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Plant-Based Plastics

Nature's Polyethylene

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What will life be like when the oil runs out in about 40 years[1] time? Most people will immediately think about how they will drive their cars or fly in planes, but that is more or less a solved problem. We can use hydrogen from renewable, nuclear or solar light derived electrolysis of water. We, as chemists, however will think of all the many products of the petrochemicals industry: shampoo, washing-up liquid, lubricants, creams, and all the plastics, which are used everywhere every day. We shall still need these attractive products, but what carbon source will we use to replace oil? In the short term we may use coal, which has a projected lifetime of a few hundred years and indeed, huge plants are already converting coal to a similar range of hydrocarbons to that obtained from oil refineries.[2] In the longer term, however, and even in the shorter term if we are to reduce CO_2 emissions, we must turn to renewable forms of carbon and that means growing plants. The carbon there comes in rather different forms, but maybe we can use those forms directly to make all the desirable products we need.

As an example, polyethylene comes in many forms, high density, low density, linear, hyperbranched. It is made by polymerising ethylene (Figure 1 a) traditionally using free radical reactions or Ziegler catalysts but. more recently using single site metallocene catalysts or late transition metal catalysts often incorporating nitrogen donor ligands, which offer fine control over the microstructure and polydispersivity.[3,4] The uses of polyethylene range from plastic bags and bottles to huge gas pipes but the ethylene used to make it comes from oil refining. In the past, ethylene has been seen as a cheap feedstock since it is not part of the fuel pool, but is a major cracking product. As an indication of the rising scarcity and cost of ethylene, one use is for ethanol manufacture by hydration, but the reverse reaction—dehydrating ethanol to ethylene— is now considered to be more commercially attractive because the price of ethylene has increased with the oil price and because ethanol is readily available from fermentation of sugar or, through methanol, from other carbon based sources such as coal or natural gas.

There are moves to find replacements for polyethylene, which derive from natural sources.[5] Dow–Cargill already sells polylactic acid, which can be a drop-in substitute for some forms of polyethylene. It is made by polymerization of lactide (a cyclic molecule formed by heating lactic acid to drive off some of the water, Figure 1 b), with the lactic acid coming from fermentation—some yeast-like organisms give lactic acid rather than ethanol when used to ferment sugar. Fermentation can be done on a large scale under mild conditions, but it represents an extra step and only produces dilute streams of the desired product. In addition, microorganisms can be sensitive and die, although, of course, they also reproduce. All chemical routes to replacement polymers would be very attractive, and different properties for the final product, closer to those of polyethylene itself would be attractive. Whereas polyethylene is only made up of carbon and hydrogen, polylactic acid has two oxygen atoms for every three carbon atoms. This makes it more polar and gives it different properties. In addition it is biodegradable, which is a good thing for plastic bags and bottles, but very bad news if you want to make gas pipes out of it.

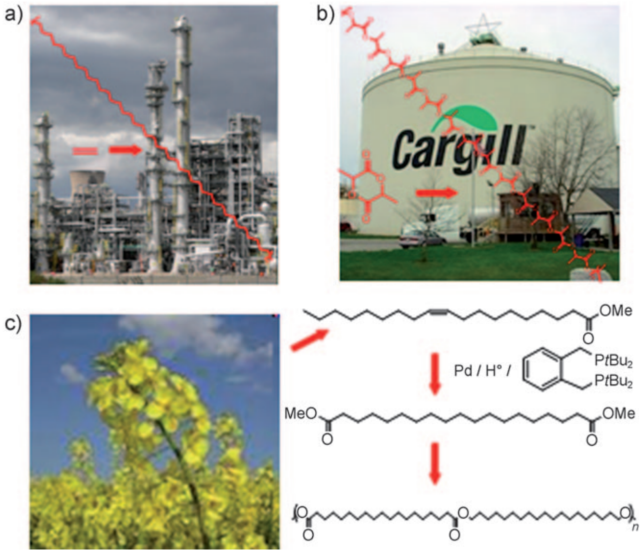

Figure 1. Polymers from a) ethylene from oil, b) lactide from fermentation and c) methyl oleate from plants.

So scientists are looking at ways in which polymers much more similar to polyethylene can be made from natural sources. This is where the recent paper "Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization" by Quinzler and Mecking comes in.[6] They have developed a new way of making straight chain

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polymers containing very little oxygen from oleochemicals, such as methyl oleate. Oleochemicals come from natural oils from such plants as oil-seed rape, sunflowers, olives, etc. Often they exist as triglyceride esters, but they can be broken down into glycerol and long chain fatty acids or esters which have up to three double bonds and chain lengths of about 12–24 carbon atoms. Indeed this is the entire basis of the biodiesel industry, where the fatty acids are used to make diesel. However, rather than burning them, the idea is to use them for making higher added value materials like polyethylene replacements. This approach has the advantage that the oils are obtained directly from the plants without the need for fermentation, they can be in high concentration and the production of the fatty acid molecules requires one simple chemical processing step, transesterification of the triglycerides with methanol.

