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Synthesis and trans-ureation of N,N'-diphenyl-4, 4'-methylenediphenylene biscarbamate with diamines: a non-isocyanate route (NIR) to polyureas

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Abstract A non-isocyanate route (NIR) of making polyureas of high molecular weight has been found through trans-ureation of N,N'-diphenyl-4,4'-methylenediphenylene biscarbamate (4,4'-DP-MDC) with a variety of diamines and mixed diamines. The preparation of 4,4'-DP-MDC was achieved readily by carbonylation of 4,4'-methylenedianiline (4,4'-MDA) with diphenyl carbonate (DPC) using organic acids as catalysts. It was found that the highest yield (99%) of pure 4,4'-DP-MDC can be isolated in a toluene solution under mild conditions co-catalyzed by benzoic acid and tertiary amine. Trans-ureation of 4,4'-DP-MDC with aliphatic amines indicated that the process is a highly solvent dependent process and was found to be extremely facile in dimethyl sulfoxide (DMSO) at 80 °C and in tetramethylene sulfone (TMS) at 140 °C in absence of any catalyst. Particularly, the most effective polymerization process was developed using tetramethylene sulfone (TMS) as the solvent under reduced pressure for concurrently distilling off phenol from the reaction mixture during the polymerization in a shifting equilibrium towards polyurea. However, this solvent-assisted trans-ureation was found to be in-efficient when N,N'-dimethyl-4,4'-methylenediphenylene biscarbamate (4,4'-DM-MDC) was used in a similar condition for comparison. Thus, an efficient green-chemistry process has been developed based on 4,4'-DP-MDC in making urea prepolymers, urea elastomers and urea plastics all in excellent yields without using reactive methylenediphenylene diisocyanate (MDI) or any catalysts in the trans-ureation polymerizations.

Primary intermediate synthesized	Specifications	Abbreviation
N,N'-diphenyl-4,4'-methylenediphenylene biscarbamate	Mw:438.47	4,4'-DP-MDC
N,N'-dimethyl-4,4'-methylenediphenylene biscarbamate	Mw:314.34	4,4'-DM-MDC
4,4'-diphenylmethanebis-[(2-hydroxyethyl)urea]$_{DMSO/80}$	Mw:372.42	[DPMHU]

Introduction

Polyurea and polyurea elastomers have been known to possess many outstanding mechanical properties. Since introduced commercially in the 1970s, polyurea elastomers have been widely applied in polyurethane-urea reaction injection molding (RIM) processes [1–5] and spray-coating systems [6–8] to harness their fast polymerization rates and outstanding mechanical properties. Currently, two important polyurea commercial markets are automotive and construction applications [9–12] with familiar finished products such as bumpers, fascia, waterproofing linings, thermal insulation materials, industrial flooring and sports facilities. However, due to the high reaction rates of diisocyanates such as methylenediphenylene diisocyanate (MDI) and diamines, the synthesis and processing of polyurea and polyurea elastomers have been heavily dependent upon the assistance of RIM-machine or high-

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pressure mixing equipments. Synthesis of polyureas in bulk through more controllable step-wise manners has rarely been reported and will be highly prized for polyurea formulation development [13–16]. If the synthesis of polyurea can completely avoid using diisocyanates such as MDI or toluene diisocyanate (TDI) as the raw materials, it would become even more attractive because of the elimination of highly toxic and reactive diisocyanates in the overall synthetic scheme. (Scheme 1)

Recently, non-isocyanate synthesis of polyurea and polyurethanes has been explored with reactions of diamines with new intermediates. For example, Meijer used di-tert-butyl tricarbonate and diamine terminated poly(tetrahydrofuran) as raw materials for making thermoplastic elastomers (TPEs) [17, 18] of urea segmented block copolymers. Another approach for preparing polyureas without isocyanate chemistry was reported in Mtilhaupt's studies [19, 20] where a carbonyl biscaprolactam served as a non-halogen building block that could convert the terminal amine-groups of functional polymers into the corresponding caprolactam-blocked isocyanates. Although these approaches appear to be non-isocyanate processes to

polyureas in nature, high cost of di-tert-butyl tricarbonate and carbonyl biscaprolactam seems limiting their wide-spread applications.

Since the 1980s, biscarbamates of methylenediphenylene diisocyanate (MDI) such as 4,4′-DM-MDC or N,N'-diethyl-4,4′-methylenediphenylene biscarbamate (4,4′-DE-MDC) have been touted as the most important precursors for non-phosgene synthesis of MDI [21–23]. These bis-carbamates are synthesized by the condensation of mono-phenylcarbamate (Scheme 1) with formalin. The mono-phenylcarbamates were prepared by oxidative carbonylations of aniline (Asahi' Process) or reductive carbonylation (ARCO's Process) of nitro-benzene. Both these carbonylations involved carbon monoxide and precious metal catalyses. However, high dilution and high temperature thermolysis of biscarbamates in excess of 250 °C are both required for MDI generation. As a consequence, those severe conditions make the overall process unattractive due to energy cost, safety concerns and process difficulties. Except for isophorone diisocyanate (IPDI) productions, no commercial diisocyanates (MDI or TDI) has been diverted to the biscarbamate process so far [24, 25]. Therefore, non-phosgene routes (NPR) to diisocyanates
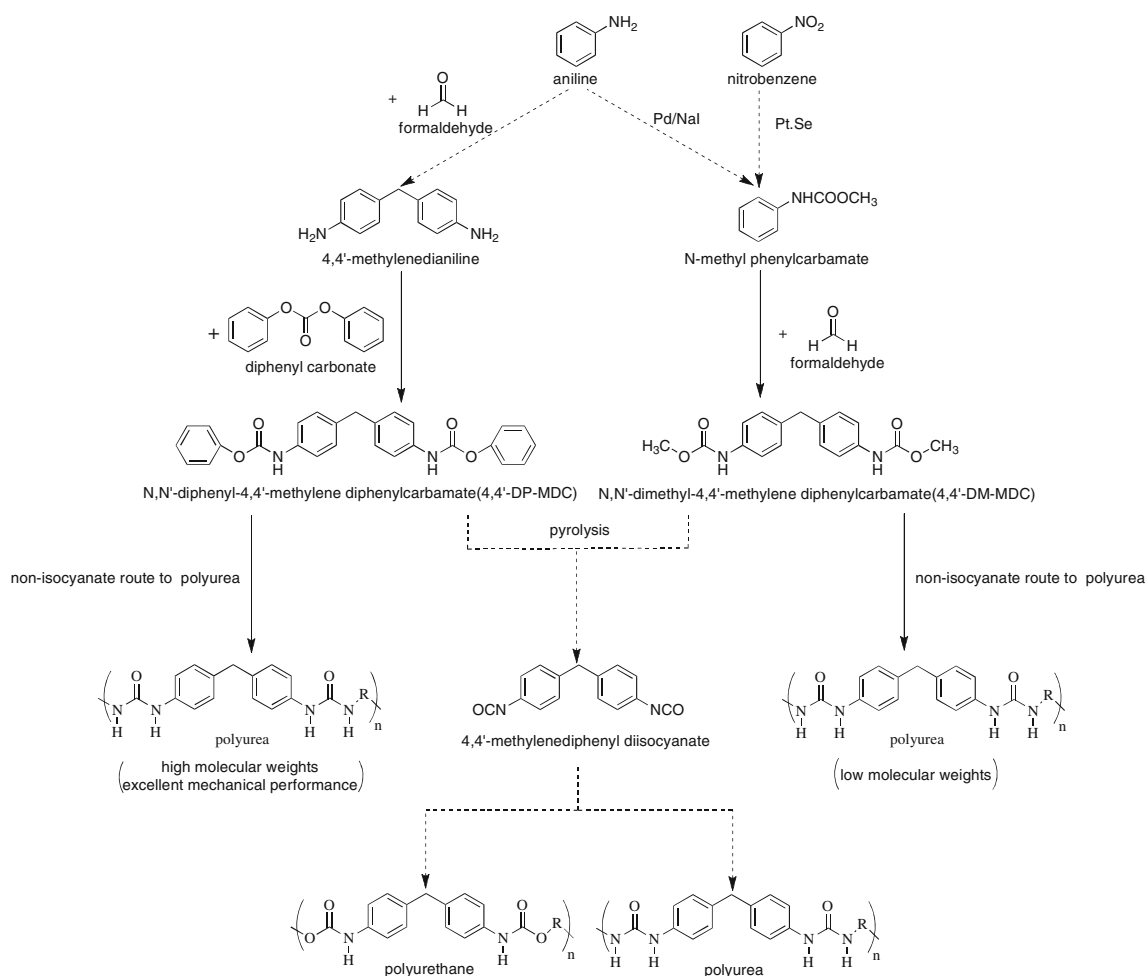
Scheme 1 Overall scheme of NIR route to polyurea. (The solid-line portions are carried out successfully in the study)

