

Polyamides Derived from Terpenes: Advances in Their Synthesis, Characterization and Applications

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Polyamides are very important polymers, with applications from commodities up to high-performance materials for, for example, fibers or for the biomedical sector. Nowadays, still most of them are synthesized from fossil resources. With regards to sustainability and bioeconomy, and especially regarding the new structures and properties that can thus be achieved, the preparation of polyamides (PAs) from natural precursors is getting more and more important. For this, especially the utilization of terpenes, a large and important group of natural products with different functions in nature (regulators, defense signals, etc.), is important, which is described herein. Similar approaches are interesting from a scientific point of view regarding, for example, structure-function-relations, but also with regards to different applications as, for example, high-performance or biomedical materials. **Practical applications:** Terpene-based polyamides can find many applications, from commodities up to high-performance fibers and special materials in (bio)medicine, for example, drug delivery, tissue engineering, etc.

or polyhydroxyalkanoates (PHAs)^[24] and lignin^[25], and also for various natural monomeric building blocks, which results mainly in the classification concept of polymer approaches versus molecular approaches.^[26–31]

In this whole context, terpenes are important molecules in nature, that have a variety of functions, for example, as defense signals for repelling insects, as growth regulators, as activators of symbiotic mechanisms (e.g., the stimulation of cross-pollination processes via the attraction of insects), as fragrances, etc.^[32] In the systematics of organic chemistry they belong to the lipids, and there are more than 80 000 terpenes and terpenoids (the latter are mainly oxygenated compounds) in nature with a variety of structures and functions. Many of them are abundant and often derived from non-edible parts of plants.^[33] A classification

1. Introduction

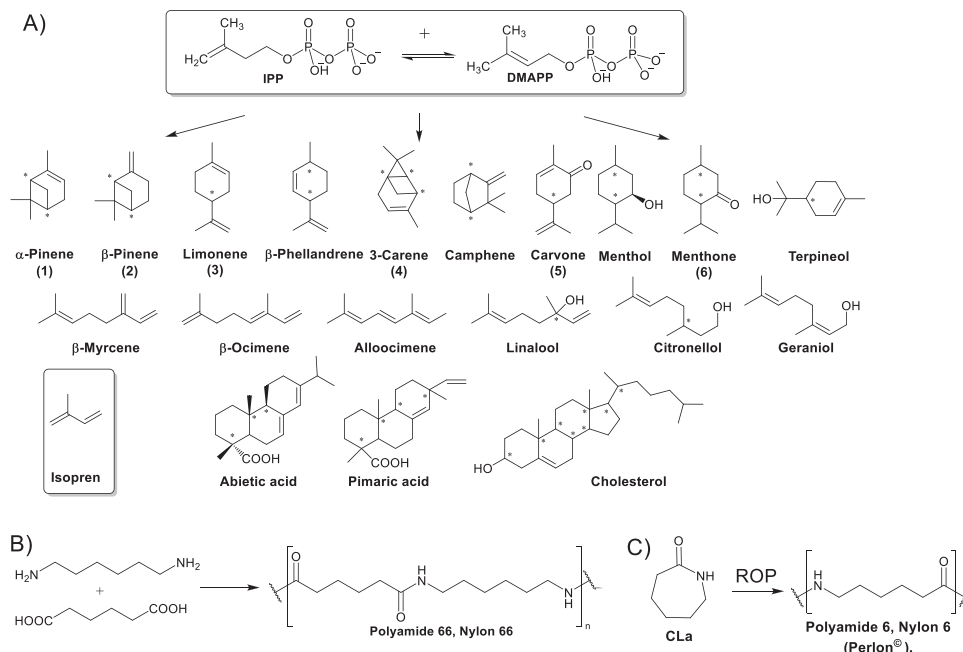
There is an increased awareness for environmental responsibility regarding different production processes, climate, etc., which also has different effects on materials and their circular economies.^[1–6] Therefore and especially in the context of Bioeconomy and sustainability, the utilization of renewable starting compounds for the preparation of sustainable polymers and materials is a main task in modern polymer chemistry.^[7–22] This is much further emphasized by the fact that Nature can provide many substances with special structural features that cannot be obtained so conveniently via fossil-based pathways. This fact is important for natural polymers (e.g., cellulose^[23]

