Ring-Opening Metathesis Polymerization for the Synthesis of Terpenoid-Based Pressure-Sensitive Adhesives

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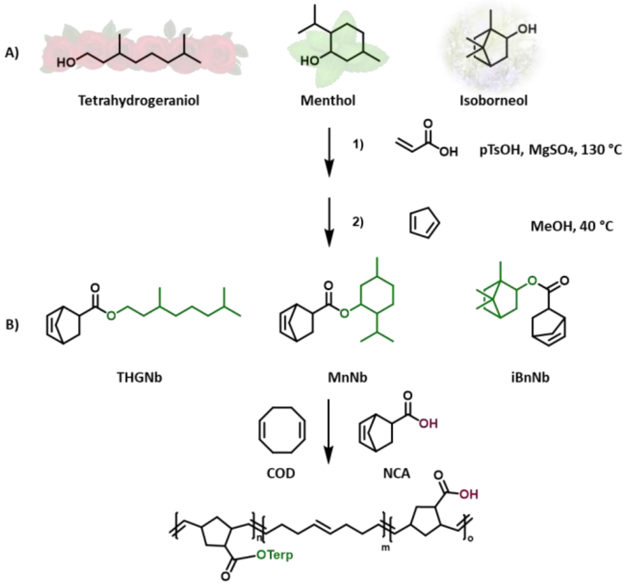
ABSTRACT: Pressure-sensitive adhesives (PSAs) made from norbornene-functionalized terpenoid-based monomers are reported as a possible alternative to the conventional petrochemically-based PSAs. For this, tetrahydrogeranyl-, menthyl- and isobornyl norbornenate monomers, with a renewable carbon content up to 72%, are synthesized and copolymerized via ring-opening metathesis polymerization (ROMP) with cyclooctadiene and 5-norbornene-2-carboxylic acid. ROMP enables a much faster and controlled polymerization process in comparison to free radical polymerization techniques when targeting high molecular weights, and therefore unlocks a potential to design a unique class of PSA materials. The moduli at bonding and debonding frequencies of the obtained PSAs are plotted in the Chang classification system and are used to predict their adhesive performance. Tack and peel measurements indicate that the terpenoid-based norbornenate formulations show similar adhesive properties in comparison to the previously investigated acrylic counterparts.

Pressure-sensitive adhesives, indispensable in industry and our daily lives, are soft viscoelastic materials that can instantly adhere to surfaces when a mild pressure is applied and that can be easily removed without leaving any residual adhesive.[1–3] Commercial PSAs often contain acrylic[4] or styrene-butadiene-based block copolymers[5] with varying formulations, depending on the desired application. So far, the majority of PSAs are still derived from petrochemicals. Nevertheless, replacing fossil resources with renewable feedstocks has been a major focus in academic and industrial research labs due to limitations in crude oil reserves and an increased demand for bio-based products as a result of increasing public awareness.[6–10] The adhesives sector and more particularly the one of PSA, is therefore seeking for an increased sustainability, both in resources and processes, without compromising the properties of the end products.[11] As a result of this rising interest, renewable building blocks based on plant oils,[2,12–14] starch,[15,16] lignin,[17,18]terpenes[19,20] or a combination thereof[21] have been investigated during the last decade. Recently, we reviewed the field of bio-based acrylic PSAs elsewhere.[22]

Terpenes and their terpenoids subclass have been of keen interest for PSAs due to their wide availability and monomer variety.[23–25] The large structural diversity of terpenoids allows to tune the glass transition temperature (T_g) of the resulting PSA copolymers and subsequently their adhesive performance, independent of the dispersity.[26] In a given formulation, different adhesive properties can be obtained by altering the ratio between so-called high T_g- and low T_g monomers, which induce flowing and wetting of the substrate, respectively.[3,27] In this way, a temperature window for the adhesive application can be targeted by employing a range of different monomers.