such as MDI or TDI have remained a long-term un-met goal yet to be achieved in the polyurethane/urea fields.

However, in a non-isocyanate route (NIR) to polyurea, the approach based on MDI-biscarbamates seems promising because no high-temperature condition is required through trans-esterification or trans-ureation. In fact, several attempts have tried to use carbamates, or biscarbamates directly as precursors for polyurethane (PU) and polyurea synthesis bypassing isolation of diisocyanate completely [26]. In 2000, ring-opening isomerization of cyclic-urethane [27–29] and trans-esterification [30, 31] to make PU are notable examples. However, both produce low molecular weight polymers. Metal or Lewis acid catalyzed trans-esterifications of diols and diamines with biscarbamates also have been studied in recent reports with some success [32].

Since improved synthesis for 4,4′-DP-MDC from carbonylation reaction of 4,4′-methylenedianiline (4,4′-MDA) with diphenyl carbonates have been accomplished recently by Harada's [33] and by Bosetti's [34] studies, we have initiated a feasibility study of NIR-polyurea process using 4,4′-DP-MDC and 4,4′-DM-MDC as key intermediates to react with diamines. Our present study has established that there are tremendous advantages of using 4,4′-DP-MDC over 4,4′-DM-MDC in trans-ureation reaction in making polyurea. Our results show that the polymerization using 4,4′-DP-MDC and diamines can lead to high molecular weight polyurea in dimethyl sulfoxide (DMSO) or tetramethylene sulfone (TMS). This NIR trans-ureation process is efficient and is achieved in absence of any catalyst.

Experimental section

Materials and reagents

Materials and reagents	Specifications	Suppliers	Abbreviation
Concentrated hydrochloric acid	37%	Tedia	Con. HCl
Formaldehyde	37%	Tedia	–
1,6-Hexanediamine	analytical grade	Acros	1,6-HDA
m-Xylylenediamine	analytical grade	TCI	m-XDA
Isophorondiamine	analytical grade	Acros	IPDA
4,4′-Diaminodicyclohexylmethane	analytical grade	Alfa	H_{12}MDA
4,4′-Methylenedianiline	analytical grade	Acros	4,4′-MDA
2-Aminoethanol	analytical grade	Tedia	AE
Tetramethylene sulfone	analytical grade	Acros	TMS
Dimethyl sulfoxide	HPLC grade	Tedia	DMSO
Amine terminated PPG-2000	Jeffamine D-2000, Mw: 2000	Huntsman	PPG-DA-2000
Amine terminated PPG-230	Jeffamine D-230, Mw: 230	Huntsman	PPG-DA-230
Polyether diamine based on a predominantly PEG backbone	Jeffamine ED-2003, Mw: 2000	Huntsman	PEG-DA-2000
1,8-Diamino-3,6-dioxaoctane	Jeffamine EDR-148, Mw: 148	Huntsman	DADO
N-Methyl-2-pyrrolidinone	analytical grade	Mallinckrodt	NMP
Diphenyl carbonate	analytical grade	Acros	DPC
Pyridine	analytical grade	Tedia	–
1,4-diazabicycle[2, 2, 2]octane	analytical grade	Alfa	TEDA

Instrumentations

Infrared (IR) spectra were recorded with Perkin Elmer Spectrum One FT-IR Spectrometer. Solid samples were prepared as potassium bromide pellets. High-pressure liquid chromatography (HPLC) was performed using a Shimadzu LC-6A with a column of Hypersil-100 C18 supplied by Thermo Electron Corporation, length 250 mm, I.D.: 4.6 mm and the UV wavelength set at 254 nm. ^{1}H-NMR spectra were recorded on a Varian Unity Inova FT-NMR (200 MHz) Spectrometer. GPC spectra were run on Waters Apparatus 515 HPLC pump 717

auto sampler, using a 2410 refractive index detector. Thermal gravimetric analysis (TGA) was performed on a Seiko SII SSC/5200 running at a heating rate of 10 °C/min. T_gs of the samples were performed a Differential scanning calorimeter (DSC) of Seiko SII SSC/5200. Stress–strain measurements of the polyurea films were performed on a Hung Ta HT-8504 tensile tester at an elongation rate of 100 mm/min. Sample bars of polyureas for the tensile strength measurement were punched from solution-cast films. Dimensions of the tensile bars were prepared in the following sizes: length = 22 mm, width =5.0 mm, and thickness =0.50 mm. Intrinsic

viscosities of polyurea were done in NMP solution at 0.5 g/dl concentration.

Experiment

1) Preparation of 4,4′-DP-MDC

4,4′-Methylenedianiline 19.8 g (0.1 mole), diphenyl carbonate 128.4 g (0.6 mol) and benzoic acid 2.44 g (0.02 mol), were added sequentially into a tri-necked reactor containing 150 ml of toluene at room temperature. The resulting mixtures were mixed with a magnetic stirrer and heated to 80 °C with an oil bath. After the dissolution of the reactants, the progress of the reaction was monitored by TLC plates.

