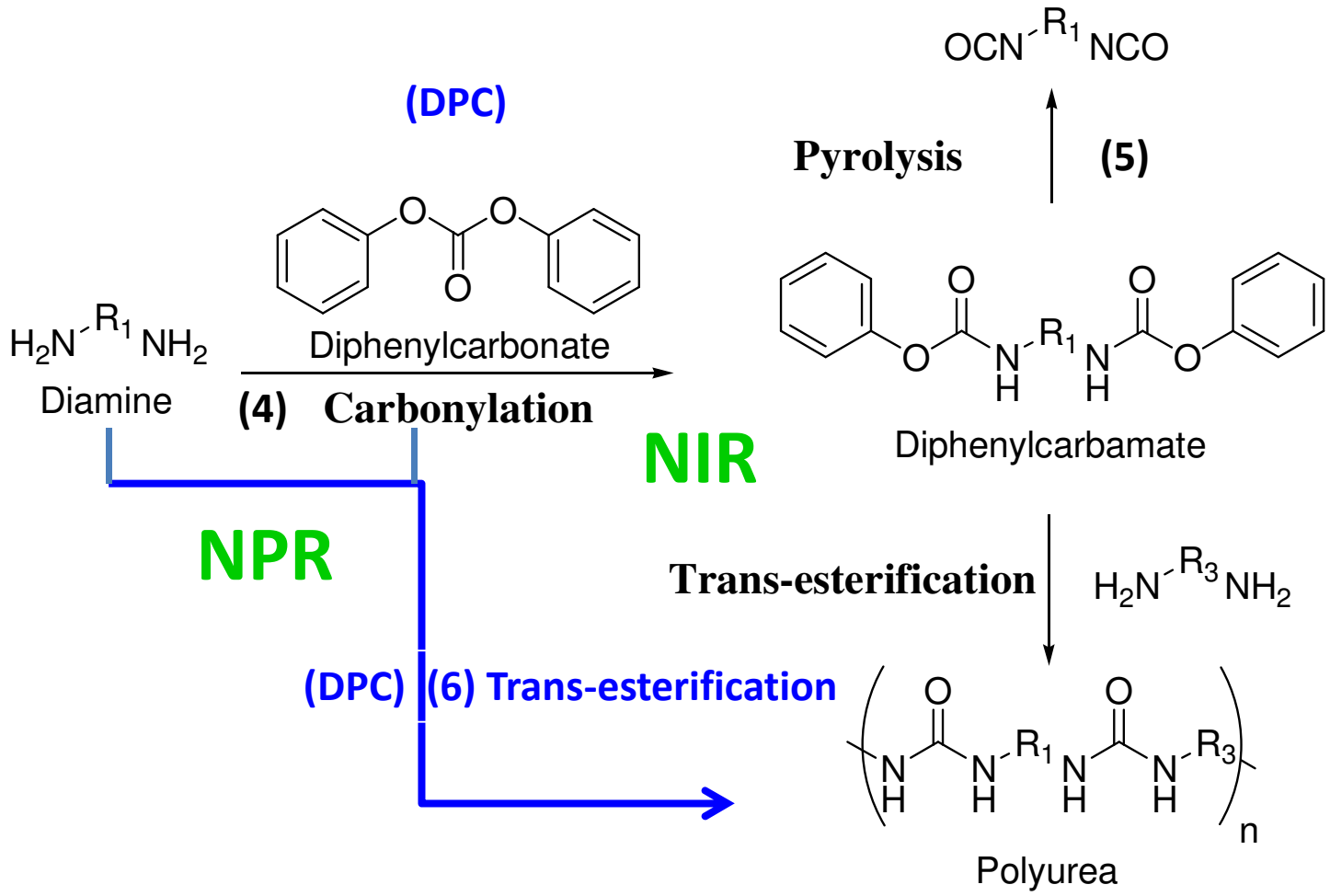
Two step (original process) → **One-pot two-stage NPR process**

	DDI	HDI		DDI	HDI
Carbonylation solvent (Reaction S.C%)	EGDEE (25%)	EGDEE (25%)		DPE (25%)	DPE (25%)
Molar ratio	DDA : DPC =1 : 2.05	HDA : DPC =1 : 2.05		DDA : DPC =1 : 2.05	HDA : DPC =1 : 2.05
Catalyst	none	none		none	none
Reaction condition	25℃、2hr	25℃、2hr		60℃、2hr	60℃、2hr
Biscarbmate Yield	98% (DMBPC)	98% (HMBPC)		100% (DMBPC)	100% (HMBPC)
Pyrolysis solvent (Reaction S.C%)	DPE (10%)	DPE (2.5%)	DPE (10%)	DPE (18%)	DPE (16%)
Cracked time (carbamate disappeared)	240℃、0.5hr (254℃)	240℃、2hr (254℃)	240℃、1.5hr (254℃)	240℃、0.5hr (260℃)	240℃、1hr (258℃)
Stabilizer (Benzoyl chloride)	Exist (1 / 145)	none	Exist (1 / 145)	none	Benzoyl chloride / HMBPC = 1 / 145 (molar ratio)
Isocyanate Yield	DDI=84% *Trimer=16%*	HDI=76% *Trimer=12%* *Biuret=8%*	HDI=47% *Trimer=14%* *Biuret=4%* *Allophanate=35%*	DDI=80% *Trimer=20%*	HDI=42% *Trimer=34%* *Biuret=16%* *Allophanate=3%*

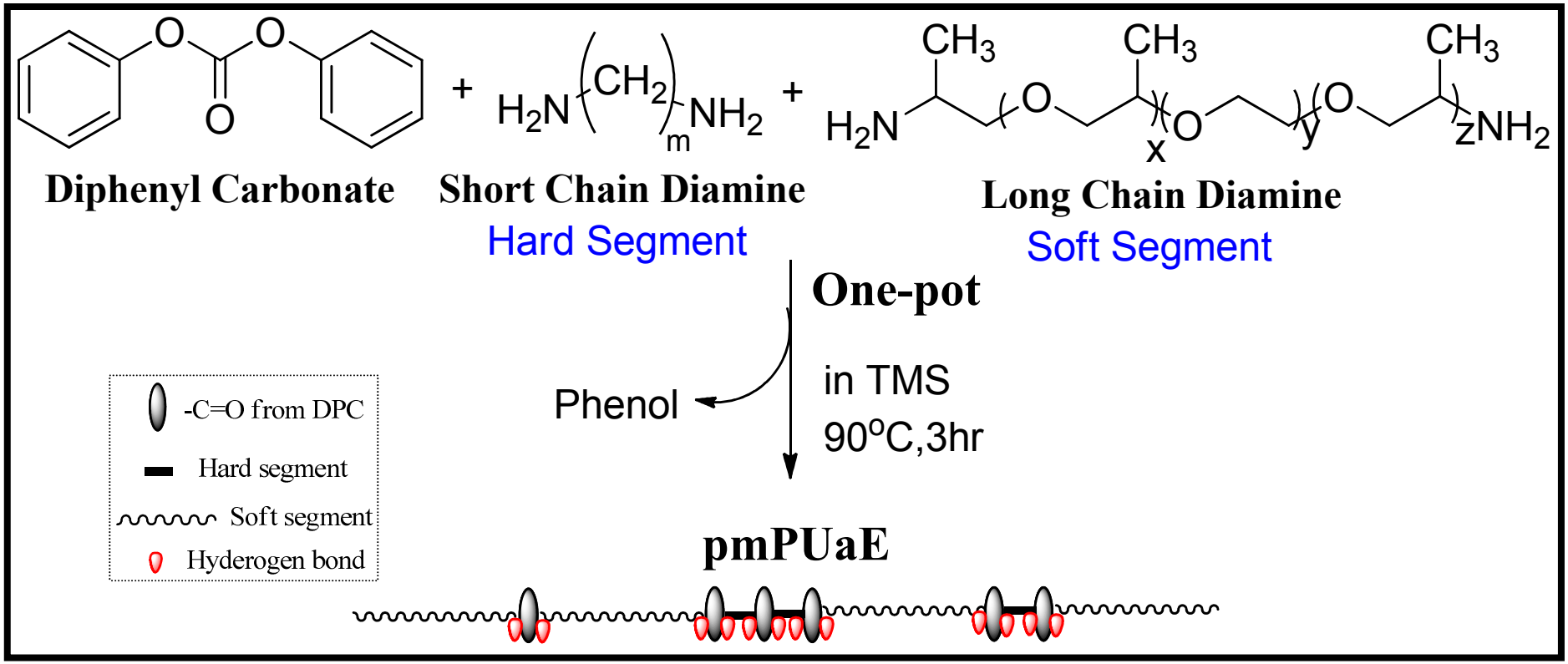
Shdai-140727

Non isocyanate / Phosgene Route (NIR/NPR)

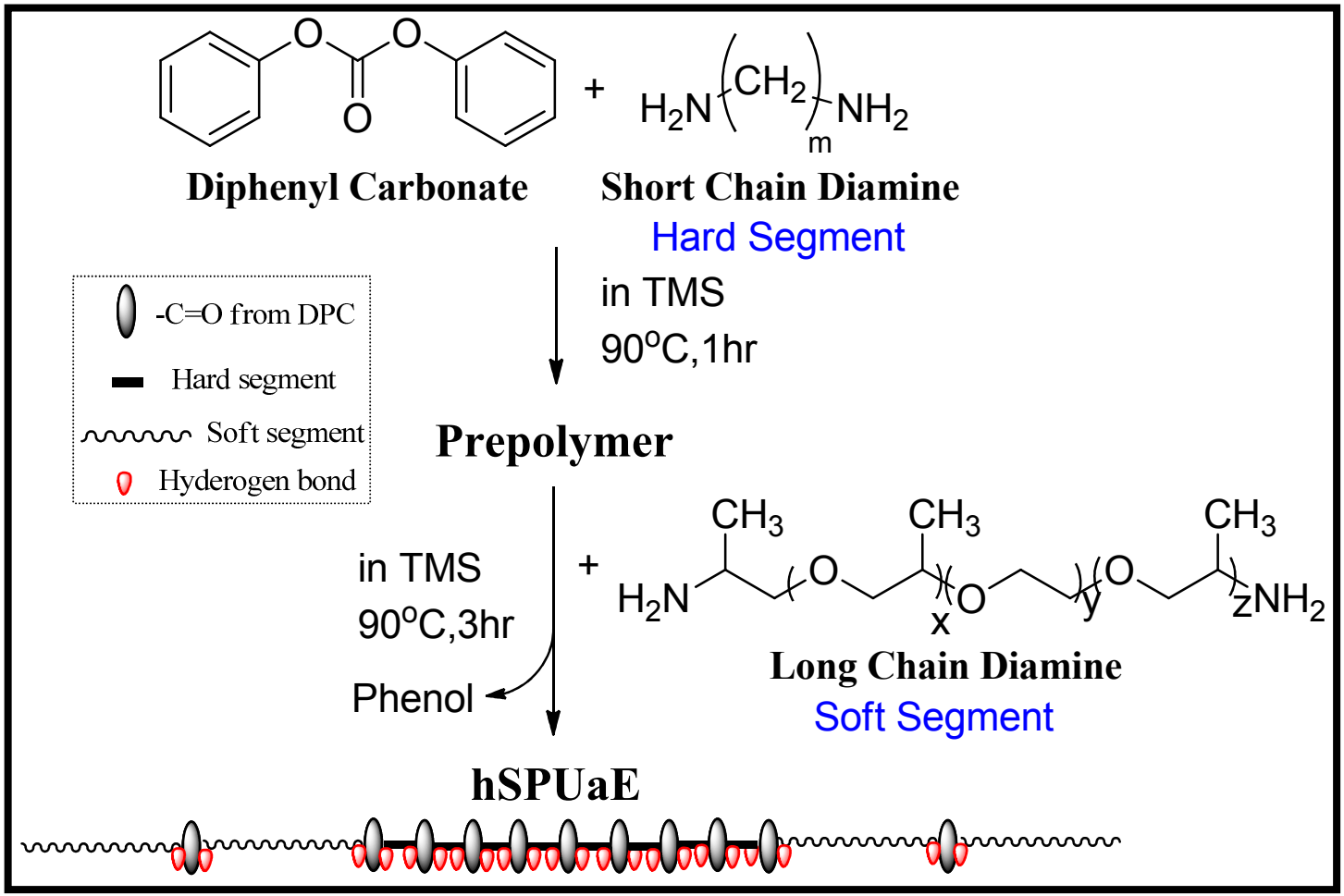
Chen, H.Y.; Pan, W. C.; Lin, C. H.; Huang, C.Y.; and Dai, S. A., *Journal of Polymer Research*, 19(2), 9754-9765,2012.



