SUSTAINABILITY OF POLYMERS : FUTURE DIRECTIONS

NATIONAL SYMPOSIUM ON CHEMISTRY EDUCATION AND SUSTAINABLE ENGINEERING
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SUSTAINABLE DEVELOPMENT (CHEMISTRY)

" Development (chemistry or chemical industry) that meet the needs of the present without compromising the ability of future generations to meet their own needs"

In other words, each generation must bequeath to its successor at least as large a productive base it inherited from its predecessor

Brundtland Report
UN World Commission on Environment and Development, 1987

www.un.org/documents/ga/res/42/ares 42-187.htm

We do not inherit the earth from our ancestors; we borrow it from our children.

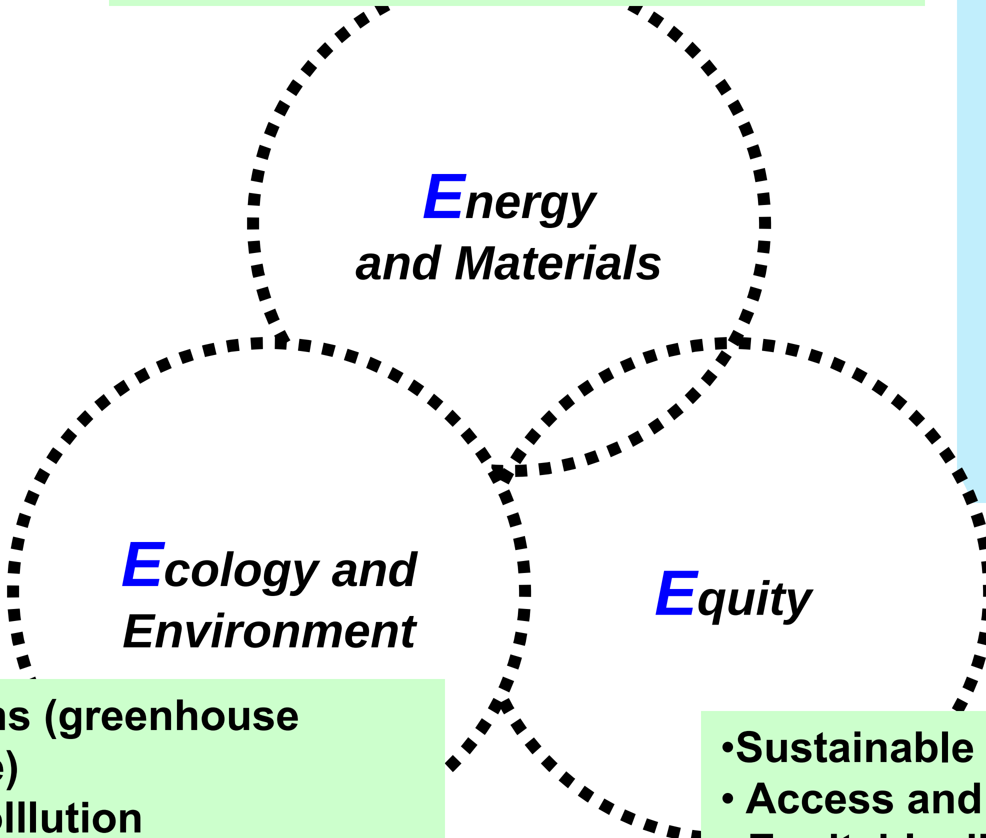
Native American Proverb

Sustainable chemistry: how to produce better and more from less? F. Jérôme et al, , Green Chemistry, 2017, 19, 4973

THE THREE E's OF SUSTAINABILITY

- Clean and renewable energy
- Energy efficiency
- Depleting material resources

Our civilization is at historic crossroads; how we think and act today will determine the future of this planet



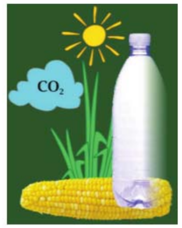
- Reduced emissions (greenhouse gas/carbon dioxide)
- Humans driven polllution
- Safety of chemicals
- Materials from renewable resources
- Circular economy concepts
- Carbon neutrality and de-carbonization

- Sustainable development goals
- Access and entitlement
- Equitable distribution of wealth
- Eliminating poverty

Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality

Rolf Mülhaupt*

Dwindling fossil resources, surging energy demand and global warming stimulate growing demand for renewable polymer products with low carbon footprint. Going well beyond the limited scope of natural polymers, biomass conversion in biorefineries and chemical carbon dioxide fixation are teamed up with highly effective tailoring, processing and recycling of polymers. "Green monomers" from biorefineries, and "renewable oil", gained from plastics' and bio wastes, render synthetic polymers renewable without impairing their property profiles and recycling. In context of biofuel production, limitations of the green economy concepts are clearly visible. Dreams and reality of "green polymers" are highlighted. Regardless of their new greenish touch, highly versatile and cost-effective polymers play an essential role in sustainable development.



1. Introduction

Modern polymer technology has green routes. In both natural and man-made technologies, polymers play a prominent role as extraordinarily versatile and diversified structural and multifunctional macromolecular materials. In 1920, the Nobel laureate Hermann Staudinger recognized that natural and man-made polymers are produced according to the same blueprint: a very large number of small monomer molecules are linked together to produce high-molecular-weight macromolecules. Properties are readily tuned by varying monomer type, sequence of monomer incorporation, polymerization processes, polymer superstructures, and processing technologies. Without polymers, modern life would be impossible because polymers secure the high quality of life and serve as pacemakers for modern technologies. During the early days of polymer sciences and engineering, almost all materials were based exclusively upon chemically modified biopolymers.[1,2] Among polymers, sugar-based cellulose, which is the major component of biomass, wood, and cotton, represents the most abundant organic compound produced by living organisms.[3] In biological cells and biotechnology labs, the incorporation of 20 amino acids is precisely controlled, producing polypeptides such as spider silk, wool, enzymes, insulin, and a great variety of other synthetic proteins for industrial and biomedical applications.[4]

In the 19th Century, natural raw materials such as casein, shellac, gum, natural rubber, and cellulose were chemically modified to convert them into useful macromolecular materials with new property profiles. An important objective was to render the infusible and frequently insoluble natural materials capable of being processed. The first horn-like plastic material was galalith, produced by reacting casein from milk (Greek *gala*) with formaldehyde to produce a stiff thermoset resin resembling stone (Greek *lithos*). Although the biodegradable and water-insoluble galalith was not moldable, sheets could be produced, thus enabling dyeing and machining. The latex of Brazilian rubber trees was collected, coagulated, dried, and vulcanized with sulfur to produce industrial rubber for making tires. Today, around 40% of rubber

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Macromol. Chem. Phys., 214, 154 (2013)

Sustainability issues of polymers and plastics is a topic of great contemporary interest occupying many pages of our scientific journals

Macromolecules 50
Perspective
pubs.acs.org/Macromolecules

50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers

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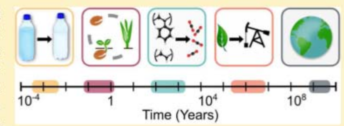
ABSTRACT: It is likely that a half-century ago even enthusiastic and optimistic proponents of the synthetic polymer industry (Mr. McGuire included) could not have predicted the massive scale on which synthetic polymers would be manufactured and used today. Ultimately, the future success of this industry will rely on the development of sustainable polymers—materials derived from renewable feedstocks that are safe in both production and use and that can be recycled or disposed of in ways that are environmentally innocuous. Meeting these criteria in an economical manner cannot be achieved without transformative basic research that is the hallmark of this journal. In this Perspective we highlight five research topics—the synthesis of renewable monomers and of degradable polymers, the development of chemical recycling strategies, new classes of reprocessable thermosets, and the design of advanced catalysts—that we believe will play a vital role in the development of sustainable polymers. We also offer our outlook on several outstanding challenges facing the polymer community in the broad area of sustainable polymers.



I. INTRODUCTION

To highlight the magnitude of an important challenge now facing polymer science, we begin this Perspective on sustainable polymers with a broad look at a seemingly unrelated topic, earth science. There is currently a rift in the field of geology. At the heart of the controversy is nomenclature, specifically whether or not the *Holocene*—the epoch which began almost 12 000 years ago at the end of the last glacial period and which encompasses all written human history—has now ended.[1,2] Although a host of climatic, atmospheric, biological, and geochemical data support the idea that we are now living in a new geological epoch, the *Anthropocene*,[3,4] some earth scientists contend that there is not enough evidence in the rock record to make this designation.[5] In 2016, a process to formalize the *Anthropocene* was launched within the International Commission of Stratigraphy (ICS). This process begins with identifying a primary signal to serve as a marker of this new epoch in the rock record. Among those currently favored are plutonium fallout and radiocarbon spikes from atomic bomb tests, increases in carbon dioxide concentration from burning fossil fuels, and, most relevant to our discussion, plastic.[6,a] The history of the synthetic polymer industry, from the localized introduction of Bakelite and Rayon in urban centers during the early 20th century to the global proliferation of commodity plastics following the Second World War, will be recorded in the sediment for centuries regardless of the specific marker chosen by the ICS.

Over the past 50 years, the uses for and production of synthetic polymers have increased exponentially. This is in large part due to the undeniable fact that these materials provide many societal benefits including those strongly and positively connected to sustainability (e.g., lightweight transportation to ... fuel consumption, membranes for efficient water purification, and food packaging to prevent spoilage). However, polymer prices often do not reflect the true costs associated with their manufacture and disposal.[7] One major issue many synthetic polymers share is that they are derived from nonrenewable resources. Today a small but non-negligible percentage of the total oil produced annually (~8%) is consumed for the manufacture of polymers, with the amount being used *directly* as the carbon source for the synthesis of monomers roughly equal to the quantity consumed *indirectly* for production processes.[8] This number is increasing monotonically; some argue that by 2050 the plastics industry alone will account for almost 20% of the total oil consumed annually.[8] The large scale on which synthetic polymers are produced can be concerning from an energy security and from an economic standpoint for the simple reason that petroleum consumed in their production (and their embedded energy content) is generally not recovered. As a specific example, currently over 40% of the ~80 million tons of plastic packaging used every year is discarded in landfills with an astonishing 32% escaping the collection system or being dumped illegally.[9]

Aside from the considerable economic losses that result from the disposal of polymeric materials after a single use (estimated at ~100 billion dollars annually for packaging materials alone), there are also the direct costs of disposal and the indirect, and often difficult to quantify, environmental costs of polymer pollution.[7,9] Synthetic polymers make up ~11% of the total municipal solid waste (MSW) stream by mass; however, they take up a disproportionate volume in landfills due to their low density.[10] Unlike many other forms of trash, most synthetic

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Macromolecules 2017, 50, 3733–3749

Macromolecules, 10.1021/acs macromol.7b00293, 2017

Circular chemistry to enable a circular economy

By expanding the scope of sustainability to the entire lifecycle of chemical products, the concept of circular chemistry aims to replace today's linear 'take–make–dispose' approach with circular processes. This will optimize resource efficiency across chemical value chains and enable a closed-loop, waste-free chemical industry.

Tom Keijer, Vincent Bakker and J. Chris Slootweg

Awareness of the finite nature of many resources — including the issue of element scarcity, shown in Fig. 1 — as well as the limited environmental tolerance towards our chemical industry has grown tremendously in the past few decades. It has become painfully obvious that the linear route of production, in which scarce resources are consumed and their value-added products are degraded to waste, is a route cause of several impending global crises such as climate change, diminished biodiversity, as well as food, water and energy shortages.