Acrylic PSAs from terpenes have been reported, through the use of low T_g tetrahydrogeranyl acrylate (THGA), combined with high T_g isobornyl or menthyl acrylate.[28,29] Optically clear PSAs were obtained via UV-light triggered photo-copolymerisation in bulk. Menthide has been copolymerized with lactide via sequential ring-opening polymerisation to obtain renewable PSAs that are hydrolytically degradable.[30] Furthermore, β-pinene was cationically copolymerized with a Lewis acid in a range of molecular weights, to be incorporated as a tackifier in triblock copolymer-based PSAs.[31] Noppalit et al. prepared block copolymers by copolymerising THGA with styrene via reversible addition-fragmentation chain-transfer (RAFT) polymerisation.[32] By employing this technique, it was shown that the length of the blocks allowed to tune the adhesion-cohesion balance. More recently, sustainable terpene triblock copolymers with varying properties were synthesized *via* RAFT using α-pinene methacrylate and butylacrylate.[33]

In other words, numerous (controlled) chain growth polymerisation techniques can be used in combination with terpenes for the design of PSAs. On the other hand, while ROMP allows for ultra-fast synthesis of high molecular weight polymers on a multigram scale,[34] the direct ring-opening metathesis polymerization (ROMP) of terpenes is currently limited to δ-pinene,[35] apopinene[36], caryophyllene[37] and humelene[38]. These cyclic monomers carry a certain amount of ring strain, which makes direct ring-opening metathesis possible to obtain low dispersity polyterpenes with molecular weights up to 20 kDa.



Scheme 1. A) The chemical structures of the terpenoids tetrahydrogeraniol, menthol and isoborneol and the structures of the corresponding norbornenate monomers after their reaction with acrylic acid and cyclopentadiene. B) The copolymerization in solution with Grubbs 3rd generation catalyst, 1,5-cyclooctadiene (COD) and 5-norbornene-2-carboxylic acid (NCA).

Tang and coworkers modified rosin acid, a resin of pine and conifer trees, with a norbornene ring, which was polymerizable *via* ROMP to obtain bio-based, tough multiblock copolymers with low dispersity.[39,40] In short, functionalising terpenes or terpenoids into the corresponding norbornenates allows for a fast and controllable polymerisation.

The limited amount of reports covering renewable resources in combination with ROMP, opens up possibilities for various lines of research. In the area of PSAs, only one specific report[41] could be found where ROMP has been applied as the polymerisation technique, in combination with a photoiniferter polymerization. In this work, the synthesis of terpene-based norbornene monomers and their copolymerization *via* ROMP in combination with cyclo-1,5-octadiene (COD) and 5-norbornene-2-carboxylic acid (NCA) will be described. The copolymers have been investigated by means of their rheological properties for PSA-application. Additionally, the monomer to initiator ratio will be altered to investigate the tunability of the viscoelastic properties of the corresponding PSA materials. Finally, it will be investigated if PSAs with viscoelastic properties in a closer range to those of a commercial acrylic PSA can be obtained by blending two copolymers with different molecular weights.

To ensure a good wettability onto a substrate, PSA mostly have a low T_g (between -5°C and -60°C). Therefore the composition of the PSA formulations mainly consists of low T_g monomers (70-90%), combined with a smaller amount of high T_g monomers (10-30%) and often a small percentage of a polar functional monomer (e.g. a carboxylic acid group), to improve the PSA properties.[42,43] In the search for more sustainable PSAs, we have chosen three specific, readily available terpenoid compounds because they are easily modified thanks to the presence of a hydroxyl group: tetrahydrogeraniol, menthol and isoborneol (Scheme 1). Tetrahydrogeraniol was chosen because of its flexible aliphatic chain, inducing a low T_g to the corresponding polymer, whereas menthol and isoborneol were introduced to finetune the T_g and the resulting PSA properties. The former terpenoid monomers were modified with a norbornene functionality in a two-step process on a scale of 20 g (Scheme 1), to allow for rapid and controllable ROMP with a Grubbs 3rd generation catalyst.[44]