into linear (acyclic) and cyclic terpenes can be defined, and furthermore into monocyclic, bicyclic, and polycyclic representatives. The number of C5 isoprene units within these compounds is another description system for these substances.^[34,35] Terpenes as constituents of different oils, that are extracted from leaves, fruits, flowers, and spices, have been known and utilized for many centuries. Interestingly, many terpenes can also be produced by insects, marine microorganisms and fungi. A biogenic isoprene rule was formulated, suggesting that the carbon-skeleton of these compounds consists of isoprene units (C5) that are linked in a regular (head-to-tail) or an irregular (head-to-head) arrangement. Accordingly, an additional specification can be defined into Monoterpenes (C10), Sesquiterpenes (C15), Diterpenes (C20), Sesterpenes (C25), and Triterpenes (C30) and so on.^[32] For these compounds, the Mevalonate-pathway is the most important synthesis route. It begins with three Acetyl-CoA units and proceeds via isopentenyl pyrophosphate (IPP) and its isomer dimethylallyl pyrophosphate (DMAPP), that are connected to geranyl pyrophosphate (GPP), which again reacts with one unit of DMAPP to form farnesyl pyrophosphate (FPP). By this synthesis sequence, the stepwise generation of all terpenes is possible through enzymatic catalysis (e.g., terpene synthases) and optionally by further modifications. Turpentine oil is a main fractions of oleoresins obtained mainly from conifers. A classification can be made into sulfate turpentine, gum turpentine and wood turpentine.^[36,37] These oils have a high global production (>330 kto year⁻¹) and they are mainly obtained during wood processing as a by-product from

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DOI: 10.1002/ejlt.202300014



Scheme 1. A) Different terpenes. Box: Basic C5 unit of the terpenes, 'Isoprene'. Importantly, for many of these terpenes, several isomers do exist; B) polyamide 66 (Nylon 66), and C) polyamide 6 (Nylon 6).

the pulp industry, for which the so-called Kraft process is an important approach.^[38] It has different terpenoid components at different percentages, which depends on the occurrence (α -Pinene (1) 45–97%, β -Pinene 0.5–28% (2) and smaller amounts of other terpenes such as 3-Limonene (3), Carene (4), Camphene, β -Phellandrene, and Myrcene, and others) (Scheme 1A). Terpenoid ketones like Carvone (5), L-Menthone (6), etc. are important flavorings.

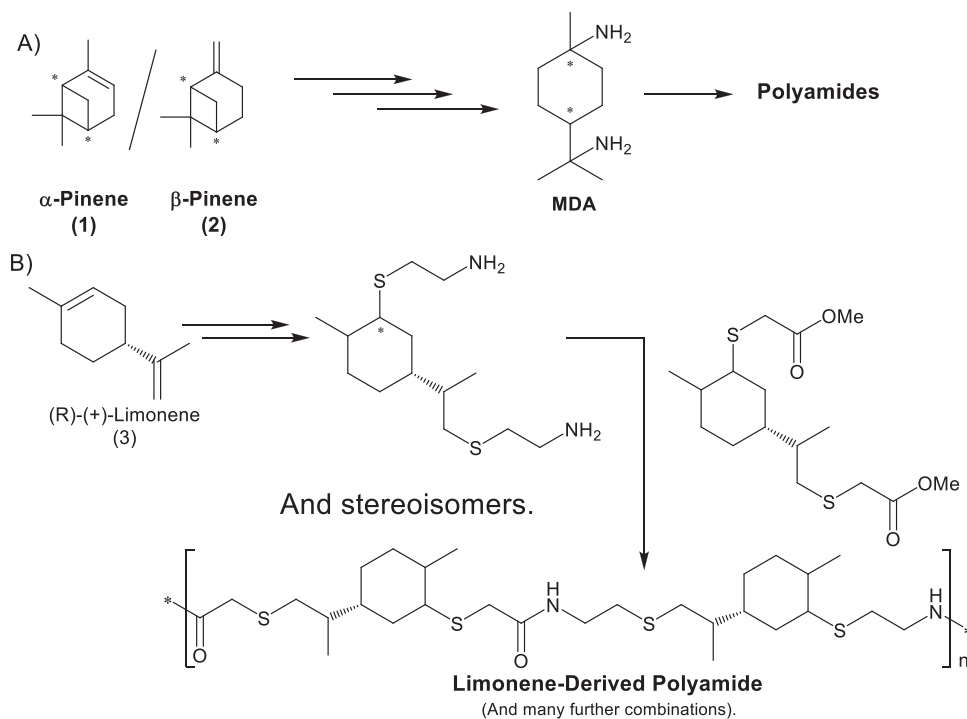
Generally, polyamides (PAs) are very important polymers and materials for a wide range of applications, from different commodities, packaging and customer products up to special fibers, engineering (thermos)plastics used for, for example, electronics and also transportation, as well as other high-performance materials or many medical products.^[39–42] They are mainly synthesized via polycondensation of dicarboxylic acids (or their derivatives) and diamines, or via ring-opening polymerization (ROP) of cyclic amides (lactams), but also further methods exist. Polyamide 66 (Nylon 66) (from adipic acid and hexamethylene diamine) and Polyamide 6 (Nylon 6, Perlon) (from cyclohexanone via ϵ -caprolactam), respectively, are important examples for these polymers (Scheme 1B,C).^[43,44] As it generally applies for many polymers, the majority of PAs are still synthesized from fossil resources. Therefore and due to the facts described above, meanwhile also many biobased PAs have been prepared and investigated that are derived from different natural products.^[1–4,39–42,45–49]