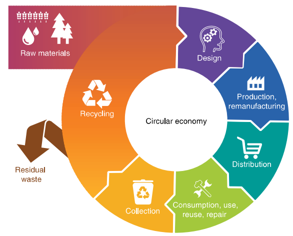
Advocates of the circular economy such as The Ellen MacArthur Foundation (https://www.ellenmacarthurfoundation.org) cleared the path for the emergence of novel policy frameworks that aim to redesign current economic systems, exemplified by the European Union's 2013 'manifesto for a resource-efficient Europe'. A circular economy is defined as "restorative and regenerative by design, and aims to keep products, components and materials at their highest utility and value at all times"[1]. Chemistry is crucial for achieving this[2–7]. Chemists understand their role in designing and developing indispensable materials and technologies, but also simultaneously recognize the potentially detrimental effects that this may have on their practice; they are therefore becoming increasingly aware that each step must be designed or reassessed with sustainability in mind.

Green chemistry for linear processes

Since it was first introduced in the 1980s, green chemistry has provided a framework for teaching and performing sustainable chemistry, and has delivered an impetus for developing cleaner products and processes[8–10] — which have enhanced chemical sustainability in industry and academia. Its twelve guiding principles (Box 1, GC 1–12) focus on the direct sustainability assessment of chemical reactions, and are perfectly suited for the optimization of linear production routes. The developments towards a circular economy, however, require a re-evaluation of what defines a sustainable chemical process, and needs to take into account the people, planet and profit level (referred to as the 'triple bottom line')[11]. Notably, innovative chemistry designed with sustainability in mind is only effective when translated into economically viable applications.

An illustrative example is the reported green synthesis of adipic acid — a key component for the manufacture of nylon-6,6 — by the direct oxidation of cyclohexene with hydrogen peroxide[12]. Solvent-free conditions are applied (GC 2), avoiding the use of the corrosive nitric acid (GC 3) and thus side-stepping the formation of the environmentally taxing gas nitrous oxide, N_2O — a waste product of the current industrial synthesis (GC 4). The green method, however, requires hydrogen peroxide, H_2O_2, as starting material, which means that this process is currently not commercially viable, since H_2O_2 is more expensive than the adipic acid product. Although this route obeys green chemistry principles, it violates the value chain. As a result, this green adipic acid synthesis has not been applied industrially, and has therefore not led to an overall increase in sustainability. Thus, accounting for the profit level of the triple bottom line is an essential component in the design of sustainable chemistry.

Other chemical processes may satisfy the green chemistry principles while being economically viable, yet remain unsustainable. For example, the Haber–Bosch process uses iron for the conversion of dinitrogen, N_2, into ammonia, NH_3, which in turn is used in the production of agricultural fertilizers. It is a key industry showcase for the use of catalysts (GC 9) in increasing energy efficiency (GC 6). The current process requires high temperatures and pressures, and further optimization has stagnated. After its use as fertilizer, large portions of the fixated nitrogen are lost to the environment, causing eutrophication, a global environmental concern, the importance of which should not be underestimated[13]. The cascade of environmental changes that results includes



Credit: European Parliament

an increase in water and air pollution, both of which threaten to destabilize the Earth's system beyond the proposed 'planetary boundaries' or "safe operating space" for anthropogenic activities[14]. This highlights the importance of looking beyond the scientific discovery and analysing the global impact of chemistry using a systems approach[15].

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Circular chemistry for sustainability

In this Comment, we provide a holistic view on how chemistry can contribute to the development of a circular economy, and formulate twelve principles for a 'circular chemistry' (Fig. 2 and Box 2, CC 1–12). In doing so, we provide a framework analogous to that of green chemistry, which has been adapted to facilitate the transition to a circular economy. This approach aims to make chemical processes truly circular by expanding the scope of sustainability from process optimization to the entire lifecycle of chemical products. It promotes, in particular, resource efficiency across chemical value chains and highlights the need to develop novel chemical reactions to reuse and recycle chemicals, to in turn enable development towards a closed-loop, waste-free chemical industry[16–19].

Waste is a resource

Regarding waste as a resource is a prerequisite for circularity. Redirecting

Nature Chemistry, March 2019, p.190

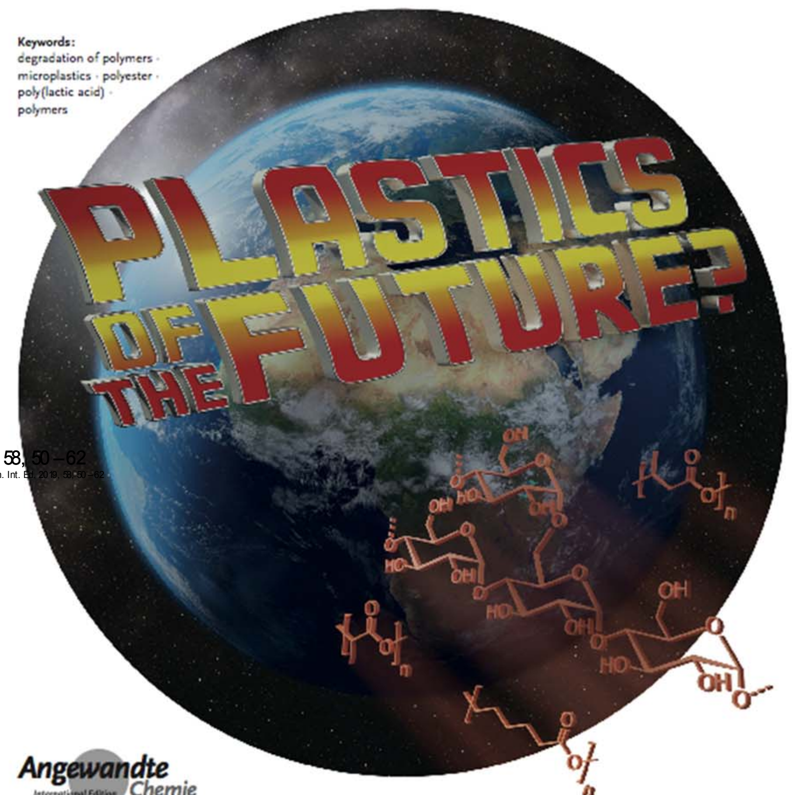
Biodegradable Polymers

International Edition: DOI: 10.1002/anie.201805766
German Edition: DOI: 10.1002/ange.201805766

Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society

*Tobias P. Haider, Carolin Völker, Johanna Kramm, Katharina Landfester, and Frederik R. Wurm**

Keywords:
degradation of polymers · microplastics · polyester · poly(lactic acid) · polymers



Angewandte International Edition Chemie

Wurm, F R et al, Angew Chem. Int.Ed, 2019. 58, 50

Sustainability of polymers is critical to the emerging interest in circular chemistry

SUSTAINABLE POLYMERS : A DEFINITION

" Sustainable polymers are defined as materials derived from ***renewable*** or ***non-renewable*** feed-stocks that are **safe** in production and consumption and which after their use can be ***recycled*** or ***disposed of*** in ways that are environmentally benign"

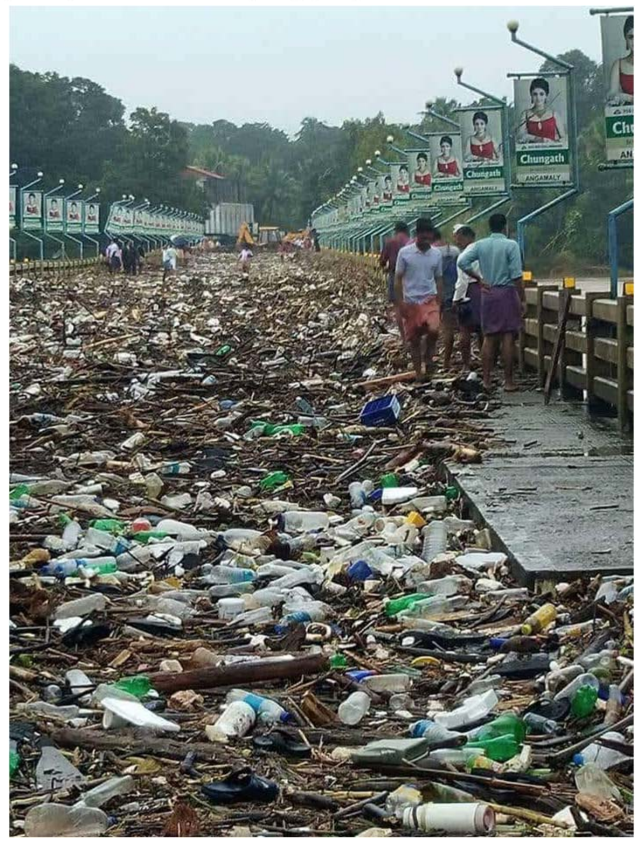
Recycle : easy and economically viable processes to recycle the material
Disposed of : in land and water and the products of degradation harmless to soil and water

INCREASING ONSLAUGHT ON PLASTICS : THE TRIGGER

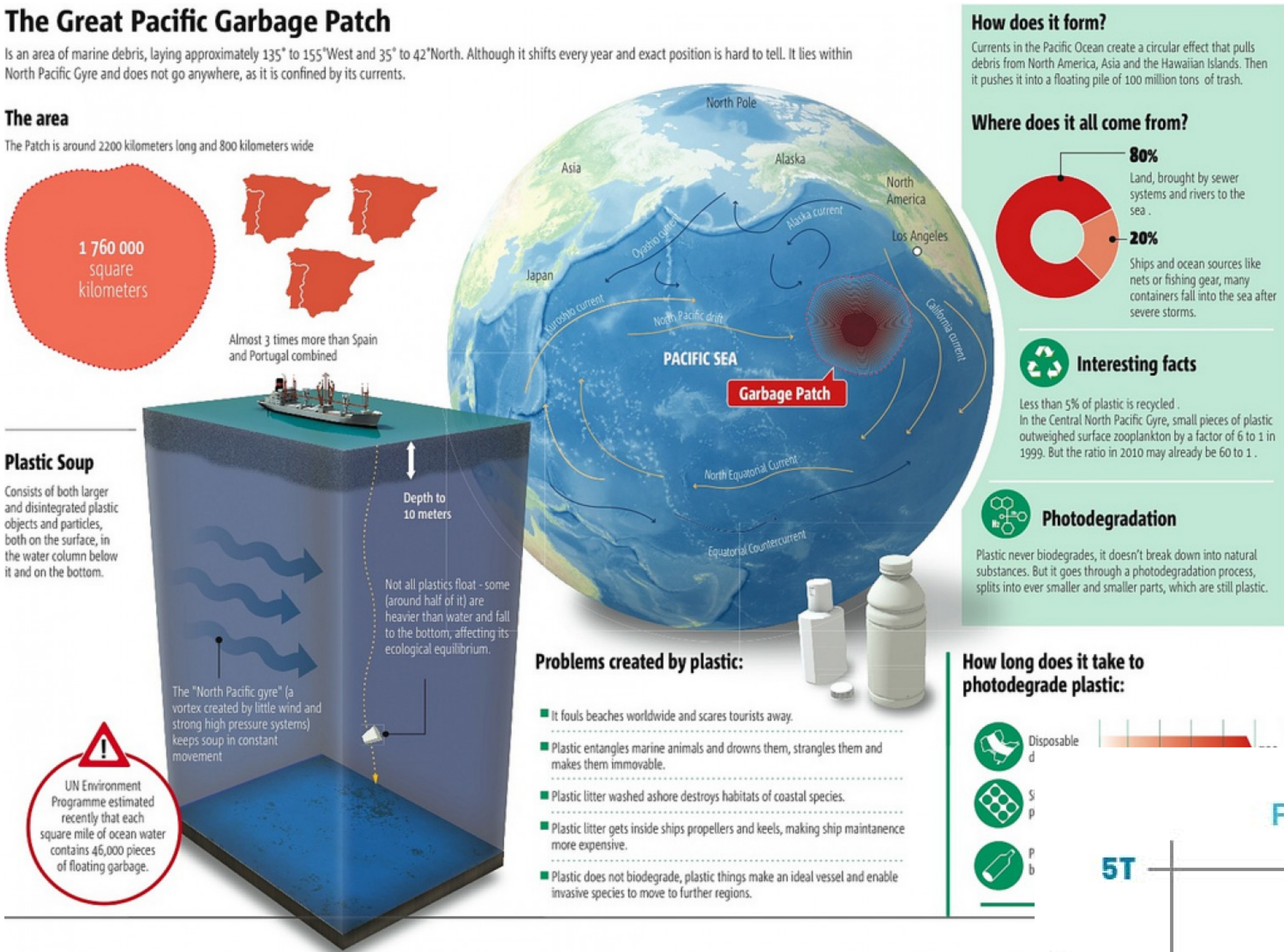
- China's National Sword Government Program implemented from January 1, 2018 and the closure of world's largest garbage dump processing 7.5 mta of and 80 % of global end-of–life plastics waste
- Ellen McArthur Foundation Report on "Towards a Circular Economy", released at WEF Meeting at Davos in January 2014 and "The New Plastics Economy", The Ellen MacArthur Foundation and WEF, January 2016
- United Nations Environment Program World Environment Day 2018 pledge to eliminate "Single-Use Plastics" and "Clean Seas Campaign"