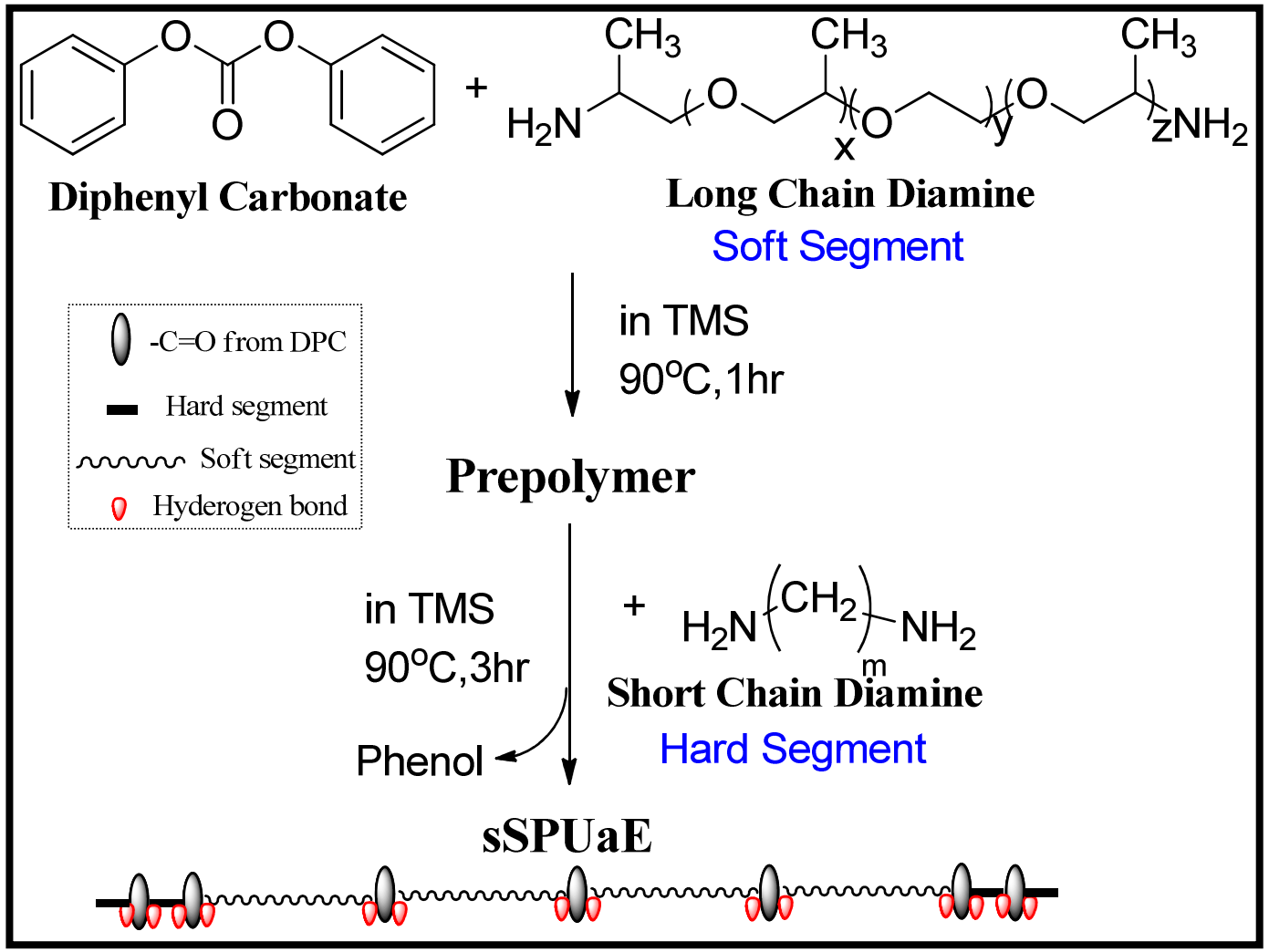
NIR- Method 1: One Step-One Pot Process



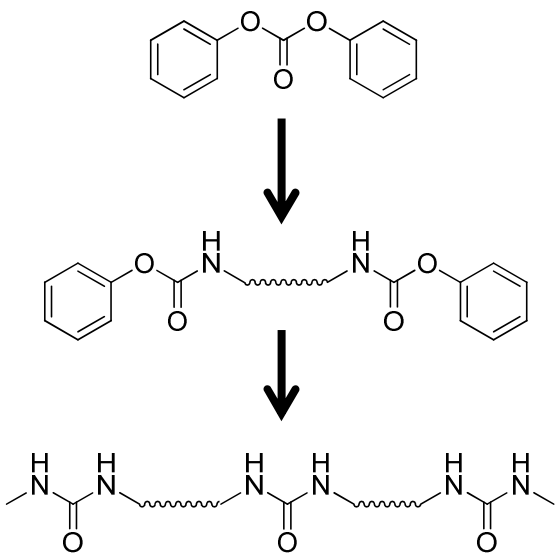
NIR- Method 2: Two-step Process with Hard Segment Prepared First

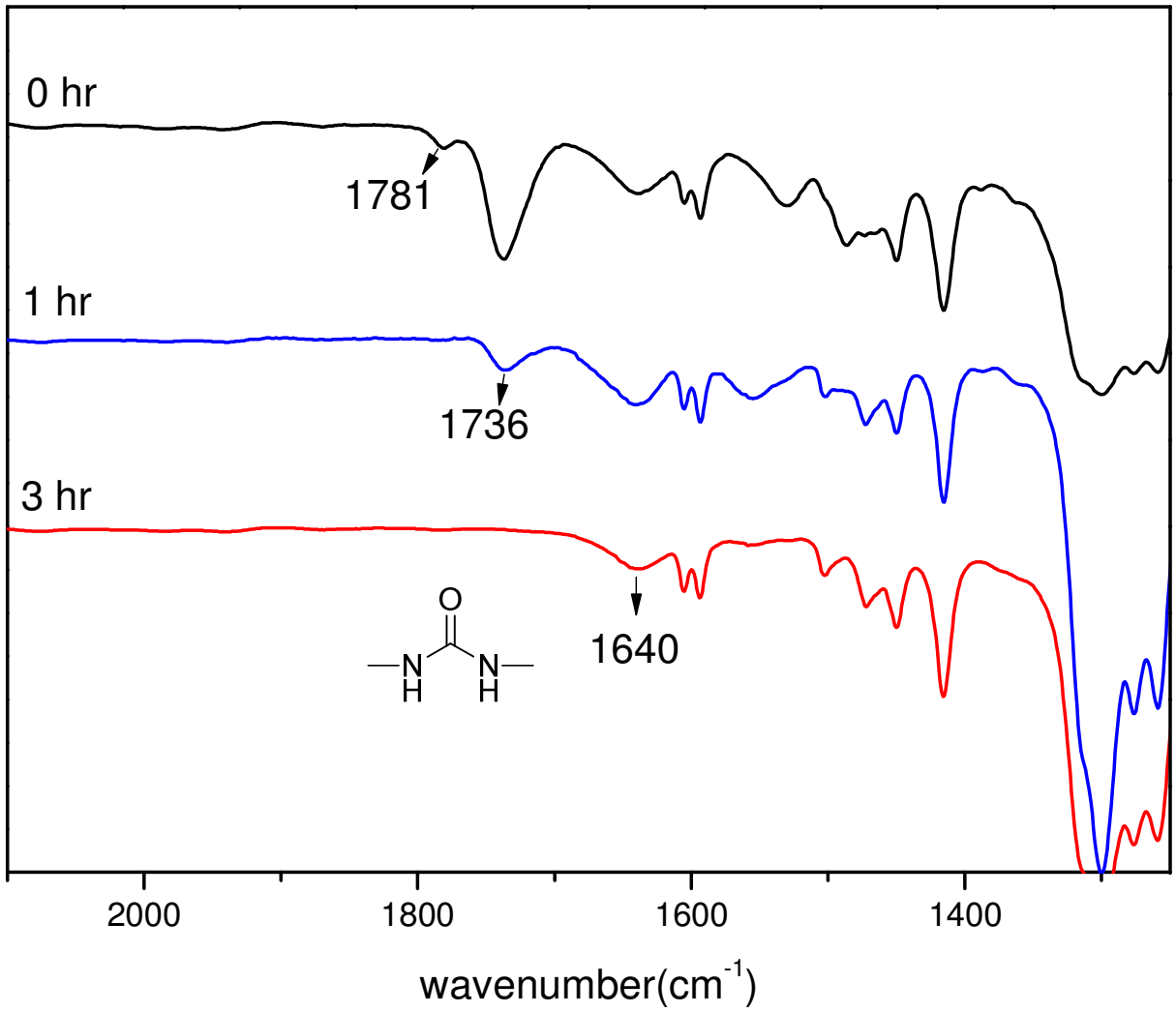


NIR- Method 3: Two-step Process with Soft Segment Prepared First



NIR- Monitoring by FT-IR in Method 3



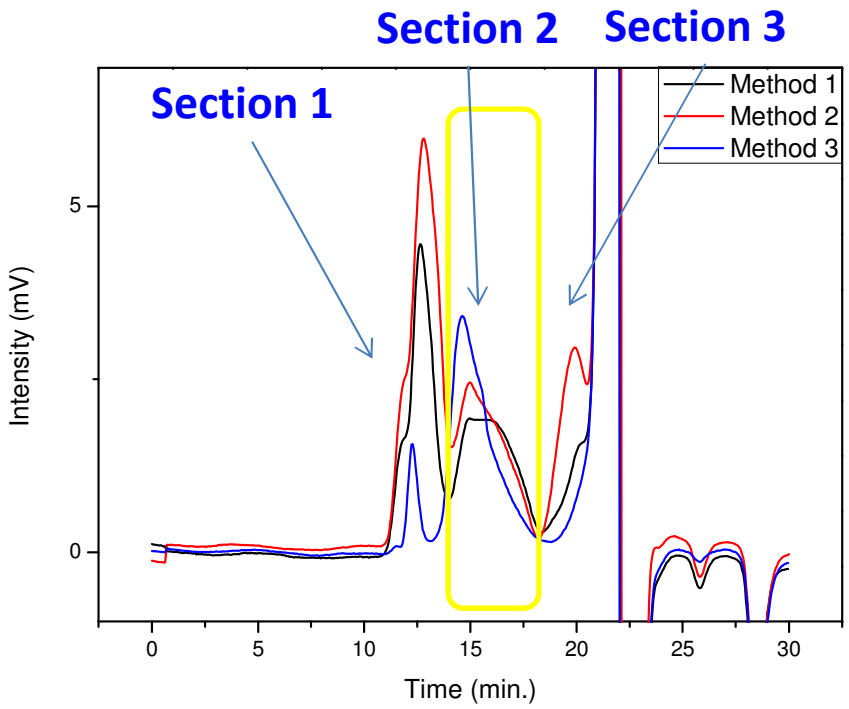


Properties of NIR-PUaE

Method[a]	HS[b] (%)	Yield (%)	phenol recycle ratio (%)	η_{inh}	T_d[c] (℃)	T_g (℃)	T_c (℃)	Elongation (%)	Tensile strength (MPa)
1	30	100	88	0.25	268	-62	/	174	3.84
2		**97**	**82**	**0.49**	**262**	**-64**	**187**	**469**	**18**
3		94	89	0.26	231	-65	170	92	3.28
1	40	94	78	0.29	250	-60	181	315	17.6
2		**96**	**85**	**0.42**	**251**	**-60**	**192**	**160**	**15.2**
3		89	84	0.28	243	-64	/	208	11.79