Quinzler and Mecking decided to make polyesters in which long hydrocarbon chains are linked by ester linkages. To do this they needed molecules with an ester linkage at each end of a long chain. Up until recently, the only way to make molecules like this from oleochemicals was to use self metathesis of methyl oleate, an 18 carbon fatty acid ester with a double bond in the middle of the chain, catalysed by Grubbs' ruthenium based catalysts to give an alkene and an α,ω-diester each with 18 C atoms and a double bond in the middle. After hydrogenation, the dimethyl 1,18-octadecanedioate can be used for making condensation polymers such as polyesters. The disadvantage of this very neat process is that only half the naturally occurring molecule can be used for making the polymer.

Very recently an alternative methodology has been developed which allows all of the methyl oleate to be converted into an α,ω-diester.[7] It involves a remarkable catalyst based on palladium and a special ligand, bis(di-*tert*-arybutylphosphinomethyl)benzene (Figure 1c). This catalyst was first used for making methyl propanoate by addition of carbon monoxide and methanol to ethylene.[8] This process has recently been commercialized and is producing 100000 tons of methyl propanoate per year as part of a new environmentally friendly route to methyl methacrylate, the monomer used to make Perspex. (The old route used acetone and hydrogen cyanide and produced more than a ton of waste for every ton of product. The only "waste" from the new process is a small amount of water.) Subsequent studies showed that this catalyst could also make esters from long chain alkenes, even if the double bond were in the middle of the chain.[9] Remarkably, the new ester group is always introduced at the end of the chain ($>95\,\%$). Even though the required isomerization of the double bond is thermodynamically uphill, the double bond is only trapped by carbonylation when it is at the end of the chain. Unsaturated carboxylic esters and acids selectively produce α,ω-diesters even if the double bond starts off conjugated to the ester function or is deep in the chain.[7] Methyl oleate gives the α,ω-diester, dimethyl-1,19-nonadecanedioate (Figure 1c).[7] This is ideal for polyester formation and most importantly allows all of the natural oil to be used. Quinzler and Mecking have optimized this reaction so that they obtain very pure dimethyl-1,19-nonadecanedioate.

Purity is essential for good polymer properties but, in addition, a partner α,ω-dialcohol is also required. Quinzler and Mecking have made this by reducing the diester and purifying the product. Both components then come from the methyl oleate in very high yields and use all the carbon atoms. A standard condensation polymerization was used for linking the alcohol with the ester groups to give a long chain molecule made up of alternating 17 and 19 carbon chains linked by ester groups. The compound is linear and has only two oxygen atoms for every 19 carbon atoms so it has properties very like those of polyethylene. To make it even more like polyethylene, a starting compound was used that is even longer (methyl erucate with 23 carbon atoms, which is available from some oil seed rape or from crambe).

This process provides an excellent replacement for linear low density polyethylene. It uses all the carbon in the oil, works well and gives high yields of material which will be more biodegradabale than polyethylene itself.

How can the process be improved? The authors themselves acknowledge that the way that have made the dialcohol from the diester (reduction with lithium aluminium hydride) is not ideal, so using some of the catalysts that have been developed for ester hydrogenation would be an improvement.[10] In addition, having to fractionate the fatty acid esters to give pure methyl oleate is energy intensive. However, it has been reported[7] that the same saturated diester is obtained from methyl oleate, methyl linoleate and methyl linolenate (containing one, two, and three double bonds, respectively), so maybe the fractionation is not necessary and crude mixed esters could be employed. Although fractionation of the natural oil to give only one chain length will important, this is easier than separation of esters of the same chain length differing only in the number of double bonds. The process described only gives a replacement for linear low density polyethylene (suitable for bags), but maybe some cross linking could be engineered. This might use residual double bonds if not all the double bonds in methyl linoleate or methyl linolenate are removed, but could possible also rely on using a slight less selective catalyst for methyl linoleate that would put more than two ester groups onto the one chain. This would allow for random cross linking and might produce a material more like high density polyethylene suitable for gas pipes, etc. The diester might also be used as an additive to alter the properties of other polyesters or for polymerization with other monomers. There is much to do, but Quinzler and Mecking have made a great start and pointed the way.

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[1] BP, Statistical Review of Energy, **2009**, http://bp.com.
[2] A. de Klerk, *Green Chem.* **2008**, *10*, 1249–1279.
[3] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170.
[4] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1203.
[5] S. Mecking, *Angew. Chem.* **2004**, *116*, 1096–1104; *Angew. Chem. Int. Ed.* **2004**, *43*, 1078–1085.

[6] D. Quinzler, S. Mecking, *Angew. Chem.* **2010**, *122*, 4402–4404; *Angew. Chem. Int. Ed.* **2010**, *49*, 4306–4308.

[7] C. Jiménez-Rodriguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* **2005**, *8*, 878–881.

[8] G. R. Eastham, R. P. Tooze, X. L. Wang, K. Whiston, World Patent 96/19434, **1996**.

[9] C. Jiménez-Rodriguez, D. F. Foster, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2004**, 1720–1721.

[10] M. Kilner, D. V. Tyers, S. P. Crabtree, M. A. Wood, World Patent 03/09328, **2003**.