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.
Rapid synthesis of diol homologs-based thermosets with tunable properties via ring-opening metathesis polymerization

Liuyang Zhang, Fei Huangfu, Wanrong Li and Po Yang*

This work aims to generate diols into thermosets with tunable properties. A series of diols-derived monomers have been synthesized and characterized. After mixing with second-generation Grubbs’ catalyst, these liquid monomers polymerize completely in two minutes to form cross-linked structures, which benefit to rapid manufacture of composites. These diol homologs-based thermosets have good thermal properties and mechanical properties, and their performance can be greatly enhanced by fabricating woven flax fibers composites. We believe these may help researchers design and explore novel promising sustainable diols-based polymers and materials with excellent properties.

Introduction

Thermosets, e.g., (for instance, phenolic resins, epoxy resins, and benzoxazines) have attracted extensive interest in scientific and industrial communities as the fascinating properties like good thermal stability and chemical resistance.1-3 Nevertheless, some disadvantages such as brittleness and tedious polymerization process limit their application. Obviously, more thermosets with tunable properties are desirable and valuable.

On the other hand, bio-based polymers and materials have become terrifically popular.4-8 This is caused by intensified environmental awareness as well as the desire to substitute dwindling fossil resources with sustainable alternatives.9-12 A promising approach is to synthesize thermosets using sustainable or bio-based compounds (for instance, diols, isosorbide and furan) as feedstocks.13-15 α,ω-diols (diols, for instance, ethylene glycol, 1,3-propanediol, 1,4-butanediol and 1,5-pentanediol) can be gotten from biomass by microbial fermentation, hydrolysis and hydrogenolysis.16-18 As an abundant source of biomass compounds, diols are used as feedstock for the synthesis of bio-based thermosets, like polyurethanes and epoxy resins.19-21 Synthesis of these thermosets, nonetheless, requires a lot of energy which produces lots of CO₂ and NOx due to the complex and tedious process.22 For example, diols-based epoxy resins need to be cured at 140 °C (1 h) and 180 °C (1 h)23, and polyurethane also takes several hours to cure 21, 24. In addition, these thermosets in general do not perform well.25, 26 Consequently, there has been still much interest in converting diols to thermosets with less energy, reducing their cost and environmental impact and furthering their application.

Ring-opening metathesis polymerization (ROMP) is a remarkable tool to rapidly generate cyclic olefins into acyclic dienes resulting in the formation of polymeric materials.27 Thanks for ROMP, numerous polymers and polymeric materials like biomedical functional materials, ion exchange membranes, photoresist and photoinitiated polymers, were synthesized easily.28-34 With the aid of frontal polymerization technique, ROMP was also applied to rapid manufacture high-performance cross-linked polymers and materials.35 If converting diols to cyclic olefins moiety-containing monomers, therefore, it will generate diols into polymers or polymeric materials via ROMP, which benefit to reduce the energy and environment and their application.

This work hence attempts to synthesize diol homologs-based thermosets and prepare composites via ROMP. Because the driving force of ROMP is the release of strain in ring structures, norbornene-functionalized monomers can polymerize quickly in the presence of Grubbs’ catalysts.36 To rapid synthesis of diol homologs-based thermosets, this contribution got a series of dinorbornenyl-diols-derived monomers from 5-norbornene-2-carboxylic acid and diols, namely, ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol and 1,10-decanediol. Thorough investigation showed that these monomers can generate into cross-linked polymers in two minutes via ROMP. And the monomers, dinorbornenyl-pentanediol and dinorbornenyl-decanediol based esters, can also be applied to prepare composites rapidly using vacuum-assisted resin-transfer molding (VARTM) technique. According to the results, diol homologs-based thermosets exhibit good properties and are fit for rapid fabricating composites, and so we developed new diols-based thermosets. Details analysis and discussions are provided below.
Diols-based thermosets were synthesized from the corresponding monomers. The GC2 solution was freshly made as described previously in ref.\textsuperscript{15} and then added to the monomers. After thoroughly mixing and rapidly transferring to PTFE mold, the monomers were polymerized at 180 °C for 2 minutes.

**Preparation of composites**

This work used five sheets of dry woven flax fibers to prepare the composites through vacuum-assisted resin-transfer moulding (VARTM) technique (Fig. S10). The formation of liquid resins is GC2/phosphite solution and NB5 or NB10. A low vacuum (-0.95 MPa) was applied to infuse the resins and compact the layup for producing the composites. After that, the layup was moved into an air oven at 180 °C for 2 minutes.

