Photo- and Metallo-responsive N-Alkyl α-Bisimines as Orthogonally Addressable Main-Chain Functional Groups in Metathesis Polymers

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S *Supporting Information*

ABSTRACT: *N*-alkyl α-bisimines were employed as main-chain functional groups in acyclic diene metathesis (ADMET)-polymers, conferring dual responsiveness for the controlled switching of the polymeric particle shape with light and metal ions. Photochemical *Z/E*-isomerization leads to a significant and reversible change in hydrodynamic volume, thus introducing simple imines as novel photoswitches for light-responsive materials. Mild imine-directed CH activation by Pd(OAc)$_2$ is demonstrated as a new single-chain nanoparticle (SCNP) folding process, enabling a controlled atom- and step-economic SCNP synthesis. The combination of light- and metallo-responsiveness in the same polymer provides the ability for orthogonal switching, a valuable tool for advanced functional material design.

The ability of matter to respond to external stimuli, e.g., by conformational changes or phase transitions, is not only a natural phenomenon essential for life as observed in many biomolecules, but also a major aim in the development of "smart" or "stimuli-responsive" materials.[1] Such materials, displaying reversible adaption to their environment, are progressively emerging and have found widespread applications in diverse fields such as controlled drug release,[2] artificial muscles,[3] or healable materials.[4] Light serves as a particularly attractive physical trigger, due to its traceless application with high spatial and temporal resolution and its multiple levels of control via wavelength and intensity.[5] The photoinduced changes of the global properties of a dynamic polymer (dynamer[6]) mainly rely on photoswitches that can alter their molecular geometry upon irradiation.[7] Azobenzene functionalities are by far the dominantly used photoresponsive main-chain units in polymers, resulting in dramatic modifications in the contour/shape of polymers by the accumulation of modest changes in the individual photochromic units.[8] For example, polyazobenzene peptides are capable of performing mechanical work as measured by tethering chains from a substrate to the flexible cantilever in a scanning force microscope.[9] Accordion-like deformation was demonstrated by incorporating azobenzene groups into rigid-rod polymers, as confirmed by a light-induced change of the hydrodynamic radius of up to −75%.[10] Not only the adaption to external stimuli but also the precise folding of biomolecules

determine their properties and functions. In order to mimic controlled folding in fully synthetic molecules, several strategies have been applied. At the oligomeric scale, the molecular geometry can be altered in a programmed manner by the coordination of metal ions to specific binding sites, resulting in defined contraction/extension motions.[11] If such modulation occurs at the polymeric scale, but intramolecularly on individual polymer molecules, a collapse of the single chain and the formation of single-chain nanoparticles (SCNPs) is induced.[12] SCNPs profit from their well-defined unimolecular structure and allow for applications as delivery agents[13] and biomimetics[14] or in catalysis.[15] Examples for so-called "repeat unit" folding induced by metal coordination have been presented for phosphine-Pd(II),[16] β-diketone-Cu(II),[17] and phthalocyanine-Cu(II) complex[18] formation with the donor ligands as pending groups, or by olefin-Rh(I)/Ir(I)/Ni(0) complexation of ring-opening metathesis polymerization-derived poly(1,5-cyclooctadiene)[19] with the donor groups in the main chain. However, all methods listed require additional catalysts or special experimental conditions of varying complexity to function efficiently. To our knowledge, there is no reported example of SCNP formation by transition-metal-mediated CH activation. The combination of the features arising from both reversible light responsiveness and the generation of SCNPs through metal cation binding represents a new type of multi-stimuli-responsive polymer,[20] resulting in materials displaying simultaneously opto-mechanical and iono-mechanical properties and thus potential applications due to the orthogonal addressability (Figure 1).

Although a number of different azobenzene polymers have been described, involving often rather laborious monomer synthesis, the restriction to just one such functional group makes progress in reversible photoresponsive polymers inherently slower. The unique features of simple imine groups,[21] their easy synthesis, their omnipresence in coordination chemistry,[22] and the recent achievements of imines in molecular machines and motors[23] call for their installation in polymeric systems and the exploration of their potential in (multi)stimuli-responsive materials.

