

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Preparation of lignin/glycerol-based bis(cyclic carbonate) for synthesis of polyurethanes

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Qin Chen^{a,b}, Keke Gao^b, Chang Peng^a, Haibo Xie^{*a,c}, Zongbao Kent Zhao^{*a} and Ming Bao^b

A bis(cyclic carbonate) was obtained via glycidylation of lignin-based bisphenol followed by cycloaddition with CO₂. Further polyaddition between the bis(cyclic carbonate) and diamines led to synthesis of polyurethanes. The structure and thermal properties of these polyurethane materials were elucidated by NMR, FT-IR, GPC, XRD, TGA and DSC.

Recently, there is an increasing demand for sustainable synthetic polymers owing to increasing environmental concerns arose from the large use of petroleum-based polymeric materials and restricted availability of petroleum resources. To meet the demand, biomass and CO₂ were regarded as the largest available and cheap resources, which can be used for the design and preparation of synthetic polymers.¹⁻³ On one hand, these polymers are regarded to be with lower carbon footprint than traditional synthetic polymers, on the other hand, taking the advantages of the new structural diversity of biobased monomers and specific molecular structure of CO₂, the as-prepared polymers should present different chemical and physical properties.^{4,5}

Polyurethanes (PUs) are important class of polymeric materials, which have been widely used in various areas owing to their diverse properties.⁶ Traditionally, the preparation of PUs involved the polyaddition of polyisocyanates and polyols, in which, great cautions have been taken to deal with the highly toxic and water-sensitive isocyanate monomers. Aiming to the development of environmentally friendly PUs, great efforts have been devoted to develop not only new, green and efficient alternative synthetic strategies, but also use environmentally benign resources as raw feedstocks. The polyaddition of multifunctional cyclic carbonate with multifunctional amines is an atom economic reaction and provides polyhydroxyurethanes containing hydroxyl groups in

their backbones and results in unique properties as compared with the conventional isocyanate-based PUs.^{7,8} The introduction of hydroxyl groups leads to the formation of hydrogen bonding, which endow the NIPUs with higher water-uptake, lower solubility in organic solvents, higher stiffness and tensile strength and improved thermal properties.⁹⁻¹¹ The advantages and greenness of the NIPUs prepared *via* the polyaddition strategy can also be valued from a point view of CO₂ fixation because cyclic carbonate can be prepared *via* the coupling reaction of CO₂ with epoxides. Therefore, the synthetic strategy of NIPUs based on the mild reaction between an amine group and cyclic carbonate group was regarded as a green and mild alternative synthetic strategy to get PUs.

With these, the well recognized starting challenge of the design and preparation of NIPUs is the molecular design and mild preparation of the bis-epoxides and the corresponding bis(cyclic carbonate)s (BCCs). In associated with the challenge, the utilization of biobased feedstocks as raw materials has attracted much attention,¹² such as vegetable oil,¹³⁻¹⁷ sugars,¹⁸⁻²⁰ terpenes²¹ and bio-polyols.²² Boyer et. al. prepared linear polyurethanes *via* the bulk polyaddition of diamines with internal and terminal carbonate fatty acid derived from sunflower oils, which exhibited low molecular weight of 13500 g/mol and low glass transition temperature (T_g) around -15 °C.¹⁴ Since the carbonate monomers contained ester groups, the aminolysis between diamines and ester could reduce the efficiency of the polyaddition. Linseed and soybean oil could be carbonated with CO₂ forming tri(cyclic carbonates) and the following curing process with different diamines resulted in corresponding NIPUs.¹⁷ Although thus obtained NIPUs showed with increased T_g to 60 °C and improved stiffness the high functionality and varied structure also led to ill-defined cross-linked NIPUs. The cyclic limonene dicarbonate prepared from the carbonation of epoxidized limonene with CO₂ have been employed in the polyaddition with different diamines to synthesized NIPUs with improved stiffness and heat distortion temperature mainly due to the cycloaliphatic structure of limonene.²¹ Recently, the bio-based content, mechanical, thermal properties and coating performance of the acrylated

^a Dalian National Laboratory for Clean Energy; Dalian Institute of Chemical Physics, CAS, Dalian 116023, PR China. Email: hbxie@dicp.ac.cn; zhaobz@dicp.ac.cn

^b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116023, PR China.