**Characterization**

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet-560 spectrometer in the range 4000–400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Bruker TD-6536 NMR (400 MHz) using CDCl\(_3\) as solvent and tetrakis(trimethylsilyl) methane as internal standard. Differential scanning calorimetry (DSC) tests were conducted using DSC Q20 (TA Instruments) at a heating rate of 10 °C/min under a constant nitrogen flow (50 mL/min). Dynamic mechanical analysis (DMA) measurements were performed using a TA Instruments DMA Q800 at 1 Hz in three-point bending mode. Specimens, 30 mm × 10 mm × 2 mm (length × width × thickness) were analyzed at a heating rate of 5 °C/min under nitrogen. Thermal gravimetric analysis (TGA) was performed with a TGA 4000 (Perkin Elmer) at 1 Hz in three-point bending mode. Specimens, 30 mm × 10 mm × 2 mm (length × width × thickness) were analyzed at a heating rate of 5 °C/min under nitrogen. Thermal graviometric analysis (TGA) was performed with a TGA 4000 (Perkin Elmer) under nitrogen atmosphere from 40 to 500°C at a heating rate of 10 °C/min. Tensile testing was conducted using an Instron 5967 with a 30 kN load cell. The dog-bone specimens were tested following ISO standard 8256 type 1BB dimensions. Tests were performed at a crosshead speed of 2 mm/min. We calculate tensile modulus over a range of load from 2N to 18N.

**Results and Discussion**

All diols-based thermosets were synthesized as Fig. 1 shown, that is, synthesis of diols-dinorbornenyl-derived monomers and polymerization of the corresponding monomers. All the monomers (i.e., NB2, NB3, NB4, NB5, NB6, NB7, NB8, NB9 and NB10) were synthesized from 5-Norbornene-2-carboxylic acid and diols, and the detailed syntheses were given in Supplementary Information. After getting these monomers, this work focused on whether these monomers could be rapidly polymerized completely in the presence of GC2. We firstly used DSC to study the polymerization behaviors of the diols-derived monomers. After mixing with GC2 (50 ppm per norbornenyl double bond), the resins were probed by DSC, Fig. S1.

As can be seen from the DSC curves, all the exothermic peaks were single peaks and appeared below 100 °C. These indicated
that these monomers can polymerize at low temperature. The measured exothermic peak temperatures and the amount of heat released ($\Delta H_P$) were respectively plotted in Fig. 1 (a) and (b). According to Fig. 1 (a), a little variation was observed in exothermic peak temperatures which located at ~72 $^\circ$C. For the amount of heat released, $\Delta H_P$ increased as alkyl chain lengths of diols increasing. For example, the $\Delta H_P$ of NB2, NB5 and NB9 were successively 58.2 kJ/mol, 70.4 kJ/mol and 75.4 kJ/mol. Whereas, the $\Delta H_P$ of NB10 decreased compared to NB9. Steric structures affect the polymerization, since driving force of ROMP is the release of strain in ring structures.36 In this work, steric structures were present in the yield monomers, namely, endo- and exo- diols-derived monomers. This is because there is the combination of isomers (endo- and exo-) in the starting material, 5-norbornene-2-carboxylic acid. To understand the effect of steric structures on polymerization, the ratios of endo- and exo- monomers were calculated by $^1$H NMR and eqns S-1 and S-2. All monomers exhibited a similar ratio of ~70/30, implying the steric structures had little influence on the polymerization. Diffusion and concentration of monomers also affect polymerization, therefore, the polymerization behaviors of diols-based monomers varied as the flexible alkyl bridge structures of diols altered.38-40

As mentioned previously, this contribution focused on rapid synthesis of diols-based thermosets, and we synthesized these thermosets at 180 $^\circ$C for 2 minutes. New issue hence introduced as: whether diols-derived monomers polymerize completely under the current process? This was investigated by detecting the heat released of diols-based thermosets using DSC, and the curves were shown in Fig. S2. As can be seen, no obvious exothermic peaks were observed, probably suggesting diols-derived monomers polymerize completely.

