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A delayed curing ROMP based thermosetting resin†

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Here, we develop a heat curing thermosetting resin using ring-opening metathesis polymerization. The resin has a prolonged working time at room temperature and cures rapidly at elevated temperatures. We detail the delayed cure activity and investigate the resulting thermal and mechanical properties of the cured materials.

Polymeric materials synthesized using ring-opening metathesis polymerization (ROMP) have seen increased importance in both industry and academia due to the versatility, functionality, and unique properties which the resulting polymers possess.[1–3] Well-defined ruthenium based catalysts have proven to be some of the most powerful metathesis catalysts due to their functional group tolerance and stability in both moisture and air.[4–7] Taming the activity of these highly active catalysts, however, remains an important challenge. High-strain monomers such as dicyclopentadiene (DCPD) and norbornene (NB) are hard to control when polymerized in concentrated solution or in bulk with Grubbs 1st and 2nd generation catalysts, due to the rapid polymerization which follows.[8–11] Additionally, these monomers are solids at room temperature, which often requires heat to perform bulk polymerization, which further worsens this problem.

To combat these challenges, a substantial amount of synthetic effort has been put into designing latent metathesis catalysts.[12–16] These catalysts aim to reduce or eliminate the activity of the catalyst until a proper chemical or physical stimulus is provided. Recently, several impressive latent ROMP catalysts

have been developed which can be activated upon the addition of heat,[17–22] light,[23–28] acid,[29–31] and mechanical energy.[32,33] These catalysts, however, often require tedious preparation. Additionally, the polymerizations involve extended reaction times and occur under dilute conditions. It remains challenging to develop a bulk system which has low ROMP activity that can be rapidly activated upon the addition of a stimulus.

One simple and efficient strategy has been the use of N-donor ligands to slow the polymerization.[34] In a simple latent catalyst system developed by Schanz *et al.*, N-donor ligands such as *N*-methyl imidazole or 4-dimethyl-aminopyridine (DMAP) were utilized as additives to slow the ROMP of cyclooctene.[29] These ligands function by competing with released PCy$_3$ for binding at the ruthenium centre during propagation.[29,30] Since dissociation of these ligands is required prior to olefin binding and catalysis, the added N-donor ligands shift the equilibrium towards the ligand associated complexes and away from the active 14-electron ruthenium species. The addition of phosphoric acid, however, regenerates polymerization activity by protonating these ligands, shifting the equilibrium back towards the active 14-electron ruthenium species. While this concept is simple in principle, chemical reactivation may not be an ideal trigger since rapid polymerization can result before efficient mixing is achieved, leading to the same problems as those with the original non-latent catalyst. A physical stimulus, such as a change in temperature, may be better suited since it can be more easily controlled. We reasoned that in the DMAP based system, heat might serve as a successful trigger to drive off the PCy$_3$ or DMAP and shift the equilibrium towards the 14-electron ruthenium species (**2**), resulting in an substantially exaggerated difference in polymerization activity in hot and cold states (Scheme 1). Additionally, we desired to use this simple additive in a bulk system which could be easily crosslinked.

To test our hypothesis (Fig. 1a), we chose to utilize the dimethyl ester of norbornene (NBMe) as a model monomer. NBMe was an attractive monomer for our final application, being a liquid at room temperature allowing easy mixing and handling in bulk. Although NBMe has low metathesis activity
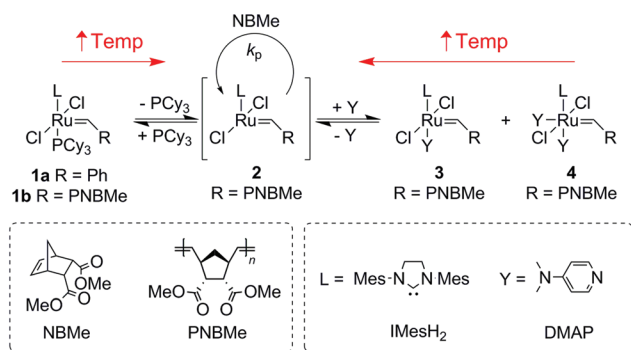
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Scheme 1 Equilibrium established during propagation in the presence of DMAP.

