

C18 Diacid Market to Grow and Expand Into an Array of Novel Products with Superior Properties

Allyson Beuhler, PhD

Overview

Diacids are a commercially important class of chemicals, produced annually in tens of thousands of tons with applications in a variety of end uses. The difunctionality of diacids makes them particularly useful building blocks in condensation polymerization applications. Due to the variable aliphatic chain length between the two carboxylic acid groups, a variety of physical properties are observed. As such, the properties of the products made can be tailored by choosing the appropriate chain length.

Octadecanedioic acid (ODDA) is a C18 diacid that is now commercially available from two pathways, one using microbial fermentation and one using metathesis of natural oils. The latter pathway is expected to dramatically increase the availability of C18 diacid and lower its cost. The products made from this diacid typically show superior properties, such as water and chemical resistance, as compared to the shorter chain alternatives. Consequently, a myriad of new products made from ODDA should now be accessible.

Aliphatic diacids, also known as α,ω -dicarboxylic acids, comprise two carboxylic acid functional groups linked by an aliphatic hydrocarbon spacer. The general formula for this class of compound is $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$. Typically, n is between 0 and 22. **Table 1** describes the diacid portfolio that is available in the market place at research and/or commercial levels.

Table 1. Selected diacids

IUPAC Name	Common Name	Carbon Number	CAS Number	Mp ($^{\circ}\text{C}$) ¹
Butanedioic acid	Succinic acid	4	[110-15-6]	187.6–187.9
Pentanedioic acid	Glutaric acid	5	[110-94-1]	98–99
Hexanedioic acid	Adipic acid	6	[124-04-9]	153.0–153.1
Heptanedioic acid	Pimelic acid	7	[111-16-0]	105.7–105.8
Octanedioic acid	Suberic acid	8	[505-48-6]	143.0–143.4
Nonanedioic acid	Azaleic acid	9	[123-99-9]	107–108
Decanedioic acid	Sebacic acid	10	[110-20-6]	134.0–134.4
Undecanedioic acid	N/A	11	[1852-04-6]	110.5–112
Dodecanedioic acid	N/A	12	[693-23-2]	128.7–129.0
Tridecanedioic acid	Brassylic acid	13	[505-52-2]	114
Tetradecanedioic acid	N/A	14	[821-38-5]	126.5
Octadecanedioic acid	N/A	18	[871-70-5]	124.6–124.8

Uses for Diacids

A variety of products and industries use diacids, which are a non-toxic, versatile class of chemical intermediates. Uses include: monomers for engineering polymers such as polyesters, polyamides, polyurethanes and hot-melt adhesives; surfactants; lubricants and additives such as grease and corrosion inhibitors; food additives; solvents and cleaning additives; personal care; plasticizers; and fine chemicals such as fragrances, insecticides and fungicides. The choice of diacid is driven by the properties of the product, which can be imparted by the length the diacid. Several notable mid- and long-chain diacids and their current and potential application areas are listed in **Table 2**.

Table 2.

Selected Diacids and Their Commercial Uses. ¹				Commercial and Potential uses
Azaleic C9	Sebacic C10	Undecanedioic C11	Dodecanedioic C12	Octadecanedioic C18
<p>Monomers or additives for polymers: polyurethanes, polyesters, copolyesters and polyamides, powder coating, polyesters</p> <p>Ingredient for: cosmetics, lubricating oils, corrosion inhibition, cleaning, candles</p>	<p>Monomers and additives for polymers: polyesters, polycarbonates, polyamides, polyurethanes, detergents, toners/inks</p> <p>Ingredient for: cosmetics, lubricating oils, flame retardants</p>	<p>Monomers and additives for polymers: polyamides, polyesters, thermoplastic polyurethanes, polyols, powder coatings</p> <p>Ingredient for: detergents, corrosion inhibitors, antifreeze additives, complexes for pharma</p>	<p>Monomers and additives for polymers: polyesters, polycarbonates, polyurethanes, polyamides, hot-melt adhesives (polyamide, polyurethane)</p> <p>Ingredient for: heat transfer fluids, corrosion inhibitors, scratch resistant hard coats, detergents</p>	<p>Monomers and additives for polymers: polyphenylene oxide, polyphenylene ethers, polyetherimides, polyurethanes, polycarbonates, epoxy, latent curing epoxies, powder coatings, reactive diluent, toners/inks</p> <p>Ingredient for: lubricating oils, cosmetics, personal care</p>