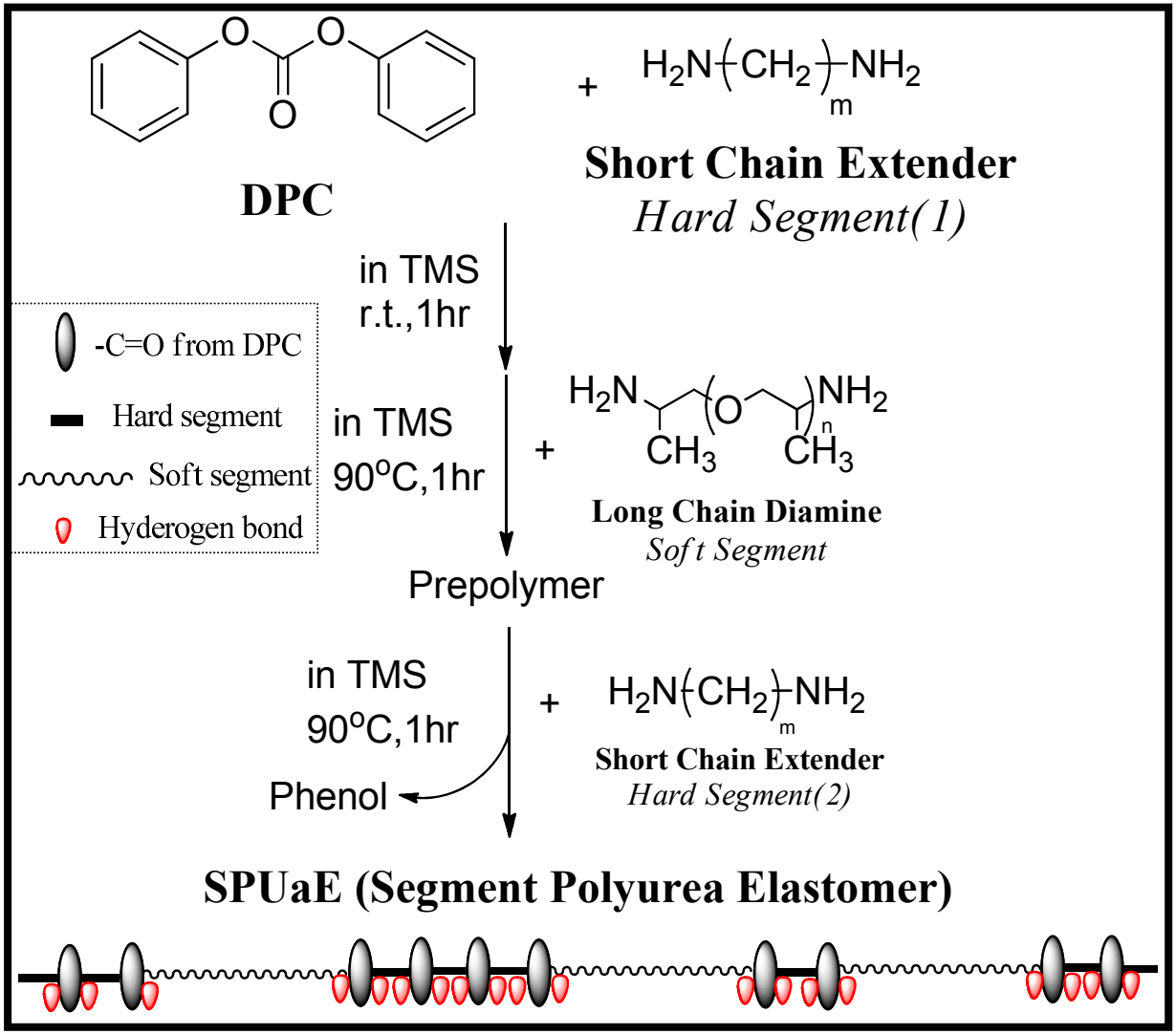
[a]: Method of synthesis(1 :one pot ; 2: two steps-Hard first ; 3: two steps-Soft first)
[b]: Hard segment ratio
[c]: 5% weight lose temperature

NIR- Polyurea Analysis of GPC

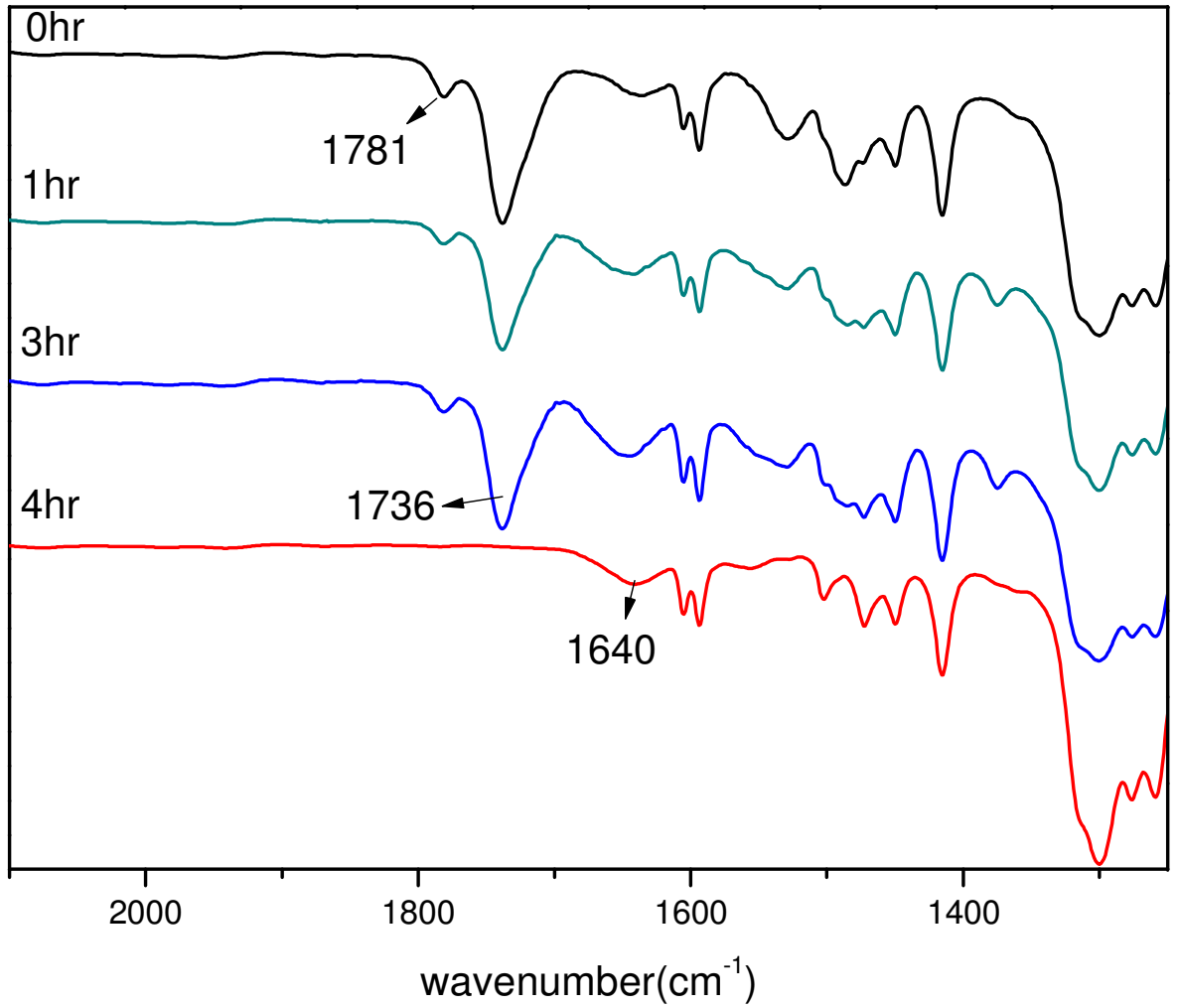


Method	Area (%)			η_{inh}
	A1 High Molecular Region	A2 Median Molecular Region	A3 Low Molecular Region	
1	37%	45%	18%	0.25
2	**44%**	**33%**	**23%**	**0.49**
3	11%	83%	6%	0.26

NIR- Method 4: Three-steps Process



NIR- Monitoring by FT-IR in Method 4



Properties of NIR-Polyurea(Method 4)

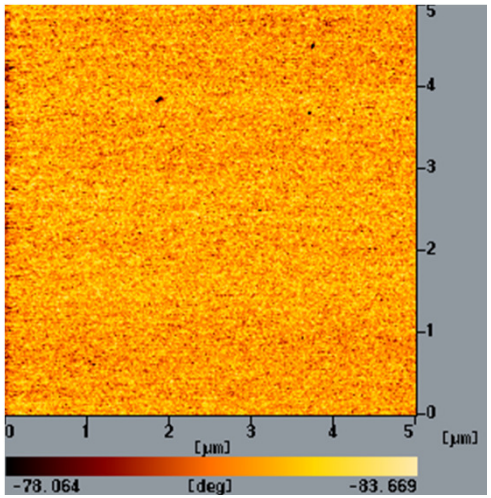
short chain diamine (1)	short chain diamine (2)	long chain diamine	HS[a] (%)	Yield (%)	phenol recycle ratio (%)	η_{inh}	T_d[b] (℃)	T_g (℃)	Elongation (%)	Tensile Strength (MPa)
HDA	**IPDA**	**D2000**		**94**	**96**	**0.56**	**264**	**-56**	**664**	**15.6**
HDA	IPDA	ED2003	**30**	89	100	0.64	298	-60	1462	0.98
MDA	IPDA	D2000		68	65	0.23	283	-55	64	0.43
HDA	**IPDA**	**D2000**	**40**	**83**	**44**	**0.62**	**284**	**-61**	**469**	**33.4**

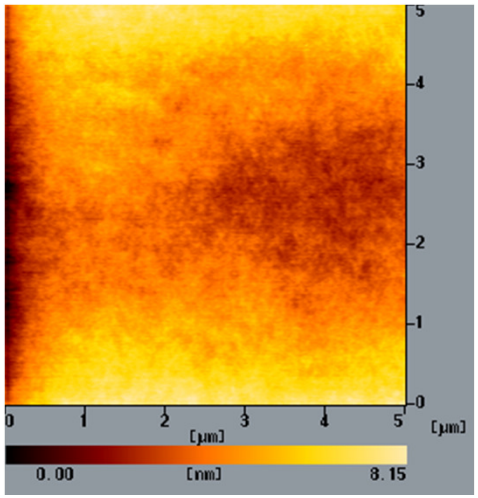
[a]: Hard Segment ratio
[b]: 5% weight lose temperature