After 16 h of continuous stirring and heating, the TLC analysis indicated the absence of 4,4′-MDA and the MDA mono-phenylcarbamate. The solid precipitate was isolated by filtration and the filtrate was washed with 50 ml of toluene. The precipitated solid product was dried under reduced pressure, and 43.1 g. of pure 4,4′-DP-MDC was obtained (m.p.=191–192 °C; yield= 98%) . ^{1}H-NMR (200 MHz, d_6-Aceton) δ (ppm): 3.9 (s, 2H, -PhCH$_2$Ph-), 7.17–7.55(m, 18H, -Ph- and -OPh-), 9.1 (br s, 2H, -NH-).

2) Preparation of 4,4′-DP-MDC with other carboxylic acid

The same procedure and quantity of reagents were carried out in similar synthesis of 4,4′-DP-MDC in as in Experiment (1), except benzoic acid was replaced by the same molar amount of other carboxylic acids listed in Table 1.(such as trifluoroacetic acid or dichloroacetic acid). After each preparation, 4,4′-DP-MDC was isolated as indicated in Experiment (1).

3) Synthesis of 4,4′-DP-MDC with different dosage of benzoic acid

The same reaction as in synthesis of 4,4′-DP-MDC [Experiment (1)] was carried out except with the varied quantities of benzoic acid weights. The amounts of benzoic acid have been reduced from 2.44 g, in Experiment (1), to 1.22 g (10 mmol), 0.61 g (5 mmol), 0.305 g (2.5 mmol) or 0.1625 g (1.25 mmol). Hence, the relative molar ratios of 4,4′-MDA/DPC/benzoic acid in this series of experiment are 1:6:0.1/1:6:0.05/ 1:6:0.025/1:6:0.0125 respectively.

4) Synthesis of 4,4′-DP-MDC with reduced amounts of diphenyl carbonate

The same reaction as in synthesis of 4,4′-DP-MDC [experiment (1)] was carried out with the following changes: the amounts of diphenyl carbonate was reduced to 85.4 g (400 mmol),64.2 g (300 mmol),53.5 g (250 mmol) or 42.4 g (200 mmol) from the original quantity shown in Experiment (1). Thus, the relative molar ratios of 4,4′-MDA/DPC/benzoic acid ran in this series were changed in the following order: 1:4:0.2/ 1:3:0.2/1:2.5:0.2/1:2:0.2 respectively.

5) Synthesis of 4,4′-DP-MDC via co-catalyst of benzoic acid with tertiary amine

The reaction procedure of Experiment (1) was carried out with an extra addition of 1,4-diazabicycle[2, 2, 2]octane [0.1 g (0.9 mmol)] or pyridine [0.07 g (0.9 mmol)], as a co-catalyst while the reaction temperature was lowered to 45 °C. The relative molar ratio of 4,4′-MDA/DPC/benzoic acid/tertiary amine run in this series was set at 1:6:0.2:0.009/1:6:0.2:0.

6) Preparation of 4,4′-DM-MDC

A 500 ml three-necked flask equipped with a magnetic stirrer, reflux condenser, and a heating mantle was charged with N-methyl phenylcarbamate (51.0 g; 33.7 mmol), 37% formaldehyde (15.2 g; 190 mmol), conc. hydrochloric acid (300 g) and methanol (101.1 g). The reaction mixture was stirred, heated to 30 °C and kept under the same condition for 40 h. After cooling to room temperature, the resulting white solid precipitate was isolated by filtration and was dried to obtain 48.2 g of DM-MDC which is amounted to 91% conversion based on N-methyl phenylcarbamate with the selectivity of 2,4′-DM-MDC, 4,4′-DM-MDC and oligomers of 2, 91 and 8% respectively (HPLC). ^{1}H-NMR (200 MHz, d_6-acetone) δ (ppm): 3.7 (s, 6H, COOCH$_3$), 3.86 (s, 2H, -PhCH$_2$Ph-), 7.1–7.5 (m, 8H, -Ph-), 8.6 (br s, 2H, -NH). M.p.=185–186 °C (recrystallized from toluene) (lit. [35], 183–186 °C).

7) Synthesis of 4,4′-diphenylmethanebis-[(2-hydroxyethyl) urea] from 4,4′-DM-MDC

A 100 ml three-necked flask, equipped with a magnetic stirrer, reflux condenser and thermometer, and an outlet in a heating mantle was charged with 4,4′-DM-MDC (4.38 g; 10 mmol), 2-aminoethanol (1.53 g;

Table 1 Effect of carboxylic acids of different pKas on 4,4′-DP-MDC yields

Carboxylic Acid Catalyst	pKa value[a]	Biscarbamate Yield (%)[b]	Urea Yield (%)[b.c]
Trifluoroacetic acid	0.23	38	1.62
Dichloroacetic acid	1.25	70	2.55
p-Nitrobenzoic acid	3.41	87	0.90
Benzoic acid	4.21	98	0.08
p-tert-Butylbenzoic Acid	4.40	96	1.28
p-Anisic acid	4.47	98	0.56
Isobutyric acid	4.86	93	1.09
Propionic acid	4.87	97	0.47
Pivalic acid	5.00	95	0.05

[a] pKa value = -log (acid dissociation constant)

[b] based on molar ratio of 4,4′-MDA:DPC:carboxylic acid =1:6:0.2

[c] Calculated by ^{1}H-NMR analysis

25 mmol) and DMSO (10 ml). The reaction mixture was heated to 80 °C under atmosphere and was kept at the same temperature for 1 h. Then, the reaction mixture was poured into water (250 ml). White solid precipitated was collected by filtration. After drying, the isolated solid was found to be pure 4,4′-DM-MDC (3.53 g. or 95%) with m.p. of 185–186 °C.

8) Synthesis of 4,4′-diphenylmethanebis-[(2-hydroxyethyl) urea] from 4,4′-DP-MDC

A 100 ml three-necked flask, equipped with a magnetic stirrer, reflux condenser and thermometer, and an outlet in a heating mantle was charged with 4,4′-DP-MDC (4.38 g; 10 mmol), 2-aminoethanol (1.53 g; 25 mmol) and DMSO (10 ml). The reaction mixture was heated to 80 °C under atmosphere and was kept at the same temperature for 1 h. Then, the reaction mixture was poured into water (250 mL). White solid precipitated was collected by filtration. After drying, it afforded 3.6 g of pure product (95% yield) with melting point measured at 226–227 °C. (lit. [36], 230 °C). ^{1}H-NMR (200 MHz, d$_6$-DMSO) δ (ppm): 3.1–3.2 (br dd, J=5.4 Hz, 4H, -CH$_2$OH), 3.4–3.5 (br dd, J=5.2 Hz, 4H, -CH$_2$NH-), 3.7 (s, 2H, CH$_2$), 4.7 (br t, 2H, -OH), 6.10 (br t, 2H, -NH), δ 7.0–7.3 (m, 8H, -Ph-), δ 8.4 (br s, 2H, -NH).

