

## Sustainable materials based on aliphatic polyesters: teaching old chemistry some new tricks

The power of chemistry was unleashed in the early fifties by the arrival of polymers as a class of new materials with a vibrant industry spawning the manufacture of myriad materials with diverse applications. Today we consume more than 250 million tonnes of polymeric materials, broadly classified as plastics, rubbers and fibres. The growth in consumption of synthetic materials has been nothing less than spectacular and has redefined the contours of our life on this planet, leading Sir Alexander Todd to remark that 'I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life.'

Yet, it was only less than one hundred years ago that the scientific world accepted the existence of large molecules (macromolecules) (Staudinger, H., *Ber. Dtsch. Chem. Ges.*, 1924, **57**, 1203). The initial reaction to Staudinger's hypothesis, derived largely from imagination and intuition, was one of ridicule. After a lecture given by Staudinger in Zurich in 1925, one of the speakers termed Staudinger's championship of long-chain molecules as akin to some traveller in Africa reporting that he had seen a zebra 400 m long!

But persistent articulation of the idea by Staudinger led to the acceptance of the 'macromolecular hypothesis'. It was Wallace Carothers, however, who significantly contributed to the establishment of 'polymerization' as a distinct class of organic reaction. His elegant exposition of rational design and synthesis of new macromolecules using well-accepted principles of C–C, C–O and C–N bond formation in organic chemistry lent this nascent discipline of science, respectability, amongst the larger body of chemists. Carothers unequivocally demonstrated that large macromolecules can be synthesized using the same laws of chemistry that define the synthesis of small molecules; he extensively explored the chemistry of esterification as applied to the synthesis of polymers, leading to a well-known class of material, known generally, as poly(ester)s today (*Chem. Rev.*, 1931, **8**, 353). Interestingly, his first line of exploration was polyesters derived from a single molecule, containing, both the hydroxyl and

carboxylic acids ( $\alpha,\omega$ -hydroxy-carboxylic acids, simplest of which are glycolic and lactic acids). He addressed a profound question, namely when an acid and a hydroxyl group react to form a poly(ester), two reactions can result: (1) a chain polymer of lower or higher molecular weight which still bears the hydroxyl and carboxyl groups in the chain ends or (2) a smaller or larger ring, which does not contain the reactive group. He asked what factors control the relative rates of these two reactions.

Polyesters became articles of commerce beginning 1941. However, polyesters that became useful materials were not derived from the monomers originally studied by Carothers, namely aliphatic di-acids and diols or  $\alpha,\omega$ -hydroxy-carboxylic acids. Polyesters useful as fibres and plastics were derived from aromatic diacids (typically terephthalic acid) and aliphatic diols (ethylene glycol) and came to be known as poly(ethylene terephthalate) or PET. Today, we consume 85 million tonnes per annum of PET with roughly 20 million tonnes per annum used for producing the ubiquitous bottles for water and beverages and the rest for making synthetic fibres. Aromatic polyesters, such as PET, are non-biodegradable and persist in the environment. Although this attribute is a boon to its application as textile fibres, it is a bane when it comes to packaging solutions. We consume 30 billion litres of bottled water annually around the world and every second we throw away about 1500 bottles, much of it ending up on the roadside and in water bodies as waste. Chemistry and technology exist for recycling PET bottles back to the monomers from which they were originally derived; this practice, however, not without difficulties, because of issues in collection, segregation and cleaning coupled with poor civic habits of consumers.

On the other hand, fully aliphatic polyesters, the kind that were initially studied by Carothers, are completely biodegradable under composting conditions. Composting is an aerobic microbial decomposition process leading to carbon dioxide and water. Yet, the world consumption of such polymers is less than 200,000 tonnes per annum, a pittance compared to aromatic polyesters. In fact, poly(lactic acid) or PLA, is an aliphatic polyester derived

from lactic acid, a product of fermentation of sugar, and has many attractive properties for use in packaging applications. PLA requires 50% less fossil fuel for its production compared to PET and has lower CO<sub>2</sub> footprint over its life cycle (0.75 kg CO<sub>2</sub> per kg PLA versus 3.4 kg CO<sub>2</sub> per kg PET). Using current-day metrics of sustainability, PLA is a more desirable material than PET. Yet, it is not part of our everyday life. Why?