Blue Planet 2: How plastic is slowly killing our sea creatures, fish and birds, 19 November 2017, Episode 7 looks at how tiny plastic particles (micro-plastics) may play a role in the uptake of industrial pollution in marine life.

https://www.nytimes.com/2018/08/06/science/plastics-polymers-pollution.html



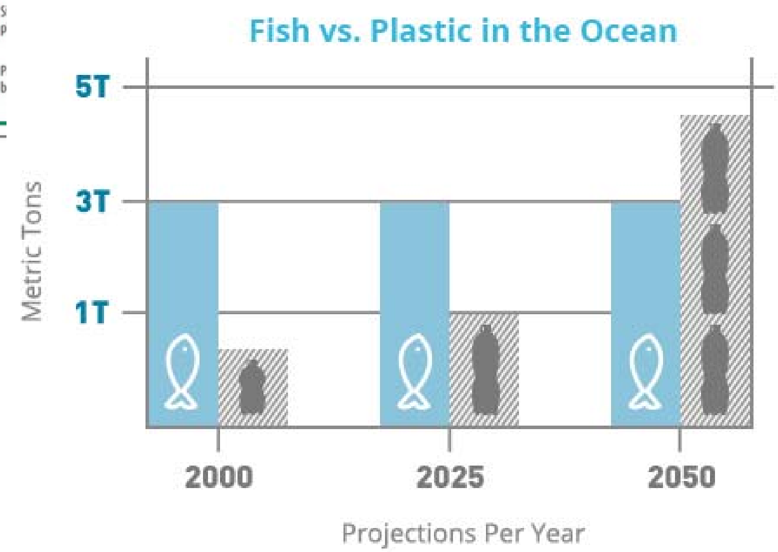
Malayattur Kodanad bridge after the floods receded, 19 August 2018



http://visual.ly/great-pacific-garbage-patch

There is an estimated 200 million tons of plastics litter in our oceans
Our oceans can be devoid of life in the not too distant future if nothing is done to stem this

The patch contains 270,000 tons of plastic waste
Microplastics upto <5 mm dia
Leachates detected : nonylphenol, Triclosan, PBDE



500 Billion bottles consumed

Poly(ethylene terephthalate)

Over 30 billion liters of bottled water is consumed annually

1
PETE

Every second we throw away about 1500 bottles

What is the solution ?

We produce 20,000 PET bottles every second

MICROPLASTICS : A NEW THREAT TO SUSTAINABILITY OF PLASTICS

June 3, 2018 TOI

TIMES TRENDS

Your polyester shirt may soon come with a warning label

When washed, synthetics shed plastic microfibres that end up in waterways

Lindsey Rupp

Lawmakers in California and New York have proposed state bills this year to raise awareness of a problem few consumers may have heard of — synthetic fabrics shedding microfibres into the water system. Reminiscent of the plastic microbeads that were banned from cosmetics, garments made with polymer-based cloth can release as many as 1,900 microfibres per wash that eventually end up in waterways, one study shows.

But research is still at the early stages, and few are in agreement about what the best response is. The bills proposed in those two states suggest requiring that all new clothing made of more than 50% synthetic material carry an additional removable tag that reads: "This garment sheds plastic microfibres when washed." The retail industry is against those proposals, claiming they wouldn't solve anything — and could create even more costs and problems.

"There's a lot of questions we don't know the answers to," said Nate Herman, senior vice president of supply chain at the American Apparel and Footwear Association, an industry trade group. "The concern with legislation is that it's getting ahead of the science."

Microfibres may pose a threat to waterways and aquatic life, according to activists and supporting research. Less than 5mm long, they're not filtered by washing machines or water treatment plants and have been found in everything from bottled water to sea salt to fish.

Like plastic microbeads washed down the drain in cosmetics the fibres are about the size of plankton, and many marine organisms may ingest the material when they're feeding. They may end up in people as well. About 83% of drinking water samples tested around the world contained microplastics, according to a study released last year.

Apparel tags or stickers would be an opportunity to raise awareness that microfibre pollution is a problem in the first place, said Rachel Sarnoff, executive director of the plastic pollution advocacy nonprofit 5 Gyres Institute. Her group isn't trying to get consumers to give up synthetic fibres altogether, but to be more aware of their possible environmental reach.

"There are certain places you're not going to give up those synthetics," Sarnoff said. "If you do wear synthetics, it's good to be aware of their impact, especially when you wash them in a machine."

Retailers say they want more research on the issue. It's not even clear that fabrics are the most to blame. It could be that garments become more prone to shed as they age, or that top-loading washing machines agitate pieces into releasing fibres. BLOOMBERG

DIRTY LINEN: Plastic microfibres from synthetics are not filtered by washing machines and have been found in everything from bottled water to fish

Machine washing your shirt may be harmful to the fish !

PLASTICS: RELUCTANCE TO CELEBRATE ITS SUCCESS !

- 2018 marked the sesquicentennial of the discovery of plastics. It was in 1868 that John Wesley Hyatt made the first billiard ball from cellulose nitrate plasticized with camphor which was introduced into the market by Phelan and Collender, NY to replace ivory
- 2020 will mark the centenary of the concept of "macromolecules", the principle that large molecules can be synthetically made from smaller molecules (Herman Staudinger)

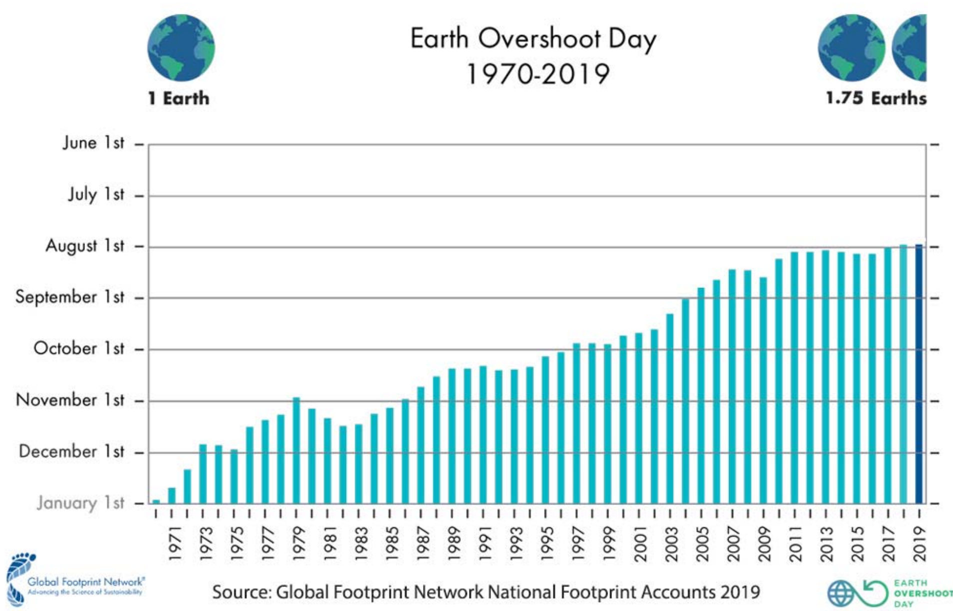
We need to shift the conversation from a binary ; the devil versus angel to something more meaningful

CHALLENGES TO SUSTAINABILE DEVELOPMENT

- Population and earth's carrying capacity (> 9 billion by 2030)
- Irreversible changes in global climate (+3˚C ⇧)
- Providing enough food for the people (land use pattern)
- **Depletion of earth resources (excessive consumption and rapid urbanization)**
- Access to affordable clean energy (societal and quality of life inequities)
- ***Increasing burden on environment by "end-of-use" objects and materials in a "throw-away" society***

OUR INSATIABLE DESIRE TO CONSUME

- The world today is using up its resources 1.7 faster than they are being renewed
- The Earth Overshoot Day this year fell on 29 July 2019, when we fully consumed our earth's resources of the entire year.



Our ecological footprint

This means that humanity is currently using nature 1.75 times faster than our planet's ecosystems can regenerate, equivalent to 1.75 Earths. Humanity first saw ecological deficit in the early 1970s. Overshoot is possible because we are depleting our natural capital, compromising the planet's future regenerative capacity.

WHAT IS THE PROBLEM WITH SUSTAINBILITY ?

For a long time we have

- Ignored the impacts of technological progress,
- Concealed the consequences of ubridled growth,
- Followed the instruction *”multiply” and “subdue the Earth”*
- Put *”having*” before *”being*”
- Kept thinking as if there were still as few people on earth as there were 200 years ago.

Our dilemma is that we live in a finite world, but behave as if it were inexhaustible.

If all the people in the world lived like they do in Switzerland, then we would need three planets as big as our Earth.