9) (9)Synthesis of P[4,4′-DM-MDC/DADO]$_{melt/160}$, P-1

A 250 ml resin kettle equipped with a mechanical stirrer, thermometer, and nitrogen inlet and outlet in heating mantle was charged with 4,4′-DM-MDC (31.4 g; 0.1 mol) and 1,8-Diamino-3,6-dioxaoctane (14.8 g; 0.1 mol) under atmosphere. The relative molar ratio 4,4′-DM-MDC/1,8-Diamino-3,6-dioxaoctane was 1/1.The reaction mixture was continuously heated at 160 °C for approximately 3 h. Methanol was removed continuously by a nitrogen purge. Polyurea prepared was characterized by GPC, TGA.

10) One-pot synthesis of P-2 in DMSO from 4,4′-DP-MDC

A 250 ml resin kettle equipped with a mechanical stirrer, thermometer, and nitrogen inlet and outlet was charged with 4,4′-DP-MDC (8.77 g; 20 mmol), 1,6-HDA (1.86 g; 16 mmol), PPG-DA-2000 (8 g, 4 mmol) in DMSO (90 ml), the mixed solution was stirred at room temperature initially under atmospheric pressure. The relative molar ratio of 4,4′-DP-MDC/1,6-HDA/PPG-DA-2000 was 1:0.8:0.2. The reaction mixture was then heated to 80 °C for about 6 h. The solvent (DMSO) and phenol generated during the reaction were removed under reduced pressure (0.5 mmHg at 120 °C oil bath temperature). Polyureas, P-2, were isolated from addition to water and was characterized by GPC, TGA and DSC.

11) Synthesis of P-7 in TMS from 4,4′-DP-MDC

A 250 ml resin kettle equipped with a mechanical stirrer, thermometer, and nitrogen inlet and outlet was charged with 4,4′-DP-MDC (5.79 g; 13.2 mmol), 1,6-HDA (0.95 g; 8.2 mmol), PPG-DA-2000 (10.0 g, 5.0 mmol) in TMS (66.96 g, solid content is set as 20%), the mixed solution was stirred at room temperature initially under atmospheric pressure. The relative molar ratio of 4,4′-DP-MDC/1,6-HDA/PPG-DA-2000 used in the preparation was 1:0.62:0.38. The reaction mixture was then heated to 90 °C for 1 h followed by a subsequent of vacuum distillation (7×10^{-3} mmHg) at about 140 °C for 2 h to drive off phenol from the mixture. After the reaction was completed, the TMS solution was dropped into 300 mL of water to precipitate the polyurea, P-7. Polymer was collected by filtration and then the product, P-7, was dried in an oven at 140 °C for 3 h and 90 °C for additional 5 h to get 12.3 g. (86%) of polyurea. P-7 was cast into film in N-Methyl-2-pyrrolidinone (NMP) solution and then were characterized by GPC, TGA, DSC and measured its elongation and tensile strength.

Results and discussions

Carbonylation of 4,4′-MDA with diphenyl carbonate (Scheme 2)

Earlier Yamazaki's study showed a carbonylation reaction of 4,4′-methylenedianiline (4,4′-MDA) with diphenyl carbonate (DPC) yielding 4,4′-DP-MDC in 68% yield with 2-hydroxypyridine as the catalyst [26]. More recently, Harada found that the yields of 4,4′-DP-MDC could be enhanced by treating 4,4′-MDA with a diphenyl carbonate in the presence of carboxylic acids such as pivalic acid or benzoic acid as the catalyst at 90 °C. Under his conditions, high conversion (>90%) with high purity of 4,4′-DP-MDC was achieved in toluene.[33]

In our study, we have repeated Harada's preparations and systematically carried out the carbonylation of 4,4′-MDA with diphenyl carbonate (DPC) each time with a different monocarboxylic acid with the intention of finding the best possible acid catalyst. The acid candidates being tested included both aliphatic and aromatic carboxylic acids with their pKa values spreading between 0.2 and 5.0. The screened candidates and synthesis condition are summarized in Table 1. The result of the 4,4′-DP-MDC yield curve plotted against pKa values is shown in Fig. 1. The result curve indicates that benzoic acid with pKa of at 4.2 out-performs the rest. Lower yields of 4,4′-DP-MDC appeared to be associated with strong acids used such as trifluoroacetic acid (pKa=0.23) and dichloroacetic acid (pKa=1.25) with low pKa values. These strong acids which form salt complexes with MDA apparently were un-favorable in carbonylation reaction.

When carboxylic acids with pKas of 4.4–5.0 were used in our screening study, the yields of 4,4′-DP-MDC were greater
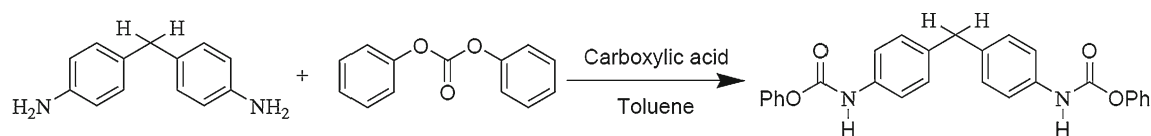
Scheme 2 Carbonylation of 4,4′-MDA with diphenyl carbonate. (Synthesis of 4,4′-DP-MDC)

than 93%. However, a slight declining trend of biscarbamate yields could be discerned as indicated in Fig. 1. This screening result supports that benzoic acid is the best choice so far. Even if the concentration of benzoic acid were reduced to 1/4 of the optimal concentration, high yield (92%) of 4,4′-DP-MDC could still be isolated (see Fig. 2 and Table 2). The effect of diphenyl carbonate concentrations on the yields of 4,4′-DP-MDC has also been investigated. The decrease of DPC concentrations shows a negative impact on yield of 4,4′-DP-MDC as indicated in Fig. 3 and in Table 3 However, about 90% yields of biscarbamate still could be achieved when the concentration of DPC was reduced to 50% of from its original optimal concentration.