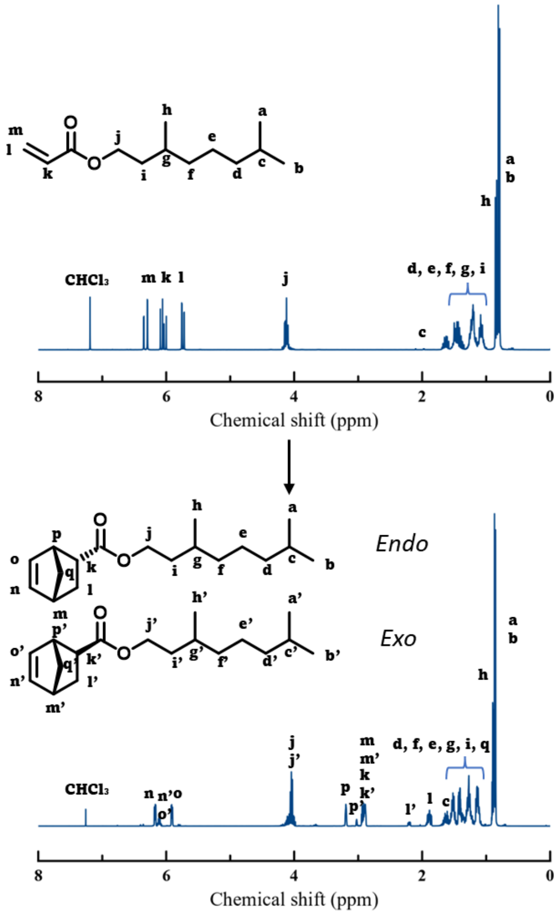


Figure 1. ^{1}H NMR spectra of the purified monomers THGA (upper spectrum) and THGNb (lower spectrum) in the absence of any impurities. The apostrophe in the lower spectrum is to differentiate the *exo*- (20%) from the *endo*-cyclic (80%) norbornenate structure. Integrations can be found in SI Figures S1-2.

Initially, a terpenoid acrylate was synthesized by means of esterification using the respective terpene alcohol and acrylic acid (Scheme 1, Step 1). The sustainable synthesis of the terpenoid-based acrylates was described in a previous publication.[45] In a next step, the obtained acrylates were modified into their norbornenate derivatives by employing cyclopentadiene in a Diels-Alder [4+2]-cycloaddition reaction in methanol at 40°C (Scheme 1, Step 2). By-products were removed via distillation under vacuum resulting in pure norbornenates (for THGNb see Figure 1, and SI Figure S1-9).

Table 1. Overview of copolymer formulations, including weight fractions, polymer and thermal properties

PSA	Copolymer formulation	Ratio [wt.%]	G^3loading ${}^{a)}$ [wt.%]	M_n ${}^{b)}$ [kDa]	$Đ$ ${}^{b)}$	T_g ${}^{c)}$ [°C]	$T_{d5\%}$ ${}^{d)}$ [°C]
PSA 1	THGNb:COD:NCA	80:18:2	0.1	59	1.98	-40	328
PSA 2	MnNb:COD:NCA	40:58:2	0.2	144	1.63	-50	329
PSA 3	iBnNb:COD:NCA	20:78:2	0.2	126	1.66	-53	330
PSA 4	iBnNb:COD:NCA	20:78:2	0.5	73	1.71	-61	330
PSA 5	iBnNb:COD:NCA	20:78:2	1	44	1.73	-63	330
PSA 6	MnNb:COD:NCA	40:58:2	1	96	1.69	-42	336
PSA 7	iBnNb:COD:NCA	20:78:2	- ${}^{e)}$	71	2.08	-74	34
Commercial sample	-	-	-	40	5.02	-50	324

a) G3 loading refers to weight percentage of 3rd Generation Grubbs catalyst employed. b) Average molecular weight (M_n) and dispersity ($Đ$) determined with THF SEC against polystyrene standards. c) Determined from the second heating ramp in DSC analysis (10 °C.min-1). d) TGA onset temperatures after 5% weight loss ($T_{d5\%}$). e) Prepared by blending PSA3 with PSA5.