Polymers from diacids are typically produced by condensation polymerization. Polyamides are the most important of these and range from very high melting point materials, such as PA 6,6, to mid-chain length materials, such as PA 6,12, to the aliphatic long-chain diacid polyamides that make up high-performance hot-melt adhesives. **Figure 1** shows some important commercial polyamides and their range of melting temperatures.

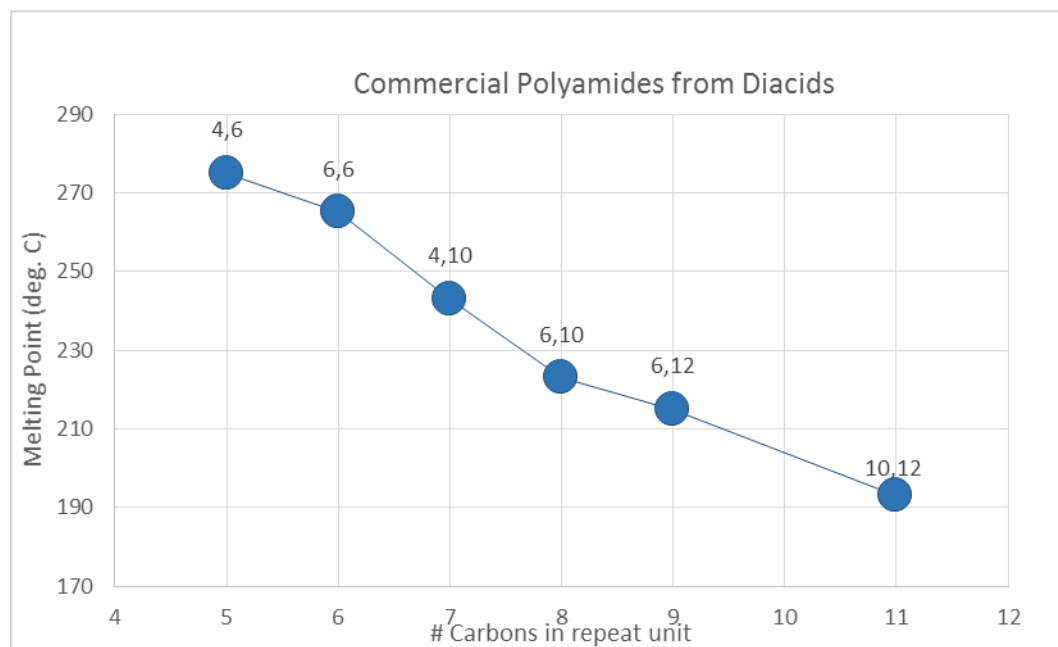


Figure 1. Commercial Polyamides

For polyamide hot-melt adhesives, the shorter chain lengths exhibit the best adhesion to surfaces due to the higher polarity of the molecule but, for the same reason, these adhesives are more susceptible to moisture pickup and can delaminate in high humidity environments. The less polar, longer chain lengths (C36) have lower moisture uptake, but also can have fewer amide linkages in the chain, and therefore lower overall adhesion. This is depicted as the performance range in **Figure 2**.