Regarding terpenes and in addition to this natural variety, catalytic upgrading of terpenes can provide accesses to many more terpenoid structures.^[50] An important example is Limonene with its many possibilities of oxidation, aminations, etc.^[51,52] All these facts make terpenes in general to be very important natural building blocks for many sustainable polymers and materials.^[53–56] Obviously, direct polymerizations of isoprene to polyisoprene

are possible via its double bonds, where different structure isomers are accessible.^[57] Polymyrcene and Polyocimene are other examples for suchlike elastomeric hydrocarbon polymers.^[58–61] Therefore, many further terpene-polymerizations have been described for many different polymers.^[62–68] As a prominent example, Limonene (3) can be polymerized and also copolymerized catalytically via different methods.^[69–72] Further examples are, for example, polyolefin polymers^[73,74] and different (hydrocarbon) elastomers.^[75] Generally, also the important polymer classes of, for example, polycarbonates,^[76–80] polyesters,^[81–84] and polyurethanes^[85] are intensively investigated with regards to their biobased alternatives. Accordingly, also different terpene-based polycarbonates,^[86–91] many polyesters,^[92–99] polyurethanes,^[100] and also polyketones^[101] have been investigated.

Therefore, especially polyamides that are derived from terpenes are very important polymers that are intensively investigated and which are described within this article. It is important to consider that classical α -Peptides and also many similar foldamers structures (β -peptides, γ -peptides,) can—due to their amide linkages—also be considered as PAs. Their elucidation would be beyond the scope of this review—they have been reviewed elsewhere in detail.^[102] Furthermore, also other N-containing polymers (polyurethanes, etc.) are very important and they are increasingly prepared by the utilization of terpenes as sustainable starting compounds. Due to the broadness of this field, for those other review articles are highly recommended.^[28]

For instance, different high-performance materials, fibers, and also biomedical applications are interesting application fields for suchlike obtained materials.^[103] In terms of the functionalities of the different terpene-based building blocks, polycondensation as well as ring-opening polymerization (ROP) are both feasible, and they are the two main methods for the



Scheme 2. A) α -pinene and β -pinene as compounds for the synthesis of MDA and polyamides; B) limonene-derived Polyamides that are obtained via polycondensation.^[110] This representative synthesis and many similar combinations are reported in the respective reference.^[110] Copyright 2013 The Royal Society of Chemistry.

preparation of Terpene-based PAs, which are addressed in the following chapters. It is important to emphasize that other *N*-containing polymers as, for example, polyurethanes (PUs) are also very important, especially with regards to their biobased and sustainable representatives.^[104] Although they are sometimes mentioned herein at appropriate passages in this text, their comprehensive elucidation would be beyond the scope of this article—similar polymers have been reviewed and described in other articles much more detailed.^[28,105] The importance of this review and the difference to the previous reviews about biobased PAs is the uptake of some very recent information and studies about this topic, as well as the structuring regarding the different polymerization mechanisms in this context. Furthermore, the fact that the focus herein is defined especially regarding the Terpene-based building blocks is important. This emphasizes the plethora and the importance of suchlike approaches that have meanwhile been investigated.