Subsequently, the bio-based *endo*-rich norbornenate monomers,[46] tetrahydrogeranyl norbornenate (THGNb), menthyl norbornenate (MnNb) and isobornyl norbornenate (iBnNb), were homopolymerized with ROMP to determine the T_g of the resulting homopolymers via differential scanning calorimetry (DSC). As expected, the lowest T_g was found for the flexible THGNb homopolymer (-7 °C), whereas higher glass transition temperatures were found for the homopolymers of MnNb (71 °C) and iBnNb (98 °C) (Figure S13). On the other hand, in order to obtain copolymers with lower T_g-values, there was a need for a monomer that would reduce the overall T_g of the corresponding copolymer significantly. COD was therefore included in this investigation, as the corresponding homopolymer showed a T_g of -85 °C and was easily polymerized via ROMP. The bio-based norbornenate monomers were then individually copolymerized to full conversion in solution with COD and a functional monomer, NCA. NCA is expected to improve the adhesive properties of the PSA, similar to acrylic acid in readily available acrylic PSAs. Short polymerization times in the order of minutes were required to obtain full conversion.

Depending on the terpenoid-based norbornenate monomer, either a high or low amount was introduced into the copolymer formulation, where the fraction of the functional monomer NCA remained constant throughout the PSA formulations (Table 1). For PSA1, a high fraction of THGNb was introduced because of the homopolymers low T_g of -7°C, whereas for the MnNb and iBnNb-based PSAs, only a small fraction was required. As reported in Table 1, the first three copolymer formulations PSA1, PSA2 and PSA3 lead to high molecular weight copolymers with low glass transition temperatures (< -40°C) and high thermal stabilities up to 330°C (Figure S12). However, it must be noted that in the thermal degradation profile of the homopolymers, an expected decarboxylation can be observed for NCA starting from 150°C (Figure S11), which could have a potential effect on the adhesive properties at elevated temperatures. Yet, the homopolymers of iBnNb, THGNb and MnNb showed a more stable thermal degradation profile (Figure S10).

Further insights on the adhesive performance of these three formulations (PSA1, PSA2, PSA3) were obtained by means of analyzing their rheology data and introducing these into the Chang classification system. The Chang classification method allows to obtain a viscoelastic window (VW) within a log-log cross-plot from the storage (G') and loss modulus (G'') at 10^{-2} rad/s, the bonding at 10^2 rad/s and debonding frequency at 25°C of the PSAs.[47,48] A correlation between different adhesive properties and the place in the viscoelastic window can be found.[43] For example, a material with a low storage modulus and a high loss modulus would result in cold temperature PSAs (lower right quadrant in Figure 2).

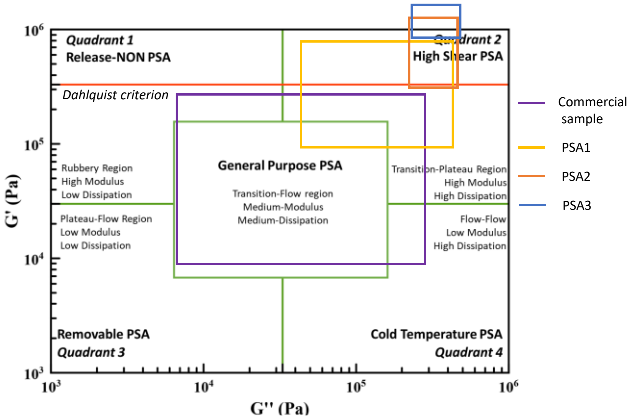


Figure 2. The customized Chang classification system of specific PSA formulations (Table 1) and of a commercial sample.

From the Chang classification plot in Figure 2, it can be observed that the commercial acrylic PSA (provided by 3M company) shows good adhesive properties for general purpose PSAs, whereas from the initially proposed formulations only PSA1 shows potential as a high shear PSA. On the other hand, PSA2 and PSA3, with a somewhat higher average molecular weight, lower dispersity but similar thermal stability to PSA1 appear to be above the Dahlquist criterion ($G' < 3.3\ 10^5$ Pa, red line in Figure 2). Above the latter criterion, the storage modulus is too high, limiting the potential flowing and the corresponding adhesion of the PSAs onto substrates.

