

Cycloadditions in Modern Polymer Chemistry

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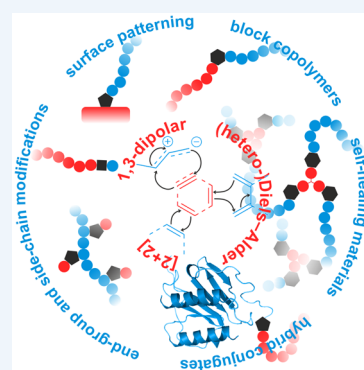
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CONSPECTUS: Synthetic polymer chemistry has undergone two major developments in the last two decades. About 20 years ago, reversible-deactivation radical polymerization processes started to give access to a wide range of polymeric architectures made from an almost infinite reservoir of functional building blocks. A few years later, the concept of click chemistry revolutionized the way polymer chemists approached synthetic routes. Among the few reactions that could qualify as click, the copper-catalyzed azide-alkyne cycloaddition (CuAAC) initially stood out. Soon, many old and new reactions, including cycloadditions, would further enrich the synthetic macromolecular chemistry toolbox. Whether click or not, cycloadditions are in any case powerful tools for designing polymeric materials in a modular fashion, with a high level of functionality and, sometimes, responsiveness.

Here, we wish to describe cycloaddition methodologies that have been reported in the last 10 years in the context of macromolecular engineering, with a focus on those developed in our laboratories. The overarching structure of this Account is based on the three most commonly encountered cycloaddition subclasses in organic and macromolecular chemistry: 1,3-dipolar cycloadditions, (hetero-)Diels–Alder cycloadditions ((H)DAC), and [2+2] cycloadditions. Our goal is to briefly describe the relevant reaction conditions, the advantages and disadvantages, and the realized polymer applications. Furthermore, the orthogonality of most of these reactions is highlighted because it has proven highly beneficial for generating unique, multifunctional polymers in a one-pot reaction.

The overview on 1,3-dipolar cycloadditions is mostly centered on the application of CuAAC as the most travelled route, by far. Besides illustrating the capacity of CuAAC to generate complex polymeric architectures, alternative 1,3-dipolar cycloadditions operating without the need for a catalyst are described. In the area of (H)DA cycloadditions, beyond the popular maleimide/furan couple, we present chemistries based on more reactive species, such as cyclopentadienyl or thiocarbonylthio moieties, particularly stressing the reversibility of these systems. In these two greater families, as well as in the last section on [2+2] cycloadditions, we highlight phototriggered chemistries as a powerful tool for spatially and temporally controlled materials synthesis.

Clearly, cycloaddition chemistry already has and will continue to transform the field of polymer chemistry in the years to come. Applying this chemistry enables better control over polymer composition, the development of more complicated polymer architectures, the simplification of polymer library production, and the discovery of novel applications for all of these new polymers.



■ INTRODUCTION

Polymer synthesis has been revolutionized in the last 20 years by two major developments: (1) the introduction of reversible-deactivation radical polymerizations (RDRP),^{1–3} allowing for fine control over macromolecular architecture with relative ease and enabling the design of complex polymers with well-defined and modifiable end-groups for a range of applications; (2) the discovery of a wealth of small molecule reactions for equipping polymers with defined terminal- and midchain-group functionalities. In particular, the *click* concept⁴ has been adapted to

polymer/macromolecular synthesis.⁵ Fundamental to the *click* concept are both chemical and biological reaction orthogonality, coupled with mild and preferably equimolar reaction conditions. Cycloaddition chemistry, which is in some cases reversible upon exposure to a trigger, is a particularly attractive class of ligation that often qualifies as *click* chemistry. In this Account, we will highlight some of the key cycloadditions that

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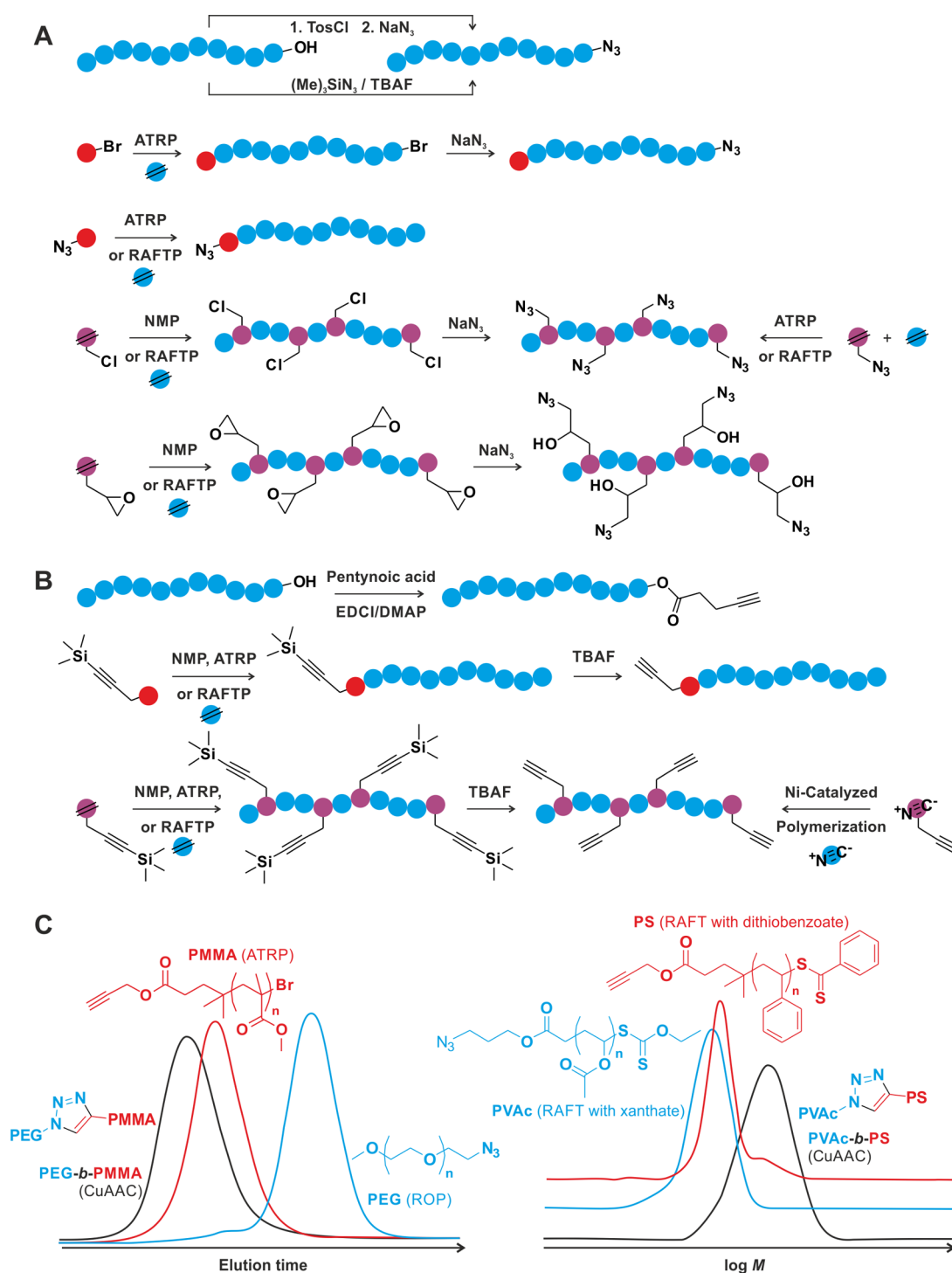