Using resources at the current rate we will need " the equivalent of more than two planets to sustain us " by 2100 ! Our planet is finite, but human possibilities are not. Living within the means of one planet is technologically possible, financially beneficial, and our only chance for a prosperous future

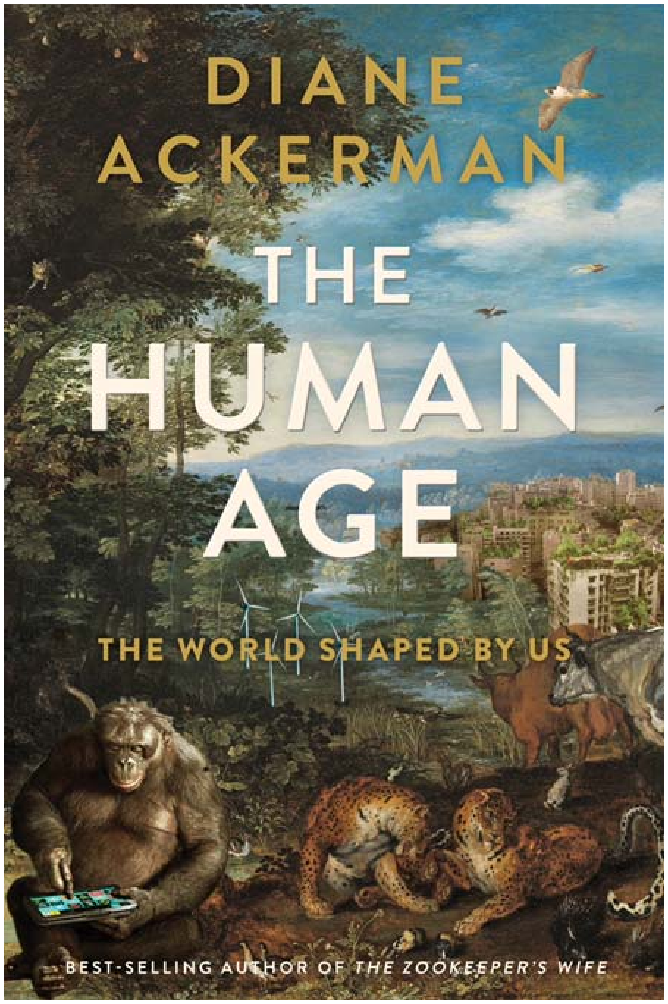
THE HUMAN ANTHROPOCENE AGE

Humans are leaving an indelible imprint on Planet Earth

Closing the cycles is a key challenge for science

- *The Carbon dioxide cycle*
- *The Hydrogen cycle*
- *The Carbon Cycle*
- *The Nitrogen cycle*
- *The Element cycle*
- *The Ocean pH cycle*
- *The Fuel cycle*

Extinction of species, habitats and material resources are at unsustainable rate



2014

However, emergence of new science & technology alone is no guarantee that its benefits will tickle down to humanity at large.

SUSTAINABILITY ISSUES ASSOCIATED WITH PLASTICS

What is the problem ?

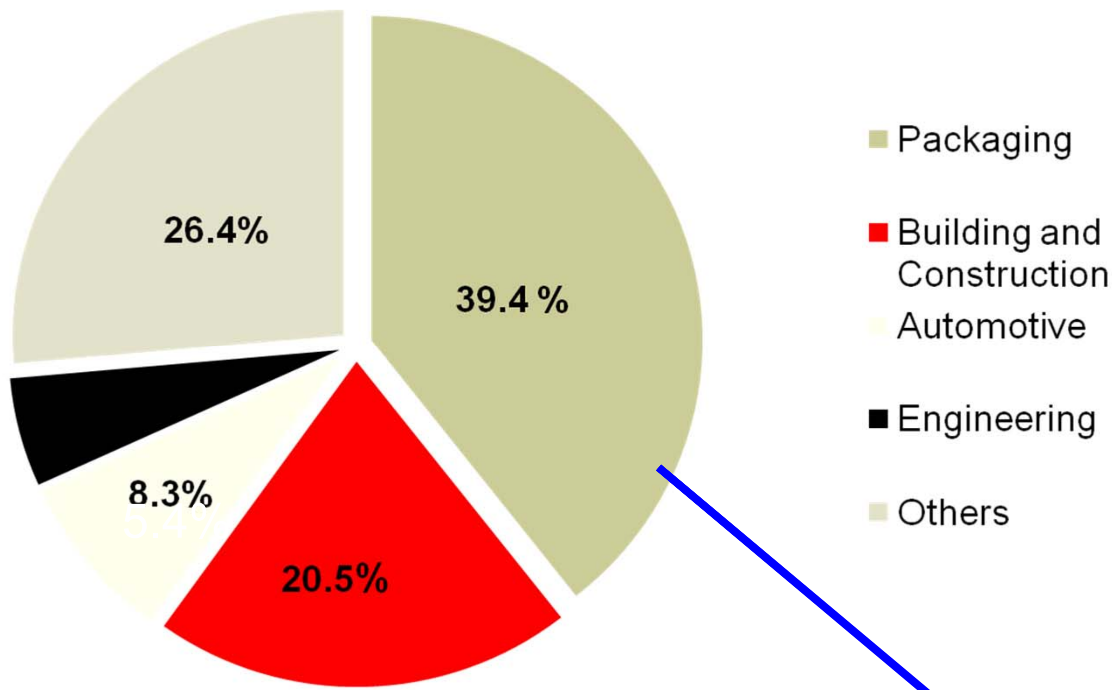
- Use of fossil hydrocarbon derived building blocks ?

or

- After use and end of life issues?

To arrive at an answer we have to frame the question correctly !

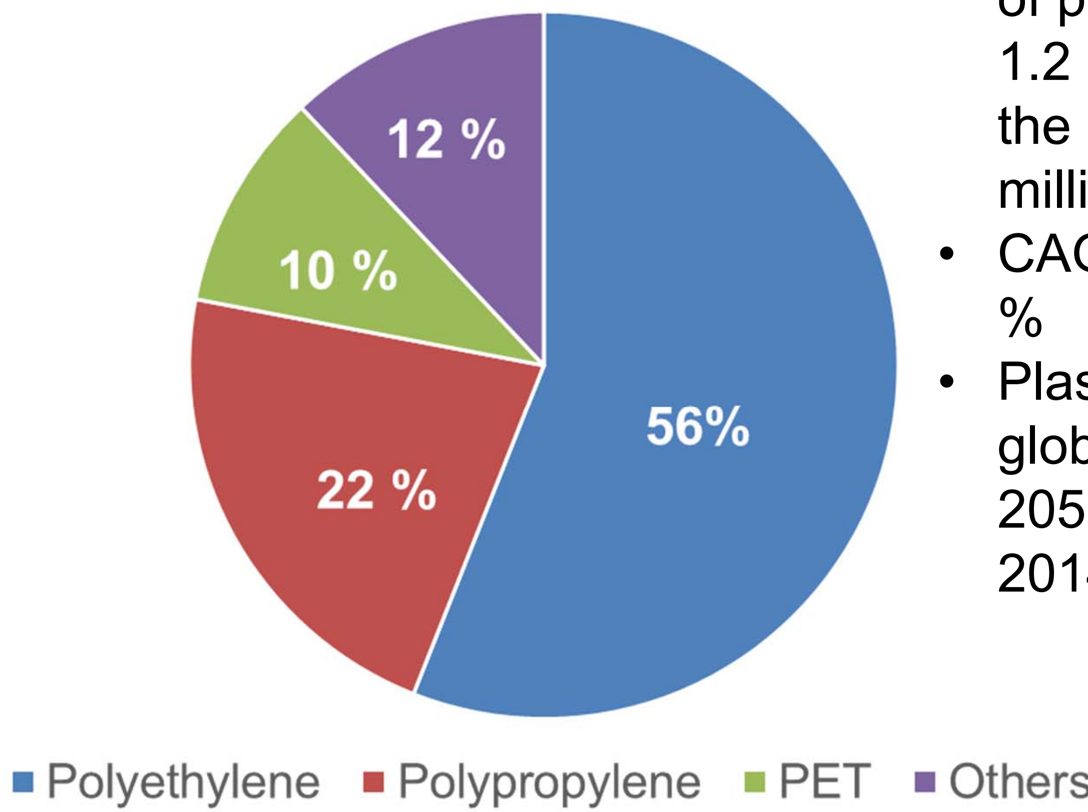
PLASTIC DEMAND BY APPLICATION SEGMENT



After use and end-of-life issues?

Segment of great concern

GLOBAL PLASTICS PACKAGING MARKETS



- Global production of plastics by 2050 : 1.2 billion tons from the present ~400 million tons
- CAGR : 3.5 to 4.0 %
- Plastics share of global oil: 20 % by 2050 from 6 % in 2014

Fundamental redesign for sustainability required for 50% of packaging items by number and 30 % by weight

PLASTICS IN PACKAGING: BANE OR A BOON ?

- Inexpensive
- Design flexibility
- Aesthetics
- Capable of mass manufacturing
- Preserves food and improves hygiene

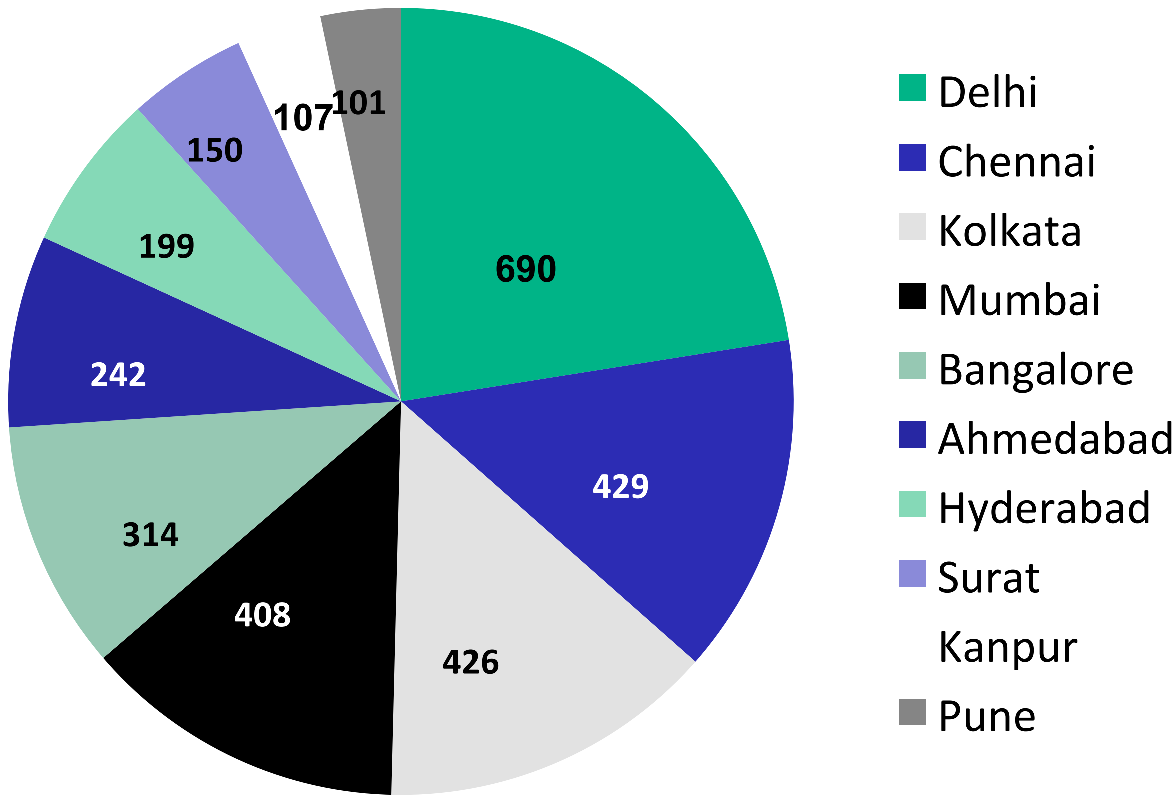
When a virtue becomes a vicissitude !