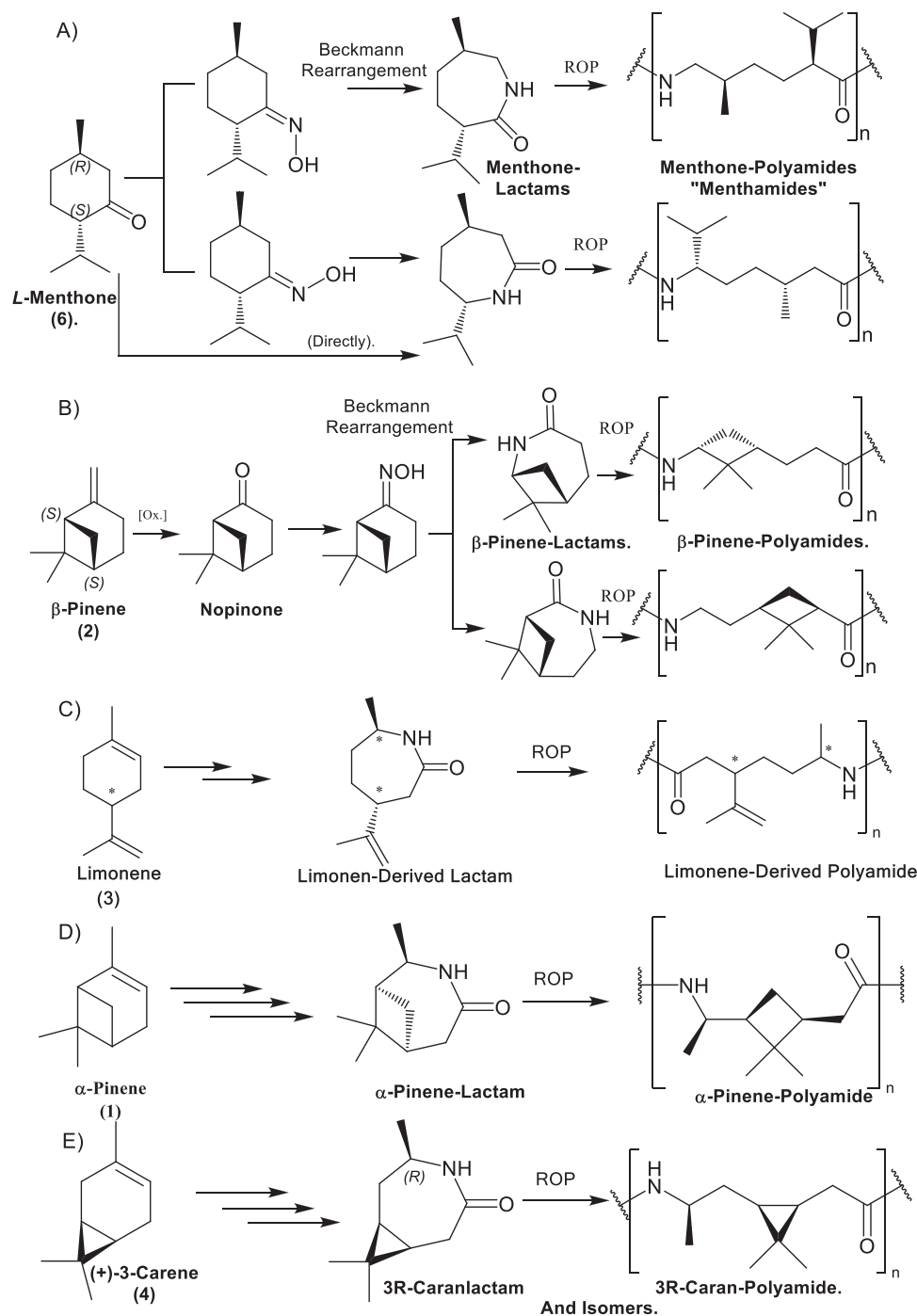
2. Terpene-Based Polyamides via Polyaddition and Polycondensation Reactions

1,8-Menthane diamine (MDA) can be prepared via different reaction pathways from Pinenes.^[106–108] This interesting compound can meanwhile be considered to be a platform chemical for a variety of biobased *N*-containing polymers including, for example, polyamides (epoxy/amine resins are other examples, where this compound can thus be used as a curing agent) (Scheme 2A).^[28,109] Also many similar amine-containing building blocks can be prepared from Limonene and polymer-

ized, which thus makes a wide variety of interesting polymers accessible.^[28] Furthermore, Polyamides (and also polyurethanes) from limonene can be prepared, for example, via polycondensation of Limonene-derived diesters and diamines (Meier et al.).^[110] Through different combinations, limonene, fatty acid, as well as Nylon 6,6 copolymers were thus prepared, and the relationships between structures and thermal properties were analyzed (Scheme 2B). It could be demonstrated by GPC and DSC characterizations that these monomers are useful for the synthesis of different polyamides with adjustable properties. Furthermore, the obtained diamines have successfully been transformed into dicarbamates by means of a phosgene-free route, and their suitability for different polycondensation reactions was studied. The resulting PUs—from amorphous to semicrystalline—were also characterized in detail, and their mechanical properties were investigated as well.