Figure 1. General methods to introduce azides (A) and alkynes (B) into radical polymer chains. (C) Earliest reports of BCP formation by CuAAC.^{24,25}

have been utilized, in particular by our group, to generate macromolecules. For brevity purposes, we will only describe macromolecules obtained by statistical monomer addition, which excludes dendrimer synthesis. We focus our compact survey on synthetic macromolecules prepared by cycloaddition chemistry alone or by RDRP followed by cycloaddition modification. Nevertheless, a handful of examples based on other controlled polymerization processes, such as ring-opening (metathesis) polymerization, are also included.

■ 1,3-DIPOLAR CYCLOADDITIONS

The most frequently employed type of cycloaddition in polymer chemistry, to date, is arguably the 1,3-dipolar cycloaddition of terminal alkynes and azides (AAC), and in particular AAC reactions catalyzed by copper (CuAAC).^{4,6} The resulting 1,2,3-triazole linkages possess a remarkable chemical and thermal inertness and, although it is rarely of concern in polymeric structures, CuAAC is regioselective toward the 1,4-disubstituted isomer. The popularity of (Cu)AAC, certainly stems from the availability of commercial alkynes and ease of

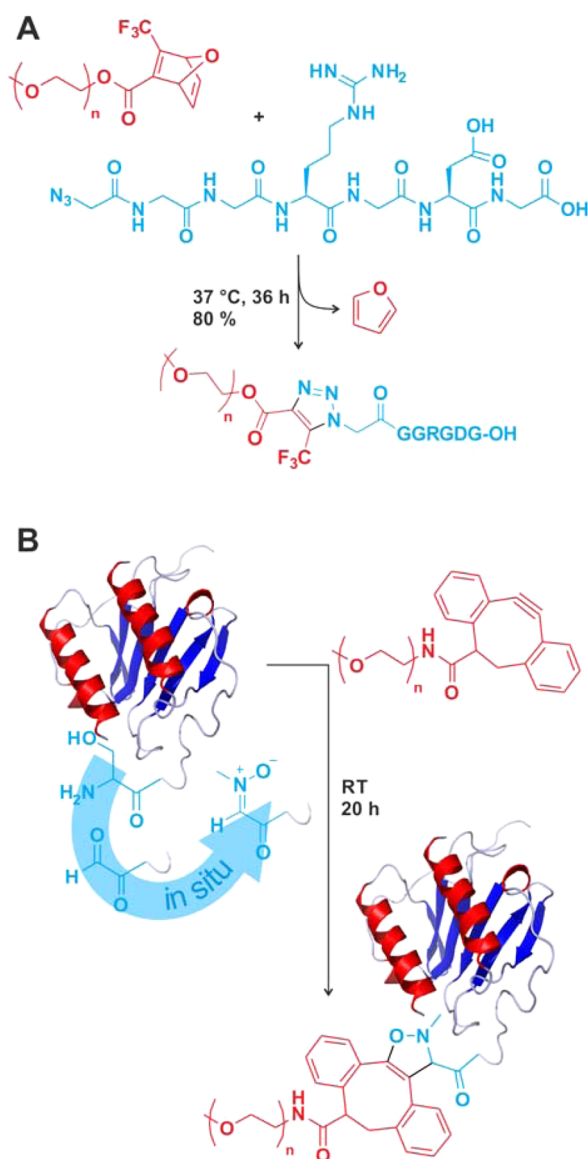


Figure 2. PEGylation of (A) a peptide by CrDA⁴¹ and (B) a protein by SPANC.⁴³

installation of azide groups by nucleophilic substitution of halides present on polymer side-chains and/or end-groups or by sodium azide-based epoxide ring-opening, for instance (Figure 1A). Albeit nonessential, ligands are often used to enhance the reaction, particularly in polar solvents. Interestingly, triazoles themselves are efficient ligands, resulting in an autocatalytic effect on the cycloaddition.⁷

The impact of CuAAC on modern polymer chemistry has been immense and certainly reinvigorated certain research areas, especially that of cycloaddition-based polymerization. The first reported use of CuAAC in polymer chemistry, apart from dendrimer synthesis,⁸ described the step-growth polymerization (CuAACP) of multifunctional azides and alkynes to produce linear and hyperbranched polymers as metal adhesives.⁹ In addition to classic alkyne/azide-terminal monomers, 1-iodoalkyne-based monomers can also undergo CuAACP to yield 5-iodo-1,4-disubstituted-1,2,3-triazole polymers, amenable to further modification by transition metal-catalyzed reactions.¹⁰ Furthermore, CuAACP has been used to introduce functionalities into the polymer backbone. For

example, we employed CuAACP to develop a library of fluorene-based copolymers for the selective dispersion of single-walled carbon nanotubes,¹¹ and libraries of catalytically active polymers containing palladium complexes¹² or ferrocenyl units.¹³ Selecting the appropriate CuAACP conditions (stoichiometry, catalyst, concentration, reaction time) permits the synthesis of high molecular weight (MW) polymers, as demonstrated with polyethers.¹⁴ Further details on CuAACP can be found elsewhere.¹⁵