OUR INSATIABLE DESIRE TO CONSUME

- To date we have produced, consumed and discarded over 8 billion metric tons of plastics; 60 % have been landfilled, 30 %are still in use and 10 % incinerated (Sci. Adv., 10.1126/sciadv.1700782, 2017)
- W. Europe consumes an average of 16 tons of materials per person per year, of which 6 tons ends up as waste, including 3 tons of landfill
- We consume 30 kg of packaging material per person per year, all of which ends up as waste.
- We discard about one trillion single use plastic bags each year; generate 2 billion tons per annum of municipal waste; 5 million tons of plastics find their way into our oceans
- Global recycling rate is only about 10 % of the materials consumed

Unsustainable consumption of finite resources

PLASTIC WASTE IN TONS PER DAY IN MUNICIPAL SOLID WASTE (2010-11)



An average of 8,5 % of the MSW is single use plastics, which when extrapolated to whole country translates into 25,000 tons per day or 10 million tons per annum

Source; CPCB

INDIAN PACKAGING INDUSTRY

- India`s plastics packaging consumption is 4.5 kg /person
- 95% of economic value of packaging lost after one use
- India’s Packaging Industry is valued at US $ 32 billion in 2015; expected to reach US $ 73 billion in 2020 with a CAGR of 18 %

What will the consequence when our per capita plastics consumption approaches the global average of 28 kg/person by 2025 ?

2018

- India's growing middle class is the largest threat
- Large scale social engineering needed to bring about behavioural changes
- Just like many other problems facing the society, there are no simple answers. So we must avoid offering simple solutions
- ***We need to change the perspectives of the society, government and the industry, in small and measured manner***

GOVERNMENT'S SIMPLE RESPONSE

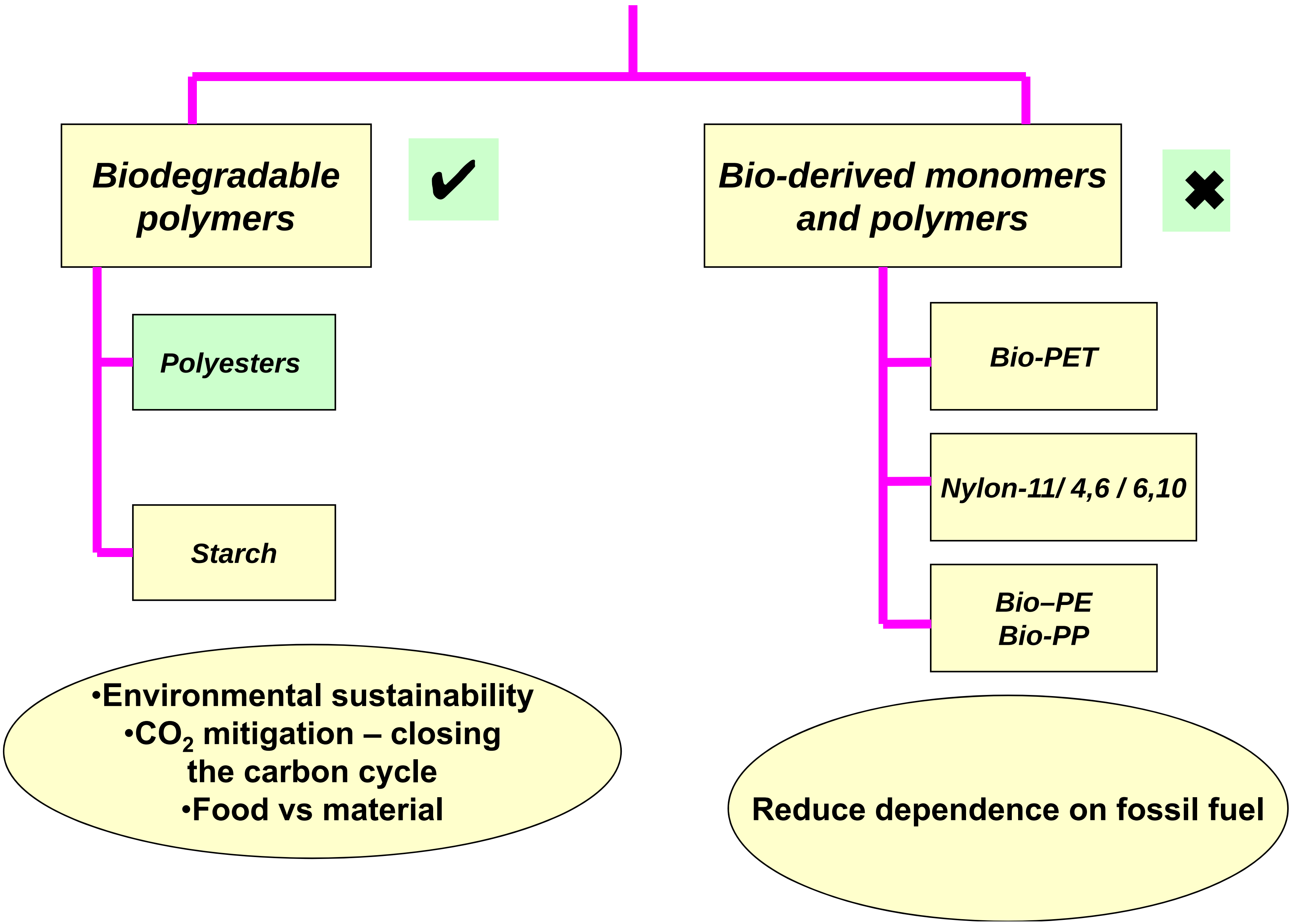
- Ban single use plastics; 25 Indian states have banned single use plastics
- Government has little choice, caught between the constraints of governance and the pressures of the civil society; Government tends to take short sighted decisions

About 127 countries in the world have enacted laws restricting the use of certain types of plastics

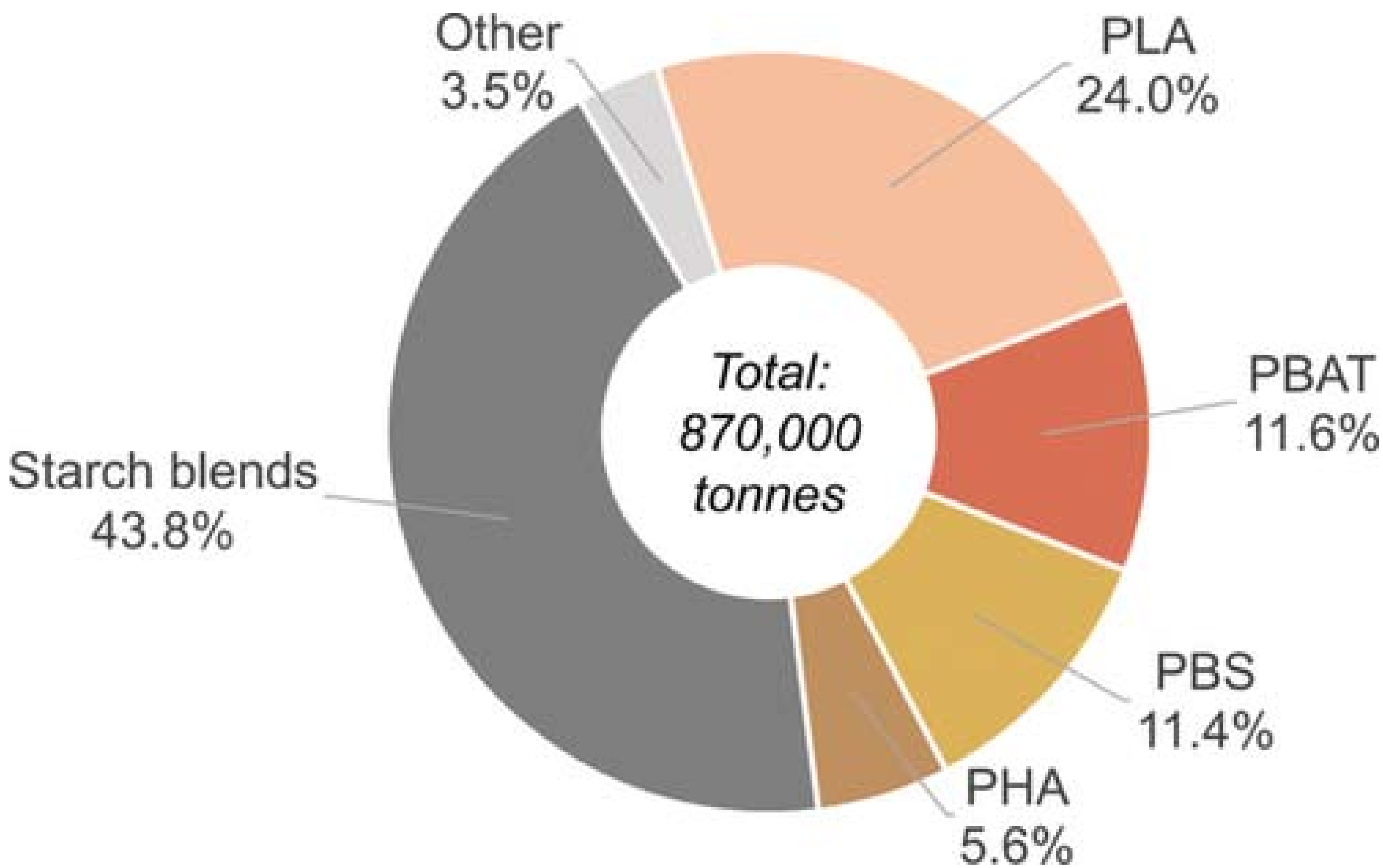
For every complex question, there is a simple answer; and it is, invariably, wrong

H. L. Mencken
(1880-1956)

POLYMERS FROM RENEWABLE RESOURCES



PLASTICS OF THE FUTURE?