3. Terpene-Based Polyamides via Ring-Opening Polymerization

It is a very useful procedure for ring-opening polymerization (ROP) to transform terpenoid ketones (that are directly available or upon oxidation of double bonds to ketones) into lactams via their oximes (so-called ‘Beckmann-rearrangement’), and then to polymerize these lactams (Scheme 3).^[111–116] An example are lactams and PAs based on *L*-Menthone (Scheme 3A).^[106–111] Furthermore, the oxidation of β -Pinene, which has an external double bond, is important and has been investigated in different contexts,^[117] also with regards to lactams and PAs



Scheme 3. Polyamides from the Terpenes a) L-Menthone; B) β -pinene; C) limonene; D) α -pinene; and E) (+)-3-Carene, which are synthesized via the corresponding oximes and lactams by means of ROP, applying different initiators. Please see the main text for the respective references.

(Scheme 3B).^[106] This procedure works thus in analogy to the established nylon-6 synthesis that starts from cyclohexanone and proceeds via ϵ -caprolactam (see also Scheme 1C). In many cases and dependent on the structures of the terpenes, the reaction conditions, etc., different oximes (*cis* and *trans*) and thus different (regioisomeric) lactams are formed, due to the conditions of the Beckmann-rearrangement. Upon polymerization, this

can also result in different polyamides. For anionic ROP, the chain length can be regulated well, for example, via the initiator content. Cationic and hydrolytic ROP are further methods. An isopropyl-substituted lactam can be also obtained from β -Pinene via a similar approach.^[99]

The PAs hats are thus obtained inherit very interesting thermal and mechanical properties, which rely on the chemical

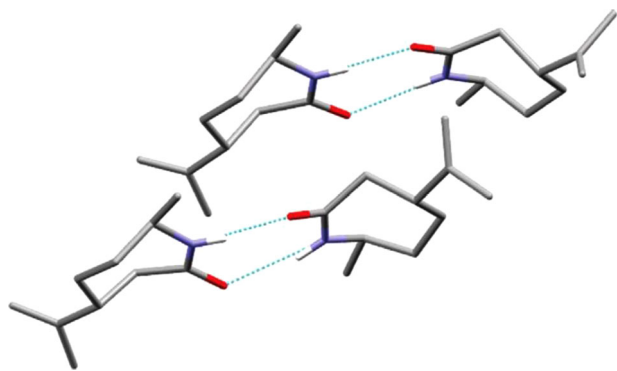


Figure 1. Crystal structure of a Limonen-based lactam. The Methyl and the iso-propyl group show equatorial arrangement. Reprinted with permission.^[120] Copyright 2022, Wiley-VCH GmbH.

structures of these polymers with regards to, for example, side groups and stereocenters, and chain (re)arrangements). An example are high melting points that can result from—for instance—the chain interactions in addition to the H-bonds. X-ray diffraction experiments show different distance parameters for the unit cells, considering different possible chain (re)arrangements.^[118,119] This is also important for the different properties of these polymers. Limonene-based PAs can also be prepared via suchlike approaches, which have double bonds suitable for further graft functionalizations (Scheme 3C).^[120,121] Furthermore, α -pinene- and (+)-3-Carene-based lactams and Polyamides have also been described, that were synthesized via similar and analogous procedures (Stockmann, Sieber et al., Schemes 3D and 3E, respectively).^[122,123] The diastereomeric 3S-Caranactam and 3R-Caranactam were thus obtained and isolated. The preparation of the isomers occurs selectively by an epoxide-ketone rearrangement and by a suitable kinetic and thermodynamic control of the intermediates. Furthermore, interesting reactor technologies that are based on a one-vessel reaction cascade have been developed for this approach, that enable also a convenient reaction control, processing and work-up. Also here, for example, *N*-benzoylated lactams were used as co-initiators. Depending on isomers and structures, the obtained PAs can be amorphous or semi-crystalline.^[117,118,124,125] The amorphicity could be shown in an absence of a melting point T_m , and the resulting transparent bio-PAs give accesses to new fields of applications. A crystal structure of the semicrystalline poly-3-S-caranamide was also presented. Furthermore, copolymers with CL and with lauroactam (LL) were synthesized with different monomer distributions and shown to have good MW values and remarkable properties. The different monomer reactivities were investigated by means of elaborated kinetic studies.