Although CuAAC can be efficiently used to generate polymers, it has mostly been utilized to postfunctionalize polymers typically based—though not exclusively—on vinyl monomers. Matyjaszewski et al. and Hawker et al. were the first to investigate lateral group modifications of azide- and acetylene-containing (co)polymers.^{16,17} Polymer-analogue modifications are also widely employed when the functionality to be installed is sensitive to the polymerization conditions (e.g., radical-initiated side reactions, thermal instability, steric hindrance). For instance, to circumvent the difficulty of polymerizing unprotected sugar-functionalized monomers, Haddleton et al. exploited readily accessible azidosugars to produce a small glycopolymer library from poly(propargyl methacrylate).¹⁸ Employing CuAAC for lateral functionalization has also proven advantageous to avoid tedious monomer synthesis. Indeed, polymer purification, typically by precipitation or dialysis, is usually easier. For instance, CuAAC postfunctionalization was employed to synthesize dye- and tetraethylene glycol-functionalized polyisocyanides, which are otherwise challenging to synthesize directly from the precursor monomers (Figure 1B).¹⁹

Thanks to the high reaction efficiency, CuAAC postfunctionalization of polymers is particularly well suited to produce libraries of copolymers possessing a common structural unit/monomer. We developed a series of Pd-containing copolymers by copolymerizing styrene with various amounts of *p*-chloromethylstyrene and subsequently converting the chlorine moieties into 2-(1*H*-1,2,3-triazol-4-yl)pyridine units through a nucleophilic substitution/CuAAC sequence.²⁰ In this case, preinstalling azides on the monomer would have been problematic due to possible reaction with propagating styryl species.²¹ Using a similar strategy, we produced phosphoric ester-functionalized styrene copolymers.²² Alternatively, Thelakkat used the modular character of side-chain-localized CuAAC to modify reactive alkyne-bearing polystyrene (PS) with one of six different perylene bisimide (PBI) groups to compare the physical properties of the resulting polymers, which differed only in the PBI motifs because all other possible parameters were decoupled.²³

CuAAC has also been employed for point modifications at polymer chain-end and midchain positions. We, for instance, synthesized homotelechic polymers bearing triphenylphosphine end-groups by performing polymerization with a dihalide-functional atom-transfer radical polymerization (ATRP) initiator, converting each terminal halide group into an azide, and coupling the azide to a triphenylphosphine alkyne derivative.²⁶ We also utilized an azido-dibromo initiator to permit midchain CuAAC modification with an alkynylated Hamilton bridge after ATRP.²⁷ Point modifications are also targeted to attach polymers through their termini to surfaces. Although this can be challenging, especially in contexts such as microcontact printing, which requires short reaction times, the exceptional efficiency of CuAAC facilitates polymer-to-surface

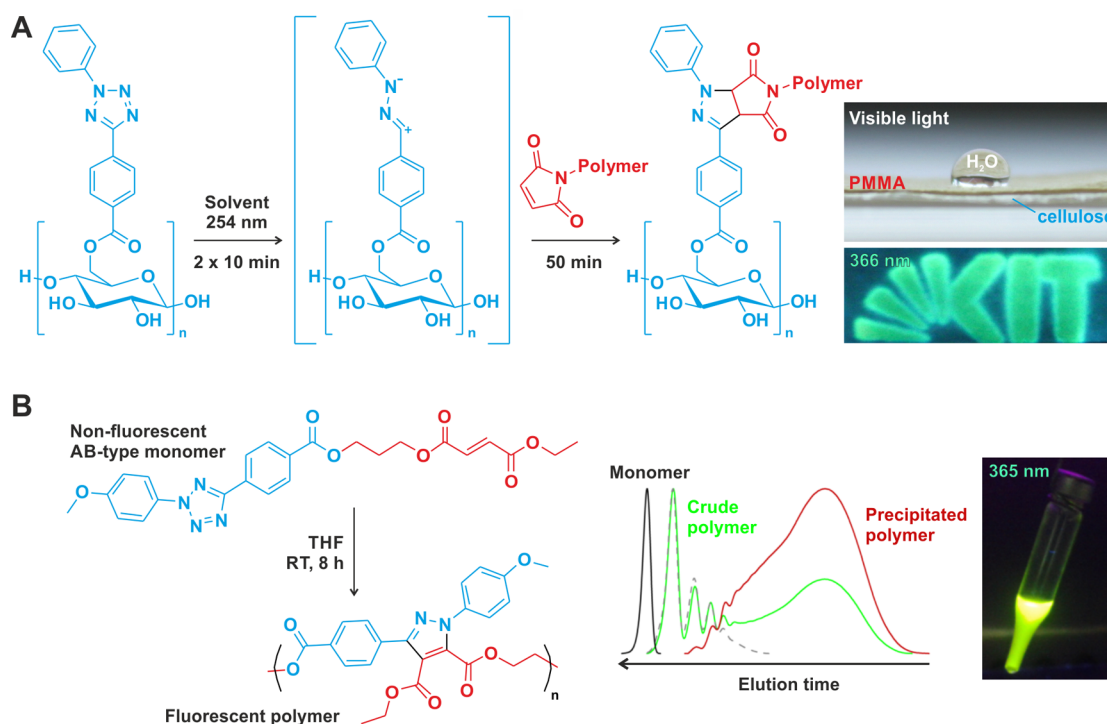


Figure 3. Two applications of NITEC: profluorescent (A) polymer grafting onto cellulose⁴⁹ and (B) cyclopolymerization.⁵²

coupling, as shown in the fabrication of glycopolymer microarrays.²⁸

The formation of block copolymers (BCPs) by coupling two polymers can also be considered a chain-end modification; however, it is certainly more challenging due to steric hindrance, stoichiometry, and the difficulties of separating polymeric species, for instance. Van Hest and Opsteen described the first CuAAC-based modular synthesis of BCPs from alkynyl- and azido-capped polymers (Figure 1C).²⁴ Nonstoichiometric ratios and further purification, however, were necessary to drive the reactions to quantitative yields. We reported the first CuAAC-driven BCP formation from equimolar ratios of poly(vinyl acetate) (PVAc) and PS.²⁵ Such a BCP cannot be obtained by consecutive reversible addition–fragmentation chain-transfer polymerization (RAFTP) due to the disparate reactivities of vinyl acetate and styrene. CuAAC polymer coupling is also a means to artificially increase MW, while maintaining a narrow distribution, when a MW limit is observed during polymerization.²⁹ Finally, we demonstrated that CuAAC can be used to obtain complex structures, such as H-shaped triblock copolymers formed from the coupling of homotelechelic azido-poly(ethylene glycol) (PEG) with a PVAc-*b*-polyacrylonitrile possessing a midchain alkyne.³⁰

Since most of the reactive species involved in cycloadditions are not present in nature, these reactions are bioorthogonal and are thus beneficial for bioconjugation and the creation of well-defined biohybrid polymeric architectures. Schultz reported the first example of CuAAC-based polymer–protein conjugation through a 4-azidophenylalanine-substituted tryptophan residue.³¹ Other bioconjugates formed by CuAAC include PEGylated proteins,³² modified capsids,³³ and giant amphiphiles.³⁴

