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Grand challenges in polymers

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Introduction

In recent years, we have witnessed a considerable diversification in the field of polymer science. On the side of fundamental research in polymer chemistry, the “hot topics” of the last decade include smart and responsive, possibly self-healing polymers, sequence-controlled polymers for e.g., information storage, and the increasingly large cut-set with the life sciences, such as peptide/protein mimetics. In the physics domain, the properties of self-organized nanostructured polymers and nanocomposites, semiconducting polymers, polymers at interfaces, and a better understanding of branched or crosslinked topologies may be mentioned. All these exciting developments have only partially addressed the need for innovations in the fields of commodity and engineering plastics as well as of thermosets and rubbers, which are naturally developed in the more applied disciplines and of course in industrial research. Improved polymeric materials are pivotal for cornerstone technologies such as electric mobility or additive manufacturing, where inexpensive high-performance construction materials, possibly as lightweight composites, have never been at a higher demand. This perspective elaborates on a few of the above-mentioned topics from a very personal standpoint, circling around the latter challenge, which brings us to the possibly most pressing question in current polymer science: How can we as scientists contribute to moving away from often single-use throwaway products and downcycling at best to a fully sustainable, cyclic plastics economy? In the end, I will give a perspective on important contributions that polymer physics and theory may be able to provide, in particular for the foundations of the life sciences.

Environmental challenges

For the longest time, degradability or recyclability of these fascinating polymer-based materials has all too often not been the primary interest. In fact, high polymers have always been defined as intrinsically non-toxic and have thus not been regulated in any way. As a result, we are now facing an omnipresence of plastics waste in our environment, ranging from the macroscopic scale (such as fishing nets in the oceans as the most abundant culprit) to micro- and nano-sized bits and pieces. While we are still far from a full understanding of the impacts and modes of action, a global consensus seems to be reached that this development must be stopped. Climate change and the quest for sustainable technologies not relying on fossil resources are

another related and no less important trigger to re-think plastics industry and thus polymer science.

Bio-based polymers made fully or partially from renewable resources, either on the monomer level or being extracted directly from living matter, may appear as an attractive solution to the sustainability problem. The diversity of such materials is growing continuously and is ready to meet even high demands (Cywar et al., 2022). However, the inevitable competition with a sustainable agriculture and thus food production (Peydayesh et al., 2022) poses challenges. Moreover, being bio-based does not imply being biodegradable, which requires separate efforts (Tian et al., 2012) to reduce the impact of littered plastics or enable a purposeful deposition in the environment or even the human body in case of biomedical applications. Fascinatingly, bacteria that practically feed on synthetic commodities like poly (ethylene terephthalate), PET, have already been found (Yoshida et al., 2016), emphasizing the great potential that biotechnological approaches may hold.

Materials-science aspects of recycling

The recycling of plastics can be significantly improved by moving to better-suited materials. The desired properties (e.g., melt flow index, crystallinity) are often the result of sensible tuning of the molecular-weight distribution or branching, which limits the chain-level recycling even after perfect waste separation by polymer type. Thus, main chains allowing for easy chemical attack appear most promising, and polyesters are arguably most relevant in this regard. The chemically selective opening of the thermally very stable ester bond enables an efficient way of recycling, either to the monomer level or to re-balance the molecular-weight distribution. It is at the heart of the commercial success of PET as the one commodity polymer with the most versatile and practically implemented recycling options (Vollmer et al., 2020). Specifically, solvolysis is an energetically and thus economically feasible option for monomer recovery of PET that is not available for other commodity plastics (Coates and Getzler, 2020). The success story of the renewable variant poly(ethylene furanoate) as reviewed by Fei et al. (2020) may serve as an example illustrating the sluggish path from a new polymer to a material in application. It is entering the markets just now, about 15 years after its efficient synthesis was published, and after a decade of fundamental research working out its superior properties and the molecular basis. It also exemplifies how a change in the regulatory framework helps establishing materials that would have been considered economically unfeasible before. To illustrate a possibly even greater potential, it was very recently shown that long-chain aliphatic “precision” polyesters have a property profile close to that of high-density polyethylene (PE).

They can also be produced from renewable resources and can be repeatedly recycled via its monomers at low cost and with very high efficiency (Häußler et al., 2021).

But also for already established polymers, new fields of (re-) use can be opened by physically informed changes in the processing strategy, which is an option that is not of primary interest for many companies with their well-implemented processing pathways. Disruptive developments are thus rare, with one prominent example being the Dyneema fiber made by gel spinning of ultrahigh-molecular-weight PE. It remains to be seen whether the ongoing development of all-polymer composites (Schirmeister et al., 2021), a strategy discussed for decades but facing conceptual problems still, can finally also attract the interest of the polymer industries. Another example is the fact that in particular polyesters are usually prohibitively brittle in their highly crystalline forms, but novel strategies such as cold crystallization of melt-stretched and quenched materials can lead to tremendous improvements without compromising the modulus (Razavi et al., 2021).

Dynamic networks

Thermosets and rubbers have so far been treated as unrecyclable, yet this paradigm has been questioned by Bowman with his “covalent adaptable network” (CAN) concept (Kloxin et al., 2010), which built upon the dynamic covalent chemistry concept developed earlier (Rowan et al., 2002). This provided new momentum in the development of new materials designed for recyclability. Actually, a first early application geared towards better recyclability of thermosets due to Endo et al. (1996) went by largely unnoticed, but soon after the conception of CANs, the concept was put to life by Leibler and coworkers in a simple chemical system that is in fact based upon a polyester material from renewable resources termed “vitrimer” (Montarnal et al., 2011). Catalyzed transesterification is in this case harnessed to impart high-temperature flow of a material with an otherwise high and constant density of crosslinks. Research in this area has been growing steadily since, and we can hope to see translations into applications in the near future.