To better explore the polymerization, a control, methyl 5-nornorborne-2-carboxylate (NB-Me) was synthesized. And its polymer, PNB-Me, was also synthesized at 180 $^\circ$C for 2 minutes. DSC (Fig. S3), FTIR (Fig. 3(a)), $^1$H NMR (Fig. S4) and GPC (Fig. S5) confirmed that NB-Me polymerized completely. In the case of $^1$H NMR, for example, cyclic double bond of NB-Me located at 5.92-6.18 ppm41,42 disappeared, and the resonances of acyclic double bonds appeared at 5.33 ppm after polymerization. For FTIR, the bands corresponding to $=$C-H stretching vibration (3142 and 3061 cm$^{-1}$) and cyclic C=C stretching vibration (1625 and 1571 cm$^{-1}$) of NB-Me disappeared, and new absorption by $=$C-H out-of-plane rocking vibration was observed at 970 cm$^{-1}$ in PNB-Me.43,44 With the aid of this control, polymerization behaviors of diols-derived monomers were explored by FTIR (Fig. S6). For these monomers, the peaks located at ~3128 and ~3060 cm$^{-1}$ corresponding to $=$C-H stretching vibration, and ~1632 and ~1570 cm$^{-1}$ assigned to cyclic C=C stretching vibration disappeared after polymerizing, while the new absorption by $=$C-H out-of-plane rocking vibration was observed.
Interestingly, it is difficult to probe the crosslinked polymers based thermosets, Fig. S7. The data gained from DMA were collected and listed in Table 1. The $T_g$ values of these thermosets exceed 100 °C. And PNB2, PNB3, PNB4 and PNB5 were close in $T_g$, but higher than those of PNB6, PNB7, PNB8, PNB9 and PNB10. This is probably caused by the crosslink density which paly an important role in the performance.

To prove the view, an equation from the statistical theory of rubbery elasticity was applied to estimate the crosslink densities.\textsuperscript{45, 46} This equation can be expressed as

$$\rho = \frac{E'}{3RT}$$

where $E'$ is the storage modulus at 40 K above $T_g$, $T$ is $T_g + 40$ K. $R$ is the universal gas constant, 8.314 J/(mol·K). The crosslink densities of diols-based thermosets were calculated and shown in Table 1. As can be seen, crosslink densities were roughly consistent with the variety of the $T_g$ values. Crosslink densities of PNB2, PNB3, PNB4 and PNB5 were higher than those of PNB6, PNB7, PNB8, PNB9 and PNB10. These might be contributed to the alkyl bridge structures of diols.

In order to assess mechanical properties of these diols-based thermosets, tensile properties were measured, Fig. S8. The results were summarized and plotted in Fig. 4. As can be seen, all the thermosets’ tensile strength exceeded 20 MPa, and PNB4 exhibited the best tensile strength (28.2 MPa). For Tensile modulus, all these polymers were over 430 MPa, among which PNB3 has the best performance of 655 MPa. In addition, all these polymers showed elongation at break in the range of 7%-12%, implying the good toughness. These suggested that diols-based thermosets have good mechanical properties.

Thermal stability of the diols-based thermosets was analyzed by thermogravimetric analysis (TGA). The TGA thermograms were shown in Fig. S9, and the data obtained from TGA were listed in Table 2. The 5% and 10% weight loss temperature respectively exceed 198 and 240 °C, suggested these thermosets have good stability and can be widely applied.

Due to good mechanical properties, thermal stability and chemical resistance, thermosets are suitable for using as matrix of composite components. Diols-derived thermosets can be the candidate of the matrix for composites, this work hence also attempted to fabricate composites. In the case of traditional processing, the manufacture of thermoset components requires the monomer to be polymerized at 180 °C for several hours.\textsuperscript{47} But this work can fabricate composites in 2 minutes through polymerizing woven flax fibers infused with the monomer solution, because diols-derived monomers can rapidly polymerize. PNB5/woven flax fibers (PNB5C) and PNB10/woven

| $T_g$ (Tan Delta) (°C) | $E'$ (298 K, MPa) | $E''$ (40 K, MPa) | $\rho$ (g/mol·m$^3$) |
|-------------------------|------------------|------------------|----------------|
| PNB2 131                | 1649             | 147              | 13.2           |
| PNB3 132                | 1499             | 122              | 11.0           |
| PNB4 129                | 1255             | 115              | 10.4           |
| PNB5 130                | 1139             | 127              | 11.5           |
| PNB6 111                | 1101             | 102              | 9.6            |
| PNB7 103                | 717              | 47               | 4.3            |
| PNB8 106                | 976              | 68               | 6.5            |
| PNB9 112                | 942              | 82               | 7.7            |
| PNB10 102               | 868              | 40               | 3.8            |
flax fibers (PNB10C) composites were manufactured through vacuum-assisted resin transfer molding (VARTM), Fig. S10.