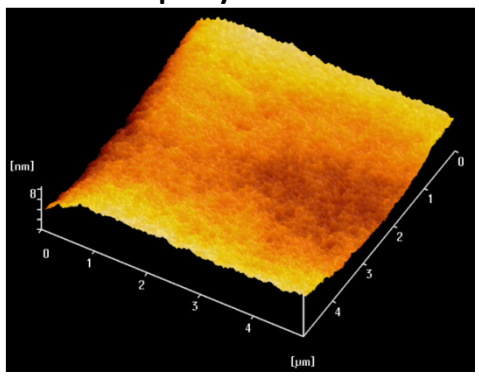
Analysis of AFM

3D-display

Method 1

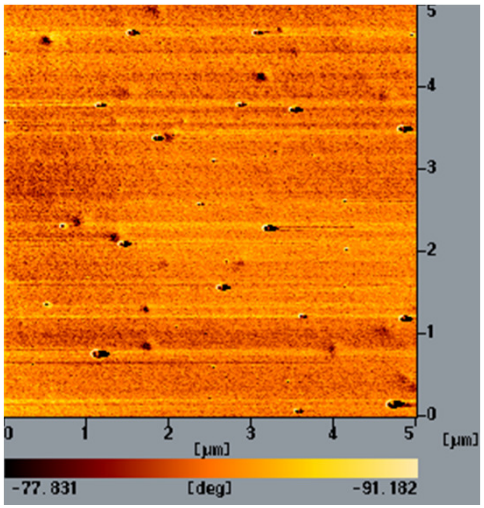


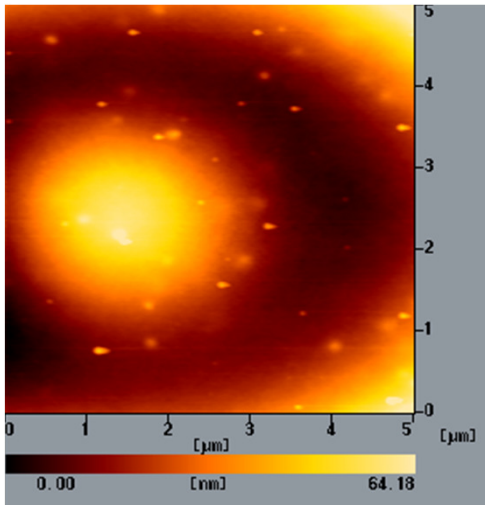


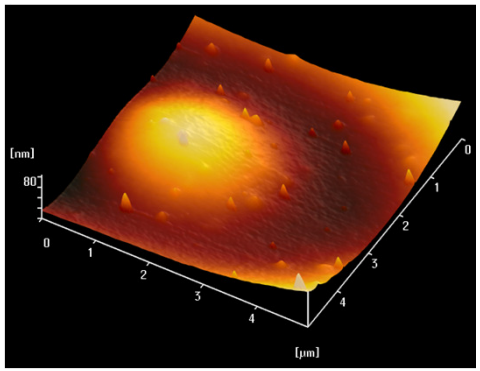


pmPUaE(DPC-D2000-IPDA)
roughness:**1.09nm**

Method 2



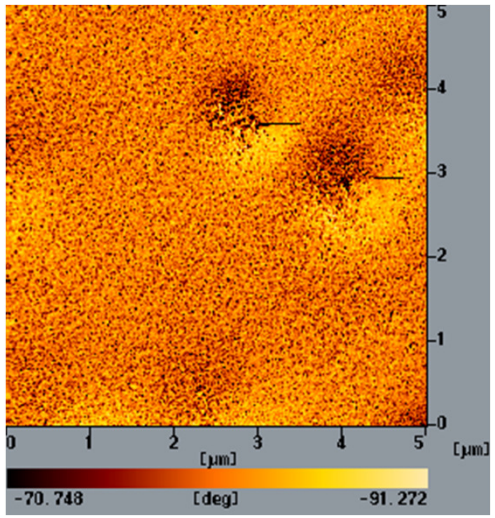


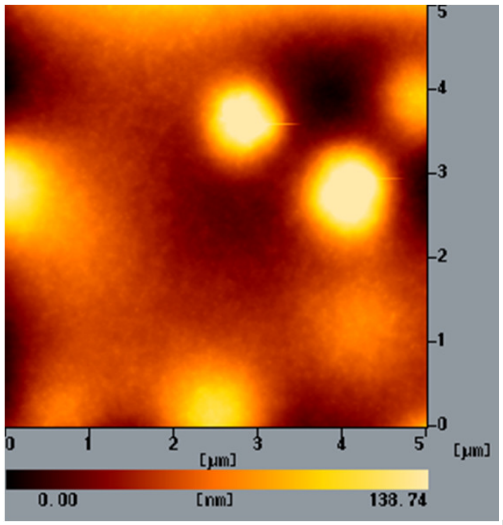


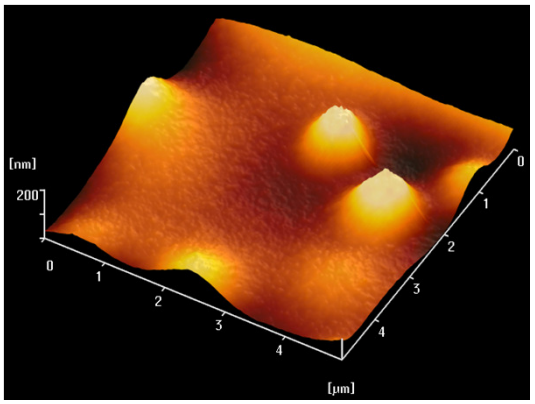
hSPUaE(DPC-IPDA-D2000)
roughness:**11.06nm**

Analysis of AFM

Method 3

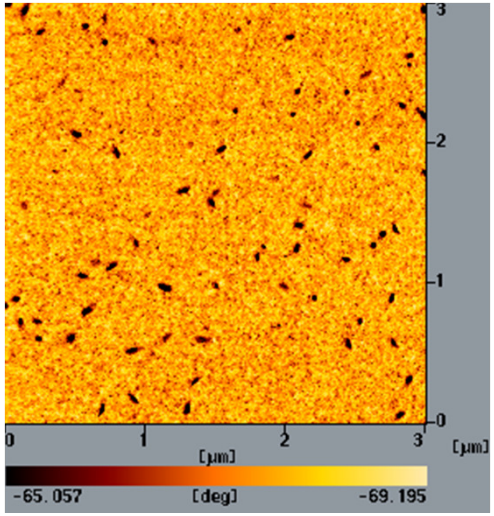


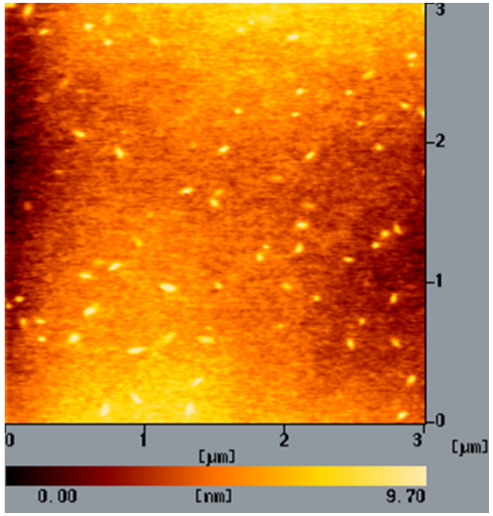


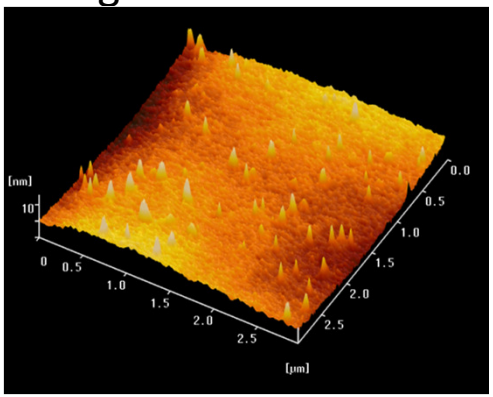


sSPUaE(DPC-D2000-IPDA)
roughness:18.85nm

Method 4







SPUaE(HDA-DPC-D2000-IPDA)
roughness:12.7nm

NIR -Conclusion

- Method 1：One step → Random → no phase separation



- Method 2：Hard segment first →gathered hard segment → clear phase separation and better properties



- Method 3：Soft segment first → scattered hydrogen bond → small phase separation and poor properties



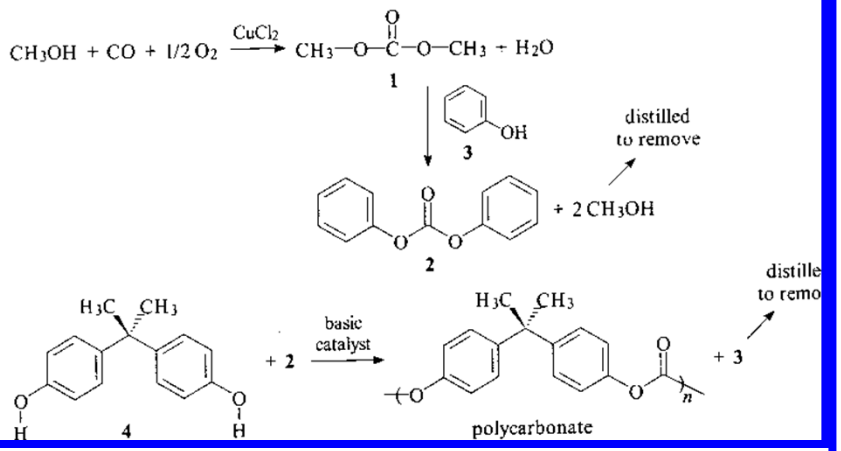
- **Method 4：Three steps → high MW and phase separation**

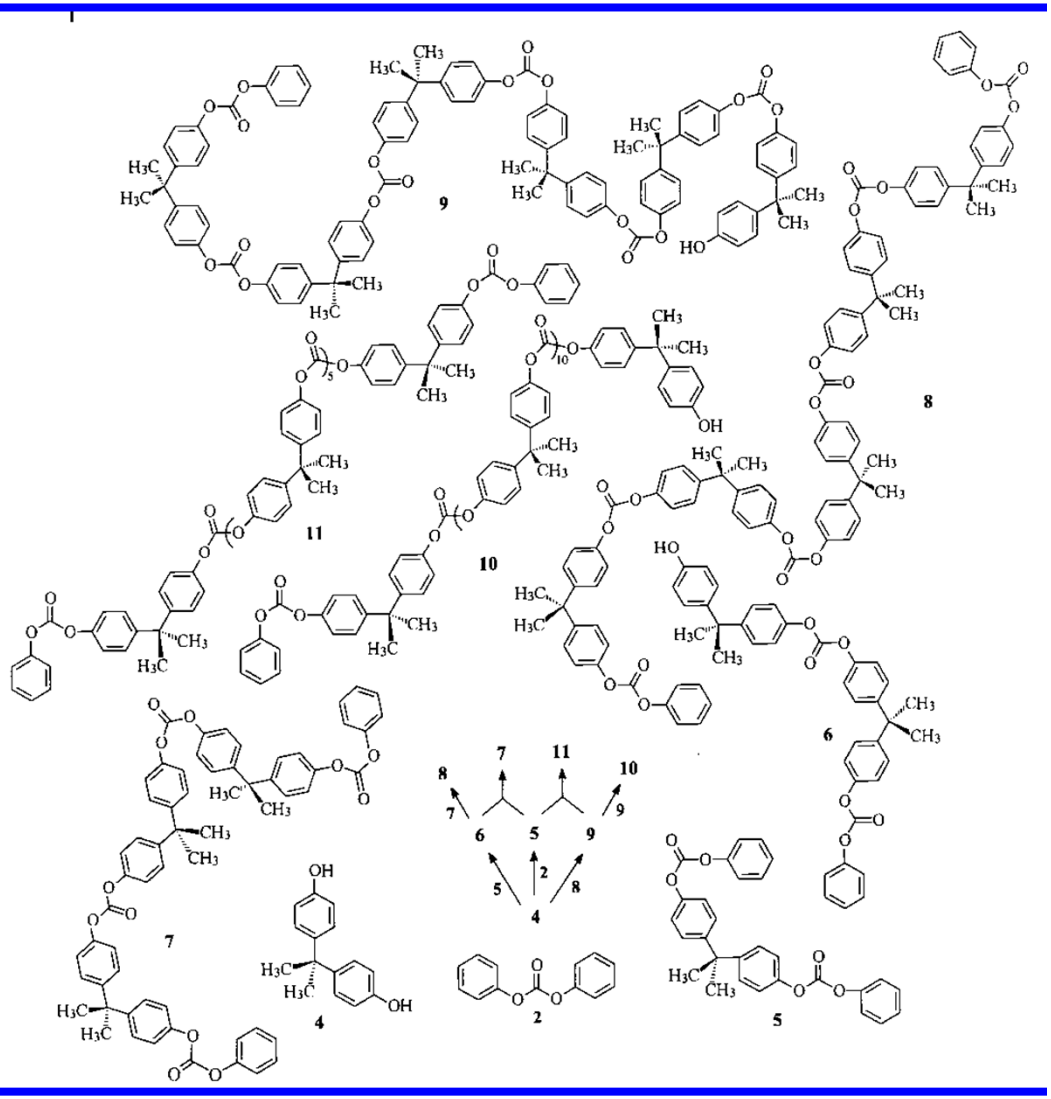


NIR Process with DPC

- **Advantages of our PUaE:**
  - ✓ Raw materials (DPC and diamines) are inexpensive.
  - ✓ Low chlorine in PUaE
  - ✓ Can synthesize segmented PU elastomers
  - ✓ Mechanical and thermal properties of PUaE are better than traditional PU.
  - ✓ In line with the principles of green chemistry
  - ✓ Lower capital expenses for scaling-up
- **Disadvantages:**
  - phenol/TMS recovery and recycle