Although the need for copper can be turned into an asset, as demonstrated by the patterning of hydrogels by photoreduction of inactive Cu(II) to active Cu(I),³⁵ it usually remains a major

issue for CuAAC as its toxicity can be detrimental for some biology-related applications. Removal can be tedious. Traces often remain in final products. Furthermore, copper can catalyze ester hydrolysis, which is particularly damaging to polyesters³⁶ and potentially poly(meth)acrylates. Although solid-supported catalysts or appropriate ligands address these issues, recent efforts have been undertaken to develop copper-free AAC methods. Strained alkynes, particularly cyclooctynes, were highlighted as extremely reactive compounds for AAC in biological and materials contexts.³⁷ Although strain-promoted AAC (SPAAC) is gaining popularity, especially as the synthesis of strained alkynes is facilitated,³⁸ SPAAC involving species as bulky as dibenzocyclooctynes can be less efficient than CuAAC (particularly in sterically congested environments).³⁹ Thus, electron-deficient alkynes may be a solution as they react with azides at low temperature, without catalyst.⁴⁰

A number of other metal-free click 1,3-dipolar cycloaddition reactions have been developed as alternatives to (Cu)AAC. For instance, triazoles can also be very efficiently obtained from azides and ring-strained, electron-deficient enes, namely oxanorbornadienes. This reaction proceeds at 25 °C in protic media through a tandem [3 + 2] cycloaddition/Diels–Alder cycloreversion (CrDA) releasing furan and is effective in preparing polymer–peptide conjugates (Figure 2A).⁴¹ Dove et al. employed a related chemistry to modify polycarbonates obtained by ring-opening polymerization (ROP) of a norbornene-containing cyclic carbonate.⁴² The norbornene moieties were reacted with various azides without byproduct formation, albeit at elevated temperatures.

Both nitrile oxide-alkyne and alkyne-nitrone cycloadditions (NOAC and ANC) not only proceed without a catalyst and are high yielding under mild reaction conditions, but are far less hazardous than other alkyne-based reactions because azides are avoided. NOAC was used to generate⁴⁴ and modify⁴⁵ polymers. Significantly, under optimized reaction conditions the nitrile *N*-oxide 1,3-dipole has been found to react equally well with

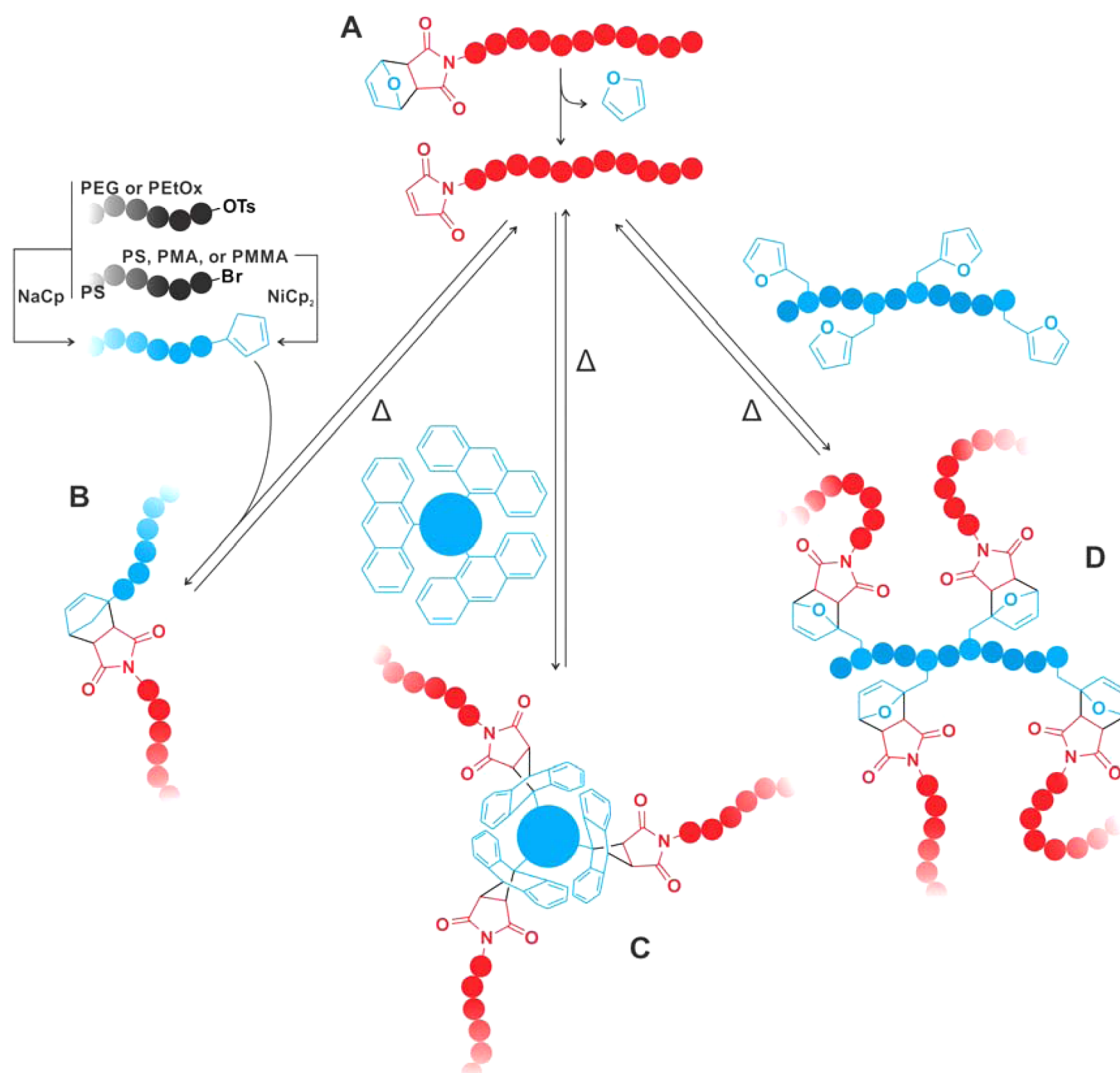


Figure 4. Examples of macromolecular engineering by maleimide-based DAC. (A) Deprotection of maleimide-capped polymer.⁵⁷ (B) Synthesis of various cyclopentadiene-capped polymers and subsequent BCP formation.^{60–62} (C) Star polymer formation from a trifunctional anthracene-functionalized core.⁵⁸ (D) Formation of branched and cross-linked structures from furan copolymers.⁶³

alkenes and nitriles as dipolarophiles, yielding polymeric cycloadducts stable up to 350 °C.⁴⁴ NOAC was also demonstrated to be orthogonal to CuAAC,⁴⁵ implying it could potentially be utilized to generate more complicated macroarchitectures in one-pot reactions. Strain-promoted ANC (SPANC) has been successfully used for PEGylating peptides/proteins (Figure 2B).⁴³ Furthermore, SPANC proceeds at ambient temperature and faster than NOAC or SPAAC.