Tensile properties of the composites were also measured, and the representative stress-strain curves were shown in Fig. 5. Tensile strength, tensile modulus and elongation at break of PNB5C were respectively 40.5 MPa, 927 MPa and 16.7%, and those of PNB10C were successively 35.3 MPa, 536 MPa and 24.4%. Compared to PNB5 and PNB10, there were great enhancements in tensile properties. These suggest that diol-based thermosets are good matrix for rapid manufacturing composites.

**Conclusions**

In summary, this work focuses on rapid manufacturing diol-based polymers and composites via ROMP. A series of diol-derived monomers were synthesized. These liquid monomers can generate into thermosets at 180 °C in 2 minutes, which benefit to fabricate composites rapidly through vacuum-flax fibers infused with the monomer solution. Diol homologs-based thermosets exhibited good thermal properties and mechanical properties, and their performance can be enhanced significantly by manufacturing woven flax fibers composites. We believe that diols-based thermosets can be widely used in many fields as a substitute for petroleum-based polymers.

**Table 2. Tensile properties of the composites**

|                | PNB5  | PNBSC | PNB10 | PNB10C |
|----------------|-------|-------|-------|--------|
| Tensile strength (MPa) | 27.3±0.9 | 40.5±2.1 | 20.1±0.5 | 35.3±1.8 |
| Tensile module (MPa)    | 648±26 | 927±60 | 469±13 | 536±43 |
| Elongation at break (%) | 7.3±1.2 | 16.7±1.3 | 8.2±0.7 | 24.4±1.8 |

**Fig. 5 Stress-strain curves of the composites.**

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

1. R. Durah and N. Karak, *Rsc Adv*, 2015, 5, 64456-64465.
2. Y. R. Xu, L. F. Guo, H. N. Zhang, H. M. Zhai and H. Ren, *Rsc Adv*, 2020, 10, 22600-22600.
3. P. Yang and Y. Gu, *J Polym Res*, 2011, 18, 1725-1733.
4. R. Hatti-Kaul, L. J. Nilsson, B. Z. Zhang, N. Rehnberg and S. Lundmark, *Trends Biotechnol*, 2020, 38, 50-67.
5. M. A. Hillmyer, *Science*, 2017, 358, 868-870.
6. D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2017, 50, 3733-3750.
7. Y. Q. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, 540, 354-362.
8. N. Teramoto, *Polymers (Basel)*, 2020, 12.
9. A. Gandini, *Macromolecules*, 2008, 41, 9491-9504.
10. A. L. Holmberg, K. H. Reno, R. P. Wool and T. H. Epps, *Soft Matter*, 2014, 10, 7405-7424.
11. R. Mulhaupt, *Macromol Chem Phys*, 2013, 214, 159-174.
12. K. J. Yao and C. B. Tang, *Macromolecules*, 2013, 46, 1689-1712.
13. S. Munoz-Guerra, C. Lavilla, C. Japu and A. M. de Ilarduya, *Green Chem*, 2014, 16, 1716-1739.
14. O. Nsengiyumva and S. A. Miller, *Green Chem*, 2019, 21, 973-978.
15. H. W. Park, M. Toan, H. J. Kim, J. H. Lee and S. Shin, *J Ind Eng Chem*, 2020, 92, 184-190.
16. G. Q. Chen and M. K. Patel, *Chem Rev*, 2012, 112, 2082-2099.
17. H. Yim, R. Haselbeck, W. Niu, C. Pujol-Baxley, A. Burgard, J. Boldt, J. Khandurina, J. D. Trawick, R. E. Osterhout, R. Stephen, J. Estadilla, S. Teisan, H. B. Schreyer, S. Andrae, T. H. Yang, S. Y. Lee, M. J. Burk and S. Van Dien, *Nat Chem Biol*, 2011, 7, 445-452.
18. J. Lu, L. B. Wu and B. G. Li, *Acs Sustain Chem Eng*, 2017, 5, 6159-6166.
19. D. Fourcade, B. S. Ritter, P. Walter, R. Schonfeld and R. Mulhaupt, *Green Chem*, 2013, 15, 910-918.
20. K. K. Tremblay-Parrado, C. Bordin, S. Nicholls, B. Heinrich, B. Donnio and L. Averous, *Macromolecules*, 2020, 53, 5869-5880.
21. H. Blattmann and R. Mulhaupt, *Green Chem*, 2016, 18, 2406-2415.
22. A. J. Timmis, A. Hodzic, L. Koh, M. Bonner, C. Soutis, A. W. Schafer and L. Dray, *Int J Life Cycle Ass*, 2018, 4510-4544.
23. F. Zia, K. M. Zia, W. Aftab, S. Tabasum, Z. I. H. Nazli, M. Mohammadi and M. Zuber, *Int J Biol Macromol*, 2020, 165, 1889-1899.
24. S. Naheed, M. Zuber, M. Barikani and M. Salman, *Mater Sci Eng B-Adv*, 2021, 264.
25. A. Gallastegui, E. Gabirondo, F. Elizalde, N. Aranburu, D. Mecerreyes and H. Sardon, *Eur Polym J*, 2021, 143.
26. J. M. Sadler, F. R. Toulan, G. R. Palmese and J. J. La Scala, *J Appl Polym Sci*, 2015, 132.
27. O. M. Ogba, N. C. Warner, D. J. O'Leary and R. H. Grubbs, *Chem Soc Rev*, 2018, 47, 4510-4544.
28. C. W. Bielawsli and R. H. Grubbs, *Progress in Polymer Science*, 2007, 32, 1-29.
29. A. E. Madkour, A. H. R. Koch, K. Lienkamp and G. N. Tew, *Macromolecules*, 2010, 43, 4557-4561.