^c Department of polymer materials and engineering, College of Materials and Metallurgy, Guizhou University, Guiyang, 550025, China

Electronic Supplementary Information (ESI) available: Experimental details and some other data. See DOI: 10.1039/x0xx00000x

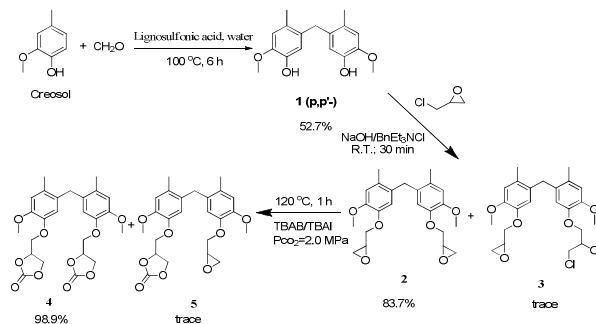
epoxidized soybean oil (AESO) based thermosetting resins were significantly improved after copolymerization with polyesters derived from itaconic acid and diols/glycerol, which were effective co-monomers to enhance the properties and bio-based content of soybean oil-based thermosets.²³

It is well recognized that the thermosetting materials containing aromatic monomers, such as bisphenol A, usually confer high mechanical and thermal properties to the network, but bisphenol A have proven harmful. Therefore, the seeking and introduction of biobased aromatic moiety into synthetic polymers have obtained great interesting recently. Lignin is the most abundant natural aromatic compounds on the planet, and the catalytic conversion of it affords a broad spectrum of aromatic derivatives, such as vanillin, 2-methoxy-4-ethylphenol and 2-methoxy-4-propylphenol.^{24, 25} Nowadays, vanillin is regarded as a promising biobased aromatic building-block for monomer synthesis. The reduction of vanillin produces 2-methoxy-4-methylphenol and the further condensation with aldehyde catalyzed by mineral acid²⁶ or lignosulfonic acid²⁷ in water provides lignin-based bisphenol. Such lignin-based bisphenol have been demonstrated to be a potential alternative to the traditional bisphenol A in the production of polycarbonate and bis(cyanate) esters.²⁸ Considering its biobased property and bisphenolic structural moiety, the bisphenol is anticipated to be a promising biobased building-block for monomer synthesis, but the research is still in its fancy. Therefore, it is still incentive to broaden the application of the lignin-based bisphenol. It is well recognized that the production of biodiesel produces surplus of glycerol as by-product, which represents as low-cost and non-food feedstock for bio-based functional derivatives and commercially valued products.²⁹ Through the Epicerol process, the glycerol can be converted to epichlorohydrin, which is an important substrate for conversion of polyols to epoxy resins.³⁰⁻³²

Herein, to prepare novel biomass derived PUs, a new bis(cyclic carbonate) was synthesized by *O*-alkylation reaction of lignin-based bisphenol with epichlorohydrin, followed by efficient cycloaddition in the presence of CO₂ and subsequent polyaddition with different diamines. The integrated use of biobased feedstocks and CO₂ *via* atom economic reaction and green catalysis for PUs synthesis outlined a good example in sustainable polymer chemistry with low carbon footprint.

Firstly, we used lignosulfonic acid, a green, effective and biomacromolecule-derived catalyst for the synthesis of bisphenol **1** through the *para-para* condensation reaction with a maximal 52.7% yield between creosol and formaldehyde in water (Scheme 1). Traditionally, glycidylation reaction of phenolic compounds is proved to be an effective strategy to construct monomers bearing epoxy moiety. For example, the glycidylation reaction between the mono-phenol alcohol and epichlorohydrin could be performed smoothly in the presence of NaOH in water/acetone mixture.³³ However, a simple adoption of this method into this study only obtains a moderate yield 51.7% of targeted aromatic bisepoxide monomer **2** when the lignin-based bisphenol **1** and epichlorohydrin was used under identical conditions (Scheme