Nitrile imine-mediated tetrazole-ene cycloaddition (NITEC) and the nitrile ylide-mediated 2*H*-azirine-alkene cycloaddition (NYAAC) are 1,3-dipolar cycloadditions that only proceed after photoirradiation. These reactions are attractive as they are bioorthogonal, high yielding, complete within 2–15 min, and require only mild reaction conditions (e.g., ambient temperature, aqueous media, no catalyst). NYAAC is highly selective and proceeds via formation of a nitrile ylide intermediate after irradiation of the azirine,⁴⁶ whereas NITEC proceeds via the loss of N₂ and is attractive because the end-product is fluorescent, allowing spectroscopic quantification.⁴⁷ Both of these chemistries are promising for temporally and spatially controlled polymer grafting to surfaces and protein functionalization *in vitro* and *in vivo*.⁴⁸ We employed NITEC to pattern

cellulosic substrates with a variety of maleimide-functionalized polymers (Figure 3A)⁴⁹ as well as for the design of cell-guiding surfaces⁵⁰ and bioadhesion-resistant paper by photografting of poly(carboxybetaines).⁵¹ We also recently reported a NITEC-based cyclopolymerization approach to generating fluorescent polymers from nonfluorescent monomers (Figure 3B).⁵²

■ (HETERO-)DIELS–ALDER CYCLOADDITIONS

The earliest reports of cyclopolymerizations are almost exclusively based on (hetero-)Diels–Alder cycloadditions ((H)DAC).^{53,54} More recently, (H)DAC were exploited to construct block and star (co)polymers, transform end-groups, modify surfaces ranging from silicon wafers to microparticles to fullerenes and carbon nanotubes with polymer strands, and design self-healing materials.

Unlike the stable and irreversible 1,3-dipolar cycloadducts, DAC linkages are often reversible at a given temperature, making them attractive for the construction of materials that can undergo bonding/debonding on demand. Additional advantages for some DACs include the absence of catalyst and the ability to achieve quantitative conversions at ambient temperatures within a few minutes. The reversible nature of the

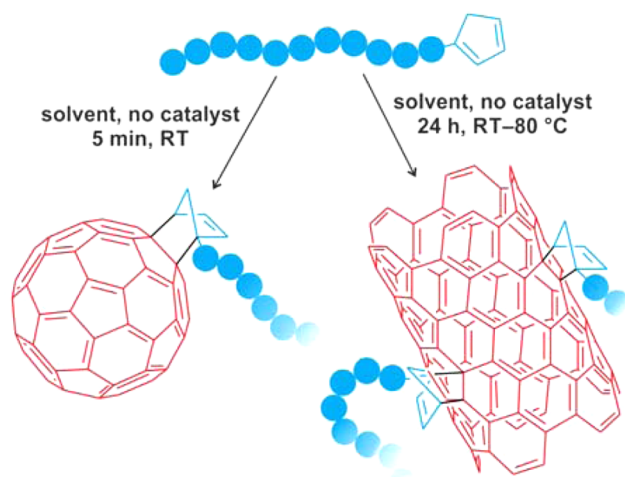


Figure 5. Synthesis of polymer-carbon nanostructures by Cp-based DAC.^{65,66}

DAC adducts at sometimes relatively low temperatures can be a disadvantage, forbidding high-temperature processing (e.g., extrusion). Nevertheless, DAC products can be made permanently stable. For instance, simultaneous or postpolymerization aromatization is reported in most ladder polymers systems.⁵⁵ More recently, maleimide-furan DAC-cross-linked networks were demonstrated to be potentially useful as negative photoresists by locking the cycloadduct through a two-photon-triggered thiol–ene reaction on the remaining double bond.⁵⁶

Arguably, the most common dienophile in polymer-based DAC is maleimide, despite the fact that it is not a fully orthogonally reactive group since it can partake in radical (e.g., copolymerization and thiol–ene addition) and nucleophilic (Michael addition) reactions. However, the reversible nature of most DACs allows dienes or dienophiles to be incorporated into polymers in a cycloadduct-based protected form. For instance, maleimide is frequently introduced into polymers prepared via a radical mechanism under its furan-cycloadduct form, and easily deprotected by thermal and/or pressure treatment (Figure 4A).⁵⁷ In the context of polymer-based DAC, maleimides have mostly been reacted with furan and anthracene derivatives due to their stability and ease of incorporation/derivatization. In a typical example of the application of maleimide in macromolecular engineering, PEG, PMMA, and poly(*t*-butyl acrylate) arms were grafted onto a core functionalized with three anthracene units via a one-pot rDA-DAC sequence (Figure 4C).⁵⁸ The popularity of the maleimide/furan couple⁵⁹ certainly stems from the relative inertness of furan, allowing it to be introduced as a side-chain in an unprotected form, such as furfuryl methacrylate, before polymerization (Figure 4D).

Besides furan and anthracene, we have recently introduced a more reactive diene into ATRP-synthesized polymers: mono-substituted Cp (Figure 4B).⁶² Ambient temperature Cp-capped polymer cycloadditions can reach completion within minutes or even seconds with maleimides,⁶⁴ fullerenes,⁶⁵ carbon nanotubes (Figure 5),⁶⁶ and appropriate thiocarbonyl derivatives.⁶⁰

To overcome the disadvantage of having to either postfunctionalize the polymer end-group(s) prior to DAC or synthesize a dedicated dienophile-containing initiator or chain-transfer agent (CTA), we designed a CTA with electron-deficient C=S bonds, which served the dual function of a CTA

during RAFTP and a dienophile during postfunctionalization (Figure 6). The most efficient RAFT-HDACs between pyridyl- or phosphoryl-CTA-based polymers⁶⁷ and cyclopentadienyl-capped macromolecules proceed within a few minutes at ambient temperatures⁶⁰ and yield BCPs with MWs up to 100 kDa (Figure 6A).⁶⁸ Unlike typical DAC, RAFT-HDAC usually requires an activator (TFA or ZnCl₂) to proceed, especially when an open-chain diene motif is employed. Interestingly, RAFT-HDAC can reach completion in 10 to 200 min in water without activator (Figure 6B).⁶⁹ Alternatively, we reported a Cp-functionalized CTA, allowing both the simultaneous grafting and growing of polymers.⁷⁰ The Cp end-functionalization of polyethylene, made by coordination chemistry,⁷¹ and poly(2-ethyl-2-oxazoline),⁶¹ obtained by ROP (Figure 4B), highlights the power of RAFT-HDAC to yield BCPs that are not accessible via consecutive polymerization of two monomers, due to disparate reactivities (ethylene vs styrenics/acrylics) or polymerization mechanisms (radical vs cationic).