Mechanism study on benzoic acid catalyzed carbonylation (Scheme 3)

The mechanism of benzoic acid-catalyzed carbonylation of 4,4′-MDA with diphenyl carbonate has been the other focal points of our study. During the course of the carbonylation reaction, we did detect a weak absorption band at $1,760$ cm^{-1} especially in the beginning of the mixing which persisted throughout the course of the carbonylation (Fig. 4). We suspected that this IR absorption band might corresponding to a probable intermediate, carbonic carboxylic anhydride A as postulated in Scheme 3. The carbonic carboxylic anhydride A was previously prepared by condensation of benzoic acid with phenylformyl chloride [37–39]. Anhydride A behaves like acid

anhydride and is an effective acylation reagent that converts alcohols into esters readily [40]. By a similar mechanism, anhydride A should facilitate the formation of carbamate if it should form in the reaction mixture and come in contact with amines. Therefore, we then added organic bases into the reaction solution hoping to promote the formation of anhydride A during the course of reaction as postulated in Scheme 3. In doing so, we did find that IR absorption band at $1,760$ cm^{-1} grew in its intensity while the added organic tertiary amines could indeed accelerate 4,4′-DP-MDC formation at 80 °C. More convincingly, tertiary amine promoted carbonylation was found to give highest yield of 4,4′-DP-MDC (99%) at mild temperature of 40–50 °C in 16 h as indicated in Table 4. Under this ambient temperature, carbonylation of 4,4′-MDA with benzoic acid alone are found to be sluggish and a lower yield of 4,4′-DP-MDC (65%) was obtained after 16 h. Among the tested tertiary amines, 1,4-diazabicycle[2, 2, 2]octane (TEDA) was found to possess the highest promoting activity so far. Thus, the catalytic role of carboxylic acid through formation of anhydride A in the carbonylation of amines has become well understood due to tertiary amine activation.

Synthesis of 4,4′-DM-MDC by condensation of N-methyl phenylcarbamate with formaldehyde (Scheme 4)

Condensation of *N*-alkyl phenylcarbamates with formaldehyde as the coupling agent have been studied for making biscarbamates of 4,4′-methylenediphenylene diisocyanate
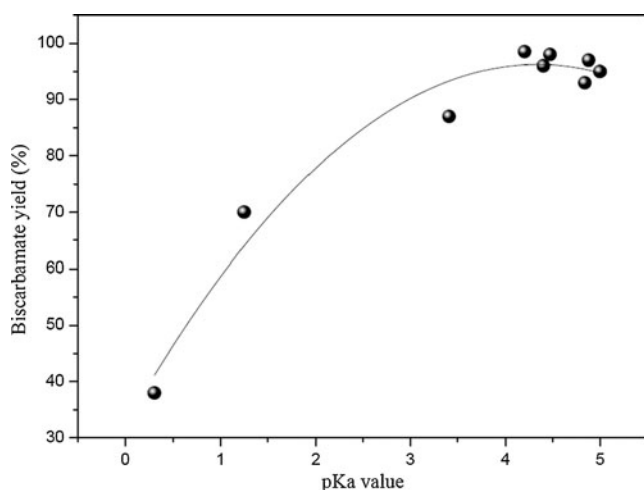

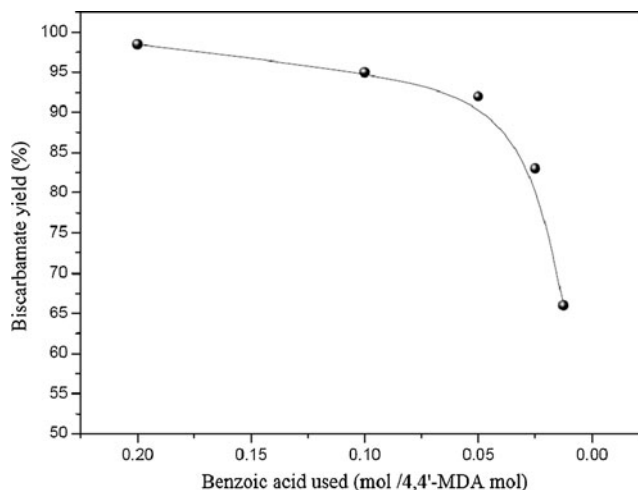**Fig. 1** Effect of carboxylic acids of different pKas on 4,4′-DP-MDC yields

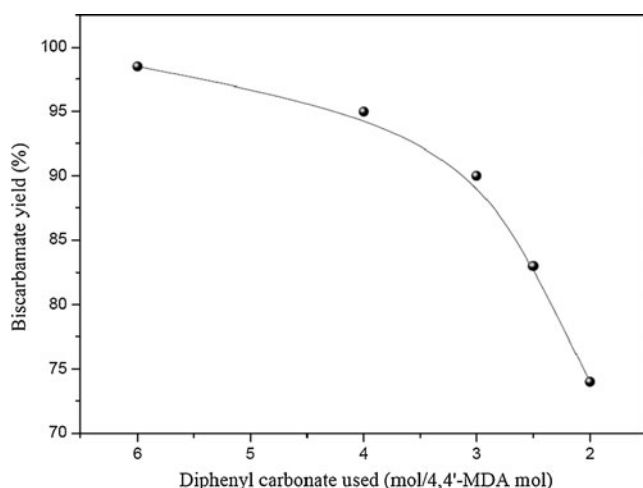**Fig. 2** Effect of different benzoic acid amounts on 4,4′-DP-MDC yields

Table 2 Effect of different benzoic acid amounts on 4,4′-DP-MDC yields

Composition[a]	Weights of Carboxylic Acid(g)	Biscarbamate Yield (%)	Urea Yield (%)[b]
MDA/DPC/Benzoic acid(1/6/0.2)	0.23	38	1.62
MDA/DPC/Benzoic acid(1/6/0.1)	1.25	70	2.55
MDA/DPC/Benzoic acid(1/6/0.05)	3.41	87	0.90
MDA/DPC/Benzoic acid(1/6/0.025)	4.21	98	0.08
MDA/DPC/Benzoic acid(1/6/0.0125)	4.40	96	1.28

[a] Molar ratio

[b] Calculated by ^{1}H-NMR analysis

Table 3 Effect of diphenyl carbonate concentrations on 4,4′-DP-MDC yields

Composition[a]	Conc. of Diphenyl carbonate(g)	Biscarbamate Yield (%)	Urea Yield (%)[b]
MDA/DPC/Benzoic acid(1/6/0.2)	128.4	98	0.08
MDA/DPC/Benzoic acid(1/4/0.2)	85.3	95	1.01
MDA/DPC/Benzoic acid(1/3/0.2)	64.2	90	0.42
MDA/DPC/Benzoic acid(1/2.5/0.2)	53.5	83	1.33
MDA/DPC/Benzoic acid(1/2/0.2)	42.4	74	1.18

[a] Molar ratio

[b] Calculated by ^{1}H-NMR analysis

(4,4′-MDI) such as 4,4′-DM-MDC. The most critical part of the synthesis has been the selection of acids for promoting the condensation reaction. The acids used so far [41] included concentrated sulfuric acid (conc. H_2SO_4, 98%), concentrated hydrochloric acid (conc. HCl, 37%), mixed conc. HCl-conc. H_2SO_4, and H_2SO_4-CF_3COOH. The pioneering studies of conc. HCl-catalyzed condensation of N-alkyl phenylcarbamates with formaldehyde were reported by Ryu's Patent in 1982–1983 [42, 43] and Ikariya's Patent in 1987 [44]. More recently, Zhao and his coworkers [45] have provided yet another alternative reagent, $ZnCl_2$, as the Lewis acid catalyst to condense N-alkyl phenylcarbamates with formaldehyde to form 4,4′-DM-MDC in 87%.