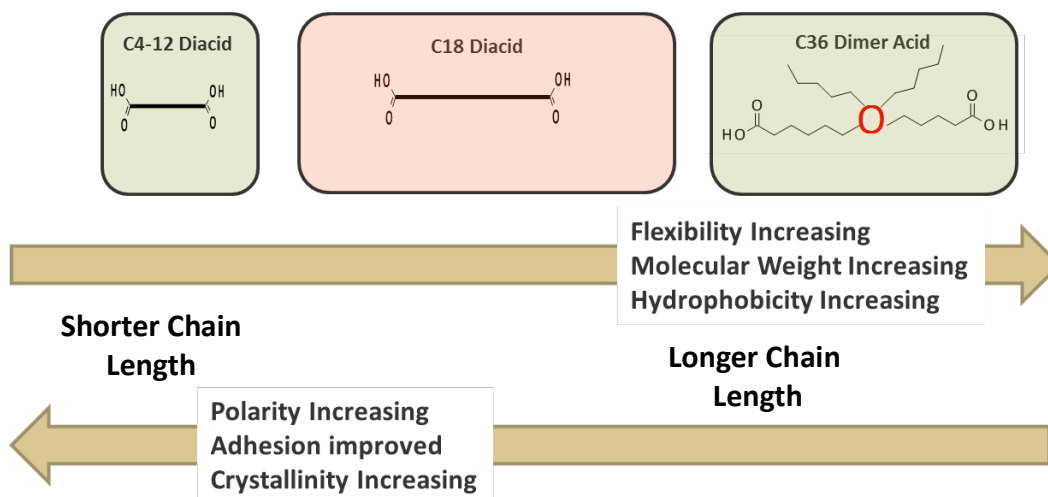


Figure 2. Structure-Property Relationships of Polyamide Adhesives

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With the use of the C18 diacid in the adhesive market space, this performance gap would be overcome. Specifically, this 18 carbon, mid-range material should impart a combination of both higher polarity and higher adhesion due to increased amide linkages and lower moisture uptake.

Methods to Produce Diacids

Historically, diacids have been obtained from both petrochemicals and oleochemicals using established, industrial chemical processes. Ozonolysis of unsaturated feedstocks is used for the preparation of suberic acid from cyclooctene, azaleic acid from oleic acid and brassylic acid from eucric acid, for instance. Multi-stage oxidation of a cyclododecane, derived from butadiene, is used to produce dodecanedioic acid. Castor oil can be oxidized with caustics to sebacic acid. Microbial fermentation of mid- and long-chain n-alkanes or fatty acids to produce diacids, notably tetradecanedioic acid and octadecanedioic acid, is also practiced. Recently, octadecanedioic acid is being produced via metathesis.

Methods to Produce C18 Diacid

C18 diacid has been prepared by the fore-mentioned fermentation pathway, and more recently, by olefin metathesis², a Nobel Prize-winning technology, utilizing natural plant oils. The key aspect of the metathesis technology is that it enables the production of this diacid from renewable feedstocks, e.g., any one of several natural oils. Overall, this biorefinery, catalyst-based technology is incentivized on an economic, renewability (life cycle analysis) and overall waste minimization basis.

Properties of Materials from C18 Diacid

A review of existing scientific literature reveals a broad appeal for utilizing C18 diacid in many of the traditional applications for diacids. Some of the advantages of C18 diacid, as compared to other diacids, is its relatively high melting point, lower volatility and increased hydrophobic nature (due to the longer aliphatic chain). The melting point is approximately the same as the C12 and C14 diacids, and significantly above most of the odd chain diacids, such as azaleic acid (**Figure 3**).