In addition, two recently reported mild, catalyst-free, and rapid DACs occurring at ambient temperature show promise: (1) Triazolinediones were found to react instantaneously with a wide variety of dienes, to produce BCPs.⁷² (2) Tetrazines, undergoing inverse electron-demand DAC with ring-strained alkenes, were utilized to modify end-groups⁷³ and side-chains,⁴² and synthesize BCPs.⁷⁴

Capitalizing on the reversible nature of many DAC linkages, we demonstrated the reversible patterning of surfaces using a maleimide/furan couple.⁶⁴ Importantly, we recently demonstrated that the DAC-rDAC equilibrium is not only governed by the nature of the diene-dienophile couple, but also strongly influenced by the chain length of the macromonomers to be coupled by DAC, providing unique design opportunities for self-healing systems.^{78,79} Nonetheless, the most common self-healing materials are based on maleimide-furan polymer systems, which have been extensively reviewed.⁸⁰ Efforts to optimize such systems through precision design have resulted in efficient self-healing materials.^{81,82} Despite these advances, much of the recent research dedicated to the development of DAC-based self-healing materials has been focused on designing optimized DAC pairs, such as dithioester-Cp^{75–77} and fulvene-dicyanofumarate couples,⁸³ permitting a very rapid (seconds) cycloaddition at ambient temperature, while having modest debonding temperatures (below 150 °C). Specifically, the dithioester-Cp couples feature a rich and versatile chemistry, as polymer strands terminated with activated dithioesters can be readily prepared by RAFTP. The first examples of reversible bonding/debonding materials based on dithioester-Cp HDAC systems from our laboratories switched rapidly between the bonded and debonded states, yet still required an activator (Figure 6C).^{75,84} Our more recent variants operate additive-free, relying on cyano-substituted dithioesters.^{76,77}

As an alternative to protected dienes/dienophiles, we introduced photoenol chemistry (inspired by Meador et al.⁸⁵) for the construction of BCPs and the attachment of polymers onto surfaces (Figure 7A). Initially in a dormant form, *o*-methylphenyl aldehydes or ketones can be activated by UV irradiation in situ yielding equilibrium concentrations of *o*-quinodimethanes (photoenols). The latter are very reactive dienophiles, capable of reacting at ambient temperature within minutes with maleimides⁸⁶ or even nonactivated thiocarbonylthio compounds, in the absence of any catalyst.⁸⁷ Popik reported similar species (3-(hydroxymethyl)naphthalene-2-ol),

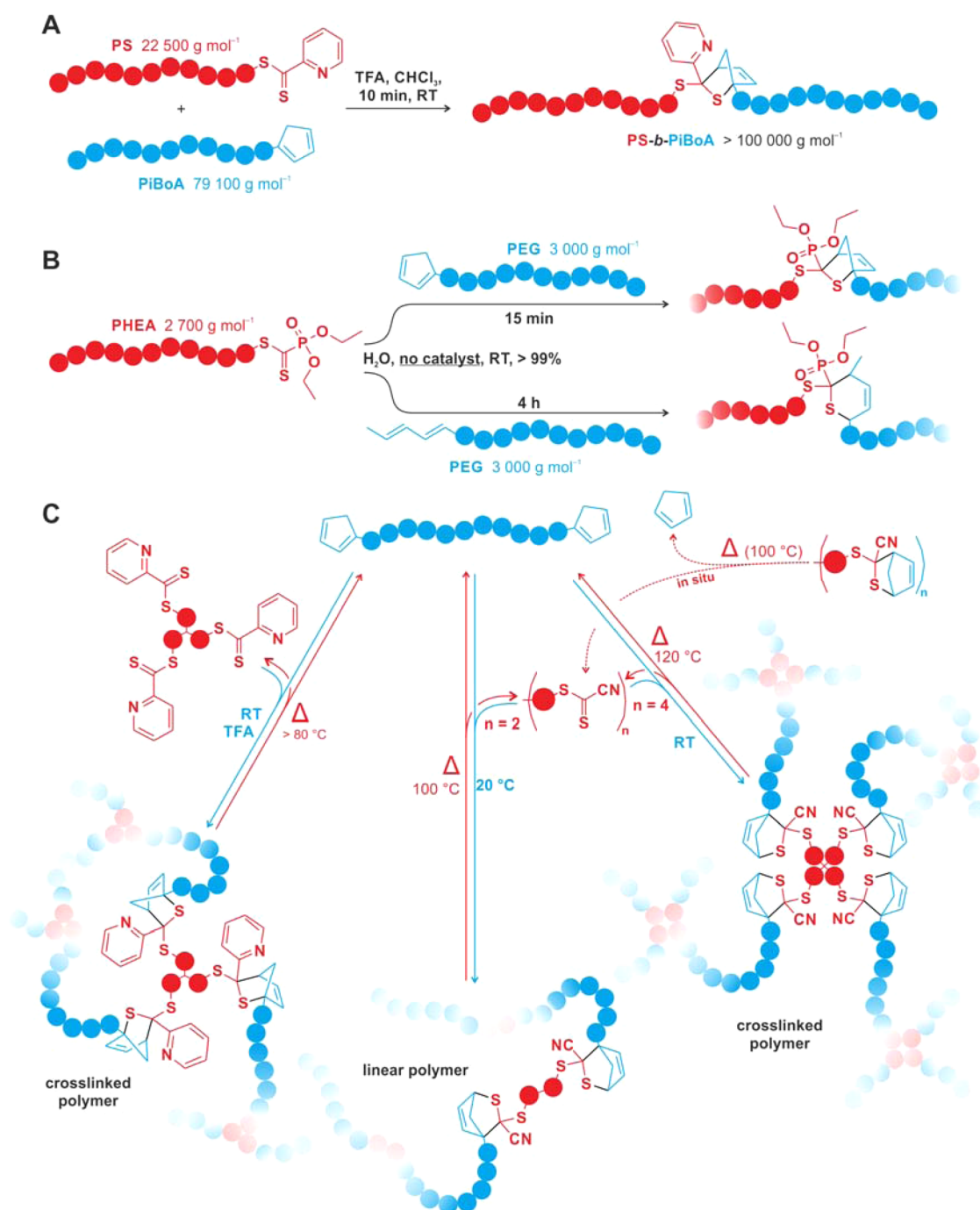


Figure 6. HDAC systems based on dithioesters: (A) Ultrafast synthesis of high-MW diblock copolymers.⁶⁸ (B) Catalyst-free (ultra)fast synthesis of BCPs in water.⁶⁹ (C) Rapid bonding/debonding on demand for self-healing materials.^{75–77}