We herein report the straightforward two-step synthesis of symmetric α,ω-diene monomers containing internal α-bisimine
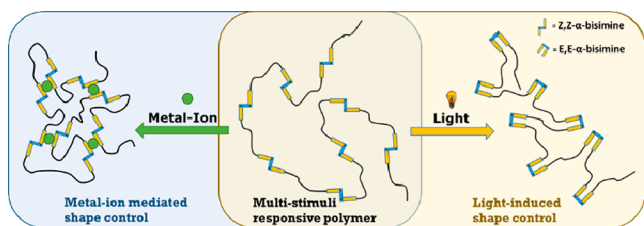
Figure 1. Combination of light-induced shape control by molecular switching (right) and metal-ion-mediated shape control by metal–ligand interaction with formation of SCNPs (left) as demonstrated in the present work.

units and their subsequent acyclic diene metathesis (ADMET) polymerization for the generation of unsaturated polymers with the unprecedented ability to react upon light and metal stimulus by shape modulation and SCNP formation, respectively. Significant reversible changes in the particle size were induced by the application of UV light, as determined by size exclusion chromatography (SEC), dynamic light scattering (DLS), and diffusion-ordered NMR spectroscopy (DOSY) measurements, thus introducing imines as novel photoswitches in polymers. Upon addition of Pd^{2+} ions, the polymers show well-defined collapse into the corresponding SCNPs, combining the potential of both fields for the first time and conferring dual-stimuli responsiveness to metathesis-derived polymers.

Amine-carbonyl condensation of the readily available benzil derivative with *trans*-4-aminocyclohexanol gave diols **1a/1b**, whose subsequent high-yielding esterification with 10-undecenoic acid chloride (a subsidiary product of castor oil) yielded the symmetrical α-bisimine diene monomers **2a/2b** (Figure 2). X-
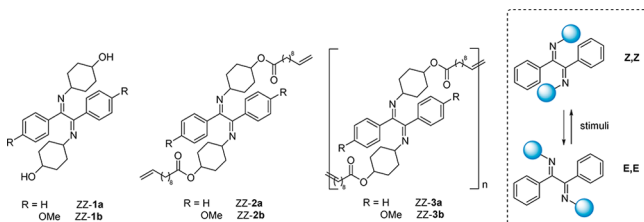
Figure 2. α-Bisimine diol (**1a/1b**), diene monomers (**2a/2b**), and ADMET polymers (**3a/3b**) synthesized for the present study, and the switching between *E,E*- and *Z,Z*-configurational states at the C=N bond (*E,Z* state not depicted).

ray crystallographic analysis and ^{1}H NOESY spectroscopy of bisimine **1a**, as well as comparison with analogue derivatives, indicate that compounds with the benzil-bisimine core structures tend to adapt their pure (*Z,Z*)-configuration as thermodynamically favored product (Figure 2).[23c,24] In the quest for a suitable method for polymerization of the diene monomers **2a/2b**, we adapted acyclic diene metathesis polymerization. Through polycondensation of α,ω-dienes, ADMET polymerization allows access to a wide variety of precision polyolefins containing diverse functional groups.[25] Moreover, the development of a wide variety of catalysts for this transformation has expanded the functional group tolerance of ADMET chemistry. Thus, the Hoveyda–Grubbs second-generation (HGII) catalyst was employed in the ADMET polymerizations (85 °C, in *o*-dichlorobenzene). The desired polymer **3a** (or **3b**) was isolated with an apparent molar mass of 11 kDa (10 kDa for **3b**) and with a polydispersity index of 1.7 (2.0 for **3b**) (as determined by SEC relative to polystyrene standards) after reacting monomer **2a** (or

2b) with 1 mol % HGII catalyst per double bond, under reduced pressure.[26] The *Z/E*-photoisomerization of the C=N bonds was inspected first for the monomeric diols (*Z,Z*)-**1a/1b**. As was expected from studies with related imines,[23c] compound **1a** underwent a clean *Z/E*-isomerization upon irradiation with UV light of 254 nm, whereas the methoxy-substituted bisimine **1b** changed configurations upon irradiation with light of lower energy (>280 nm), determined by ^{1}H NMR spectroscopy. Full reversibility was observed upon standing at ambient temperature for 15 h, consequently providing the desired properties for the installation of such units in photoresponsive polymeric structures. Indeed, polymers **3a/3b** revealed *Z/E*-photoisomerization similar to the monomers. Polymer **3a** was switched by irradiation with light of 254 nm, and polymer **3b** responded with a clear change in diastereomeric distribution upon the application of light of >280 nm. Even though the difference in required excitation wavelengths for the switching of compounds **3a** and **3b** is not very large, it demonstrates the ease of tuning such photoresponsive groups by simply changing the C-substituent of the imine group.[27] High switching efficiency of **3a** led to almost pure (*E,E*)-**3a** polymer and complete reversibility via a subsequent thermal back reaction. More intriguingly, it was possible to reconvert (*E,E*)-**3a** back to the initial (*Z,Z*)-configuration by irradiation with light of 365 nm, thus offering dual-gated light control by the usage of such imines as photoresponsive units. Changes in particle size of **3a** were analyzed by SEC, DLS, and DOSY techniques. The initial apparent molecular weight of polymer **3a** changed dramatically upon UV irradiation from 11 kDa for (*Z,Z*)-**3a** to 5 kDa for the irradiated (*E,E*)-enriched sample. After standing for 24 h at ambient temperature, the initial molecular weight distribution was almost fully regained, as determined by SEC (Figure 3a).
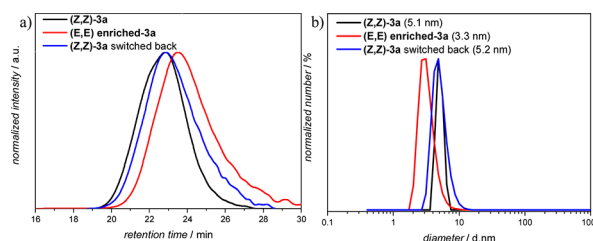