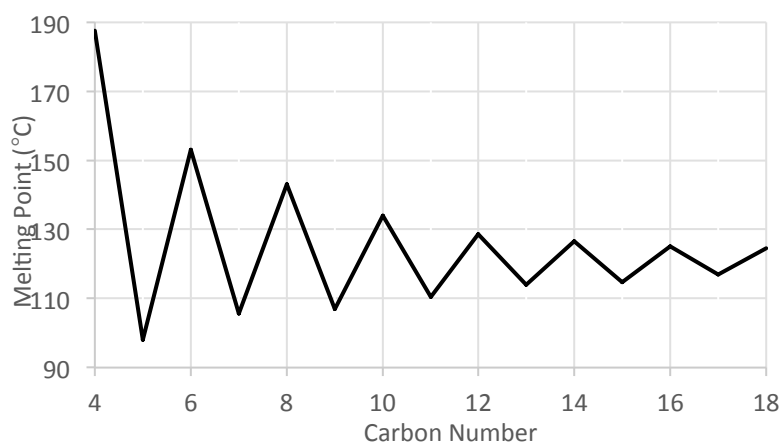


Figure 3. Melting points for selected diacids as a function of carbon number¹

With its molecular weight higher than that of short- and mid-chain diacids, C18 diacid is less volatile. The long hydrophobic chain of this diacid makes it and its condensation products more resistant to water (hydrolysis) and other chemicals, thus yielding products with lower dielectric constants, lower density and lighter weight, improved optical transparency, and lower refractive indices.

Amides have been synthesized from dimethyl 9-octadecene-1,18 dioate.³ The di-ester was produced via self metathesis of methyl 9-dodecenoate over a ruthenium catalyst. The di-ester was further derivatized with dimethyl amine to produce the diamide – 80% trans compounds were synthesized using this approach.

Some noteworthy products using C18 diacid are polyesterification products and polyamides. Aliphatic polyamides, based on C18 diacid (from PA 2,18 to PA 12,18), have been synthesized via melt condensation.³ Note the trend (**Figure 4**) in the polyamide series as the spacing between amide groups increases with the longer diacids. The resulting polyamides are still highly crystalline, however, the melting point decreases as the length of the amide repeat unit increases. With higher aliphatic content, the polyamides become more resistant to moisture and organic solvents. With the exception of PA 3,18 (which appears to be amorphous), the C18 diacid-based polyamides possess the stable α form crystallites, typical for even-even polyamides. Interestingly, even the long-chain and highly aliphatic PA 4,18 and PA 6,18 polyamides exhibit very high melting points, greater than both PA 10 and 11, enabling a very high-use temperature for these C18 diacid polyamides.

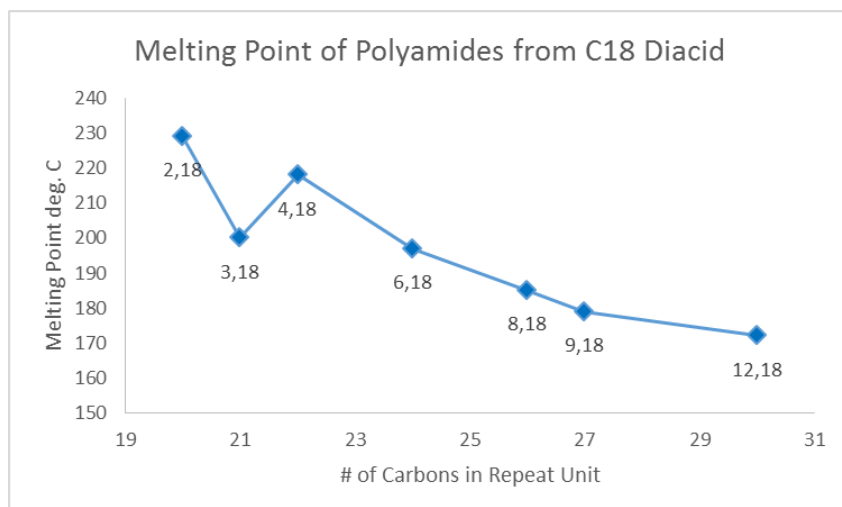


Figure 4. Melting points of x,18 polyamides from C18 diacid⁴

Copolyamides of 6,18 with other monomers have been reported in existing scientific literature. PA 6,18 was co-polymerized with PA 6 for use in molded and extruded thermoplastics. The resulting polyamide was reported to be more resistant to salt stress corrosion cracking and to have a lower melting point than PA 6,6 and PA 6,10.⁴