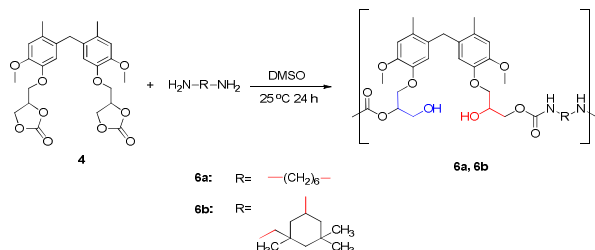
1). The mono-epoxy compound **3** was also separated as a by-product in 14 % yield. It was found that the addition of phase transfer catalysts (PTC), such as tetrabutylammonium bromide (TBAB) and benzyltriethylammonium chloride (BnEt₃NCl), into the system can significant accelerate the reaction and increase the selectivity, which was evidenced by the increased yields up to 73.5% and 83.7% in the case of TBAB and BnEt₃NCl, respectively, and only trace of mono-epoxy compound was detected (Scheme 1). With the particular introduction of methoxyl and methyl groups onto the benzene ring, it is found that the as prepared aromatic bisepoxide product has a melt point of 98-99 °C, which is higher than that of traditional bisphenol A diglycidyl ether (42-44 °C).³⁴



Scheme 1 The integrated use of biomass-derived feedstock and CO₂ for the design and synthesis of a new bis(cyclic carbonate) monomer via green catalysis

The cycloaddition of CO₂ with mono-epoxy compound have been widely studied and numerous catalysts have been developed to obtain high yield and selectivity, such as halide salts,³⁵ quaternary ammonium salts,^{36, 37} ionic liquids (ILs)^{38, 39} and metal catalysts.^{40, 41} With the significant progress in NIPUs preparation *via* the polyaddition between BCC and multifunctional primary alkyl amines, the screen of highly effective catalysts for the conversion of bisepoxy compounds into BCC is of great important, as the structures and properties of as prepared NIPUs are greatly influenced by the ratio of carbonate to amine groups.²¹ Therefore, it is of great important to convert bisepoxide to BCC in high yield and selectivity.⁴⁰ Although the metal catalysis were highly active for organic carbonate formation, the organocatalysis could be a greener alternative.⁴²⁻⁴⁴ Firstly, LiBr was applied due to its good performance during the cycloaddition of CO₂ with mono-epoxy compound,³ however only 14.4% yield of **4** and a 25.7% yield of **5** were obtained under identical conditions (Scheme 1). Large amount of **2** remained unreacted. The tetrabutylammonium bromide/tetrabutylammonium iodide (TBAB/TBAI) was regarded as a green and effective catalytic system for the cycloaddition of CO₂ with mono-epoxy compounds,⁴⁵ usually, a homogeneous system was formed at the beginning of the reaction, and a heterogeneous system was formed after the reaction due the immiscibility of the cyclic carbonate with TBAB/TBAI, which offer significant advantages from a facile and green products separation and catalyst reuse point of view. Therefore, the catalytic system was adapted directly for the conversion of **2** into **4**. It was found that a 98.9% yield was obtained, which demonstrates a

quantitative conversion of **2** into corresponding **4**. The structures of **4** and **5** were confirmed by nuclear magnetic resonance spectroscopy (NMR), fourier transform infrared spectroscopy (FT-IR) and high-resolution mass spectra (HRMS). With the particular introduction of methoxyl and methyl groups onto the benzene ring, it is found that the as prepared BCC has a melt point of 156 °C, which is slightly lower than that of the BCC derived from bisphenol A diglycidyl ether (159-163 °C).¹¹



Scheme 2. Polyaddition of the new bis(cyclic carbonate) **4** and traditional diamines