Fig. 1 (a) Scheme showing reduced catalytic activity of **1a** in the presence of DMAP at room temperature. (b) Conversion of NBMe in CDCl₃ monitored by ¹H NMR at various temperatures in the presence or absence of DMAP. [NBMe] = 1.0 M, [**1a**] = 2.0 mM, [DMAP] = 2.0 mM. (c) Gel time at room temperature and conversion of NBMe upon heating at 100 °C for 1 h at varying ratios of NBME, **1a**, and DMAP. Polymerizations were performed in bulk.

and requires higher temperatures or long polymerization times, it proved to be advantageous for our application as it can provide an extended time for mixing,[35,36] and has low odor, in contrast to the widely used DCPD and NB. Lastly, because of the importance of crosslinked metathesis based polymers such as poly(dicyclopentadiene) (PDCPD), we anticipated that we could incorporate a crosslinker into this liquid monomer to create a thermosetting resin. Norbornene containing polyesters synthesized through alternating polymerization with various epoxides have been previously developed in our group[37] and others,[38,39] and should serve as ideal multifunctional crosslinkers due to their easy synthesis and structural variety.

Utilizing ruthenium catalyst **1a** (Scheme 1), we first determined the extent to which DMAP was able to inhibit the polymerization of NBMe at room temperature (Fig. 1b). In the absence of DMAP, the conversion of NBMe reached over 95% conversion after 3 h with a rate constant $k_p = 0.76$ M^{-1} s^{-1} (see ESI for details†). Upon the addition of 1 equiv. DMAP relative to **1a**, an over 20 fold decrease in polymerization rate ($k_p = 3.3 \times 10^{-2}$ M^{-1} s^{-1}) resulted, with less than 15% monomer conversion after the same time period. If the temperature is increased to 55 °C, however, a rapid conversion of the monomer takes place when initiated with **1a** both in the absence ($k_p = 6.2$ M^{-1} s^{-1}) and presence of DMAP ($k_p = 3.1$ M^{-1} s^{-1}), with both polymerizations reaching completion in under 20 minutes. This demonstrates that heat can serve to recover the diminished polymerization activity of the DMAP inhibited system. Isolation of catalyst **4** and subsequent kinetic studies revealed polymerization activity that was comparable to, but slightly faster than the **1a** + DMAP system. The catalyst, however, was less stable in solution and eventually lost activity after the first 2 h under ambient conditions (ESI, Fig. S1†). The instability of **4** and the stability of **1a** + DMAP likely stem from differences in equilibrium concentration of **2**, which can react with either monomer or oxygen. Additionally, **4** was not as active as the **1a** + DMAP system at elevated temperatures, demonstrating the improved performance of the latter system (ESI, Fig. S1†).