Figure 3. Light-induced (254 nm, 5 h) contraction of (*Z,Z*)-**3a** to (*E,E*)-enriched-**3a** and thermal back-reaction as determined by SEC (a) and DLS (b).

The increased retention volume corresponds to a change of hydrodynamic volume of $\Delta V_h = -36\%$ (based on SEC data).[28] Similar results were obtained by DLS, showing that the parent polymer features a hydrodynamic radius of 5.1 nm, shifting to 3.3 nm upon irradiation with UV light and full retention in size after the thermal back-reaction (a shrinkage of $\Delta V_h = -35\%$), in accordance with the SEC results (Figure 3b). Diffusion coefficients were determined by DOSY experiments (in THF-d_8), showing an increase from 1.64×10^{-10} m^2 s^{-1} to 2.05×10^{-10} m^2 s^{-1} after irradiation—being inversely proportional to the hydrodynamic radius—indicating a decrease of the particle size (see the Supporting Information for spectra and further details).

The molecular mechanics-calculated Boltzmann average distance of the β-carbon next to the ester function in the monomers yields 13.6 Å for the initial (*Z,Z*)-isomer and 17.0 Å for the photoinduced (*E,E*)-isomer, i.e., an *increase* in the end-to-end distance (for computational details, see the Supporting

Information). Therefore, the collapse of the particle cannot be rationalized by geometrical contraction of the individual photoresponsive units during the change of the (Z,Z)- to the (E,E)-configuration. It is rather likely that the observed contraction stems from an increased flexibility in the polymeric chain upon photoisomerization, since the energy barrier for the internal C−C bond rotation in the N=C—C=N system is reduced by interconversion of (Z,Z) to (E,E).[23c] Thus, the increase in conformational entropy after photoisomerization may counteract the loss in conformational entropy during the folding process of the polymer chain and consequently allow for a tighter average packing of the coil ensemble.[29] Bearing in mind the unique coordination abilities of α-bisimines toward transition metals, we were interested in the behavior of monomeric **1a** and polymeric **3a** upon the addition of Pd(II) ions. After addition of 1 equiv of Pd(OAc)$_2$ to diol **1a** in CH$_2$Cl$_2$, significant changes of the characteristic imine bond IR stretching frequencies and changes in the ^{1}H NMR spectra indicated quantitative a reaction. Surprisingly, a clean o-CH activation at one of the two phenyl rings, likely directed by the imine group, generated the Pd(II) complex **Pd-1a**. X-ray diffraction analysis (see Figure 4) showed the formation of a dinuclear compact complex structure, in which two Pd-bisimine units are bridged by two acetate anions.[30]
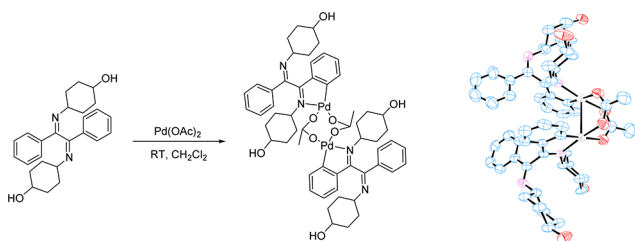
Figure 4. Synthesis and X-ray diffraction analysis of CH activation product **Pd-1a** (solvent molecules and hydrogen atoms are omitted for clarity).