30. J. A. Johnson, Y. Y. Lu, A. O. Burts, Y. Xia, A. C. Durrell, D. A. Tirrell and R. H. Grubbs, *Macromolecules*, 2010, 43, 10326-10335.

31. T. K. H. Trinh, G. Schrodi, S. Rigolet, J. Pinaud, P. Lacroix-Desmazes, L. Pichavant, V. Herogev and A. Chemtob, *Rsc Adv*, 2019, 9, 27789-27799.

32. R. Weitekamp, H. Atwater and R. Grubbs, *Abstr Pap Am Chem Soc*, 2015, 249.

33. C. W. Cheng, X. H. He, S. M. Huang, F. Zhang, Y. Guo, Y. F. Wen, B. Wu and D. F. Chen, *Int J Hydrogen Energy*, 2020, 45, 19676-19690.

34. I. M. Rutenberg, O. A. Scherman, R. H. Grubbs, W. R. Jiang, E. Garfunkel and Z. Bao, *J Am Chem Soc*, 2004, 126, 4062-4063.

35. I. D. Robertson, M. Yourdkhani, P. J. Centellas, J. E. Aw, D. G. Ivanoff, E. Goli, E. M. Lloyd, L. M. Dean, N. R. Sottos, P. H. Geubelle, J. S. Moore and S. R. White, *Nature*, 2018, 557, 223-226.

36. A. H. Hoveyda and A. R. Zhugralin, *Nature*, 2007, 450, 243-251.

37. J. M. Pollino, L. P. Stubbs and M. Weck, *Macromolecules*, 2003, 36, 2230-2234.

38. Y. Song, S. Zhang and P. Yang, *Thermochim Acta*, 2018, 662, 55-63.

39. Y. Bai, P. Yang, S. Zhang, Y. Q. Li and Y. Gu, *J Therm Anal Calorim*, 2015, 120, 1755-1764.

40. E. Skliutas, M. Lebedevaite, E. Kabouraki, T. Baldacchini, J. Ostrauskaite, M. Vamvakaki, M. Farsari, S. Juodkazis and M. Malinauskas, *Nanophotonics-Berlin*, 2021, 10, 1211-1242.

41. C. H. Liu, L. D. Dugas, J. I. Bowman, T. Chidanguro, R. F. Storey and Y. C. Simon, *Polym Chem-Uk*, 2020, 11, 292-297.

42. B. J. Sundell, J. A. Lawrence, D. J. Harrigan, S. B. Lin, T. P. Headrick, J. T. O'Brien, W. F. Penniman and N. Sandler, *Acs Macro Lett*, 2020, 9, 1363-1368.

43. T. J. Cuthbert, T. Li, A. W. H. Speed and J. E. Wulff, *Macromolecules*, 2018, 51, 2038-2047.

44. H. W. Thompson, D. L. Nicholson and L. N. Short, *Discuss Faraday Soc*, 1950, 222-235.

45. H. Ishida and D. P. Sanders, *J Polym Sci Pol Phys*, 2000, 38, 3289-3301.

46. L. R. G. Treloar, *The physics of rubber elasticity*, Clarendon Press, Oxford, 2d edn., 1958.

47. D. Abliz, Y. G. Duan, L. Steuernagel, L. Xie, D. C. Li and G. Ziegnman, *Polym Polym Compos*, 2013, 21, 341-348.