In a next step, the molecular weights of the copolymers were altered to increase the adhesion performance of the former PSA2 and PSA3 formulations. It was believed that a

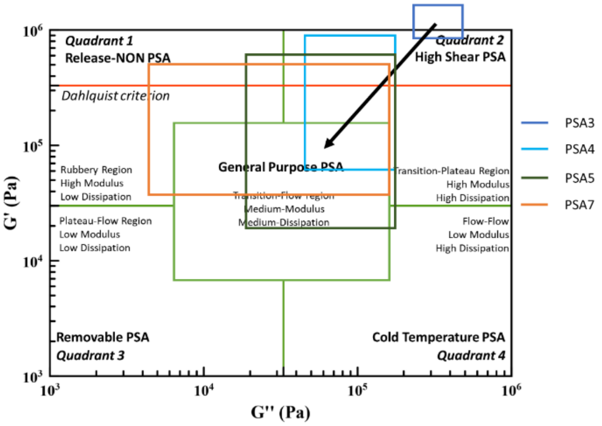


Figure 3. The customized Chang classification system and the viscoelastic windows of the PSA formulations PSA3, PSA4, PSA5 and PSA7. The arrow shows the shift to a more general purpose PSA from PSA3 to PSA5, with an increase in catalyst loading. A similar shift to more general purpose PSAs is seen from PSA3 to PSA7, by blending PSA3 and PSA5.

decrease in molecular weight would also result in a cohesion decrease and as a result, an increase in adhesion.[49] Indeed, from the data of the commercial sample (Table 1), it could be seen that a lower molecular weight of the copolymers, in combination with a broad dispersity, could allow for better flowing that results in good PSA properties. Thus, aiming to decrease the average molecular weight, different loadings of catalyst (Grubbs 3rd generation) were investigated. For this part of the study, the isoborneol-based PSA (PSA3) was selected and the catalyst loading was varied from 0.2 wt.% for PSA3 to 0.5 wt.% for PSA4 and 1 wt.% for PSA5. Upon increase of the catalyst loading, a decrease in average molecular weight was observed in the SEC trace (Figure S17). It can be observed from Figure 3 that this effect also resulted in better adhesive properties, as can be seen by the shift of the viscoelastic window towards the general purpose area. Moreover, the rheological master curves from PSA3, PSA4 and PSA5 were constructed by using the Williams-Landel-Ferry (WLF) time-temperature superposition (Figure S18), confirming a steeper decay at lower frequencies (the bonding frequencies), which means that an increased flow of the adhesive and thus better wetting of a substrate is expected.

A similar trend was observed for PSA6 based on menthol in MnNb. Upon increasing the catalyst loading to 1 wt.%, a decrease in average molecular weight was observed (Table 1) from 144 kDa to 96 kDa (SEC traces Figure S16) while maintaining a similar dispersity. The decreased average molecular weight for PSA6 resulted in a shift of the viscoelastic window in the Chang classification plot from PSA2, located above the Dahlquist criterion, to a viscoelastic window located in the general purpose PSA region (Figure S21). A similar result, e.g. an increased flow at the bonding frequencies, as for PSA3 to PSA5 *(vide supra*), was also seen in the master curves for PSA2 to PSA6 (Figure S19).

As previously mentioned, the commercial benchmark sample showed a much higher dispersity in comparison to the ROMP-based copolymers. It is indeed expected that the dispersity has a significant impact on the adhesive

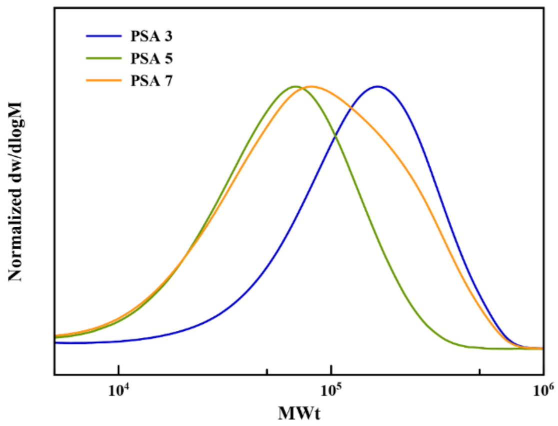


Figure 4. The normalized SEC traces of the polymer blend PSA7 compared to PSA3 and PSA5.