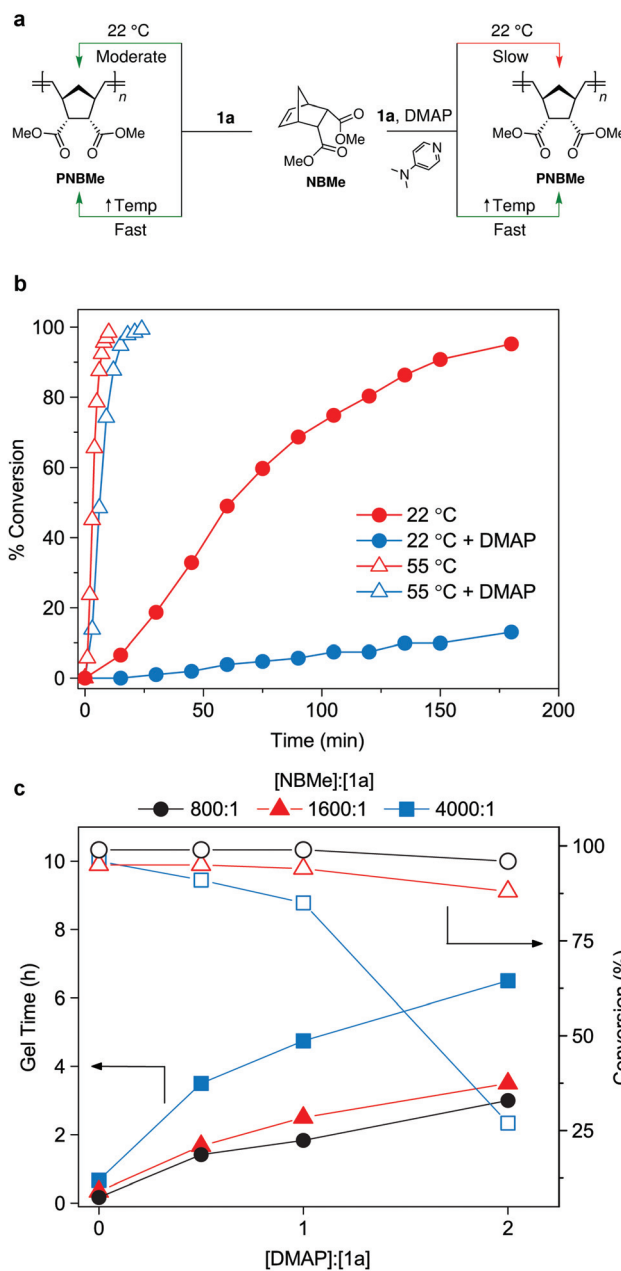Polymerization conducted in the absence of DMAP resulted in an approximately 8-fold increase in rate upon increasing the temperature from 22 °C to 55 °C. In contrast, addition of 1 equiv. DMAP resulted in a 100-fold difference in the rate between the same temperatures. This drastic difference stems from the inhibited ROMP activity of **1a** and DMAP at 22 °C, which can be understood from the dynamic equilibrium which exists between a complex mixture of species including **1a**, DMAP, and mono- and bis-DMAP coordinated ruthenium

species (Scheme 1 and ESI, Fig. S2 and S3†). During propagation, the addition of DMAP shifts the equilibrium away from the active 14-electron intermediate (**2**) and towards species **1b**, **3**, and **4**, decreasing the rate of propagation. At elevated temperatures, however, this equilibrium shifts away from the ligand associated species to account for the greater temperature sensitivity, and substantial recovery of the rate. Ligand dissociation is thermodynamically more favoured at elevated temperatures, and the equilibrium thus shifts towards species **2**, resulting in a faster propagation rate. It should be noted that species **2** cannot be observed spectroscopically as it exists transiently and in low quantity.[40] In addition to the shift in equilibrium, higher temperatures also increase the propagation rate (k_p) as well as the initiation efficiency (*vide infra*), further leading to the exaggerated temperature dependence of this catalyst system.

The final molecular weights of the polymers (PNBMe) synthesized in solution were all higher than predicted by the [NBMe] : [**1a**] ratio, which is typical of **1a** due to incomplete initiation of the catalyst.[4] The polymerization conducted at room temperature without DMAP, for instance, showed approximately 20% catalyst activation, resulting in a polymer with M_n = 503 kDa and PDI = 1.26. At 55 °C, the initiation efficiency increased to about 50%, resulting in a polymer with M_n = 204 kDa and PDI = 1.19. Adding DMAP to the polymerization at this temperature had the effect of further increasing the initiation efficiency to 70%, in agreement with the effects of other amine based ligands on **1a**.[30,41]