With the successful preparation of **4**, a series of NIPUs were prepared *via* polyaddition reaction with diamines as a proof of concept application. Considering the high melting temperature and high reactivity of BCC, we applied solution polymerization in polar aprotic solvent, dimethyl sulfoxide, at an initial concentration of 1 M at 25 °C, which could avoid side reaction. Firstly, two kinds of diamines, 1,6-hexamethylene diamine (HMDA) and isophorondiamine (IPDA) (Scheme 2) were employed under various reaction conditions, which were widely studied for the preparation of NIPUs. The conversions of the **4** were determined by the ¹H NMR integration ratios of the phenyl proton of **4** and NIPUs, and the molecular weight of the NIPUs was analyzed by GPC analysis. The structure was also confirmed by ¹H NMR and ¹³C NMR. The results were shown in Table 1. It was found that the catalyst and reaction temperature affect the NIPUs preparation to some extent (Table 1, entries 1-6). Basically, increasing temperature and adding a superbasic catalyst results in an increase in the conversion of the BCC and the molecular weight. For example, in the case of HMDA, the conversion of **4** is 92.7%, and the M_n of the **6a** is 23000 when the polyaddition reaction was performed at 25 °C, without adding TBD as an organocatalyst (Table 1, entry 1); while the results are 100% and 46000, respectively when the polyaddition reaction was performed at 100 °C (Table 1, entry 3). The addition of TBD as an organocatalyst not only increased the conversion of **4** from 92.7% to 100%, but also increased the M_n of **6a** from 23000 to 30000 (Table 1, entries 1 and 2). The results also demonstrated that HMDA is more active than IPDA. Although high molecular weight of NIPUs were prepared when IPDA was used in previous studies, only low molecular weight of **6b** with broaden PDIs were obtained either increasing the reaction temperature or adding TBD as an organocatalyst (Table 1, entries 4-6). The low activity of IPDA in this study may be due to the high steric hindrance arose from both of **4** and IPDA. As

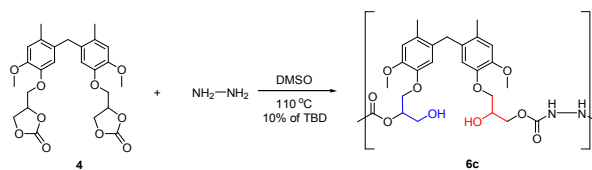
HMDA can be produced by fermentation process, the **6a** can be considered to be a polymer with low carbon footprint.

Table 1. Polyaddition of bis(cyclic carbonate) with diamine^a

Entry	NIPUs	TBD mol%	Conv % ^b	Yield %	1°:2°OH ^b	M_n ^c g/mol	PDI ^c
1	6a-1	-	92.7	84.0	59:41	23000	1.9
2	6a-2	5	100	96.0	50:50	30000	1.7
3 ^d	6a-3	-	100	89.1	60:40	46000	1.5
4	6b-1	-	77.0	73.9	46:54	3300	1.5
5	6b-2	5	92.8	86.9	30:70	6300	9.4
6 ^d	6b-3	-	90.1	75.6	42:58	4800	5.4
7 ^e	6c-1	10	72.0	53.5	51:49	6600	2.6
8 ^f	6c-2	10	83.9	56.1	51:49	1300	1.1
9 ^g	6c-3	10	69.6	50.2	49:51	1100	1.2

a: Reaction condition, bis(cyclic carbonate) 0.5 mmol, diamine 0.5 mmol DMSO 0.5 mL, 25 °C, 24 h; b: calculated from ¹H NMR; c: determined by GPC calibrated with polystyrene; d: 100 °C; e: 110 °C; f: 110 °C, 72 h; g: 110 °C, 7 d

In order to lower the carbon footprint of the as-prepared NIPUs, diaminehydrate (DAH) was further selected as a diamine (Scheme 3), which does not have carbons in the molecule. The results showed that only low molecular **6c** were obtained even 10% of TBD was added as catalyst at 110 °C due to the low nucleophilicity of the amine group in DAH (Table 1, entries 7-9). Furthermore, the prolongation of reaction time from 24 h to 72 h decreased molecular weight from 6674 to 1359, which implied that subsequent depolymerization of the formed NIPUs occurred when the reaction time was prolonged (Table 1, entry 9). Although only low molecular NIPUs were obtained in this study, to the best of our knowledge, this is the first investigation to use DAH for the preparation of NIPUs.



Scheme 3. Polyaddition of the new bis(cyclic carbonate) and hydrazine hydrate.