In addition to NMR spectroscopy, mass spectrometry, etc., the integrity, the stereochemistry and the orientation of the lactam monomers can be determined by means of X-ray crystallographic measurements, as shown in **Figure 1** for the Limonene-based lactam.

For the polymerizations that are shown in Scheme 3, kinetic studies show interesting correlations between the reactivities of the monomers and also the progress of the polymeriza-

tion reactions. Different initiators can be applied for the regulation of the chain lengths and of the reaction speed/times, and it is possible to reach PAs with high molecular weights. Different copolymers of these terpene-based lactams with other monomers have also been described.^[126,127] As an example, copolymerization of pinene-lactams with ϵ -caprolactam leads to different copolyamides.

There are various and manifold processing possibilities for these PAs. For instance, films of some of the (+)-3-Carene-based PAs and copolyamides were prepared by means of dissolution of the PAs in HFIP and slow evaporation of the solvent, for the evaluation of the optical properties (**Figure 2**). While commercial and self-made PA6 and PA12 resulted in colorless non-transparent films here, from the amorphous co-polymers, however, relatively transparent films (foil-like) could be prepared (obvious despite of occasionally little amounts of residual monomers or inclusion of solvent and other regularities due to the preparation methods).^[123]

Dynamic-mechanical analyses (DMA) are also performed for many of these polymers. For the Pinene-based PAs, a good tensile strength and E-modulus can be reached, which can be modulated via different parameters, and Copolymerization with ϵ -caprolactone results in polyesteramides with tunable properties including adjustable biodegradability.^[122,128] Such copolymers can be synthesized in random, gradient or block structures, which can be regulated, for example, via the applied initiators, the reaction conditions, the monomer reactivities and also the order of monomer additions. These approaches result in a general “construction box” for Terpene-based copolymers and their blends. The processing of these polyamides, for example, with regards to the production and testing of different specimen, components, surfaces, coatings, or also for fiber spinning, has been investigated and is also topic of ongoing investigations. Hydrolytic polymerization is also under investigation, where polycondensation and cationic ROP can occur in parallel. Accordingly, also the isolation of the ring-opened lactams as amino acids and/or their corresponding salts can (and has been shown to) be an interesting option prior to the further procedure. Also different combinations of, for example, cyclic monomers and linear/acyclic monomers are possible. Upscaling of the reactions is a main challenge here. With regards to applications, also the hydrophilization of the PAs can be important. Especially PA/PEG (PEG = polyethylene glycol) blends and copolymers are interesting for cell-material-interactions with regards to, for example, cell adhesion, proliferation, and clustering, mainly due to their tunable hydrophilicity and surface character.^[129] As it is well known that many inherent materials properties (stiffness, biodegradation by-products, chemical functionality, etc.) influence the behavior of living cells with regards to, for example, adhesion, proliferation, and clustering,^[41,103] these approaches give various accesses to very interesting (bio)materials suitable for, for example, regenerative medicine and tissue engineering. The grafting of functional molecules as, for example, biomolecules is another very interesting option for the functionalization of these PAs, especially if pendent modifiable groups such as, for example, double bonds are present (see above, e.g., for the limonene-based PAs). In this case, “click chemistry” can be applied, which enables olefins, spring-loaded electrophiles, and heteroatom connections to be key elements in a fast, modular process-driven

