

Cite this: *Polym. Chem.*, 2012, **3**, 1677

www.rsc.org/polymers

EDITORIAL

New methods of polymer synthesis

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DOI: 10.1039/c2py90007f

What's new in polymer synthesis? 80 years after Staudinger's discovery of the covalently linked nature and indeed the existence of large macromolecules, one can reasonably ask if there is still room for innovation in synthetic polymer science. After all, synthesizing polymer chains still consists in tethering monomer units together. Is what we are doing in 2012 significantly different to what Staudinger, Carothers, Kwolek and many others did before? With the current themed issue on *new methods of polymer synthesis*, the three of us would like to convince the readers of *Polymer Chemistry* that, indeed (!), there are still plenty of opportunities for invention in synthetic polymer science – probably much more so than ever before. In fact, it is sometimes amazing to see how fresh and dynamic our field is after 80 years of intense international research. Although the industrial large production of commodity polymers such as polyethylene has not evolved much during the past decades, the rise of specialty polymer applications has dramatically changed the face of academic and high technology driven industrial polymer research. This becomes obvious by comparing the table of contents of specialized polymer journals over the past few decades. Most of the popular polymerization techniques used in academia today were discovered at the end of the 20th century. For instance, approaches to π -conjugated polymers,

ring-opening metathesis polymerization, controlled/living radical polymerization, click chemistry, bio-orthogonal ligations, and bioconjugation are all very recent developments in polymer chemistry. In this context, the present themed issue compiles a selection of topics, which represents the current priorities in the field of synthetic polymer chemistry. These themes are described in detail below and we hope to have collated an exciting mixture of studies of the latest developments in contemporary synthetic methodology. It seems apt to commence our journey into the themed issue with fundamental considerations of polymer chemistry, *i.e.* mechanistic aspects, where three contributions highlight the latest in understanding radical and cationic polymerization processes. Detrembleur and colleagues (DOI: 10.1039/c1py00443c) investigate the effect of light on the powerful $\text{Co}(\text{acac})_2$ mediated radical polymerization (CMRP) process, providing evidence that light – here UV irradiation – can be an additional controlling factor for achieving molecular weights for well over a million Da with low polydispersity. Han and Tsarevsky (DOI: 10.1039/c1py00495f), on the other hand, report on a new method making use of efficient exchange reactions between at hypervalent iodine centers to convert carboxylic acid moieties into initiating sites for radical polymerization processes and employ it for generating semi-stable cross-linked networks. In the realm of new photo-initiation system development, Tehfe, Gimes, Lalevée and colleagues (DOI: 10.1039/c1py00460c) report new initiators – alongside their initiation mechanism – capable of cationically polymerizing epoxides with variable diode lasers, allowing for the visible light

design of shrinkage limited materials for optoelectronic applications.

As the mechanistic understanding of polymerization processes forms the basis of designing new polymeric materials, control of polymer microstructure (*i.e.* tacticity and monomer sequences) of synthetic polymers remains a key aim entailing significant challenges for macromolecular chemistry. Indeed, the structural (*e.g.* crystallization) and functional (*e.g.* solubility) behaviour of synthetic polymers is closely related to their microstructure. In the current themed issue, three contributions describe routes for controlling tacticity or monomer sequences. Kamigaito and colleagues (DOI: 10.1039/c1py00401h) report a very interesting pathway for controlling tacticity in reversible addition–fragmentation chain-transfer (RAFT) polymerization. These authors provide evidence that complex stereogradients can be generated using bulky methacrylates. Thomas and his team (DOI: 10.1039/c2py00472k) describe an in-depth study of the surface-induced stereoselectivity in neodymium-catalyzed methacrylate polymerizations, while Moad and colleagues (DOI: 10.1039/c2py00529h) have investigated new macro-RAFT agents for the sequential insertion of functional monomers: the successive incorporation of styrene and *N*-isopropylacrylamide is reported. Moving from the control over polymer microstructure to the next higher level, block copolymers and nano-structured polymer formation is represented with four contributions, once again providing evidence that we are probably at a stage where virtually any sequence of block copolymer is achievable with the latest in polymerization technology. The team of Hawker (DOI: 10.1039/c1py00484k)

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reports a synthesis strategy *via* which acid cleavable linkers can be introduced into block copolymer structures prepared *via* nitroxide mediated radical polymerization. Hillmyer and colleagues (DOI: 10.1039/c1py00450f) report the preparation of triblock copolymers *via* a tandem ring opening approach, which are shown to undergo self-assembly into nano-structured thermosets. An interesting combination of RAFT and azide/alkyne click chemistry with a de-grafting process is employed by Zhao and colleagues (DOI: 10.1039/c1py00396h) for the generation of very pure di- and triblock copolymers. Finally, d'Agosto, Boisson, Drockenmuller and their teams (DOI: 10.1039/c1py00459j) tackle ethylene polymerization, when they graft amino-capped poly(ethylene) onto epoxide-unit-carrying silicon substrates, which were coated with RAFT prepared poly(glycidyl methacrylate).