which, upon irradiation, form *o*-naphthoquinone methides that are able to undergo a HDAC with vinyl ethers.⁸⁸ Similarly to phototriggered 1,3-dipolar cycloadditions, photoenol-based DAC gave us temporal⁸⁹ and spatial⁹⁰ control over polymer ligation and surface grafting, such as the two-photon-triggered genuine 3D functionalization of microstructures (Figure 7B).⁹¹ Further, we recently demonstrated the λ -orthogonality of this reaction with another phototriggered cycloaddition, NITEC (Figure 8A).⁹²

In addition to the photogeneration of (transient) dienes, we showed that the photocleavage of phenacyl sulfides into thioaldehydes—dienophiles—was an efficient method for

polymer surface patterning (Figure 7C).⁹³ Interestingly, we could combine it with photoenol chemistry to produce sequence-defined monodisperse oligomers up to 10 units long (Figure 8B).⁹⁴

■ [2 + 2] CYCLOADDITIONS

[2 + 2] cycloadditions are photochemically allowed pericyclic ligations that have not typically been utilized as a ligation tool in macromolecular research as they appeared to be beset with disadvantages, specifically the requirement for long and intense UV irradiation and nonequimolar equivalents of reactants. Flow systems, however, can reduce reaction times and reagent

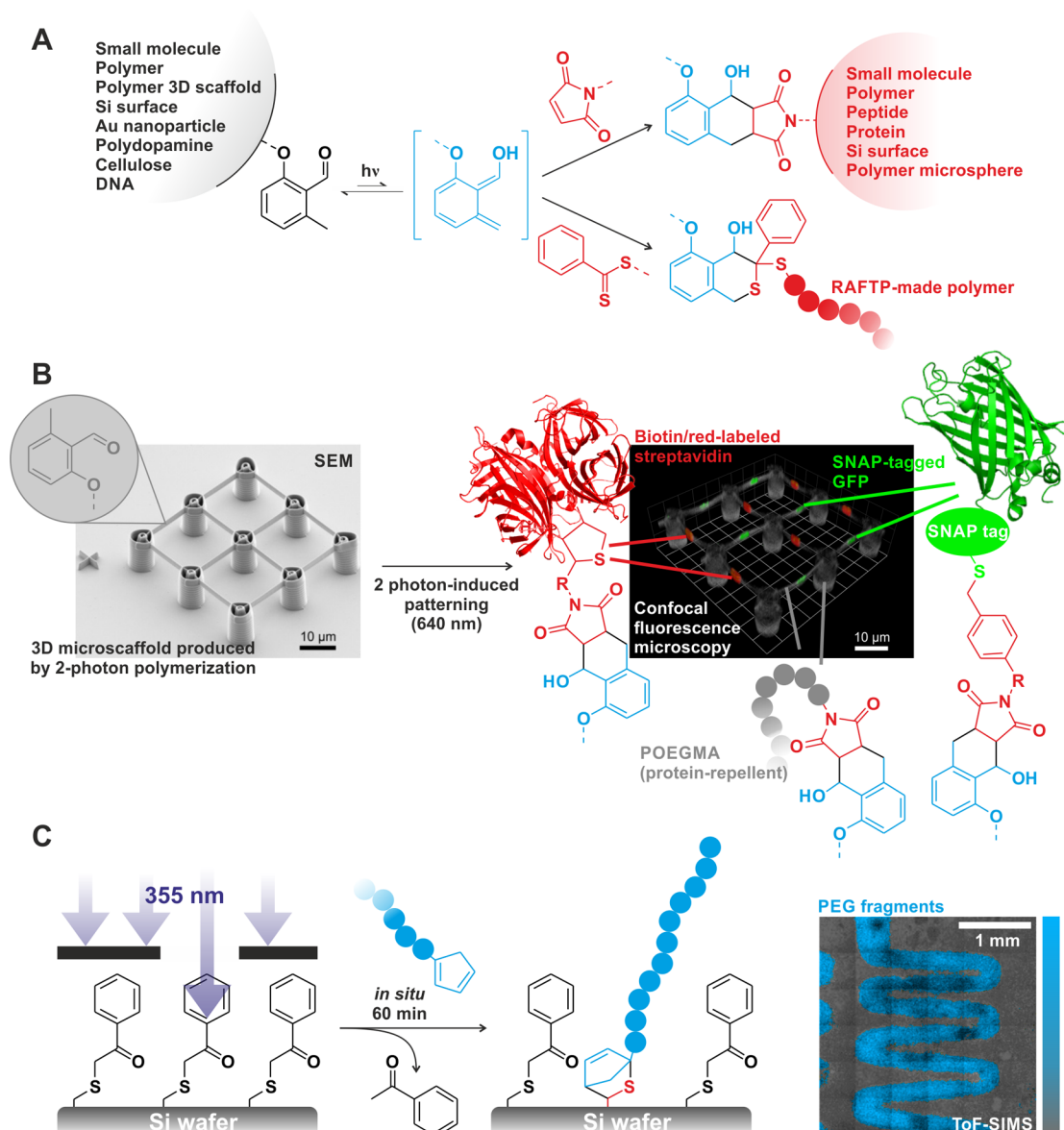


Figure 7. Phototriggered DACs. (A) Scope of applications of the photoenol chemistry. (B) Photoenol-based patterning of proteins in 3D.⁹¹ (C) Surface PEGylation by thioaldehyde-mediated DAC.⁹³

excesses.^{95,96} In the past, thermally stable networks, including (nano)gels based on coumarin⁹⁷ or dimethylmaleimide,⁹⁸ and cinnamoyl-cross-linked films for channel waveguides⁹⁹ or tissue engineering,¹⁰⁰ were generated. The Paterno-Büchi variant does not proceed through self-dimerization, which can be undesirable for some syntheses. For instance, this reaction was carried out in flow for the end-group modification of aldehyde-capped polymers using various enes, however, with a rate reduction and a moderate ene excess compared to the small molecule ligations.¹⁰¹

CONCLUSION

Cycloadditions first took prominence in macromolecular chemistry for generating polymers, taking advantage of the generally high yields of these reactions, which is required to drive polyadditions to high conversions and, thus, high MWs. Until the late 1990s, the majority of studies concerning cycloadditions in polymer chemistry were related to polyadditions. Since then, the field has evolved considerably and the

strengths of these reactions have been demonstrated in complex polymer synthesis, surface functionalization as well as advanced material design. Future challenges lie in unlocking the power of these ligations for the design of monodisperse, sequence-controlled polymers, which can serve as building blocks for precision surface and network design for advanced applications in catalysis, separation, optoelectronics, and analytical media.