¹H NMR and ¹³C NMR were employed to confirm the structures of as prepared NIPUs (Figure 1 and Figure S3-S6) and the stereo-selectivity of the ring-opening polyaddition of the BCC and diamines. The results are collected in Table 1. Taking ¹H NMR spectrum of **6a-2** as an example (Table 1, entry 2), it was found that the typical chemical shifts at $\delta = 4.89$ and 4.52 ppm disappeared, which were belonged to methylene and methine protons of carbonate groups. Meanwhile, two distinct chemical shifts appeared at 5.09 and 3.53 ppm which would be attributed to the protons of newly formed primary and secondary hydroxyl groups, respectively. Besides, the ¹H NMR spectrum of **6a-2** also exhibited the characteristic chemical shifts derived from the protons of amines at $\delta = 7.13$ -7.06, 2.92 and 1.34-1.20 ppm, which are consisted with the structural information in previous publications.^{7, 8, 46} In the ¹³C NMR spectrum of **6a-2** the chemical shifts at $\delta = 29.8$ and 26.4

ppm could be assigned to the new formed carbons of carbamide (Figure 1). Similar results can be found in the ^1H NMR and ^{13}C NMR spectra of NIPUs prepared from IPDA and DAH. In the case of DAH, the ^1H NMR spectrum also showed chemical shifts of the methylene and methine protons of carbonate groups, indicating the BCC was not completely converted to NIPUs, which is consistent with the FT-IR results.

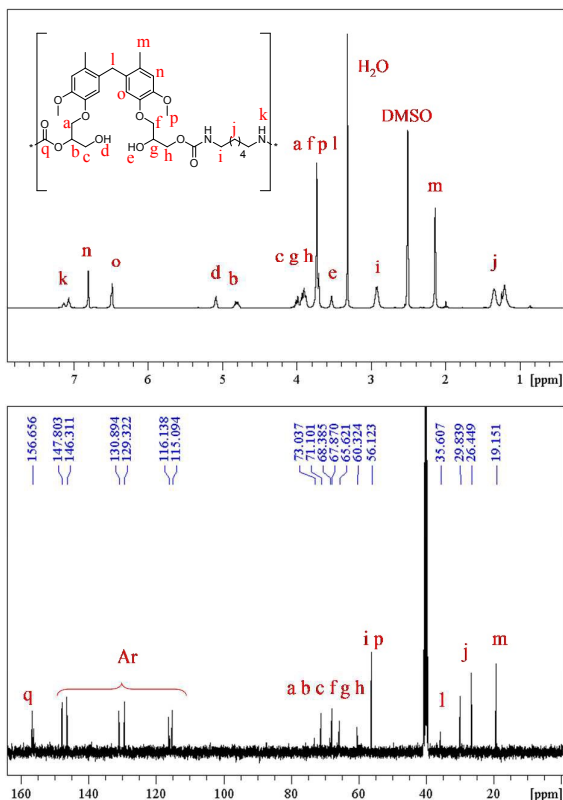


Figure 1. ^1H NMR and ^{13}C NMR spectra of **6a-2** (Table 1, entry 2)

The results of NMR also indicated that the BCC had been successfully converted to NIPUs *via* ring-opening polyaddition through two routines resulting in primary and secondary hydroxyl groups. The formation ratios of the primary OH and secondary OH were determined by the ^1H NMR integration ratio at 5.09 and 3.53 ppm according to the previous publications.^{7,47} To illustrate the reaction pathway, we firstly carried out the model ring-opening reaction between BCC and *n*-butyl amine in DMSO with initial concentration of 1 M at 25 °C for 24 h in the absence of catalyst. The result indicated that the ratio of primary and secondary hydroxyl group was 32 : 68, which was in quite agreement with the literature.^{7,8,48} It has been demonstrated that the electron-withdrawing group (PhOCH_2) would stabilize the transition state but more efficiently for the secondary hydroxyl group structure.⁸ Besides, the NIPUs with secondary hydroxyl groups are more stable than that containing primary hydroxyl groups.⁴⁸ Obviously, our model reaction was thermodynamic control. However, when three kinds of diamines were employed to

prepare NIPUs the obtained NIPUs contained increased amount of primary hydroxyl groups (Table 1). These results indicated that the polymerization between BCC and diamines was faster than the model reaction thus switching the reaction from thermodynamic control to kinetic control.⁴⁹ Furthermore the NIPUs obtained from HMDA showed higher amounts of primary hydroxyl group than those from IPDA and DAH, which would be originated from the higher reactivity of HMDA than IPDA and DAH as evidenced by ^1H NMR and FT-IR results.