Non-phosgene Route to PCs

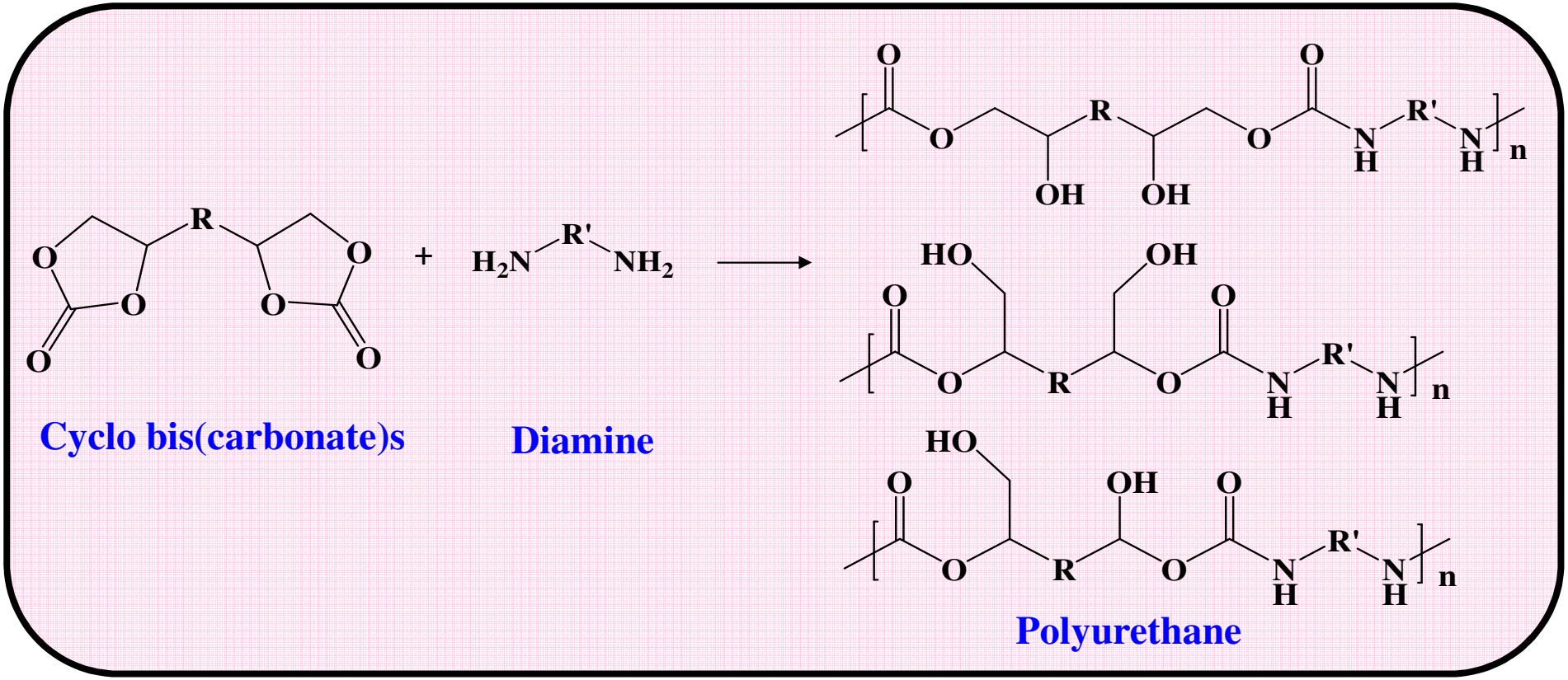




- In essence, our NPR process to PU is comparable to that BPA to PC of Asahi'process both using DPC as the key reagent. (taken from Principle of Indstrial Organic Chemistry)

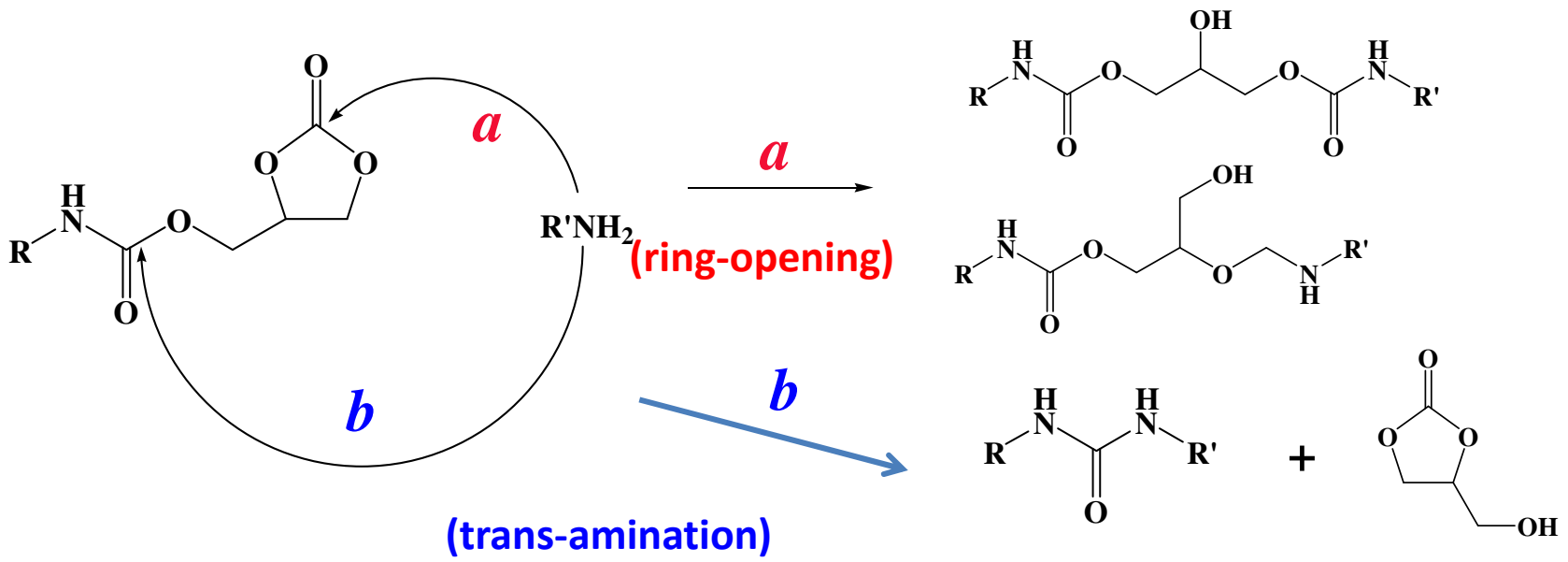
Non-Isocyanate Route to Polyurethane via Cyclic Carbonates

- **Ring-opening reaction with no by-product generation**



Oleg L.Figovsky,Features of Reaction Amino-cyclocarbonate for Production of New Type Nonisocyanate Polyurethane Coatings. Macromol.Symp, **2002**,187(325~332)

(7) Products Found in CC-Amine Reactions



Model Compound / Amine	A	B
NH2 pKa=10.78	About 1.6%	About 0.35%
NH2 pKa=10.7	About 7.7%	About 1.7%
NH2 pKa=9.35	About 1.9%	About 0%

- **Ring-opening of Glycerin cyclic carbonate formed un-desirable urea by-products in 0.3~8%**

- 使用Model compound C（由epoxy合成之CC）並無出現副產物的問題

- 所以在製備NIPU時,盡量使用Compound C types之CC進行non-isocyanate為佳.

(7) Comparison of PU and NIPU

Conventional PU (Iso/alc.)

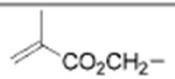
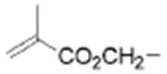
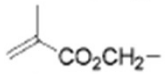
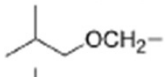
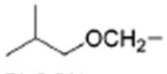
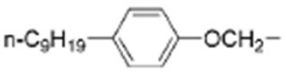
- The system must be strickly free from water until used.
- The hydrolytically unstable chemical bonds.
- The use of toxic/reactive isocyanate.

NIPU using CC/ amines

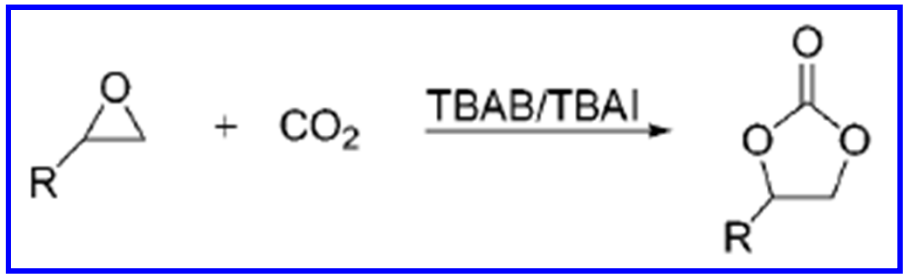
- Porous-free and moisture-insensitive.
- Intermolecular hydrogen bond endow NIPU with good properties.
- Without using isocyanate.

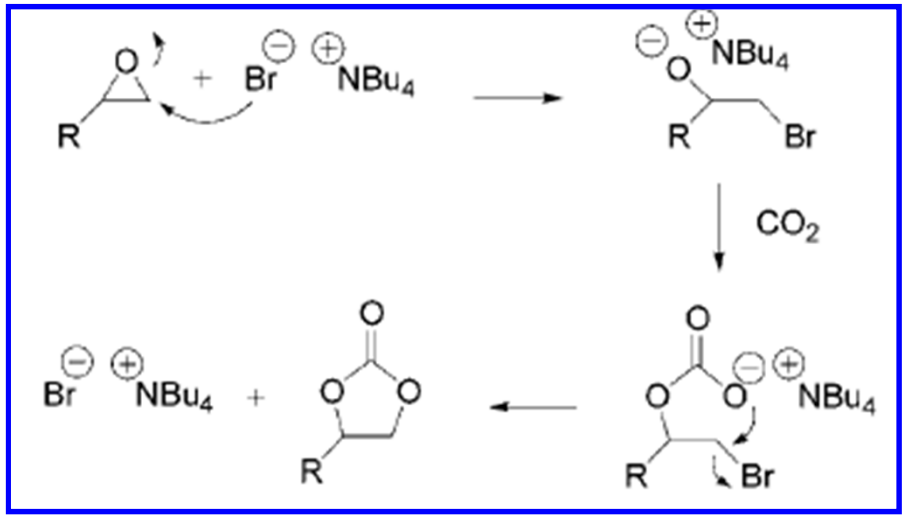
(7) Cyclic Carbonate Formation from CO_2 and Oxiranes

Table 1. Synthesis of Cyclic Carbonates in Tetralkylammonium Salts

entry	R	method	time/h	yield[a]
1		A[b]	4	90
2		A	1	88
3		B	7	91
4		A	2	90
5		B	8	87
6	$PhOCH_2-$	A	1	90
7	$PhOCH_2-$	B	4	87
8	$Ph-$	A	4	83
9	$Ph-$	B	22	80
10	$PhCH_2-$	A[b]	4	90
11		A	8	80
12		B	9	83
13	$ClCH_2-$	B	22	78
14	$PhOCH_2-$	B[c]	24	10
15	$PhOCH_2-$	B[d]	24	85
16	$PhOCH_2-$	B[c]	24	10

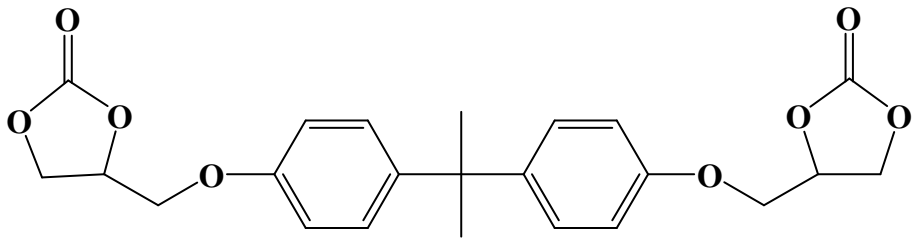
[a] Isolated yields are average of at least two runs; >95% pure as judged by ^1H NMR and GC. [b] As method A but with TBAB as solvent. [c] Catalyst 1. [d] Catalyst 2. [e] Catalyst 3.