At an even higher structural level, the design of complex topologies and architectures is key for preparing materials with designed properties. Besides block copolymers, modern polymer chemistry allows for the synthesis of a wide range of highly complex polymer architectures – some scientists even suggest that at the current state any architectural design can be achieved within certain limits of molecular weight and end group fidelity. For instance, three examples of advanced cyclic topologies are described in the current themed issue. Laurent and Grayson (DOI: 10.1039/c1py00378j) report the synthesis of amphiphilic ring-shaped polymers using copper-catalyzed azide-alkyne click chemistry. These innovative architectures behave as individual micelles and can be used in solvents of various polarities. In the study of Tezuka and colleagues (DOI: 10.1039/c1py00475a), an alternative interesting strategy for preparing amphiphilic macrocycles is presented. Cyclic polystyrene-*b*-poly(ethylene oxide) was synthesized *via* a combination of atom-transfer radical polymerization (ATRP) and ring-closing metathesis (RCM). Lutz and his team (DOI: 10.1039/c1py00514f) describe a reliable route for preparing α -shaped macromolecules. In their approach, linear precursors containing precisely positioned reactive functions were first synthesized by

sequence-controlled polymerization and were afterwards folded using a three-step modification procedure. Without doubt, the control of polymer end groups with high precision is one of the key aims of synthetic polymer science, as precision end group control is indispensable for a wide range of applications. In the current issue, we include two contributions on the topic, one from Schlaad and colleagues (DOI: 10.1039/c1py00388g), the other one from the laboratory of Du Prez (DOI: 10.1039/c2py00444e). The former provide evidence for exquisite group control for polymers comprising terpenes and poly(ethylene oxide) synthesized *via* metal-free anionic ring-opening polymerization, whereas the latter reports a very efficient one-pot controlled method for the nitroxide end-group removal from synthetic polymers generated *via* nitroxide mediated polymerisation (NMP).

It is no exaggeration to state that, in recent years, synthetic polymer science has been primarily driven by the advent of polymer modular transformations, often adhering to the stringent criteria of click chemistry. Naturally, the latest developments in the field of click chemistry have to be included in the present themed issue. A sequential click-based strategy – entailing one efficient linking and one true click reaction – is employed by Gao and coworkers (DOI: 10.1039/c1py00367d) in a couple-monomer approach for generating hyperbranched polymers, while Drockenmuller and colleagues (DOI: 10.1039/c1py00446h) review the preparation and polymerization of vinyl-1,2,3-triazole regioisomers with respect to their polymerization as well as the properties of the resulting materials and their potential for designing stimuli-responsive polymeric materials. While click chemistry leading to triazole linkages is certainly the most widely used click technology, other efficient and equally powerful click ligations exists. For example, Sumerlin and his team (DOI: 10.1039/c1py00451d) make use of oxime ligations to a RAFT prepared lateral alkoxyamine group containing polymer in a small molecule conjugation study. The release of lateral thiol entities along a polymer backbone *via* a mild ambient temperature photo-deprotection of an ATRP prepared

photo-reactive polymer is reported by the team of Barner-Kowollik (DOI: 10.1039/c1py00372k). The released thiols are subsequently employed in a Michael-type click reaction. If one wishes, however, to stay with triazole based click chemistry, yet wants to avoid the use of a potentially toxic transition metal catalyst, the study of Van Hest and coworkers should not be missed (DOI: 10.1039/c2py00466f), as they employ copper-free click chemistry in a study that contains detailed insights into the accessibility of functional groups on the surface of polymeric vesicles.

No themed issue on synthesis would be complete without what has become a trade-mark sign of synthetic polymer chemistry, *i.e.* the provision of biocompatible and biorelevant polymers, as synthetic polymers are more and more used in biomedical applications and biotechnologies. As a consequence, there is very active fundamental research in this area. Three examples for the synthesis of biocompatible/biorelevant polymers are included in our collation. Li and Matyjaszewski (DOI: 10.1039/c1py00431j) describe the activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) of oligo(ethylene glycol) monomethyl ether methacrylate in inverse microemulsion. Their method allows for the preparation of biocompatible hydrogel nanoparticles, which may be relevant for drug-release applications. In a highly timely minireview article (DOI: 10.1039/c2py00489e), Frey and coworkers describe the preparation of biocompatible polyethers with reactive groups *via* anionic ring-opening polymerization (ROP), while Hoogenboom and colleagues (DOI: 10.1039/c1py00380a) have studied the nitroxide mediated polymerization of 4-vinylphenylboronic acid. It was shown that the formed polymers can be used as efficient glucose sensors. A similar motivation that drives the design of biocompatible macromolecular systems motivates the preparation of bio-hybrid macromolecular materials, and we have included two examples in the current issue: Perrier and colleagues (DOI: 10.1039/c2py00510g) find that the ligation of several synthetic polymer chains at the same time to

a cyclic peptide sequences can face limits with triazole click chemistry, while Malmstöm and Carlmark (DOI: 10.1039/c1py00445j) review the latest state of heterogeneous grafting of synthetic polymer stands to cellulose fibers, showing that there is indeed much more to cellulose in advanced materials design than cardboard and paper!

Finally, the realm of conducting polymers must find its place in a synthetic themed issue, as areas such as solar cell

and light emitting diode design are unthinkable without the underpinning polymer chemistry. Junkers and colleagues show for the first time that poly(*p*-phenylene vinylene) materials are readily accessible *via* an efficient method for chain length control in their polymerizations by adding large amounts of bromine containing transfer agent to the polymerization (DOI: 10.1039/c2py00551d). Pauly and Theato (DOI: 10.1039/c2py00503d) demonstrate the

preparation of poly(ethynylbenzoates) and their detailed analysis, while Stefan and coworkers (DOI: 10.1039/c1py00453k) review Grignard metathesis polymerization routes to conjugated poly(3-hexylthiophenes).

We sincerely hope that you like our collation of articles in the present themed issue and agree with us that synthetic polymer chemistry is in the midst of its most productive period ever: enjoy the read!



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