The structures of NIPUs were also confirmed by FT-IR as illustrated in Figure 2. After polyaddition with HMDA the typical carbonyl group vibration of **4** at 1794 cm^{-1} completely disappeared. New peaks appeared at 3363 and 1712 cm^{-1} , which were corresponding to hydroxyl groups and the carbonyl absorption of the urethane groups, respectively.²¹ However, both NIPUs synthesized from IPDA and DAH showed weak vibration at 1794 cm^{-1} which were in accordance to their ^1H NMR results.

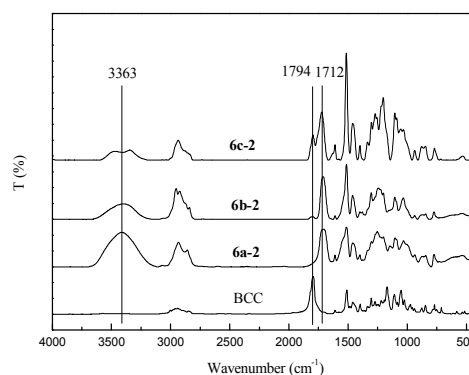


Figure 2. FT-IR spectra of bis(cyclic carbonate) and NIPUs

The thermal properties of as-prepared NIPUs were examined by TGA and DSC. The thermal decomposition analysis was carried out under nitrogen from 40 to 700 °C and the evaluated data are presented in Table 2. These NIPUs showed high thermal stability with the initial decomposition temperature ($T_d = 5\%$) in the range of 244 and 308 °C, and the maximum degradation rate was between 366 and 376 °C, which mainly depend on the structure of NIPUs. NIPUs derived from HMDA possessed higher initial decomposition temperature than those derived from IPDA and DAH, which may originate from the higher M_n and the longer space length.⁵⁰ Although NIPUs with higher M_n was obtained in the presence of TBD, the thermal stability decreased to some degree as evidenced by the decreased T_d and T_{dmax} . It is reasonable to assume that the possible TBD residual in the **6a-2** would accelerate the degradation process *via* nucleophilic attack of the polymer backbone led to the lower thermal stability.⁵¹ The DSC results indicated that the T_g was largely determined by the chemical structure of NIPUs. For example the HMDA based NIPUs in this study has a T_g over 60 °C, and IPDA based NIPUs has a T_g at 90 °C, and DAH based NIPUs has a T_g at 44 °C. In

contrast, the traditional bisphenol A diglycidyl ether and HMDA derived NIPU has a low T_g of 34 °C.¹¹ The solubility of the as-prepared NIPUs in traditional solvents is one of important properties that need to be considered during their subsequent applications. The results show that the NIPUs are insoluble in water and are soluble in DMSO, DMF and THF despite the extra pendent hydroxyl group in the side chain comparing with traditional PUs.

Table 2. Thermal properties of NIPUs

Sample code	T_d 5% °C	T_d 10% °C	T_d max °C	T_g °C	T_m °C
6a-1	308	321	371	60	—
6a-2	256	283	366	61	—
6a-3	308	321	371	63	—
6b-2	244	277	374	90	149
6c-2	244	272	376	44	—

Further WXR D analysis of the as-prepared NIPUs demonstrated that the HMDA based NIPUs are amorphous, and some content of crystalline detected in the case of IPDA based NIPU, which is consisted with the DSC results (Figure S10). Although some content of crystalline detected in the case of DAH based NIPUs, T_m was not detected, and the possible reason is still unclear at the early stage of this study.

Conclusions

In summary, novel lignin/glycerol-based polyurethanes were prepared via the corresponding bis(cyclic carbonate) intermediate without utilization of toxic isocyanates. The lignin-derived bisphenols-glycerol-HMDA based polyurethane has higher T_g than that of traditional BPA-glycerol-HMDA based NIPUs. The integrated use of biobased feedstocks and CO₂ via atom economic reaction and green catalysis for polyurethanes synthesis outlined a good example in sustainable polymer chemistry with low carbon footprint.