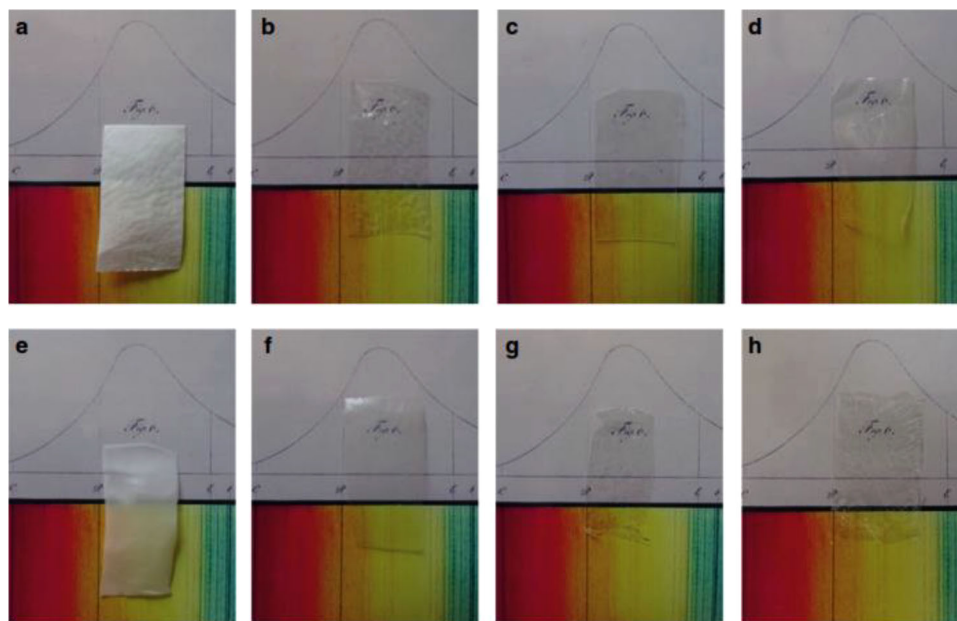


Figure 2. Transparent polyamide films of different LL-based copolymers and also others. a) PA12; b) copol(3S-Caranlactam_{32%}:LL_{68%}); c) copol(3S-Caranlactam_{33%}:LL_{67%}); d) copol(3S-Caranlactam_{41%}:LL_{59%}); e) PA6. f) copol(3S-Caranlactam_{18%}:LL_{82%}); g) copol(3S-Caranlactam_{48%}:LL_{52%}); h) poly-3R-Caranlactam. Reprinted with permission.^[123] Copyright 2020, Springer Nature.

approach to molecular and polymeric discovery, modification, and functionalization.^[130]

4. Conclusion

Due to the importance of many polyamides (PAs) in the polymer and materials fields for different applications, and generally of terpenes as building blocks for sustainable polymers and materials, terpene-based PAs are very important polymers, and their impact is further growing. They can be conveniently synthesized, for example, via polycondensation or via ROP (of lactams), and they have prosperous properties. The availability of the building blocks as well as their prices are and will be crucial factors for suchlike further developments. Although resistance is more important for PAs regarding their application fields, also the option to make Nylons (partially) biodegradable (e.g., via approaches) is worth to be investigated.^[131] The structure variety, the properties and the abundance of the terpenes (see also introduction) have the potential and are thus anticipated to give further accesses to many other terpene-based PAs in the future. This is driven also by the combination of sustainability, useful properties and high performances.^[132] These PAs are very interesting from a scientific point of view, and they are anticipated to play an increased role also for industrial applications. The compatibility tests with commercial polymerization systems as well as the investigation of polymer blends and different additives will also be important for their further evaluation and for applications with regards to their further utilization in different areas. Different further modifications are possible and expand the possible applications. This can be done, for example, via different click chemistry approaches (see above). As the (bio)medical aspects of PA from lactams are getting increasingly important, these new PAs have a huge potential to find applications also in these fields, for

example, with regards to tissue engineering and drug delivery.^[42] This is emphasized by the fact that also Nylon-3 (co)polyamides are getting increasingly important for similar applications, which brings the view also to Nylon-6 (co)polymers (from modified ϵ -lactams as described above) in this context.^[133,134] The tunability of the properties is and will be an important factor for this, which can be adjusted by several factors. For suchlike terpene-based materials—in addition to the natural resources—also other factors as, for example, energy consumption and procurement logistics should be considered for the comprehensive sustainability considerations and for the evaluations in what way “bio can be better” for the considered applications.

Acknowledgements

The work of M.W. on Terpene-Based polyamides (PAs) is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project Number 445011287. The author also thanks the TU München for the support.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The author declares no conflict of interest.

Author Contributions

M.W.: Conceptualization; Funding acquisition; Supervision; Writing—original draft; Writing—review and editing.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords

bioeconomy, polyamides, ring-opening polymerization, sustainable polymers, terpenes

Received: January 31, 2023

Revised: March 22, 2023

Published online: April 20, 2023

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