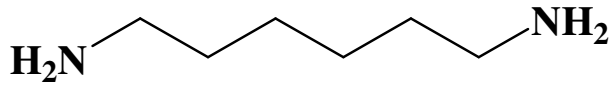
V. Calo, A. Nacci, A. Monopoli,Org. Lett. 2002,4,2561-2563

(7) Crosslinked PU from HAD/CC from BPA-DGE



CO2

BPA-DGE
(Epoxy)



HDI
Aluminium triisopropoxide

Crosslinking PU

Table V. Crosslinking Reaction of Poly(hydroxyurethane)[a]

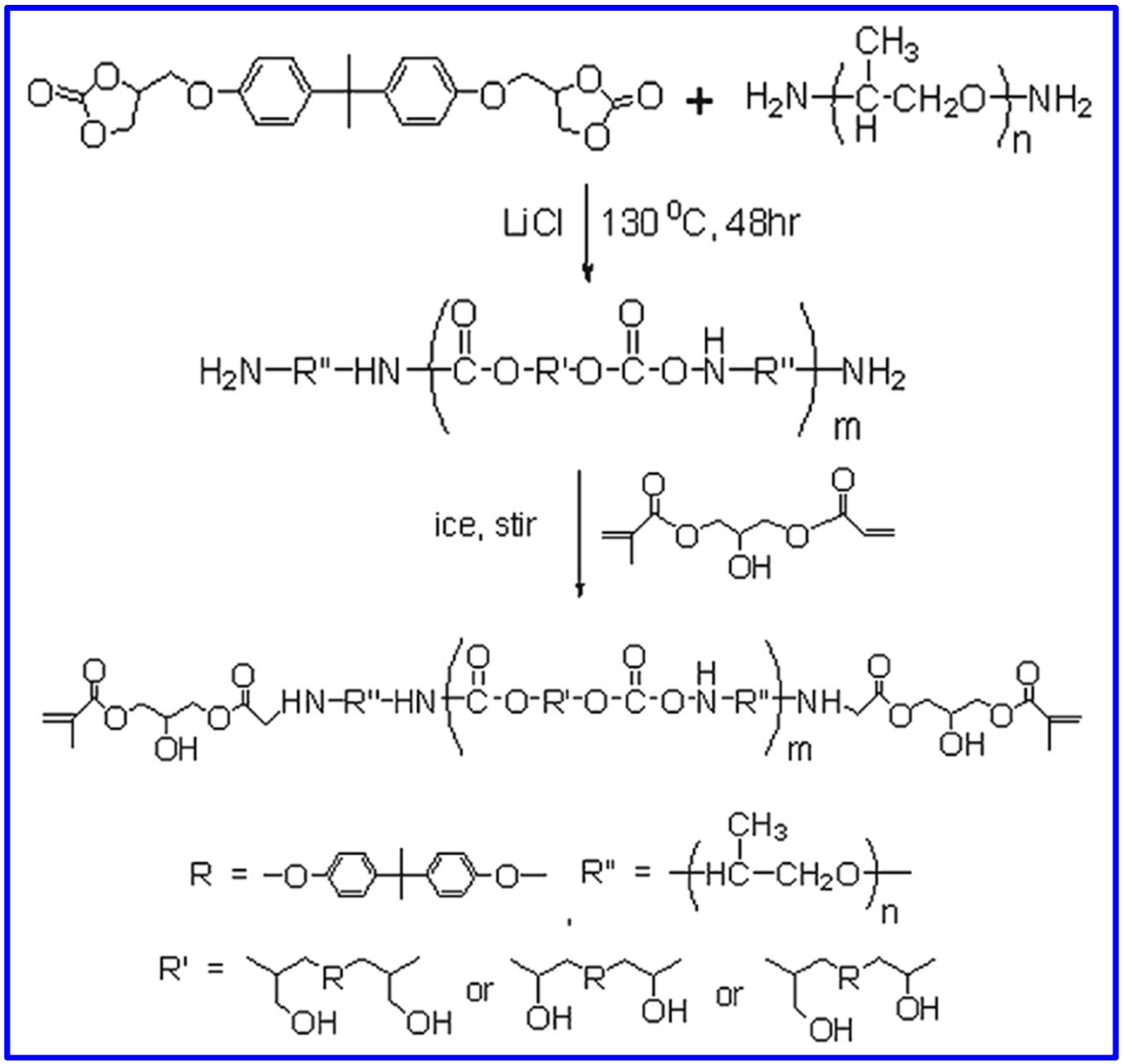
Crosslinking Agent[b]	Solvent	Concentration of Polymer (mol/L)	Gelation Time
Hexamethylene diisocyanate	DMAc	0.25	3 day
Hexamethylene diisocyanate[c]	DMAc	0.25	8 min
Aluminium triisopropoxide	THF	0.20	< 1 min

[a] Poly(hydroxyurethane) obtained from **1a** and **2a** ($\bar{M}_n$: 24,000) was used. Reaction was carried out at room temperature.
[b] One equivalent.
[c] Five mol % of dibutyltin dilaurate was used as catalyst.

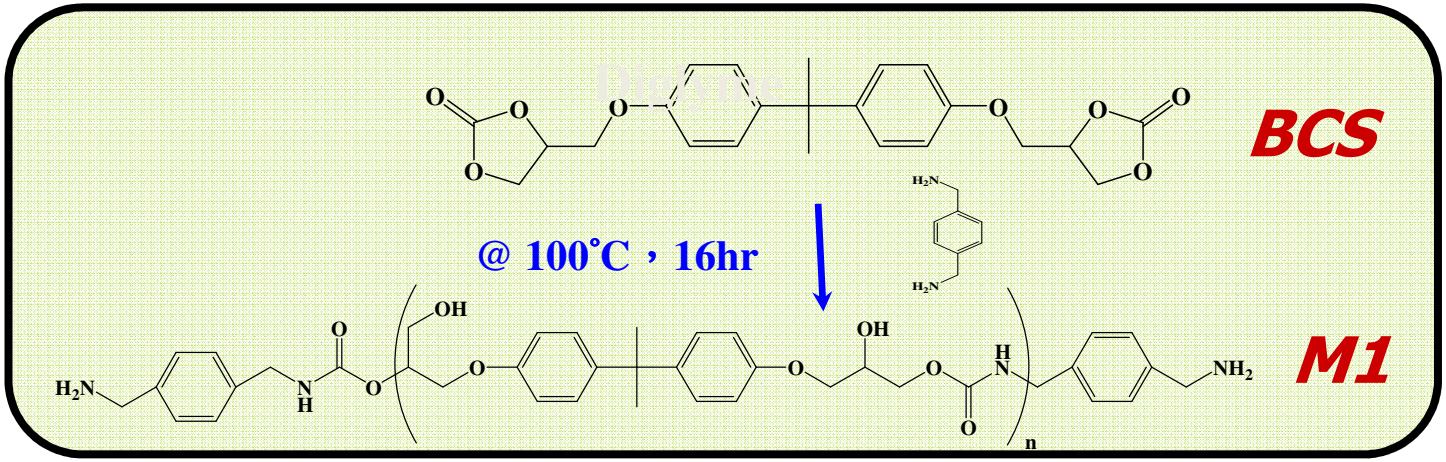
N. Kihara, T. Endo, J. Polym, Sci, **1993**,31,2765-2773