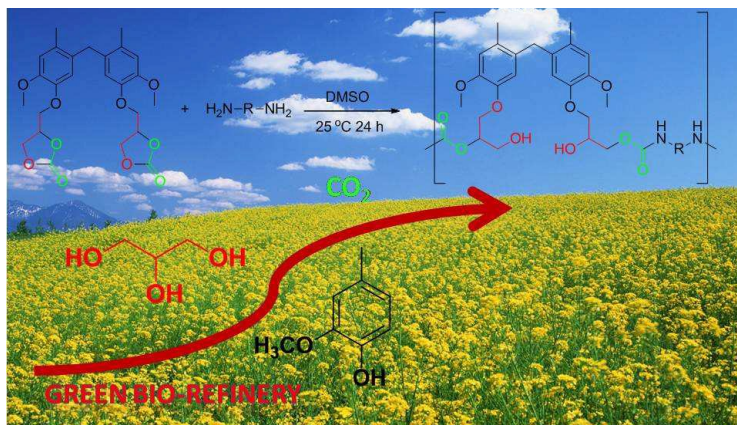
Notes and references

- V. K. Thakur, M. K. Thakur, P. Raghavan and M. R. Kessler, *Acs Sustain. Chem. Eng.*, 2014, **2**, 1072-1092.
- R. Mülhaupt, *Macromol. Chem. Phys.*, 2013, **214**, 159-174.
- H. Blattmann, M. Fleischer, M. Bähr and R. Mülhaupt, *Macromolecular Rapid Communications*, 2014, **35**, 1238-1254.
- J. J. Bozell and G. R. Petersen, *Green Chemistry*, 2010, **12**, 539-554.
- A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484-489.
- H.-W. Engels, H.-G. Pirkel, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann and J. Dormish, *Angew. Chem.*, 2013, **52**, 9422-9441.
- H. Tomita, F. Sanda and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, **39**, 851-859.
- H. Tomita, F. Sanda and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 2001, **39**, 3678-3685.
- I. Javni, D. P. Hong and Z. S. Petrović, *J. Appl. Polym. Sci.*, 2008, **108**, 3867-3875.
- O. L. Figovsky and L. D. Shapovalov, *Macromolecular Symposia*, 2002, **187**, 325-332.
- N. Kihara and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 1993, **31**, 2765-2773.
- J. Guan, Y. Song, Y. Lin, X. Yin, M. Zuo, Y. Zhao, X. Tao and Q. Zheng, *Industrial & Engineering Chemistry Research*, 2011, **50**, 6517-6527.
- R. A. Holser, *J. Oleo Sci.*, 2007, **56**, 629-632.
- A. Boyer, E. Cloutet, T. Tassaing, B. Gadenne, C. Alfos and H. Cramail, *Green Chemistry*, 2010, **12**, 2205-2213.
- K. M. Doll and S. Z. Erhan, *Green Chem.*, 2005, **7**, 849-854.
- B. Tamami, S. Sohn and G. L. Wilkes, *J. Appl. Polym. Sci.*, 2004, **92**, 883-891.
- M. Bahr and R. Mülhaupt, *Green Chemistry*, 2012, **14**, 483-489.
- G. Prompers, H. Keul and H. Hocker, *Des. Monomers Polym.*, 2005, **8**, 547-569.
- D. M. Fidalgo, A. A. Kolender and O. Varela, *J. Polym. Sci. A*, 2013, **51**, 463-470.
- V. Besse, R. Auvergne, S. Carlotti, G. Boutevin, B. Otazaghine, S. Caillol, J. P. Pascault and B. Boutevin, *React. Funct. Polym.*, 2013, **73**, 588-594.
- M. Baehr, A. Bitto and R. Muelhaupt, *Green Chemistry*, 2012, **14**, 1447-1454.
- M. Fleischer, H. Blattmann and R. Mülhaupt, *Green Chemistry*, 2013, **15**, 934-942.
- J. Dai, S. Ma, Y. Wu, L. Han, L. Zhang, J. Zhu and X. Liu, *Green Chem.*, 2015, **17**, 2383-2392.
- Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energ. Environ. Sci.*, 2013, **6**, 994-1007.
- Q. Song, F. Wang and J. Xu, *Chem. Commun.*, 2012, **48**, 7019-7021.
- H. A. Meylemans, T. J. Groshens and B. G. Harvey, *Chemsuschem*, 2012, **5**, 206-210.
- Q. Chen, W. Huang, P. Chen, C. Peng, H. Xie, Z. K. Zhao, M. Sohail and M. Bao, *Chemcatchem*, 2015, **7**, 1083-1089.
- H. A. Meylemans, B. G. Harvey, J. T. Reams, A. J. Guenther, L. R. Cambrea, T. J. Groshens, L. C. Baldwin, M. D. Garrison and J. M. Mabry, *Biomacromolecules*, 2013, **14**, 771-780.
- M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem.*, 2007, **46**, 4434-4440.
- P. Krafft, P. Gilbeau, B. Gosselin and S. Claessens, WO2005/054167 2013.
- M. McCoy, *Chem. Eng. News.*, 2006, **84**, 7-8.
- D. Siano, E. Santacesaria, V. Fiandra, R. Tesser, G. Di Nuzzi, M. Di Serio and M. Nastasi, WO2006111810, 2006.
- A. S. Voisin-Chiret, M.-A. Bazin, J.-C. Lancelot and S. Rault, *Molecules*, 2007, **12**, 2533-2545.
- S. Ore and O. G. Tjugum, *Acta Chem. Scand.*, 1970, **24**, 2397-2407.
- L. Guo, C. Wang, X. Luo, G. Cui and H. Li, *Chem. Commun.*, 2010, **46**, 5960-5962.