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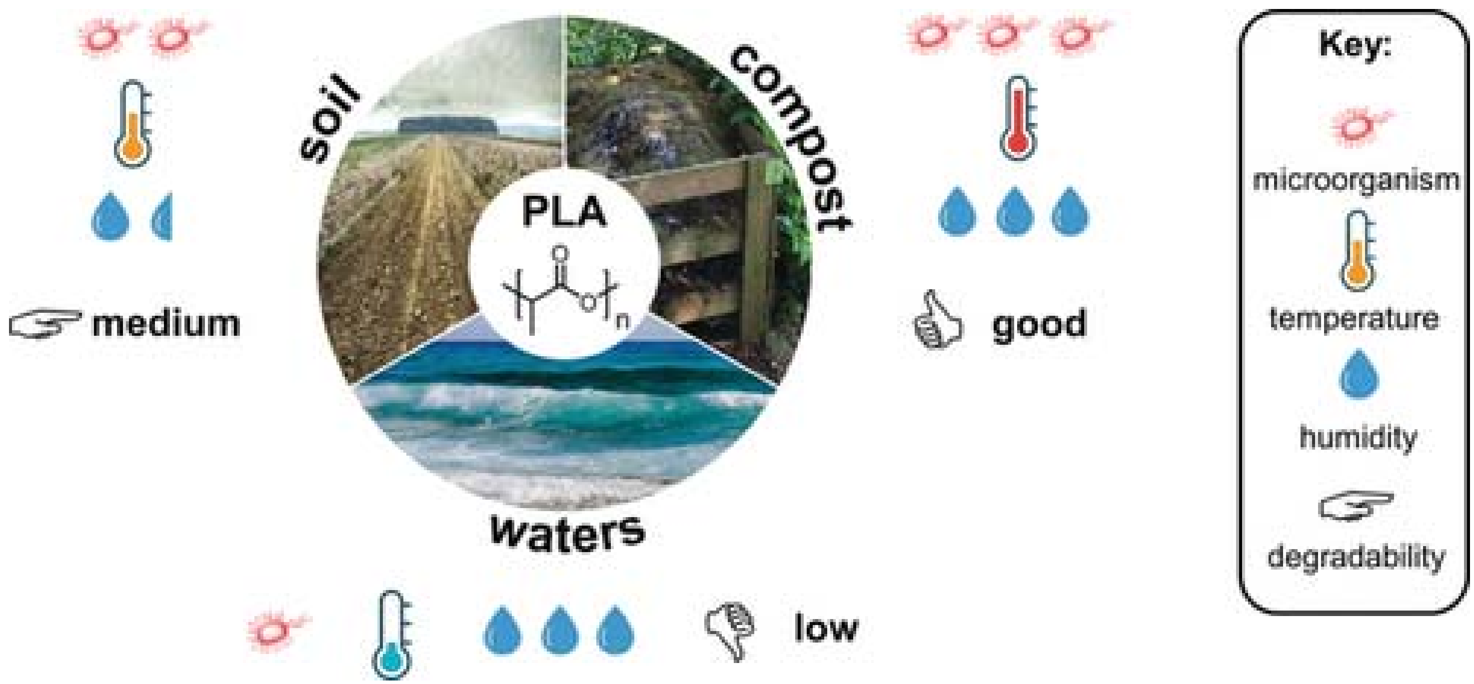
THE IMPACT OF BIODEGRADABLE POLYMERS ON THE ENVIRONMENT



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4 July 2018, DOI: (10.1002/anie.201805766)

CHALLENGES FOR BIODEGRADABLE AND COMPOSTABLE POLYMERS

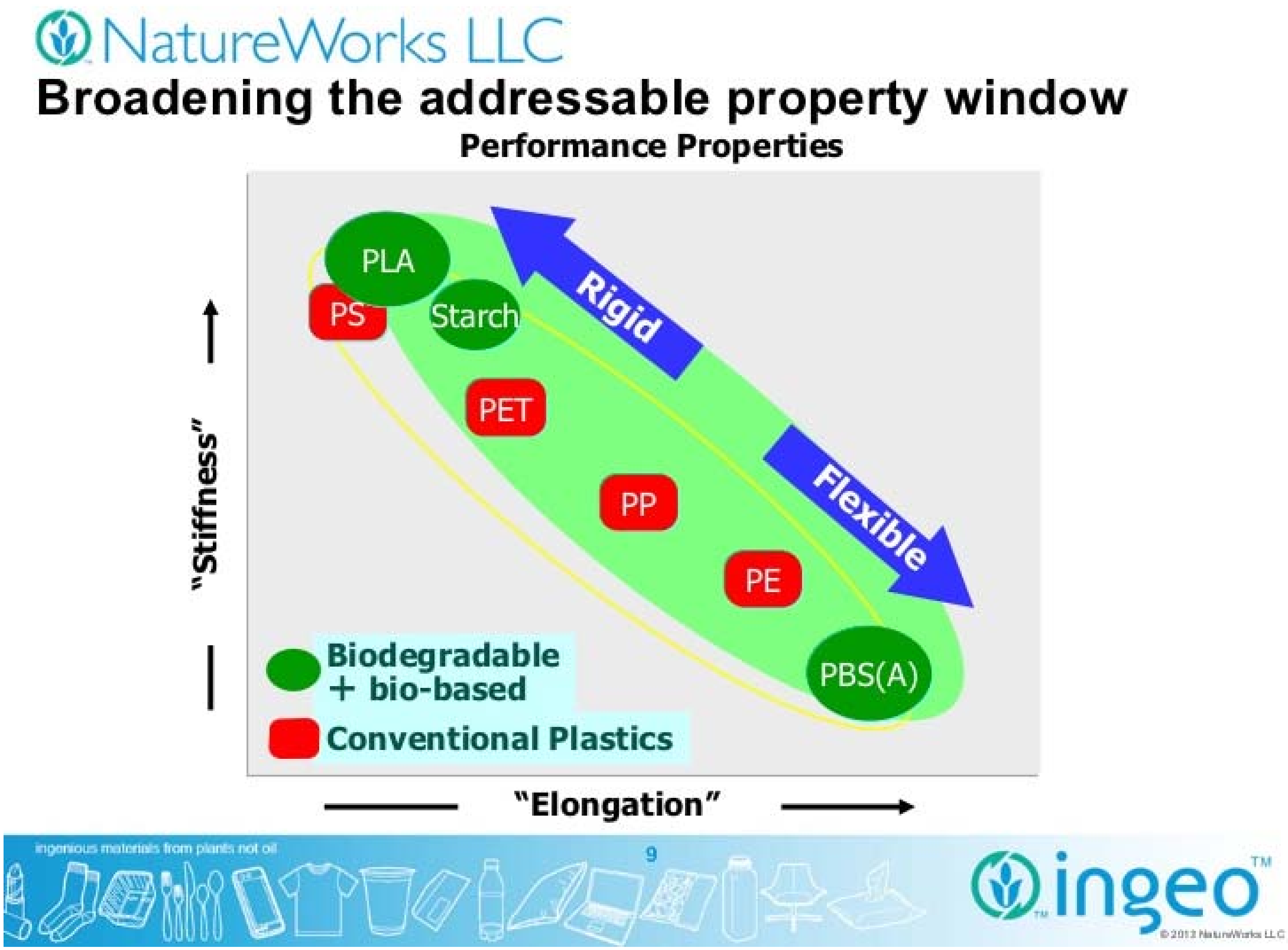
- Implications of contamination of compostable and bio degradable polymers with those which are generally recycled or landfilled
- Inadequate availability of industrial composting infrastructure
- Technology gaps in using waste agricultural residues as feedstocks for making polymers; all biopolymers today are derived from edible sugars
- Range of accessible properties; polyesters are the only class of polymers that are compostable and biodegradable; no performance differentiator for bio polymers, except their biodegradability

SUGAR AS A FEEDSTOCK FOR COMMODITY MONOMERS AND POLYMERS : ARE THEY VIABLE?

INPUT CONUNDRUM

FEED-STOCK	$ per million BTU
Natural Gas	1.80
Biomass	4.0
Crude Oil	7.9
Corn	8.0
Sugar	22.6

C&EN, May 2, 2016, p.26



Furthermore the addressable property window of biodegradables is still very narrow

PLLA : PROPERTY DEFICITS AND METHODS FOR IMPROVEMENT

Poor melt viscosities on account of poor chain entanglements

- *Branching and chain end aggregation*

Brittle material : Poor toughness and elongation

- *Improving toughness using star branched polymers*

Slow rates of crystallization (t1/2 : 2.5 hours)

- *Nucleation using well defined comb-graft copolymers*

Poor heat stability (Tm : 180 ºC ; Tg : 60 ºC)

- *Stereo-complexation of PLLA-block-PLDA*

BIODEGRADABLES: MYTHS AND MISCONCEPTION

- Biodegradable polymers do not break down under kitchen waste composting conditions. They need industrial composting conditions
- Biodegradable polymers do not degrade in aquatic environments, especially in ocean depths
- We still do not have a material which have compostability equivalent to paper or vegetable matter !

Introduction of biodegradable materials may be a double edged sword; it can cause consumers to litter more rather less because of the perception that biodegradable materials will harmlessly dissolve in the environment, thereby removing the responsibility from the individual. Sound waste management practices are as important to bio-degradable materials as non-biodegradables

Seen in Delhi Airport, Terminal 3

Compostable in 12 weeks under industrial composting conditions

YET THERE IS TOO MUCH FOCUS ON BIO DERIVED MONOMERS FOR NON BIO-DEGRADABLE POLYMERS

- Of the 4 million tons of bio derived polymers currently in commercial production, 70 % are bio-based non-biodegradable polymers; hardly 30 % is truly biodegradable polymers; by 2020, this ratio will be closer to 80:20 !
- Emphasis appears to be towards replacement of fossil hydrocarbon derived monomers for polymers
- Little focus on compostable and biodegradable polymers

A clear example of research focus that is defined by what ***can be*** *done rather than what* ***needs to*** *be done*

NO ECONOMICALLY VIABLE RECYCLING OPTIONS FOR MANY POLYMERS AS YET !

- Multi- phase polymers: ABS, Impact PP, HIPS, blends
- Multilayer coextruded films, barrier films, PE/PET, aluminum/polymer, paper/ PE. Tetrapack®, laminated tubes etc
- Polystyrene, flexible PVC, Polyurethanes
- All cross-linked rubbers (including natural rubber!)
- All thermosets
- Low bulk-density materials, such as foams, bubble wraps, blister packs and the like
- Polymers that have come in contact with food, beverages, body fluids or household chemicals

SOME SCIENCE AND TECHNOLOGY GAPS

- Convert short life time post-consumer waste to long life time products
- Polymers for packaging with single composition and the functionality of multilayer materials
- Transparent packaging films which can filter UV radiation
- Improved heat sealabilty and higher weld strengnth in biodegradable polymers (high Tg polymers)
- Redesign additive packages and make them more compatible with recycling
- Adhesives that can be easily degraded by application of a trigger; bio-degradable and bio-compatible adhesives
- Polymers capable of degrading in marine and aqueous environments (poly(hydroxy alkonoates)
- Compostable polymers with a WVTR of $< 8 g/m^2/day/atm$ and OTR of $< 55 cm^3/m^2/day/atm$

SOME SCIENCE AND TECHNOLOGY GAPS

- Biodegradable polymers with resistance to oleochemicals
- Coatings on paper to impart nominal oxygen, water vapor and oleochemical transmission barriers (re-engineering cellulose)
- More environmentally benign, small, modular and efficient waste to energy technologies
- Molecular recycling technologies (MRT); polyethylene and polypropylene back to ethylene and propylene
- Polymers that can be cleanly converted to monomers under suitable triggers (chemical or physical)
- Biodegradablity (enzymatic degradation)of polymers under home composting and under-water marine conditions
- Polymers designed for death (Immolative polymers or apoptosis)

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.www.mcp-journal.de

Recyclable Vinyl-Functionalized Polyesters via Chemoselective Organopolymerization of Bifunctional *a*-Methylene-*d*-Valerolactone

Tie-Qi Xu, Zhi-Qi Yu, and Xue-Min Zhang*

_a_-Methylene-_d_-valerolactone (MVL) is a bifunctional monomer comprising of a highly stable six-membered _d_-valerolactone ring and highly reactive C□C bond. Previously, the vinyl-addition polymerization (VAP) product, namely $P(MVL)_{VAP}$, has been formed exclusively. In this study, this conventional chemoselectivity is reversed, wherein organic catalysts are used to enable the first ring-opening polymerization (ROP) of MVL, exclusively affording a metal-free, unsaturated polyester, namely $P(MVL)_{ROP}$. This challenging goal is achieved by investigating different catalysts, initiators, and reaction conditions. In addition, the formation of two polymers, namely $P(MVL)_{ROP}$ and $P(MVL)_{VAP}$, is easily regulated by varying the polymerization solvent. The resulting $P(MVL)_{ROP}$ can be easily post-functionalized to form crosslinked or sulfurized materials; notably, it can be almost completely converted into its monomer thermochemically.