In our study, conc. HCl acid-promoted condensation was found to be the most convenient acid system among those tested because high purity DM-MDC could be isolated as the precipitate from the reaction solution at the end of the

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

reaction. Further refinement of preparation with the addition of methanol as a diluent has shown to have added advantages. Addition of methanol up to about 20% based on conc. HCl in the reaction mixture would allow continuous stirring of the mixture solution at 30 °C in achieving high conversions. The optimal relative weight ratios of methyl N-phenylcarbamate, formalin, and concentrated HCl in methanol solution were found at 10/3.3/20/40 respectively (Scheme 4). After 24 h of reaction, the yield of the product based on N-methyl phenylcarbamate was 91% while the selectivity of 2,4-DM-MDC, 4,4′-DM-MDC and polycarbamate oligomers in the precipitated product mixture were analyzed to be 2, 90 and 8%. Thus, the acid-catalyzed condensation of formalin and N-methyl-phenyl carbamate did not give pure 4,4′-DM-MDC rather produced it only as the major component in form of oligomeric mixtures.

Non-isocyanate route to polyureas by melt-polymerization

In our initial NIR process development, trans-ureation of 4,4′-DM-MDC and 4,4′-DP-MDC were carried out by mixing the same equivalent of polyetherdiamines such as 1,8-diamino-3,6-dioxaoctane (DADO), at 160 °C in the absence of solvent and catalyst. During the melt-polymerization, methanol or phenol was flushed out from the reaction mixture by continuously purging with nitrogen stream under reduced pressure. Powdered Polyurea[4,4′-DM-MDC/DADO]melt/ 160, P-1, were isolated after 60 min of reaction, and GPC analyses indicated that P-1 were with molecular weights of only about 6,000~7,000. This low-degree of polymerization could be attributed in part to the poor mixing between high melting biscarbamates and diamines and high viscosity of resulting polyurea. Moreover, if melt-polymerization was carried out at temperatures higher than 200 °C to reduce the product viscosities, Polyurea [4,4′-DM-MDC/DADO]melt/
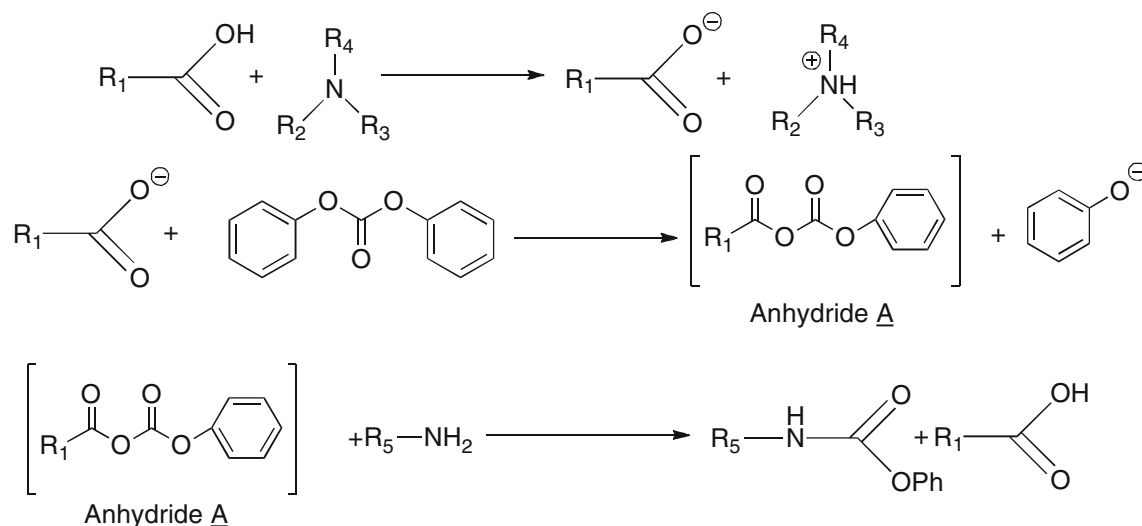
Scheme 3 Mechanism of carbonylation: co-catalyzed by benzoic acid-tertiary amine

200 turned dark rapidly due to degradation and oxidation, and the molecular weights also did not increase. Thus, a direct mixing of biscarbamates and diamines by melt-polymerization failed to yield high molecular weight polyureas.

Trans-ureation of 4,4′-DP-MDC and 4,4′-DM-MDC in DMSO and TMS by amino-ethanol (a model reaction study, Scheme 5)

In 1999, Thavonekham [46] discovered that a facile trans-ureation method of N-phenyl phenylcarbamates with N,N'-di-butyl amine in solvent, and the urea product was prepared in high yield. Interestingly, the solvent with high polarity or high-solubility parameter are the most efficient,

Fig. 4 Carbonyl regions of infrared monitoring spectra of Carbonylation of 4,4′-DPMDC. (**a**) without tertiary amine added (**b**) tertiary amine added for 2 h. (**c**) for 5 h