36. J.-Q. Wang, K. Dong, W.-G. Cheng, J. Sun and S.-J. Zhang, *Catal. Sci. Technol.*, 2012, **2**, 1480-1484.
37. M. North and R. Pasquale, *Angew. Chem.*, 2009, **48**, 2946-2948.
38. J. Sun, S. Zhang, W. Cheng and J. Ren, *Tetrahedron Lett.*, 2008, **49**, 3588-3591.
39. Z.-Z. Yang, L.-N. He, C.-X. Miao and S. Chanfreau, *Adv. Synth. Catal.*, 2010, **352**, 2233-2240.
40. C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228-1231.
41. M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, **15**, 3083-3090.
42. C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij and M. A. Pericas, *Green Chem.*, 2014, **16**, 1552-1559.
43. G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375-1389.
44. C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032-2038.
45. V. Calo, A. Nacci, A. Monopoli and A. Fanizzi, *Organic Letters*, 2002, **4**, 2561-2563.
46. B. Ochiai, S. Inoue and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 2005, **43**, 6613-6618.
47. R.-j. Wei, X.-h. Zhang, B.-y. Du, Z.-q. Fan and G.-r. Qi, *RSC Advances*, 2013, **3**, 17307-17313.
48. A. Steblyanko, W. Choi, F. Sanda and T. Endo, *Journal of Polymer Science Part A: Polymer Chemistry*, 2000, **38**, 2375-2380.
49. B. Ochiai, S. Inoue and T. Endo, *J. Polym. Sci. A*, 2005, **43**, 6282-6286.
50. X. Sheng, G. Ren, Y. Qin, X. Chen, X. Wang and F. Wang, *Green Chem.*, 2015, **17**, 373-379.
51. C. N. Tang, H. B. Nulwala, K. Damodaran, P. Kaur and D. R. Luebke, *Journal of Polymer Science Part a-Polymer Chemistry*, 2011, **49**, 2024-2032.

Graphical Abstract

**Preparation of lignin/glycerol-based bis(cyclic carbonate)
for synthesis of polyurethanes**



A bis(cyclic carbonate) was obtained via glycidylation of lignin-based bisphenol followed by cycloaddition with CO₂. Further polyaddition between the bis(cyclic carbonate) and diamines led to synthesis of polyurethanes. The structure and thermal properties of these polyurethane materials were elucidated by NMR, FT-IR, GPC, XRD, TGA and DSC.