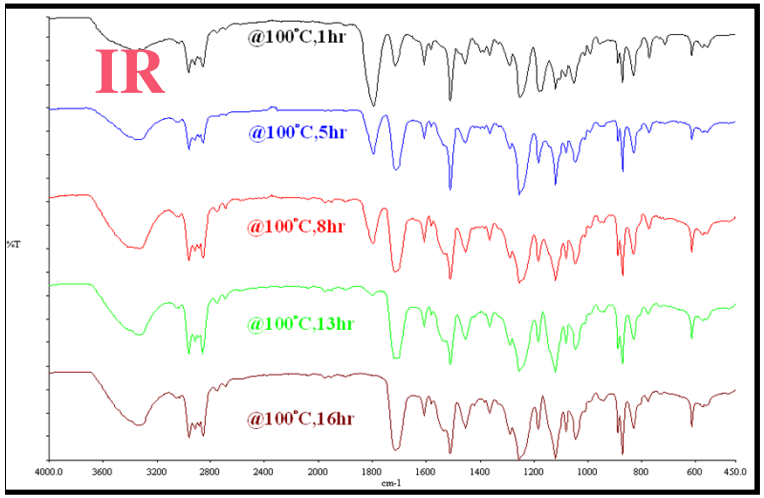
Chen Kan-Nan's Crosslinking Approach

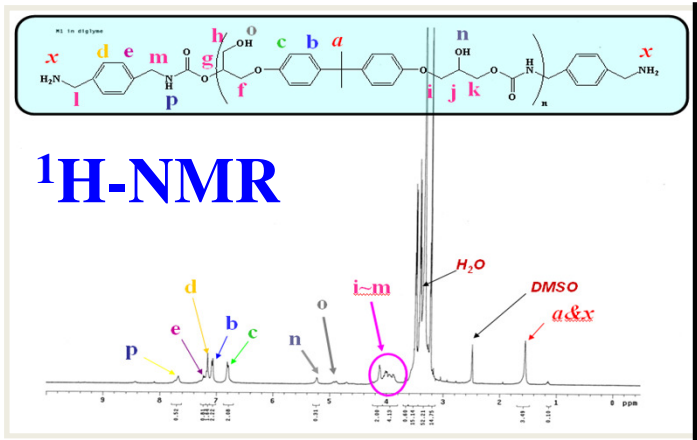
J. Polym. Res., 2012, 19, 9900



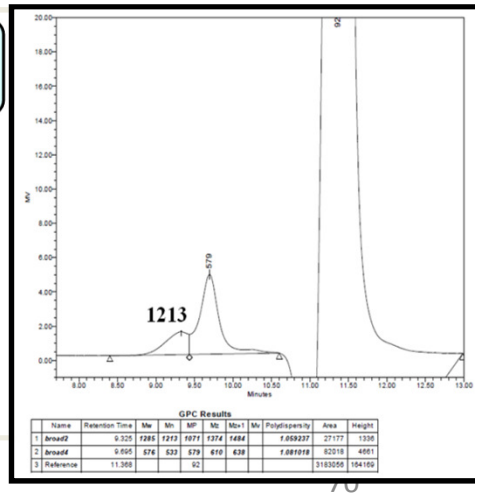
(7) : Synthesis of M1 Prepolymer



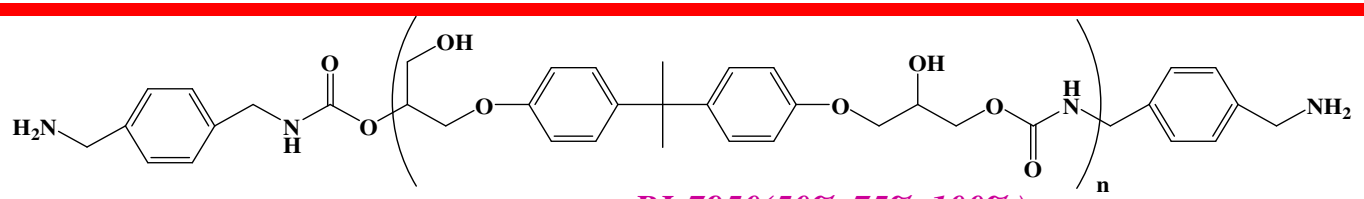




GPC



(7): Chain Extending of M1 Prepolymer with Blocked Isocyanate

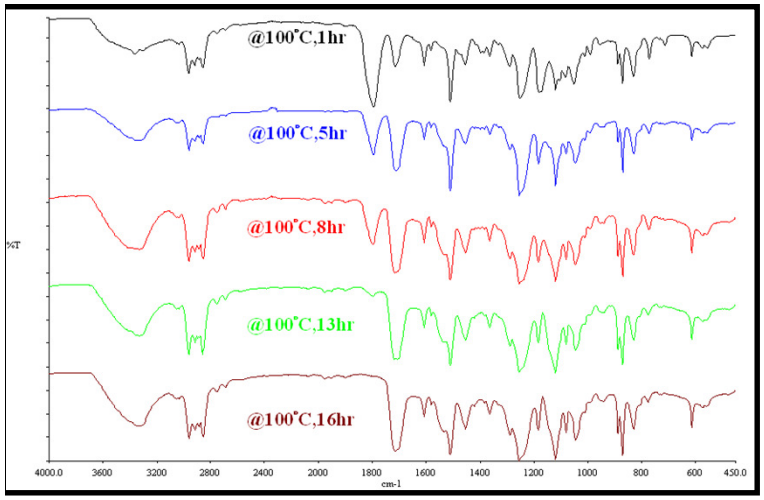


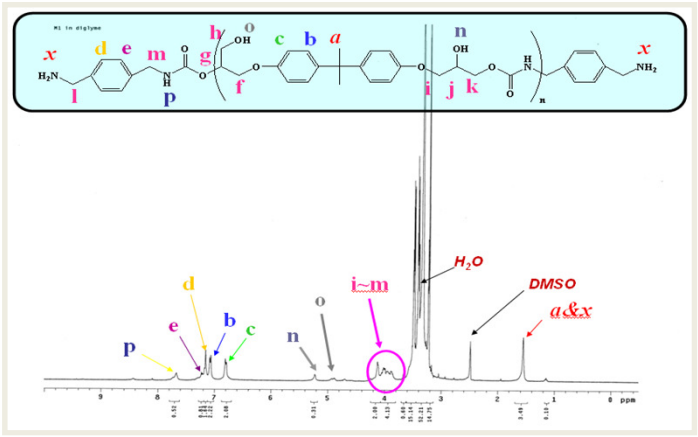
其中(50%, 75%, 100%)
代表其末端胺的反應程度

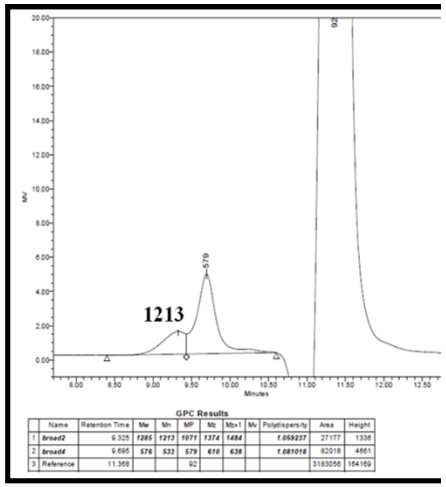
BI-7950(50%,75%,100%)
BI-7960(50%,75%,100%)
BI-7982(50%,75%,100%)

Chain Extending by Adding Blocked Isocyanate

PU(MBI-79XX-XX)

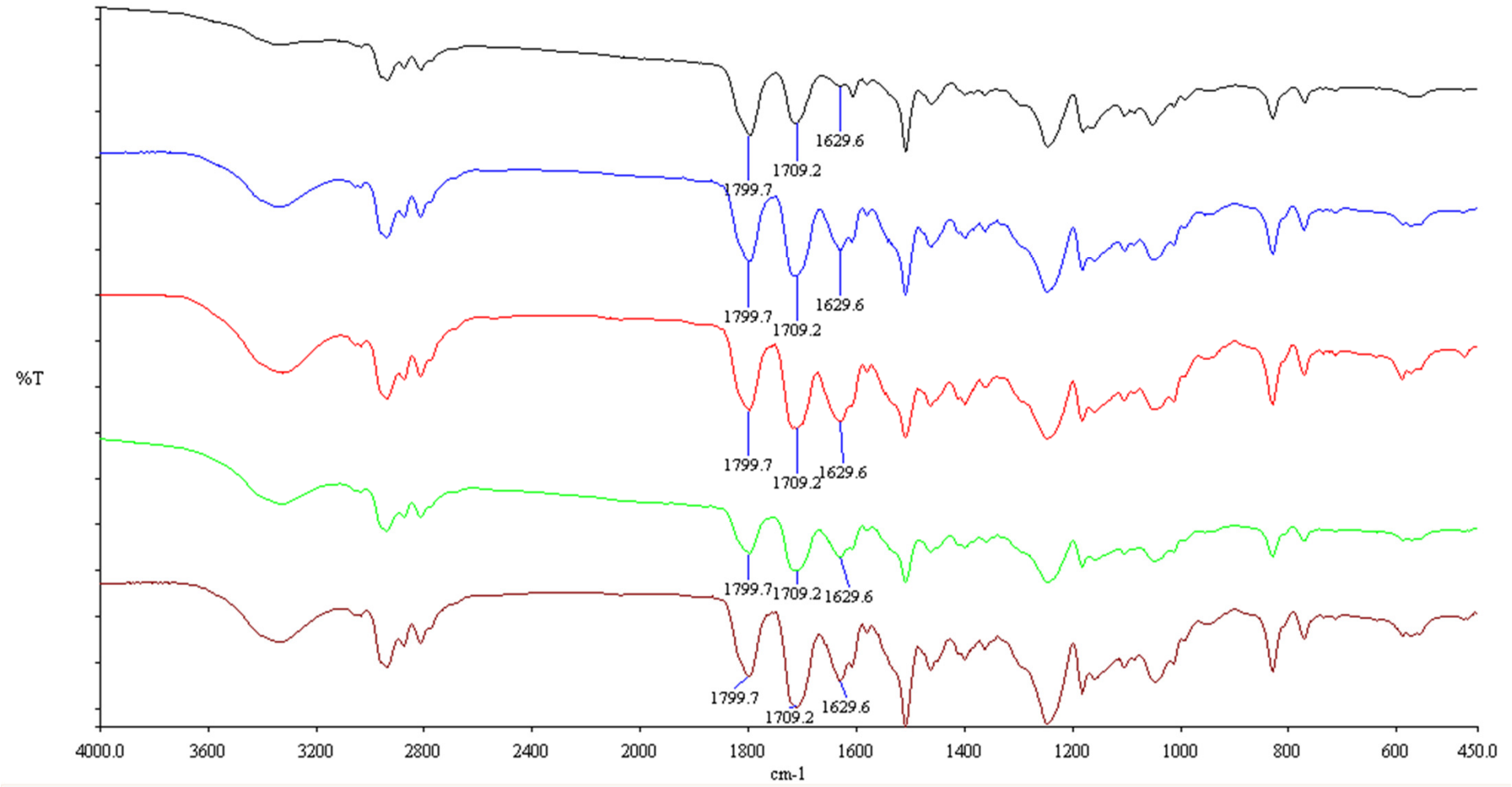






1. 由Epoxy Resin(BE-188)合成出的Amine-terminated prepolymer 不會出現 urea by-product, 但其分子量約在1200左右, 而加入了商業化的Blocked isocyanate作鏈長時, 其分子量呈現多區塊的分布, 無法避免仍存在小區塊分子產生.
2. 由添加的blocked isocyanate之不同, 交聯程度增加, 可看見大分子區塊面積些微增加, 第一區塊比例由4%~10%, 區塊由三個(MBI 7950)變為四個(MBI-7982)最佳.
3. 但主區塊的分子量成長有限, 此部份仍未完全作最佳化.

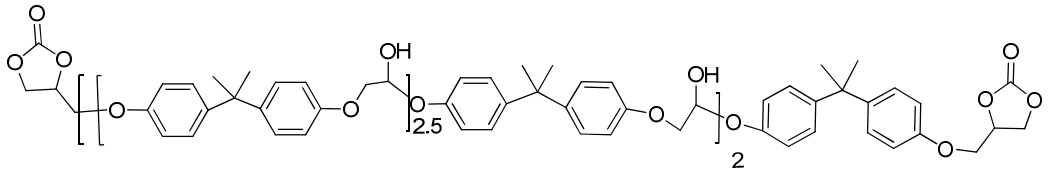
FTIR Monitoring of Preparing BCS I+ 1,4-Bis(3-aminopropyl)-piperazine at eq ratio 1.25:1 in DMAc



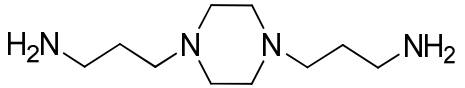
產物命名： BCS type-amine-BCS過量比例-solvent-溫度-solid content