Polymer **3a** reacted upon addition of Pd^{2+} ions in a similar fashion, as indicated by a clear shift of the IR C=N stretching mode and ^{1}H NMR spectroscopy. The change of the particle size of **3a** after addition of varying amounts of Pd(OAc)$_2$ was investigated by SEC and DLS methods. Upon metal complexation, a clear collapse to SCNPs **4a** was visible by SEC, showing the strongest decrease in hydrodynamic volume after addition of 1.0 equiv of Pd^{2+} ions (curve 1, Figure 5a) and a gradual reduction in shrinkage on addition of smaller amounts of complexing agent, i.e., 0.5 (curve 2) and 0.1 equiv (curve 3) of Pd^{2+} per bisimine unit. Coherent results were observed by DLS, showing the strongest collapse with 1.0 equiv of Pd^{2+} ions
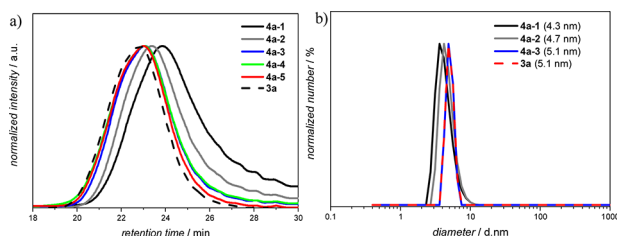
(4.3 nm, curve 1) to almost no change with 0.1 equiv (5.1 nm, Figure 5b curve 3, cf. Figure 3b). As additional feature, the polydispersity of the samples decreased, presumably due to a better-defined folding around the complexed metal ion centers, compared to the more flexible free polymer chain. No collapse could be detected with 0.05 equiv (curve 4) or 0.01 equiv (curve 5) of Pd(OAc)$_2$. The mode of Pd (II) binding in the polymer may not be exactly determined, but it seems reasonable that, in the polymer with analogue structural features around the imine units as in monomer **1a**, CH activation at the *ortho*-position of the aryl rings and the formation of more compact, binuclear, acetate-bridged Pd(II) complexes occurs. In a polymer with 15 repeating units on average, this translates into a threshold of around 0.133 equiv per ligand units present in the sample, to provide at least two Pd ions per polymer chain—a value slightly higher than the ratio (0.1 equiv) at which almost no change was detected.

The above explains the strongest collapse of the polymeric chain upon addition of 1.0 equiv of Pd(OAc)$_2$, leading to a 1:1 stoichiometry, similar to the monomer complex (see Figure 4) as well as the contraction dependence for varying amounts of added Pd salt (see above). On the other hand, reacting the polymer solution with an excess of Pd(OAc)$_2$ (2.0 equiv) led to soluble cross-linked nanoparticles with an apparent hydrodynamic radius of 32 nm (see Supporting Information), indicating a threshold loading for Pd(OAc)$_2$ which controls either an exclusive intra- or an intra-/intermolecular complexation of polymer **3a**. The formation of SCNPs by CH activation and shape contraction due to bridging intramolecular complex formation offers new opportunities based on the rich follow-up chemistry for σ-aryl-metal complexes, such as the post-functionalization of the polymer or redox processes at the metal center to induce a change in the complex geometry, thus yielding a secondary shape modulation of the polymer.[30b,31]

In conclusion, the present study describes an imine-containing polymer, obtained by facile monomer synthesis and easy-to-control ADMET-polymerization, capable of responding reversibly to light by Z/E-isomerization with a pronounced decrease in hydrodynamic radius of the particles, thus introducing imines as new and easily accessible functional units in light-responsive polymers. The capability of the α-bisimine unit to direct Pd(II) ions for CH activation introduces such transition-metal-mediated processes as a new strategy for the generation of SCNPs as method of choice for a nanoparticle synthesis in an atom- and step-economic manner, displaying the following advantages over the already reported irreversible approaches: (i) the CH activation can be carried out under mild conditions in good polymer solvents (either THF or CH$_2$Cl$_2$) and with no additional trigger besides Pd(OAc)$_2$, (ii) the CH activation does not cause any disruption on the polymer backbone, as indicated by the aforementioned characterization methods, and (iii) it offers potentially straightforward access to a variety of analogues by post-functionalization of the obtained polymeric σ-aryl-metal complexes. The implementation of imines as simultaneous light-responsive units and potential directing groups for CH activation merges both attractive features and gives access to an orthogonally addressable/doubly stimuli-responsive system. It enables the exploitation of the unique properties of a simple C=N bond, whereby the orthogonal pathways of thermal and photochemical switching of imines might lead to the generation of macromolecular motors.[23a,b] Finally, the possibility to perform dynamic covalent chemistry along the C=N bond (in this special ADMET case also by inducing dynamic metathesis[32])

Figure 5. Metal-ion-mediated (Pd(OAc)$_2$) contraction of (Z,Z)-**3a** to SCNPs **4a** with varying amounts (1 = 1.0 equiv, 2 = 0.5 equiv, 3 = 0.1, 4 = 0.05, and 5 = 0.01 equiv) of Pd(OAc)$_2$ as determined by SEC (Figure 3a) and DLS (Figure 3b).

allows for the generation of imine-based dynamers[6,33] capable of executing three types of dynamic operations, i.e., in response to light, metal ions, and constitution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12198.

All experimental and analytical data (PDF)
Crystallographic data for **1a** (CIF)
Crystallographic data for **Pd-1a** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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