1. Introduction

Synthetic polymers are indispensable for modern society. With an annual production of hundreds of millions of tons, these durable, multi-functional materials are widely used in food packaging, insulated buildings, and lightweight transportation.[1,2] However, the extensive use of these non-degradable polymers not only results in issues related to waste management but also impacts the environment significantly.[3,4] Therefore, a key goal in modern polymer research involves the generation of degradable substitutes with comparable performance to the currently used polymers. To overcome the limitations of material sustainability and degradability, biodegradable functional groups have been reportedly introduced into the polymer structure.[5] However, biodegradable polymers often require strict degradation conditions. Moreover, researchers need to consider whether it is beneficial to degrade polymers into intangible small molecules or to treat more macroscopic solid plastics from the viewpoint of environmental consequences.[6]

Recently, a few studies have reported the production of chemically recyclable polymers,[7] which comprise macromolecules that can be degraded into valuable molecular fragments, most typically converted into their constituent monomers; these monomers can be repolymerized in the same manner as the original monomer. The currently reported chemically recyclable polymers include polyesters obtained by the ring-opening polymerization (ROP) of lactone,[8–15] polyamides obtained by lactam's ROP,[16] and polycarbonates obtained by the copolymerization of carbon dioxide and 1-benzyloxycarbonyl-3,4-epoxy pyrrolidine.[17–20] Only one polymer obtained by the chemoselective ROP of the α-methylene-γ-butyrolactone (MBL) monomer is a functional material consisting of an unsaturated C□C bond, which can be further modified to form novel materials by the thiol–ene click reaction or crosslinking.[11] It is extremely difficult to achieve the chemoselective ROP of MBL in the presence of an active extracyclic C□C bond and a highly stable γ-butyrolactone (BL) monomer. This reaction must be conducted at an extremely low temperature (−60 °C) over long periods to obtain acceptable yields of the required polymer. Hence, it is challenging to prepare C□C bond-containing chemically recyclable polymers under mild conditions. The ring strain of δ-valerolactone (VL) was greater than that of BL, making it more susceptible to ROP; thus, VL exhibits good reactivity, and it is typically obtained under mild conditions.

Recent studies have also found that some polymers obtained from substituted VL monomers are promising as recyclable materials.[8–15] Therefore, a fundamental question that arises is whether this conventional chemoselectivity can be reversed by switching on the ROP of α-methylene-δ-valerolactone (MVL) while simultaneously ceasing the vinyl-addition polymerization (VAP), thereby enabling the synthesis of a chemically recyclable unsaturated polyester, $P(MVL)_{ROP}$ (**Scheme 1**). MVL is a readily available, well-established lactone monomer. For the past 30 years, the free-radical-initiated vinylic double-bond polymerization to form the VAP product, $P(MVL)_{VAP}$, has been investigated.[21] However, the ROP of this monomer has not been reported yet. Recently, the Lu group has reported the formation of an intermediate obtained by the reaction between the

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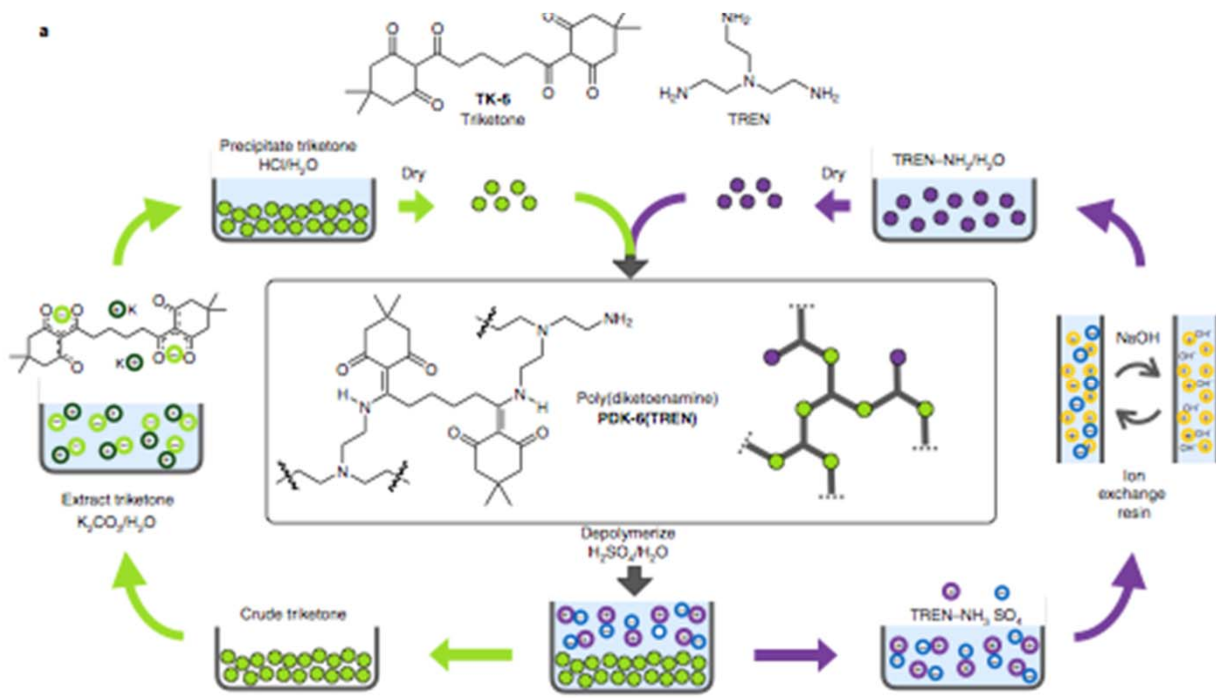
Towards Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters,
X. Tang, Eugene X-Y Chen
Chem., 2918, 5, 1-29

Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds

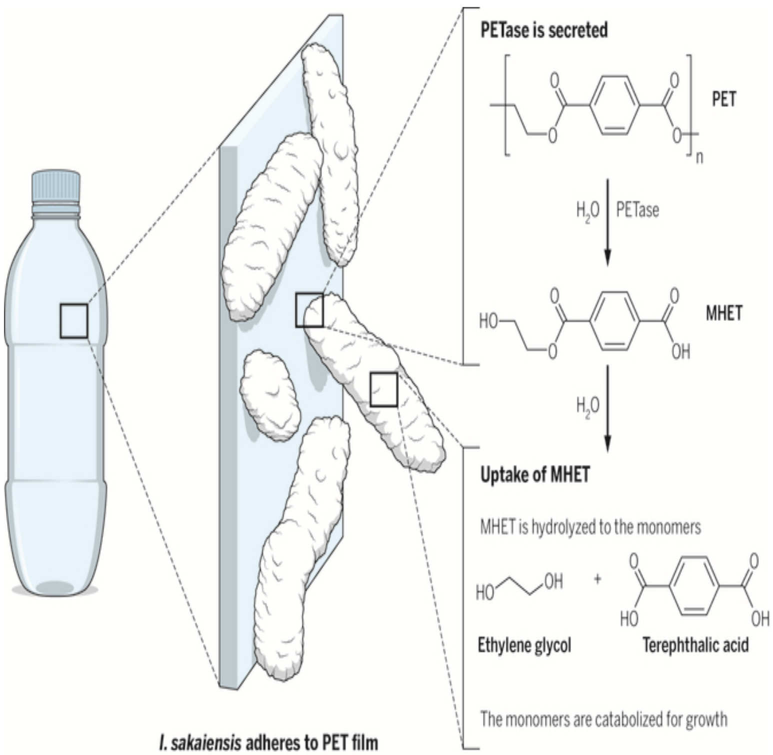
Peter R. Christensen[1], Angelique M. Scheuermann[1,2], Kathryn E. Loeffler[1] and Brett A. Helms[1,3]*

Recycled plastics are low-value commodities due to residual impurities and the degradation of polymer properties with each cycle of re-use. Plastics that undergo reversible polymerization allow high-value monomers to be recovered and re-manufactured into pristine materials, which should incentivize recycling in closed-loop life cycles. However, monomer recovery is often costly, incompatible with complex mixtures and energy-intensive. Here, we show that next-generation plastics—polymerized using dynamic covalent diketoenamine bonds—allow the recovery of monomers from common additives, even in mixed waste streams. Poly(diketoenamine)s 'click' together from a wide variety of triketones and aromatic or aliphatic amines, yielding only water as a by-product. Recovered monomers can be re-manufactured into the same polymer formulation, without loss of performance, as well as other polymer formulations with differentiated properties. The ease with which poly(diketoenamine)s can be manufactured, used, recycled and re-used—without losing value—points to new directions in designing sustainable polymers with minimal environmental impact.

Nature Chemistry, 2019, 11, 442



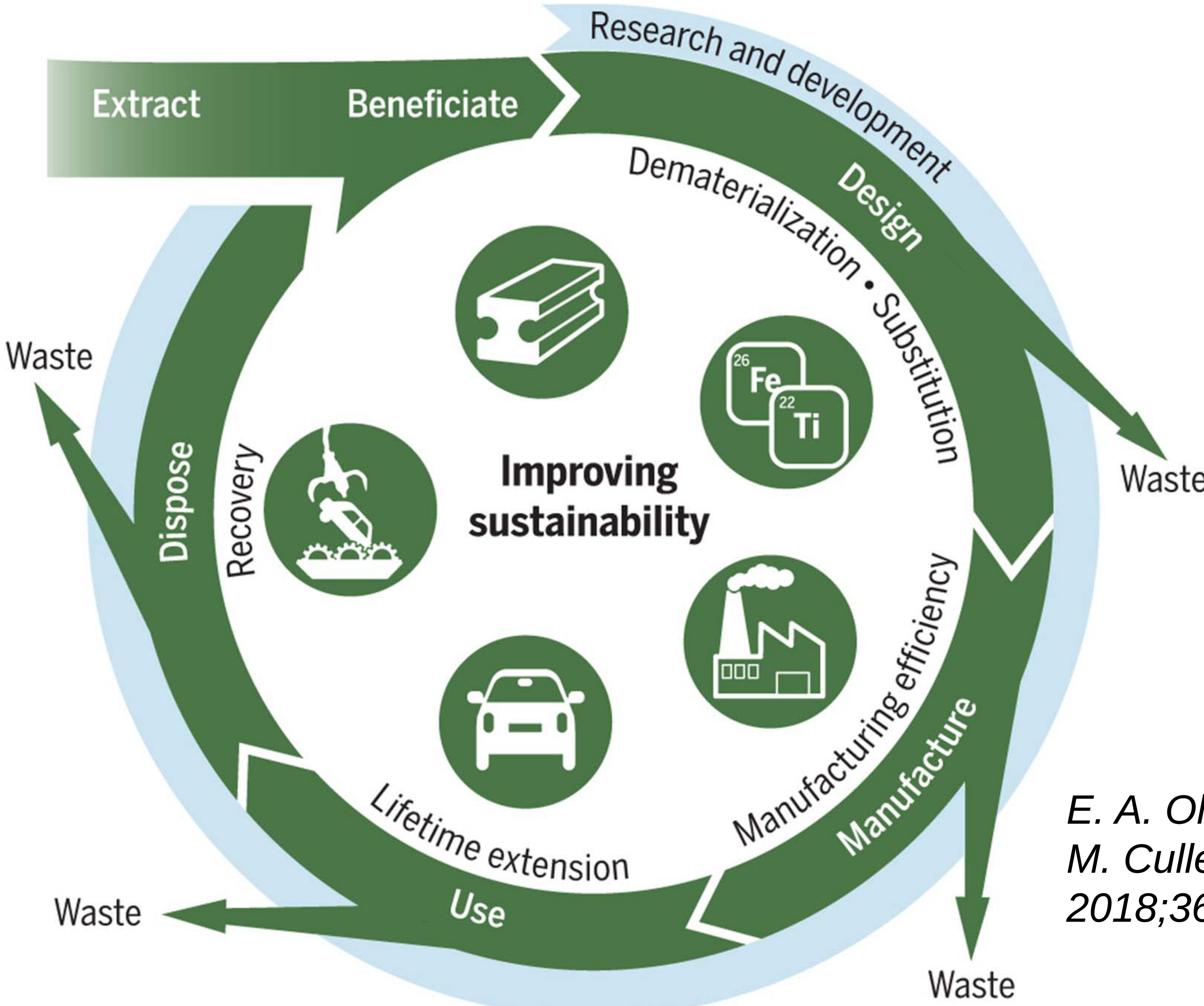
DIRECTED EVOLUTION: CAN WE DESIGN ENZYMES THAT CAN DEGRADE PLASTICS UNDER HOME COMPOSTING CONDITIONS?