若沒特別註明溫度為100°C solid cotent 為 low

Reaction of BCS II with1,4-Bis(3-aminopropyl)-piperazine



+

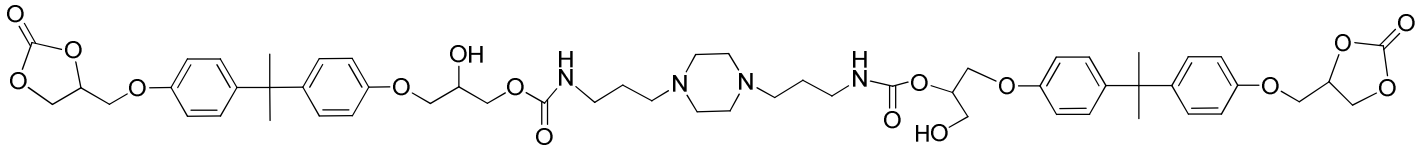


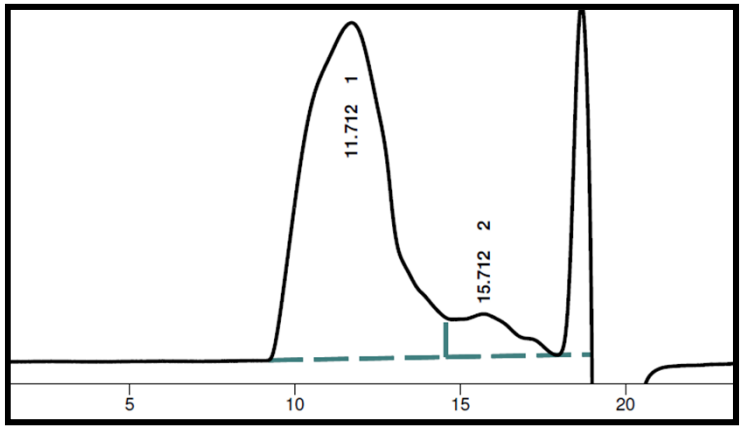
Molecular Weight: 200.32

1,4-Bis(3-aminopropyl)-piperazine

@100°C

In anisole

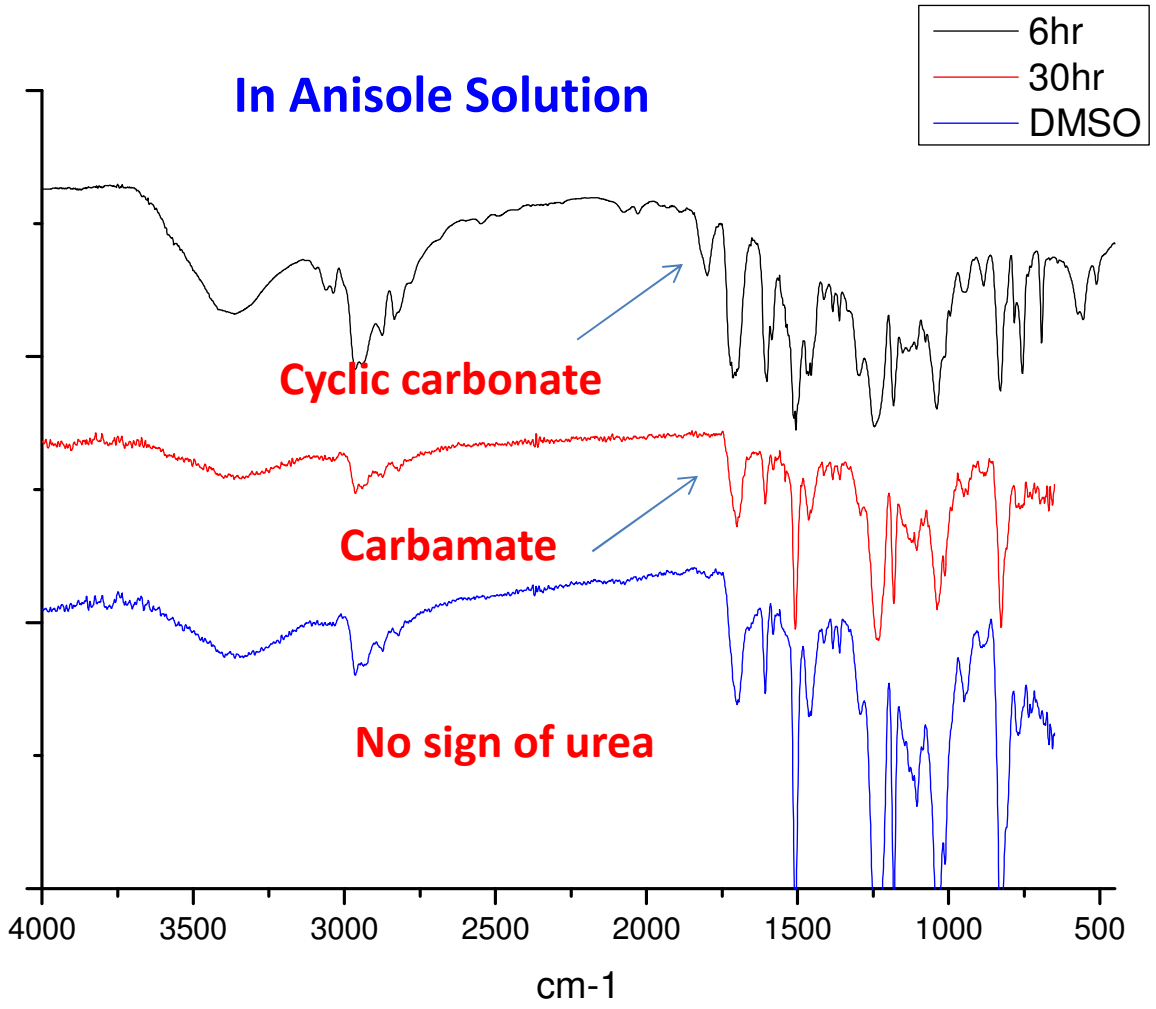




	Mn	MW	PD
20130903	56,192	846,578	15.0657

- Tg = 78.1 C
- Td (5%) = 274 C
- Char Y = 1.64%
- E% = 7%
- TS = 20.84 Mpa
- %wt increase in water = 0.23% (2wks)

Reaction of BCS II with1,4-Bis(3-aminopropyl)-piperazine

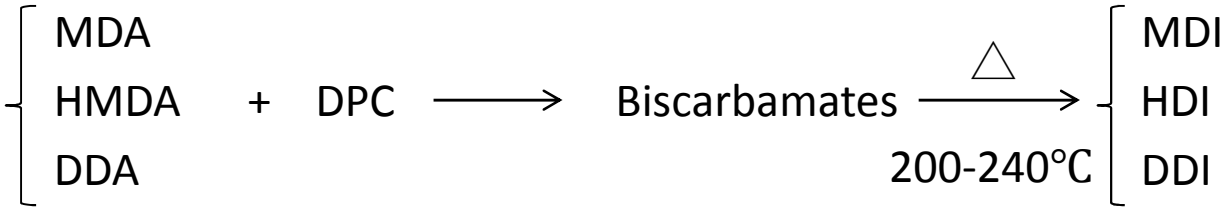


Keys to High Molecular Weights PUs from Ring-Opening of CC

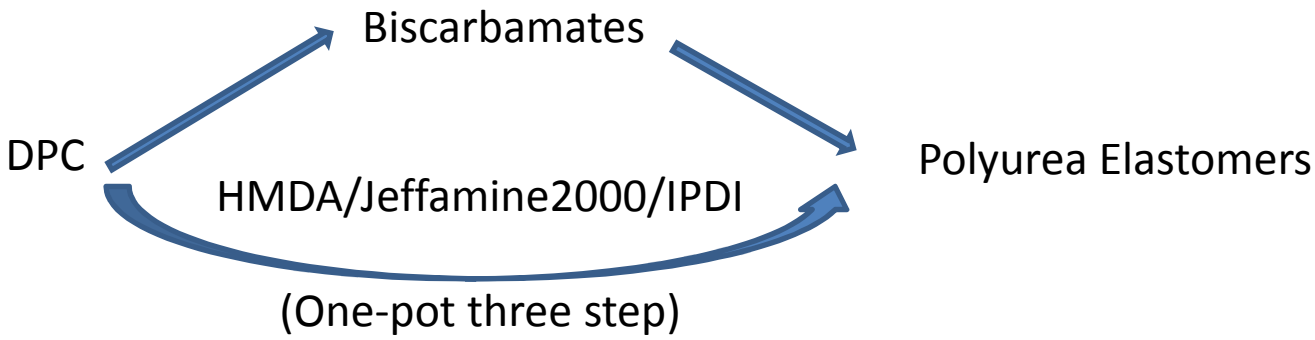
- Selection of reactive diamines and bis-cyclic carbonates
- Suitable solvent to maintain efficient mixing
- High shear mixing of high viscosity products
- Mild reaction without by-product formation (< 100 C)
- Promoted by efficient catalyst: (Data obtained in different reaction time)

Summary

- **Successful NPR Developed Using DPC as Carbonylating agent**:



- **Successful Polyurea Elastomers Development via NIR**

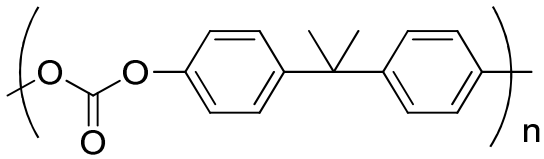


- **PU Plastics Synthesized through NIR:**



Other NIR Process under Study(Dai Group)

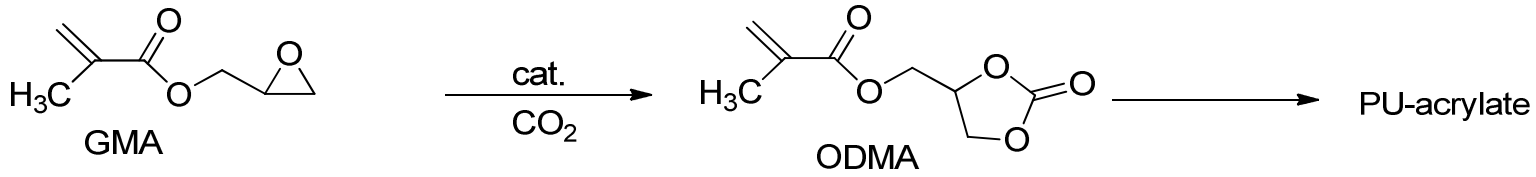
A.



(PC recycle and re-use as PU)

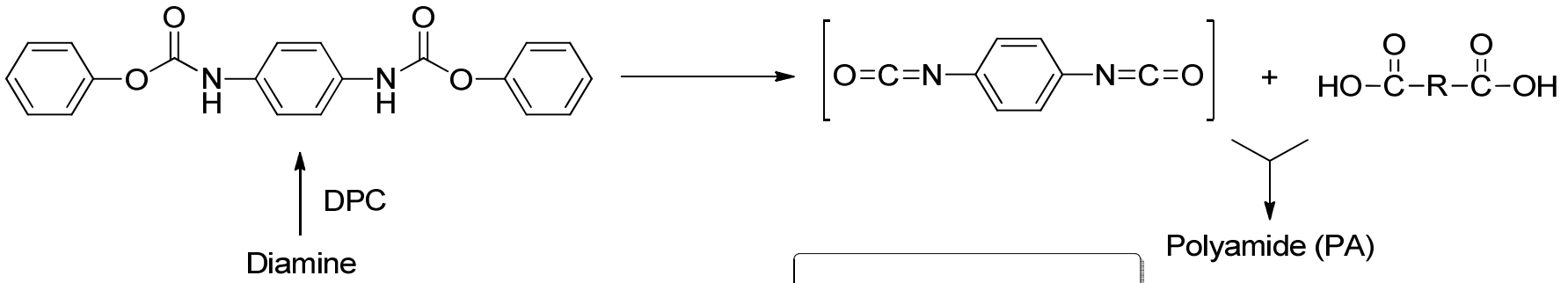
(GMA to ODMA to PU-acrylate/ DSM)

B.



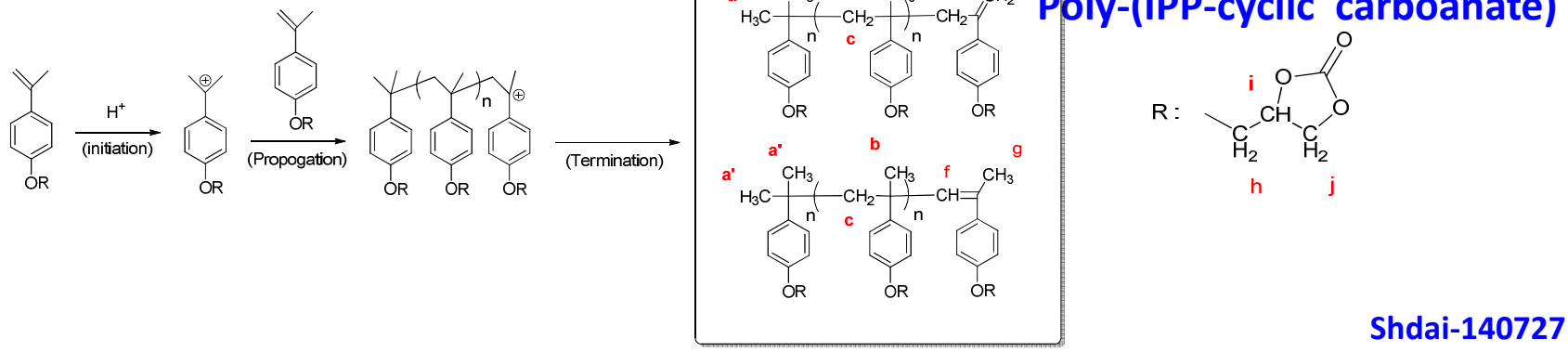
(Biscarbamate as blocked isocyanate)

C.



Poly-(IPP-cyclic carboanate)

D.



Acknowledgements

- 大東公司(GRECO)　新力美(DSM)
- National Science Concil of Taiwan
- Chen, S. Y (MDI);
- Pan, Elisa (Polyurea elastomers)
- Lin, W-S (HDI,DDI)
- Ku, K.T.(CC to PU)　Li, 紫菁(CC to PU)





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(1) Chen, 陳學永

(2) Ku, 顧冠增

(3) Pan, 潘玫蓁

(4) Li, 李紫菁

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(5) Lin, 林維興

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