properties. As ROMP is a controlled polymerization technique, thus typically leading to relatively low dispersities, it was opted to blend two different polymers, PSA3 and PSA5, in a one to one ratio with two different average molecular weights of 126 kDa and 44 kDa respectively to obtain a new material, PSA7 (Table 1). By this blending process, an increase in dispersity above 2 (Figure 4), a decrease in average molecular weight to 71 kDa and a lower Tg of -74 °C was obtained. The latter can be ascribed to the plasticiz ing effect through the introduction of the lower molecular weight polymer chains of PSA5. By blending the two polymers, a desired shift of the viscoelastic window of PSA3 was indeed observed in the direction of the general purpose PSAs for PSA7 (Figure 3). In an application oriented research, a more systematic study should be envisaged to fully explore the potential of the finetuning option for the dispersity.

To establish a comparison between the obtained PSA and the commercial sample, the adhesive performance of these materials was characterized by means of tack and peel measurements on a stainless steel surface. As described above, PSA1 has promising viscoelastic properties according to the Chang classification system and has also the highest wt.% of bio-based norbornenate monomer (80%). For reasons of comparison with an earlier report on bio-based acrylic PSAs (THGA:methyl methacrylate:acrylic acid in a 84:14:2 ratio), the initial tack of the PSA1 to the substrate was determined via probe and loop tack testing.[20] The peel test was performed in a 180° peel setup to measure the peel strength of the PSA. A peel resistance of 5.2 ± 1.0 N/25mm and a tack resistance of 4.1 ± 0.6 N/25mm was determined. While a slightly lower adhesion was determined for PSA1 in this research, the obtained results lie within a similar range (Table S2). This is an indication that ROMP can be a suitable technique to obtain terpenoid formulations with similar adhesive properties compared to the acrylic counterpart formulations, yet follow-up application-oriented research should be performed to confirm this statement.

In comparison to the crude-oil formulation in the previous work (Table S2), the obtained values for adhesion of the norbornenate PSA are considerably lower, which is attributed to at least two reasons. First, the monomer compositions of the above mentioned formulations are significantly different. While the side chains of the monomers are important to define adhesion, the backbone of the polymer will significantly contribute to the nature of the physical and adhesive properties as well. Second, there is a considerable difference between polymer dispersities. The broader dispersity in the commercial sample results in a plasticizing effect via the lower molecular weight fraction, leading to better PSA properties. Nevertheless, a more systematic study on the adhesive properties would be required to confirm this further.

In summary, bio-based PSAs with controllable viscoelastic and adhesive properties prepared via the ROMP have been described. First, norbornenate monomers were synthesized by means of an esterification of a terpenoid alcohol with acrylic acid, followed by a Diels-Alder [4+2]-cycloaddition with cyclopentadiene. The renewable terpenoid-based norbornenates were polymerized in solution within minutes of polymerization time with a Grubbs 3rd generation catalyst in different loadings to obtain PSAs. The performance of the adhesives was verified with the Chang classification system by introducing the viscoelastic properties (G' and G'' modulus of the adhesives) at the bonding and debonding frequencies of the PSA. By altering the catalyst loading or by blending two different polymers, different average molecular weights and dispersities could be obtained, allowing to improve the rheological properties of the adhesives. We believe that this sustainable approach opens a wide range of new possibilities for PSA synthesis. In the long run, redefining such systems to be compatible with emulsion polymerization could reveal their industrial potential as a step towards sustainable PSA development.

ASSOCIATED CONTENT

This material is available free of charge at http://pubs.acs.org. Experimental procedures for polymerizations and characterization of the monomers and polymers, experimental procedures (PDF)

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