2016 : A bacterium that degrades and assimilates PET; Science , 351, issue 6278, 1196-99, 2016
Sp : Ideonlla Sakaiensis

2018 : Structure of the enzyme active for degradation and design of a mutant enzyme which works even better ; PNAS, DOI: org / 10.1073 /pnas.1718804115

DEMATERIALIZATION AND THE CONCEPT OF A CIRCULAR ECONOMY



E. A. Olivetti, and J. M. Cullen Science 2018;360:1396-1398

OUR COLLECTIVE RESPONSIBILITY

- De-materialization : Generate more economic value from less natural resources
- Proactive engagement with society , both at local and national level; earn license to operate from the society
- Improve public communication as well as transparent and voluntary disclosure
- Innovation aimed at sustainability
- Embed sustainability as a business strategy
- Embed sustainability principles into early stage chemistry education

Sustainable development in chemistry education, Chem. Educ. Res.Pract, 13, 57-58, 2012; Life cycle inventory assessment as a sustainable chemistry and engineering tool, ACS Sust. Chem. Eng., October 2017

HOW DO WE DESIGN "NEXT GENERATION" CHEMISTRY FOR SUSTAINABILITY ?

- Build sustainability and life cycle concepts in materials and product design
- Ground-up solution, not tinkering with existing chemistry
- Define product value as a tangible cost (raw material, energy, manufacturing, waste disposal etc.) and an intangible cost (cost on impact on the environment and sustainability discounted over the product life cycle) to reflect the true product value
- Proactive, rather than reactive to potential or unintended consequences
- Invest in deeper understanding the interface of chemistry with biology; learn lessons in sustainability from biology

Focus on Chemistry that is desirable, not feasible

SUMMARY

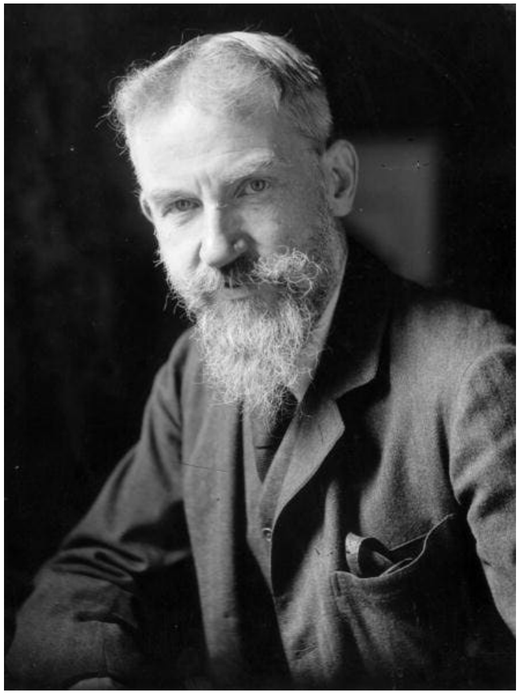
- Creation of sustainable and environmentally friendly polymers for diverse applications and capable of substituting what we currently use appears to be a formidable challenge.
- There are no easy answers
- We need to focus on, both consumption as well as end of use disposal of short life cycle materials

Remember

- *The four R's : Reduce, Reuse, Recycle & Re-invent*
- *Sustainability thinking begins with us, in our homes, teaching our children, in our work place and spaces surrounding us*

In the end, the power that plastics wields comes from all of us. All of us benefit from it even as we suffer from its ill-effects. In its failings. plastics shows our own collective failure, as a society, industry and Government

We are made wise not by the recollection of our past, but by the responsibility of our future

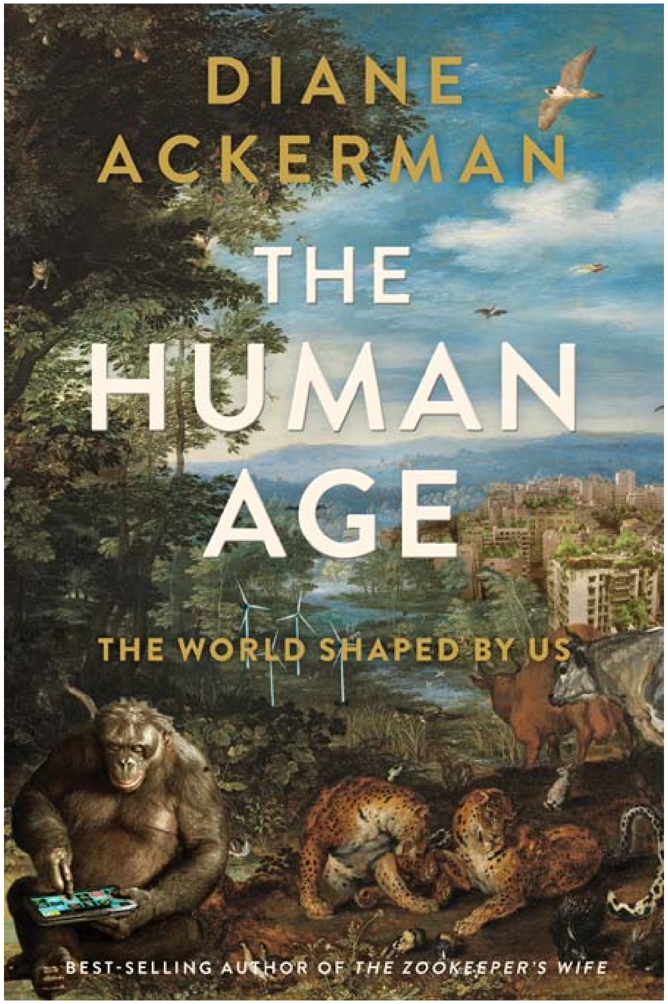


George Bernard Shaw (1856-1950)

THE HUMAN ANTHROPOCENE AGE

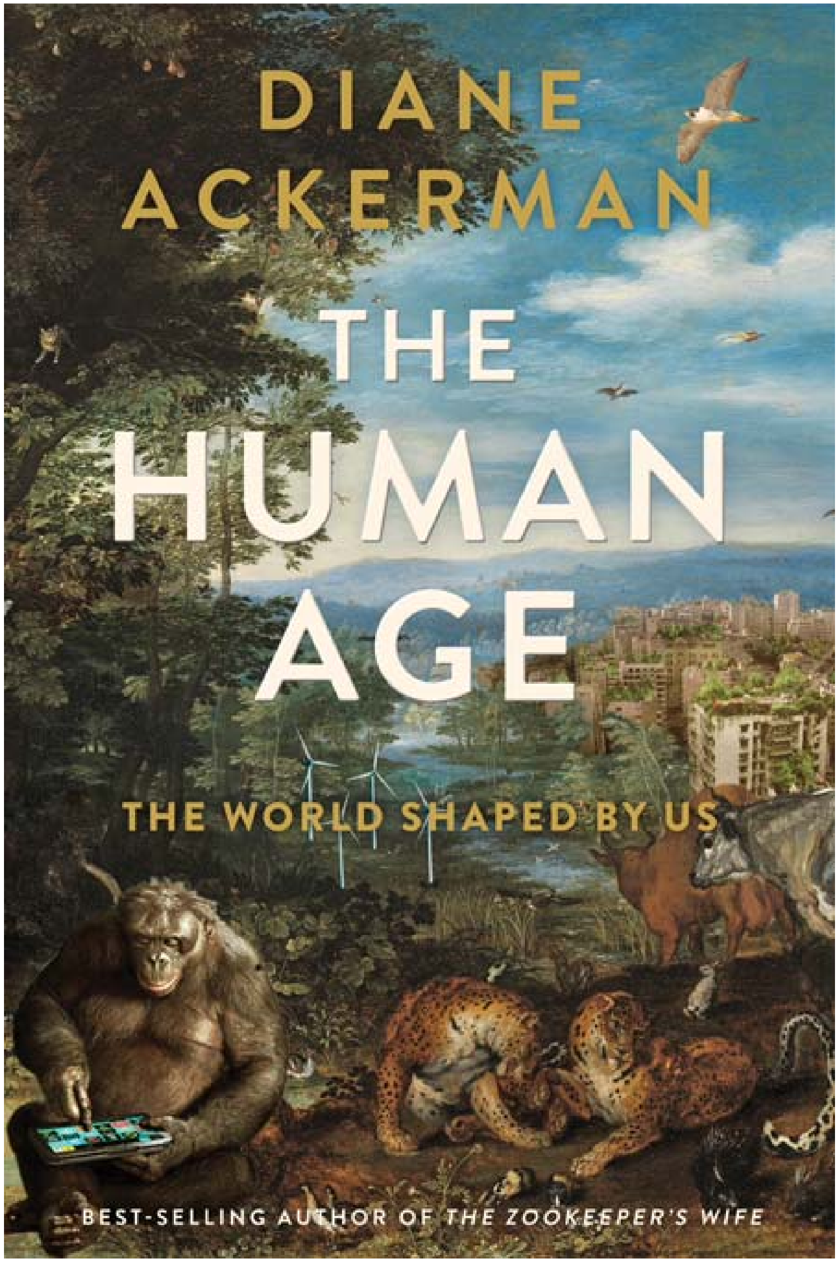
"Our relationship with nature has changed radically, irreversibly, but by no means all for the bad. Our new epoch is laced with invention. Our mistakes are legion, but our talent is immeasurable"

However, we cannot afford to make more mistakes; the society will not forgive us , if we do



2014

If you do not change direction, you may end up where we are heading: Lao Tzu



Our relationship with nature has changed radically, irreversibly, but by no means all for the bad. Our new epoch is laced with invention. Our mistakes are legion, but our talent is immeasurable."

Diane Ackerman,
The Human Age


targets
zero-waste
cascade-circles
action-plan
research
renewable-materials
eco-innovation
knowledge
eco-design
LCA
renewable-energy
EMAS
multiple-circles
production-processes
products
inner-circles
ISO


SUSTAINABILITY
AHEAD

THANK YOU