and DMSO was found to be the best solvent among those tested. In our study, trans-ureations of both biscarbamates with 2-aminoethanol in DMSO were carried out at 80 °C as in our model reaction study prior to our polyurea synthesis. The result confirms that high yield (94%) of 4,4′-diphenylmethanebis-[(2-hydroxyethyl)urea], [DPMHU], was isolated readily in a short reaction time from 4,4′-DP-MDC (60 min). Conversely, under an identical condition, trans-ureation of 4,4′-DM-MDC failed to give urea product [DPMHU], and the un-reacted 4,4′-DM-MDC, could be recovered from the mixture. These results strongly suggest that 4,4′-DP-MDC is a more effective intermediate than 4,4′-DM-MDC for carrying out trans-ureation reactions to make urea derivatives. The difference in reactivity between these two biscarbamates undoubtedly reflects the fact that the phenoxy group of 4,4′-DP-MDC is a better leaving group than the methoxy group of 4,4′-DM-MDC when 4,4′-DP-MDC were attacked at carbonyl center by nuclephilies. The use of polar solvents such as DMSO seems to further activate the urethane bond in 4,4′-DP-MDC for easy replacement of phenol. At 80 °C, tetramethylene sulfone (TMS) behaves like DMSO and also perform as the solvent for making [DPMHU]
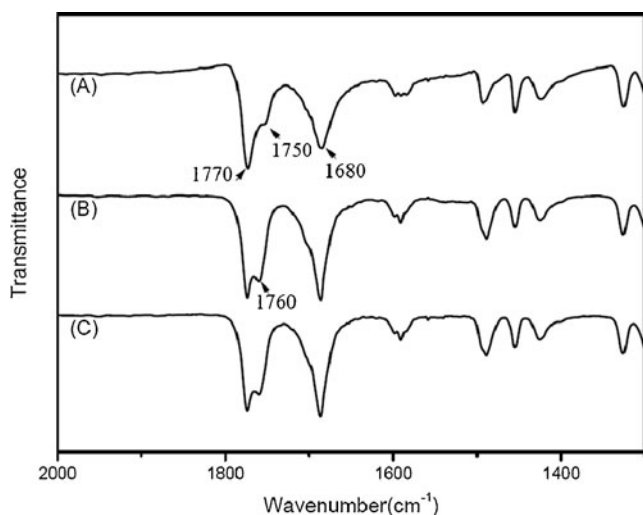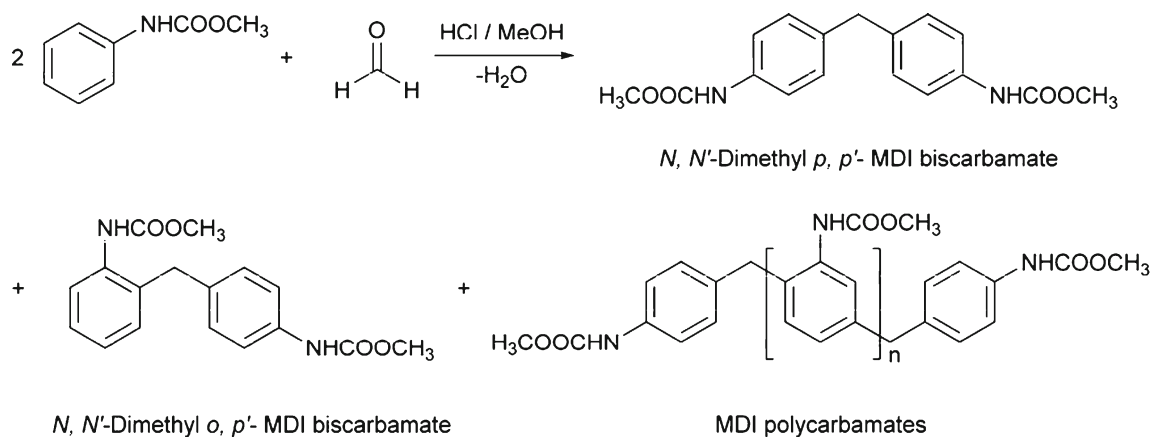
Table 4 Effect of co-catalyst on 4,4′-DP-MDC yields

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

[b] Calculated by [1] H-NMR analysis

Scheme 4 Condensation of *N*-methyl phenylcarbamate with formaldehyde. (Synthesis of 4,4′-DM-MDC)

in 90% through a similar trans-ureation. If the trans-ureation of 4,4′-DP-MDC was done in TMS under vacuum at 80–140 °C, the removal of phenol became rapid and phenol could be recovered from the distillate for easy separation. These experimental observations have been applied to our polyurea synthesis.

### NIR preparation of polyureas from 4,4′-DP-MDC and diamines in DMSO (Scheme 6)

DMSO and TMS not only are excellent solvents to dissolve both biscarbamates, but also they can serve as a good media for polyurea synthesis. For instance, Polyurea [4,4′-DP-MDC/DADO]DMSO/80, P-2, was synthesized simply by mixing 4,4′-DP-MDC with 1,8-diamino-3,6-dioxaoctane (DADO) in DMSO solution at 80 °C for 6 h. The prepared P-2 product has a molecular weight (Mw) of 40,400, which is about seven times greater than that of P-1 made by the melt-polymerization (Table 5.). P-2 showed higher T_d (280 °C) and T_g (80 °C) than those of P-1 with Td (268 °C) and Tg (50 °C), although both possess the same repeating units.

This one-shot DMSO assisted process of making polyureas with 4,4′-DP-MDC was applied to varieties of polyurea elastomer synthesis. For example, synthesis of segmented polyurea elastomers was accomplished by reacting 4,4′-DP-MDC with mixture of long-chained polyether diamines such as PPG-DA-2000 along with a short-chain amine extender such as 1,6-HDA, 1,8-diamino-3,6-dioxaoctane or diamine-PPG-230 in DMSO at 80 °C in an one-shot reaction. From IR monitoring

of the reaction solutions, it was observed that carbonyl group of 4,4′-DP-MDC at 1,722 cm^{-1} disappeared completely in just 30 min of mixing, while a new carbonyl absorption of polyurea group at 1,640 grew in intensity. After 5~6 h of reaction, molecular weights of synthesized polyurea elastomers, including P[4,4′-DP-MDC/DADO/PEG-DA-2000]DMSO/80, P-3, P[4,4′-DP-MDC/PPG-DA-230/PPG-DA-2000]DMSO/80, P-4, and P[4,4′-DP-MDC/1,6-HDA/PPG-DA-2000]DMSO/80, P-5, were found to be greater than 54,000 g/mol.

NIR preparation of polyureas from 4,4′-DP-MDC and diamines in tetramethylene sulfone (TMS)

In the course our synthetic study, some deficiencies of the one-shot DMSO process have been noted. First, because of the proximity of boiling points of phenol (b.p. = 182 °C) and DMSO (b.p. = 189 °C), separating them into individually components after the reaction is problematic. Second, the less reactive diamines such as hindered, cyclic or aromatic diamines cannot make high molecular polyureas in DMSO-assisted trans-ureation at 80 °C. In order to remedy these situations, we have found a new and improved experimental strategy that overcomes these problems. When the solvent was switched from DMSO to TMS (b.p. = 289 °C), we could carry out the trans-ureation polymerization at higher temperatures (140 °C) and while appling vacuum to the reaction mixtures. By doing so simultaneously, phenol removal from the mixture was found to greatly facilitate the forward reaction that speed up the rate of polymerization resulting in
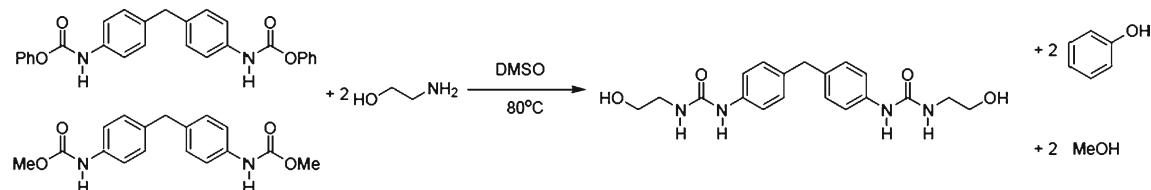
Scheme 5 Synthesis of 4,4′-diphenylmethanbis-[(2-hydroxyethyl)urea]. (Model trans-ureation reaction)
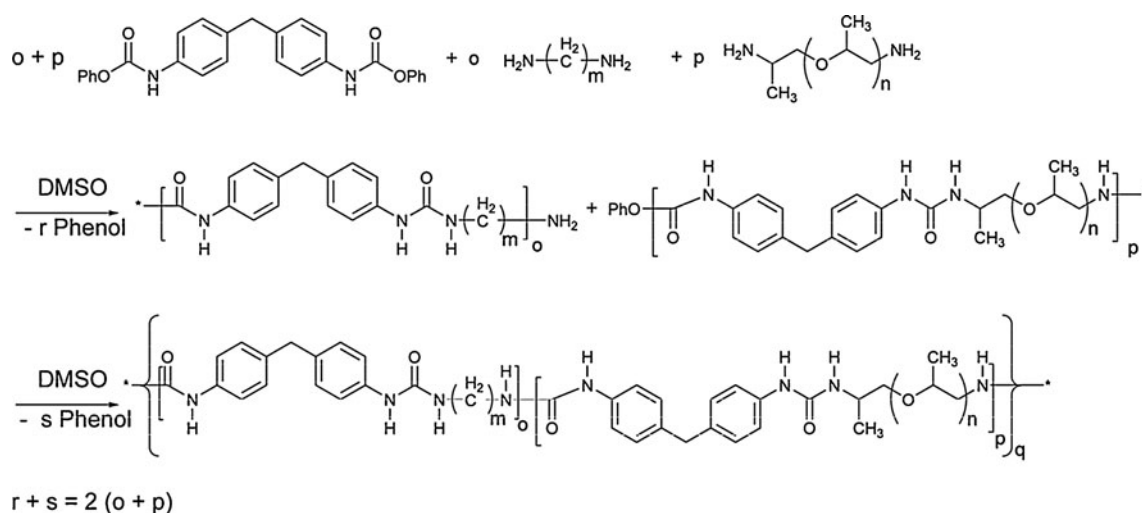
Scheme. 6 Polyurea elastomer synthesis from 4,4′-DP-MDC in DMSO/80 °C