Due to the significant temperature dependence of the polymerization containing DMAP, it is likely that bulk reactions might also be susceptible to a delayed polymerization. Several bulk polymerizations of NBMe with varying ratios of DMAP and **1a** were performed to assess this assertion and find the optimal conditions. From the results shown in Fig. 1c, we observed that in the absence of DMAP, the gel time (defined as the time when the inverted reaction supports its own weight) for the polymerization conducted at [NBMe] : [**1a**] = 800 occurred at 10 min. The addition of 0.5 equiv. of DMAP (relative to **1a**), however, increased the gel time to 85 min. As more DMAP was added, the gel time continued to increase to 110 and 180 min for 1 equiv. and 2 equiv., respectively. In contrast, when the system was heated to 100 °C to ensure complete conversion, a rapid and complete polymerization of NBMe resulted, even in the presence of 2 equiv. DMAP. Lower catalyst loadings resulted in higher molecular weight polymers (ESI, Fig. S4†); however, conversion decreased, which is likely due to decreased diffusion upon vitrification or inactivation of the catalyst by heat, moisture, or oxygen as these polymerizations were carried out under ambient air. The condition which maximized conversion at 100 °C and resulted in the longest time to gelation at room temperature was found with [NBMe] : [DMAP] : [**1a**] = 800 : 1 : 1. These conditions were also used for the development of the thermosetting resins.

The broad utility of metathesis derived polymers which can be crosslinked, such as PDCPD, has made way for their use in several commercial applications.[42–44] Since few liquid, metathesis based thermosetting systems exist and because of the heat activated activity of this monomer/catalyst system, we found it particularly advantageous for use as a thermosetting resin.[45–47] The low MW (8.0 kDa) norbornene containing polyester NB-CL (Fig. 2a) served as an ideal crosslinking agent as it shares structural similarity with NBMe, which should enhance its incorporation into the thermoset.

Utilizing various amounts of NB-CL, we were able to successfully synthesize the crosslinked material with high gel content. This was accomplished by first heating NB-CL with liquid NBMe to aid dissolution. After cooling, a clear monomer/crosslinker mixture resulted, which was stable indefinitely (Fig. 2a). We could then add **1a** as a concentrated solution in xylenes, mix, and pour the resulting resin into a mould to cure at elevated temperature. These resin mixtures showed an elongated gelation time upon the addition of the catalyst, in analogy to the bulk polymerizations performed in the absence of the NB-CL crosslinker. For example, at room temperature, a mixture of 10 wt% NB-CL in NBMe took 50 minutes to gel, while 20 and 30 wt% NB-CL amounts took 100 and 150 minutes to gel, respectively, due to the concomitant increase in the DMAP which was conveniently loaded into the NB-CL during synthesis (see ESI for details†). The resulting cured thermosets were non-tacky, insoluble in organic solvents, and had altered thermal and mechanical properties compared to PNBMe (*vide infra*).
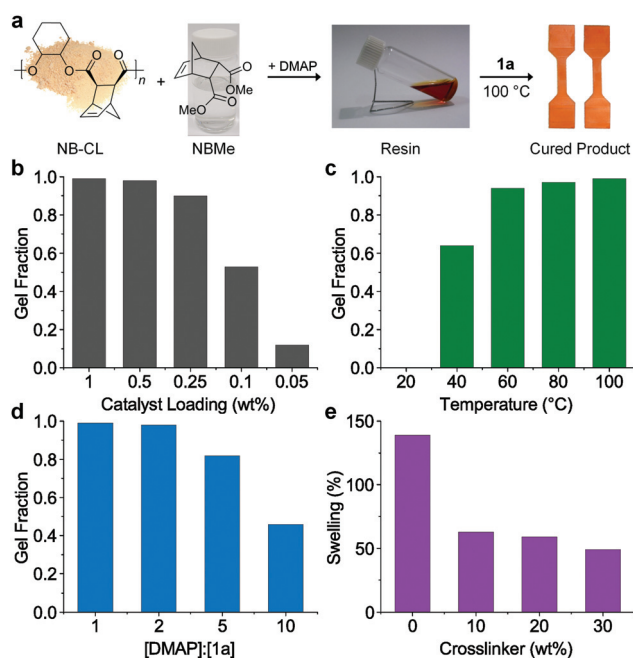