Rubbery materials and gels are widely used for their favorable rheological properties, and our current ability to understand these on a theory level is intimately connected to the concept of entanglements and their long-time relaxation enabled by de Gennes' famous concept of reptation in an effective tube (de Gennes, 1971). Until today, the tube model has gone a long way, forming the basis of many of the currently used, nowadays fully predictive models explaining the viscolastic behavior of these materials (Read et al., 2008). An exciting challenge tackled most currently in this context is the unification of the entanglement concept across qualitatively different kinds of polymer materials, spanning

from melts of flexible chains to solutions of rather stiff chains (Milner, 2020; Dietz et al., 2022). This will close an important gap in our quantitative understanding of the origin of elasticity in these materials, spanning from simple rubbers to biological tissues.

These developments went along with continuous improvements in computer simulations of polymer systems capable of addressing relevant polymers' properties on large-enough length- and timescales. The direct link of the molecular structure of polymers (affecting the glass transition and thus the temperature range of use) and large-scale phenomena such as reptation is just starting to become possible. The latter are the domain of simple lattice models (Binder and Paul, 2008) or coarse-grained molecular dynamics simulations (Peter and Kremer, 2009), which can be hooked up to molecular reality through multiscale approaches (Everaers et al., 2020). Such approaches are ultimately invaluable to test analytical theories, which can be the key ingredient to new predictions and developments, also in the form of constitutive modeling of whole parts. Along a completely different line, machine-learning approaches are now increasingly being discussed for applications in the development of new soft materials (Jackson et al., 2019). It remains to be seen whether such "model-free" approaches may ultimately be able to reach our long-term sustainability goal, or whether the scientific method shall still have its contribution.

Smart and responsive, possibly charged

The vitrimer concept mentioned above provides a link to even more dynamic associative networks or gels based upon physical rather than chemical bonds, relying on supramolecular or associative interactions (Seiffert and Sprakel, 2012). These comprise phase separation (such as in block copolymers), and more specifically hydrogen-bonding or π - π stacking groups, guest-host or metal-ligand as well as ionic interactions. On the one hand, such building blocks can impart a self-healing functionality in polymers, which has thus become a topic of major interest in the last two decades (Wang and Urban, 2020), serving the quest for more durable and better recyclable materials. On the other hand, these moieties are particularly susceptible to external stimuli such as heat, light, pH or ionic strength. This can be harnessed in a variety of applications much beyond simple construction materials, where a well-designed responsivity enables more advanced applications. Naturally, improved drug delivery is among the most-sought goals (Hoffmann, 2013), for which also main chains with biocompatible degradation pathways are required. These may also be of use outside of the biomedical domain and thus contribute to improved sustainability.

Charged polymers, often able to take up large amounts of water and thus act as superabsorbers when being highly charged and crosslinked, have been known since the earliest days of polymers science. The most-used one, namely poly(acrylic acid), PAA, has in fact been conceived in Staudinger's institute in Freiburg (Kern, 1938). Besides its overwhelming use in sanitary products, we also find applications involving its deliberate deposition in nature, most notably for humidity control in soil. It is worrisome that PAA is neither biodegradable nor ever recycled, calling for sustainable alternatives.

Novel, more sustainable polyelectrolytes or ionomers with lower charge density may also become instrumental as improved and recyclable ion-conducting barrier materials in batteries. Notably, polyester-based variants have already been reported (Lee et al., 2011). From the theory point of view, understanding the physical behavior of polyelectrolytes, in particular their solution phase behavior, represents one of the most prominent outstanding challenges (Dobrynin and Rubinstein, 2005; Muthukumar, 2020), with great implications for our understanding of life itself.

Biophysics links

There has always been a strong cross-fertilization between polymer science and the life sciences. One may start with the debate about the existence of polymer crystals, with constituent (macro)molecules being much larger than the crystallographic unit cell, which was a seemingly strong argument turned against Staudinger and his macromolecular hypothesis (Staudinger, 1934). This was ultimately resolved only much later by Watson and Crick's interpretation of Rosalind Franklin's famous "Photo 51," revealing the double helix in crystals of DNA. Also, biological macromolecules have often served as mesoscopic model materials enabling the study of polymer- and colloid-science concepts. This concerns in particular DNA, which is monodisperse and has a huge persistence length, making it a random coil that can be imaged at optical resolution. In this way, fluorescence-labeled DNA in semidilute solution has for instance served as a probe to visualize the reptation tube (Perkins et al., 1994).

In current times, polymer models are increasingly appreciated in attempts to understand the foundations of protein stability, folding and interactions (Zhou, 2004). For instance, well-established concepts to understand the thermodynamics of polymer solutions, namely the Flory-Huggins (FH) model and its extensions, proved instrumental for the description of the structure of intrinsically disordered proteins (IDPs) and crowding effects in cells (Schuler et al., 2016). Arguably one of the most exciting findings of current biology is the that of "membraneless organelles." These are an integral constituent of the function of living cells, and turn out to be formed simply by liquid-liquid phase separation, a process

well familiar to polymer scientists (Zhou et al., 2018; Mezzenga, 2021). In this context, the original FH concept of course requires non-trivial extensions to include charge effects as well as concepts from colloid science, in order to understand the qualitative differences found in phase separation of folded proteins vs. IDPs (Zhou et al., 2018).

With these perspectives on sustainability and a better understanding of life, polymer science will certainly continue to be in the limelight of Soft Matter.

Author contributions

The author confirms being the sole contributor of this work and approved it for publication.

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