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Notes

The authors declare no competing financial interest.

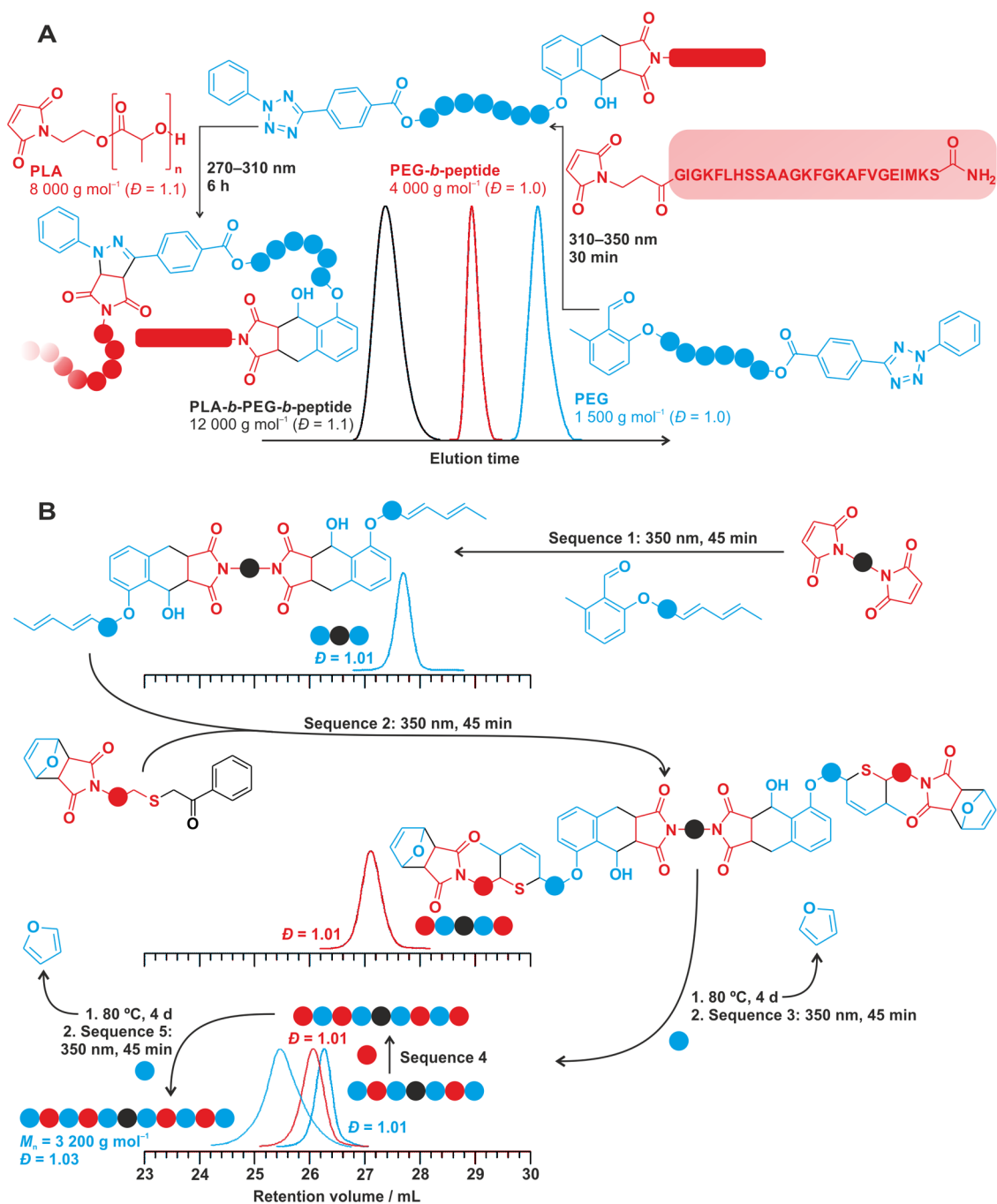


Figure 8. Combination of two phototriggered cycloadditions: (A) photoenol-based DAC and NITEC for λ -orthogonal end-group modification⁹² and (B) photoenol- and phenacyl sulfide-based DACs for sequence-controlled oligomerization.⁹⁴

Biographies

Dr. Guillaume Delaittre obtained his Ph.D. in Polymer Chemistry in 2008 from UPMC, Paris (Prof. Charleux). After a postdoc with Profs. Nolte and Cornelissen (Radboud University Nijmegen), he earned an Alexander von Humboldt fellowship to work with Profs. Barner-Kowollik and Bastmeyer at the Karlsruhe Institute of Technology (KIT). Since 2013, he is heading an independent research group at the KIT.

Dr. Nathalie K. Guimard completed her Ph.D. in Chemistry (UT Austin) (Profs. Schmidt and Sessler) in 2008. She spent 18 months as a postdoctoral fellow in Professor Roy's lab at UT Austin before moving to the Barner-Kowollik group at the KIT. In 2013, she joined

the INM-Leibniz Institute for New Materials where she was ultimately promoted to Assistant-Head of the Functional Microstructures group (2014). Since the end of 2014, she has embarked on a career change into industry.

Prof. Dr. Christopher Barner-Kowollik received a Ph.D. in Physical Chemistry in 1999 (Göttingen University). Subsequently, he joined the Centre for Advanced Macromolecular Design at the University of New South Wales in Sydney as a postdoctoral fellow, before being appointed Full Professor of Polymer Chemistry in 2006 at the same institution. Since 2008, he holds the chair for Macromolecular Chemistry at the KIT and is an Adjunct Professor of Materials Science at the Queensland University of Technology (QUT).

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