Hot-melt adhesives containing PA 6,18 have been reported in the manufacture of filters. Incorporation of the long-chain diacid is reported to decrease water absorption (the Achilles' heel of polyamides) and to provide significant increases in chemical and solvent resistance of the polyamide, including resistance to gasohol.^{5,6}

The cycloaliphatic polyamide of *bis*(2-methyl-4-aminocyclohexyl)methane and C18 diacid was synthesized and shown to be a moldable amorphous polymer with lower density, increased flexibility, better chemical resistance and reduced clouding as compared to the corresponding polymer derived from dodecanedioic acid. In addition, the optical transparency was improved over dodecanedioic acid — equivalent to PMMA and superior to polycarbonate and polystyrene.⁷

Block copolymers of polyamides and polyethers, also known as polyetheresteramides, have been formed into shaped articles such as fibers, fabrics, films, sheets, rods, pipes, injection molded components or shoe soles. The polyetheresteramides that utilized C18 diacid afford a product with improved optical properties as compared to its shorter chain homologues.⁸

In the polyester space, C18 diacid was condensed with fluorinated alcohols to produce esters that are incorporated into thermoplastic fibers. The resulting fibers, fabrics, films and molded articles are reported to exhibit improved oil and water repellency.⁹ The esterification products of polyhydric alcohols and this diacid are capable of gelling silicones, dimethylsiloxanes and oil agents for cosmetic products, which have favorable feel in their use applications.¹⁰ Acrylate or methacrylate resins with pendant functional groups, such as glycidyl groups for epoxy resins, can be combined with C18 diacid to improve adhesion as these groups react with the substrate. Advantages of using this diacid are its low volatility, together with its low melting point, that imparts desirable flow properties, which, in turn, can eliminate the need to add a third component flow control agent to the powder coating.¹¹

Polyurethanes are typically synthesized via condensation polymerization of a di-isocyanate (typically MDI), a chain extender (typically butane diol) and a longer chain polyol (typically polyester or polyether). Long-chain diacids (such as C18) can also be used to make polyester polyols that make up the soft segment in polyurethanes. The use of the longer hydrophobic chain in the polyols is expected to result in a new class of polyurethanes with a very flexible, less polar soft segment that exhibits better elasticity at low temperatures and better hydrolytic stability (due to the lower ester content and lower moisture pick-up in high-humidity environments such as automotive).

Condensation polymers based on C18 diacid are also expected to have much lower moisture pick-up than shorter chain diacids. When C18 diacid is incorporated into polar polymers such as polyamides, polyesters and polyurethanes, the resulting polymers are expected to have high temperature performance in high-humidity environments and exhibit better hydrolytic stability. This set of features is critical in under-the-hood automotive applications such as air intake manifolds, tanks for power steering fluids, coolant pumps, electronic housings, connectors and fuel lines. Other applications requiring high-humidity performance include sporting goods (e.g., roller wheels, ski boots, bicycle tires, horseshoes, athletic shoes), power tool housings, mobile phone housings, gears, sprockets, automotive panels, bumpers and airbags.

When incorporated into highly aliphatic polyesters and polyamides, the long linear chain in C18 diacid is expected to increase the crystallinity and melting temperature for applications such as hot-melt adhesives. The use of hot-melt adhesives is growing and includes consumer packaging, woodworking, shoes, laminated security glazing, aerospace, marine, magnetic media binders, construction and bookbinding.

Compounds made from C18 diacid are typically non-polar, and thus can be used in modifying surfaces to make them less sticky and more water repellent. When this diacid is incorporated into an otherwise polar compound formulation, the C18 diacid-containing component is expected to migrate to the surface, lower the surface tension and make the surface more water repellent. Surface modification using this long-chain diacid can be applied in mold release agents, surfactants, cosmetics, carpet fiber, films, water repellent fabric coatings, paints, synthetic leather, and glass coatings for tablet and cell phone screens.