Fig. 2 (a) Synthesis scheme of crosslinked thermosetting resins. Gel fractions of 20 wt% NB-CL containing thermosets at various (b) catalyst loadings, (c) temperatures and (d) DMAP contents. (e) Swelling of thermosets in toluene after curing at 100 °C for 1 h at various NB-CL contents. All thermosets were cured for 1 h at 100 °C unless otherwise specified. DMAP content was held constant at 0.07 wt% with the exception of (d). Catalyst **1a** was loaded at 0.5 wt% when not specified.

Optimizing the loading of catalyst and cure temperature (Fig. 2b and c) revealed that curing at 100 °C for 1 h at a catalyst loading of 0.5 wt% was sufficient to achieve high gel fractions of 0.98 for the 20 wt% NB-CL containing thermosets. Decreasing the temperature or catalyst loading led to decreased cure of the thermoset due to incomplete monomer conversion, as evidenced by lower gel fractions and tacky materials. While increasing the DMAP content further did increase the gel time, it also lowered the gel fractions (Fig. 2d). We found that 1–2 equiv. DMAP relative to **1a** resulted in optimal gel fractions. The swelling of the resulting thermosets in toluene was also relatively low (Fig. 2e). Even at 10 wt% NB-CL loading, swelling reached a maximum of 63%, in contrast to the widely used PDCPD which has been reported to undergo swelling of over 300% when polymerized with **1a** at higher temperatures.[8] In addition, the viscosities of the resins are comparable to those of commercially used DCPD based liquid resins (300–1000 cP).[48] The monomer alone has a viscosity of 25 cP at 25 °C. Upon the addition of 10, 20, and 30 wt% of NB-CL, the viscosities increased to 60, 250, and 960 cP, respectively.

The degree of cure was also determined using differential scanning calorimetry (DSC). Using a temperature ramp of 10 °C min^{-1}, the energy released upon the polymerization of NBMe with **1a** was determined to be 10.5 kcal mol^{-1} (Fig. 3a), in agreement with previously determined values.[49] Assuming that the same energy is released upon polymerization of each olefin in NB-CL, we determined the percentage of olefin groups which reacted in each formulation. For the 10, 20, and 30 wt% formulations, the degree of cure was 99, 93, and 91%, respectively. Extraction of the crosslinked thermosets with chloroform and analysis by ^{1}H NMR

revealed only small amounts of NBMe and NB-CL which was not incorporated into the material. The major species extracted were xylenes used to dissolve catalyst **1a** (ESI, Fig. S5†). The decreasing degree of cure at higher NB-CL loadings is likely due to the concomitant increase in DMAP loading. This is supported by the retardation of the temperature at which the peak exotherm occurs in the DSC thermogram.

The thermal and mechanical properties of the thermosets were also measured using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) and were compared to those formed without the crosslinker (PNBMe). Analysis by TGA shows high thermal stability, with a T_d of 389 °C for PNBMe (ESI, Fig. S6 and S7†). Addition of NB-CL slightly decreased the T_d, providing a T_d of 355 °C for the 30 wt% NB-CL thermoset. The DMA analysis revealed good mechanical properties for PNBMe without the addition of NB-CL, resulting in a storage modulus (E') of 2160 MPa at 30 °C (Fig. 3b). Upon addition of NB-CL, an increase in E' was observed in accordance with increasing crosslinker amount. The addition of 30 wt% NB-CL, for example, resulted in a 26% increase in E' to 2720 MPa, compared to PNBMe alone. Additionally, increasing the NB-CL content resulted in the formation of a rubbery plateau at elevated temperatures, typical of crosslinked networks. The plateau increased upon increasing crosslinker content, suggesting good incorporation of NB-CL into the network and an increasing number of crosslinks, in line with the DSC analysis.