The answer lies in both chemistry and economics. The questions that Carothers raised in the early thirties still continue to haunt us, i.e. how do we control the relative rates of inter-molecular and intra-molecular esterification that is observed during aliphatic polyester-forming reactions. Use of rigid aromatic di-acids favours largely inter-molecular esterification, obviating this problem and leading to simple and inexpensive polymerization processes. However, this is at the cost of biodegradability. There is a resurgence of interest in aliphatic polyesters in recent years. This is illustrated by an exponential increase in studies dealing with aliphatic poly(ester)s (over 2300 patents and 2000 papers in 2012). Many new synthetic strategies are being examined. These include ring-opening polymerization of cyclic lactides, use of rigid aliphatic co-monomers, polymerization in the solid state, use of mild chain end coupling methods and converting equilibrium polymerization chemistry to non-equilibrium chemistry, thereby reducing the severity of polymerization conditions. Nevertheless, the challenges in chemistry persist.

The economics is also daunting. The archetypical monomer, lactic acid, can be obtained from sugar or starch by fermentation. Recovery of anhydrous lactic acid from a dilute fermenter broth is still expensive. This apart, the question of whether sugar or starch should be used for food or as a raw material for meeting the materials needs of humankind is a matter of continuing public debate. In this context effort to efficiently convert non-edible biomass to lactic acid has assumed importance.

Responsible and sustainable use of all materials, whether synthetic or natural, is the need of the hour. If consumers need bottled water, due to heightened awareness of health and hygiene, optimal packaging solutions are also needed. PET bottle offers the most economical solution today; yet, it is not sustainable because its raw materials are derived from fossil fuels and its use generates waste that persists in the environment. India's per capita consumption of PET bottles is 0.5 kg against the global average of 2.7 kg. If our consumption approaches

closer to the global average for a billion plus population, it will pose a severe problem to our environment.

Ideally speaking, a virtuous cycle of monomers and polymers for polyesters derived from biomass, which when composted will degrade to CO<sub>2</sub> and water, is most desirable. However, this remains an elusive dream due to limitations of both chemistry and economics. Till such time chemistry and biology are able to resolve the problem, we have no choice but to use PET more responsibly.

The habits of a consumer are often determined by public policy. In many countries of the world there is an increasing trend towards mandating the use of compostable polymers in institutions such as airports, hospitals, food courts, large offices and university campuses. Large supermarket chains are voluntarily adapting the use of sustainable packaging materials on their shelves, thereby demanding new innovations from the suppliers. Unambiguous labelling of consumer products in terms of petro-carbon and bio-carbon content and easy identification of plastics capable of being composted or recycled are becoming more common, creating heightened awareness amongst consumers on the choices they have on materials and their manner of disposal.

What can each one of us do? We can avoid use of bottles of smaller capacity. We can carry our water with us when we travel and use the bottles more than once. In public places, we can use water dispensers which employ larger containers and are reused by refilling. Manufacturers can levy a small cost that provides an incentive to the consumer to return the bottle to a central collection point for recycling. Beijing Subway has installed a machine that can accept used PET bottles, and in return, give a rebate on the train tickets purchased from the machine (<http://www.upgyres.org/subway-travelers-pay-with-plastic-bottles/>; accessed on 4 September 2013).

Till such time chemistry provides us the answers to meet the chemical and materials needs of humankind based on the concept of sustainability, both of resources and environment, we as citizens must proactively think and act to minimize the impact of polymer materials on our environment using the time-tested principles of reduce, reuse and recycle.

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