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Polymers and pre-polymers made from aliphatic and cycloaliphatic methylene chains exhibit greatly improved optical transparency over aromatics since aromatics tend to absorb in the UV and visible spectrum. Polymers made from C18 diacid are expected to have high optical transparency compared to aromatics and shorter chain diacids. In optically transparent polyurethanes, polymers made from C18 diacid can thus be used for adhesives for safety glass and ballistic glass, laminated films, taillights, medical tubing and containers, and laser weldable parts such as automotive housings and UV curable adhesives.

Low dielectric constant materials are needed in many electrical, electronic component and semi-conductor applications. Polymers made from C18 diacid are expected to exhibit a low dielectric constant, making them useful for electronic connectors, passivation coatings, conformal coatings, low k dielectrics, capacitors, electrical cabling and electrical adhesives.

In summary, the advantages of long-chain diacids such as C18 are numerous and varied. Incorporation of this monomer into polymers, pre-polymers and low molecular weight compounds is expected to impart low surface tension, better dispersion and miscibility, high crystallinity, low moisture pick-up, high optical transparency, low dielectric constant, and increased hydrolytic stability over shorter chain diacids.

Derivatives of C18 Diacid

C18 diacid can be converted to numerous derivatives using standard chemical and industrial processes. It can be converted to diesters via esterification with alcohols, including diols and polyols, while amide derivatives are produced when the diacid is reacted with amines. Reduction or catalytic hydrogenation of the diacid or diesters produces 1,18-octadecanediol, which can be used as a monomer or chemical intermediate. The C18 diamine, similarly, can be obtained directly from the diacid via amidation and reduction. Titration of the C18 diacid with base provides a route to a variety of salt derivatives. Examples of compounds that can be derived from C18 diacid are shown in **Figure 5**.

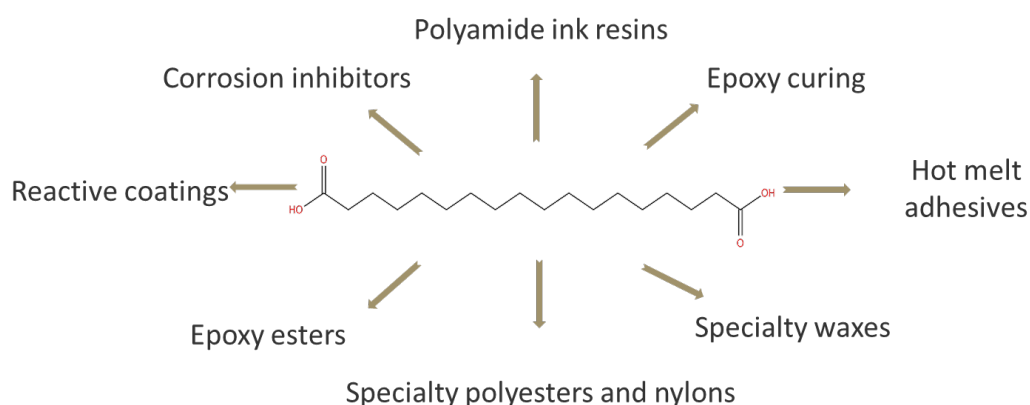


Figure 5. Derivatives of C18 diacid

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C18 diacid and its various derivatives are expected to enable a variety of new application attributes in a variety of market segments.

Summary

Diacids have a broad use across multiple market segments and application areas. With the advent of the metathesis production of Inherent™ C18 Diacid — offered by Elevance Renewable Sciences — the supply for this diacid with a demonstrated ability to impart enhanced properties, such as better solvent resistance, chemical resistance, toughening and hydrolytic stability (as compared to other diacids), will enable the market for C18 diacid to grow and expand into an array of novel products with superior properties. The expected growth of this diacid will rival and possibly exceed that of other diacids. Multiple programs are underway to advance this material broadly.

Also contributing to this article: Brian Albert, PhD; Steve Cohen, PhD; Paul Bertin, PhD; and Jordan Quinn, PhD

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