The glass transition of PNBMe measured by DMA occurs at 88 °C, marked by a peak in the loss modulus (E'') (Fig. 3c). Increasing the content of NB-CL continues to raise the T_g, reaching 92 °C and 95 °C for 10 wt% and 20 wt% loading of crosslinker. Higher loadings of NB-CL resulted in a slightly decreased T_g of 92 °C, possibly due to decreased conversion of the monomer (supported by DSC analysis); however, the accompanying loss tangent contains two maxima in this region (Fig. 3d). This feature is evident for all samples, including PNBMe which contains no crosslinker, at cure temperatures ranging from 100 °C to 140 °C (data not shown). Analysis of PNBMe without a crosslinker shows that the first peak occurs around 95 °C, and the second peak of higher intensity appears at 122 °C. DSC analysis of the glass transition region of PNBMe reveals an unusually broad step transition centered at 111 °C, suggesting that the true T_g may include both regions (ESI, Fig. S8†). Literature reports on analogously prepared PNBMe, however, resulted in a T_g of 156 °C.[49] This appears to be due to differences in thermal history of the PNBMe. Subjecting PNBMe to a higher maximum temperature of 300 °C and measurement of the T_g again had the effect of narrowing and raising the T_g to 138 °C (ESI, Fig. S8†). Additional DMA experiments confirmed an increase in T_g when running the sample through two heating cycles with a maximum temperature of 175 °C (ESI, Fig. S8†). When this doubly heated sample was analyzed by GPC and ^{1}H NMR, no changes were observed (ESI, Fig. S9 and S10†), suggesting the absence of further reaction or chemical alteration of the sample, and instead, the
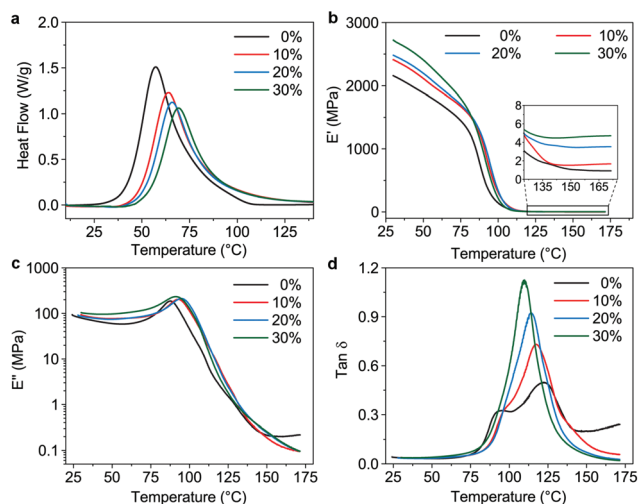

Fig. 3 (a) DSC scan showing the exotherm released upon polymerization of bulk NBMe with varying amounts of NB-CL in the presence of 0.5 wt% **1a** at a heating rate of 10 °C min^{-1}. (b) Storage modulus, (c) loss modulus, and (d) loss tangent of cured PNBMe based thermosets containing varying amounts of NB-CL cured with 0.5 wt% **1a**. The DMA was operated at a heating rate of 3 °C min^{-1} in tension mode.

added thermal energy may alter the packing of the polymer in the solid state. This phenomenon undoubtedly complicates the thermal analysis of these polymers and warrants further investigation.

Conclusions

In summary, we have devised a delayed curing ROMP based thermosetting resin using NBMe as a monomer, DMAP as a polymerization inhibitor, and a norbornene containing polyester (NB-CL) as a crosslinker. These materials can be formed under ambient air at reasonable temperatures and have high gel contents, forming thermosets with mechanical properties that rival those of widely used ROMP based thermosets such as PDCPD. The ability to further tune the properties of this polymer system through both the structure of the liquid monomer and the polyester crosslinker should enable similar materials to be created, providing access to new potentially commercially relevant ROMP based thermosets.

Acknowledgements

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