high polymer formation in a short time. As indicated in Table 5, a series of new plastics and elastomers have been prepared all in isolated yields of more than 85% with molecular weight of exceeding 50,000. Particularly, aromatic diamine (4,4′-MDA) and cyclic diamine (H12MDA) which previously failed to make polyurea elastomeric films in DMSO at 80 °C, because of an in-sufficient high molecular built-up, now has been achieved obtaining using our method.

The prepared polyurea elastomers, P-3 to P-14, all had hard segment contents of about 30–55% and characterized by their soft segment glass transition temperatures between

−55 −58 °C not far from −61 °C of that of pure PPG-DA-2000. Nevertheless, all polyureas do not show T_gs or T_ms of hard segments in DSC. The T_ds of these polymers are mostly measured at 280–301 °C as shown in Table 5, and they seem to be higher than normal polyurethane elastomers. Tensile strength and elongation of polyurea elastomers differ greatly with the changes in hard segment diamines used in each formulation. Since polyureas made from TMS/140 °C have the highest molecular weight of those made from DMSO (80 °C) or in TMS at 80–90 °C, these polyureas generally possess the highest elongation of 400–600% and tensile

Table 5 Overall properties of polyurea synthesized

Polymer	Composition	T_d^a (°C)	T_g (°C)	Hard Segment (%)	M_w^b/g mol^{-1}	η_{inh}^c	Tensile Strength (MPa)	Elongation (%)
P-1	P[4,4′-DM-MDC/DADO]$_{melt/160}$	268	37	100	6,000	–	–	–
P-2	P[4,4′-DP-MDC/DADO]$_{DMSO/80}$	280	80	100	40,400	–	–	–
P-3	P[4,4′-DP-MDC/DADO/PEG-DA-2000]$_{DMSO/80}$	301	−50	58	131,700	–	–	–
P-4	P[4,4′-DP-MDC/PPG-DA-230/PPG-DA-2000]$_{DMSO/80}$	291	−59	61	71,600	–	–	–
P-5	P[4,4′-DP-MDC/1,6-HDA/PPG-DA-2000]$_{DMSO/80}$	285	−54	57	54,400	–	–	–
P-6	P[4,4′-DP-MDC/1,6-HDA/PPG-DA-2000]$_{TMS/90}$	288	−61.6	30	57,170	0.36	10.1	321
P-7	P[4,4′-DP-MDC/1,6-HDA/PPG-DA-2000]$_{TMS/140}$	291	−57.3	30	79,000	0.42	10.4	548
P-8	P[4,4′-DP-MDC/m-XDA/PPG-DA-2000]$_{TMS/90}$	291	−60.6	31	–	0.21	4.2	34
P-9	P[4,4′-DP-MDC/m-XDA/PPG-DA-2000]$_{TMS/140}$	280	−58.4	31	–	0.35	3.6	186
P-10	P[4,4′-DP-MDC/IPDA/PPG-DA-2000]$_{TMS/90}$	299	−61.3	33	57,170	0.36	8.7	448
P-11	P[4,4′-DP-MDC/IPDA/PPG-DA-2000]$_{TMS/140}$	282	−57.3	33	61,338	0.5	18.1	546
P-12	P[4,4′-DP-MDC/H$_{12}$MDA/PPG-DA-2000]$_{TMS/90}$	293	−59.5	32	68,000	0.58	18	273
P-13	P[4,4′-DP-MDC/H$_{12}$MDA/PPG-DA-2000]$_{TMS/140}$	290	−56.9	32	84,269	0.71	25.5	425
P-14	P[4,4′-DP-MDC/MDA/PPG-DA-2000]$_{TMS/140}$	286	−60.2	30	–	0.45	4.7	241

[a] 5% weight loss

[b] Measured by GPC with DMF as solvent relative to polystyrene standard

[c] $\eta_{inh} = \ln\eta_r/conc.$ (dl/g), conc. =0.5 wt%

strengths among each series. More detailed analyses of individual polyurea morphologies with their relationships to their respective methods of preparation and formulations shall be discussed in more detail in our forthcoming report in near future.

Conclusions

Both 4,4′-DP-MDC and 4,4′-DM-MDC were synthesized in good yields and were tested as polymer intermediates for synthesis of urea-prepolymers and polyureas by trans-ureation in this study. We found that trans-ureation of 4,4′-DP-MDC in DMSO is a rapid and selective reaction, and the synthesis could be done under an atmospheric pressure without catalyst. However, to overcome the separation of phenol from the solvent, trans-ureation using a high-boiling-point TMS as the solvent thereby replacing DMSO has some advantages. Also, the TMS-modified method could recover and separate greater than 95% of TMS and 85% of phenol from TMS solution after the polymerization for re-use. Furthermore, trans-ureation of 4,4′-DP-MDC in TMS at 140 °C is capable of producing highest molecular weight polyureas greater than 50,000 among different approaches consistently with varieties of diamines and diamine mixtures. Therefore, it becomes feasible to simplify the overall polyurea synthetic process bypassing the step of making 4,4′-MDI from biscarbamates altogether. In other words, the new polyurea process based on 4,4′-DP-MDC in TMS is a general, economical and effective green-process free from using toxic isocyanates and metal catalysts, and has the potential for wide-spread applications.

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