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Polymer up-cycling by mangana-electrocatalytic C(sp³)–H azidation without directing groups†

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The chemical up-cycling of polymers into value-added materials offers a unique opportunity to place plastic waste in a new value chain towards a circular economy. Herein, we report the selective up-cycling of polystyrenes and polyolefins to C(sp³)–H azidated materials under electrocatalytic conditions. The functionalized polymers were obtained with high retention of mass average molecular mass and high functionalization through chemo-selective mangana-electrocatalysis. Our strategy proved to be broadly applicable to a variety of homo- and copolymers. Polyethylene, polypropylene as well as post-consumer polystyrene materials were functionalized by this approach, thereby avoiding the use of hypervalent-iodine reagents in stoichiometric quantities by means of electrocatalysis. This study, hence, represents a chemical oxidant-free polymer functionalization by electro-oxidation. The electrocatalysis proved to be scalable, which highlights its unique feature for a green hydrogen economy by means of the hydrogen evolution reaction (HER).

Introduction

Commodity polymers are indispensable in modern society, considering *inter alia* their broad applications in food packaging, construction materials, and electronics.[1] However, the end-of-life fate of post-consumer plastics is a growing concern for modern society as the global production scale is continuously increasing (Fig. 1A).[2] Indeed, in 2018 on average less than one fourth of the overall collected polymer waste was recycled (Fig. 1A). The process-related requirement of near-pristine polymer sorts as well as degradation of the polymer chain during the reprocessing yields low grade recycling material in conventional melt and reform strategies (Fig. 1B).[3] Chemical recycling can circumvent these issues, yielding monomers for the *de novo* synthesis of commodity polymers.[4] However, energy-intensive protocols are largely required, jeopardizing the practicality of these methods, particularly with respect to the societal demand for a transition to green energy usage. Thus, sustainable alternatives continue to be in high demand to add value to reprocessed polymer waste, and thereby increase the economic incentive for closed loop polymer recycling.

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Thus far, up-cycling[5] strategies typically rely on either scission of the polymer chain[6–9] or modification of the polymer by introduction of functional groups.[10–13] Here, the merger of C–H functionalization[14–19] and polymer science has witnessed considerable advances by leveraging polymer waste to up-cycled materials.[13,20] For instance, Hartwig and Hillmyer reported on the borylation of polypropylene using a rhodium catalyst in a polymer melt.[12] Likewise, the oxyfunctionalization of polyethylene,[21,22] and polyisobutene[10] was accomplished. Under photochemical conditions, Leibfarth and Alexanian devised elegant C–H xanthylation of polyolefins,[23,24] and C–H functionalizations *via* amidyl radicals.[25]

The azido moiety plays a key role in among others the Staudinger ligation or the 1,3-dipolar cycloaddition for bio-orthogonal click reactions.[26] In this context, Tsarevsky reported a C–H azidation of polystyrene using stoichiometrically hypervalent iodine (Fig. 1C),[27] while Bielawski and Liu used stoichiometric amounts of hypervalent iodine reagents for the mediated azidation of polypropylene.[28] Despite this indispensable progress, the use of superstoichiometric amounts of hypervalent iodine reagents significantly reduces the overall sustainability of this approach.

In stark contrast, electrochemistry[29–32] has surfaced as an increasingly viable tool to perform C–H functionalizations in a sustainable and cost-effective manner (Fig. 1D).[33–45] However, thus far electrosynthetic approaches have proven to be limited to chlorination and cyanation of π-conjugated polymers in the solid film state.[46–54] Consequently, we wondered whether metallaelectro-catalyzed C(sp³)–H azidation[55] would enable selective electrooxidation for the up-cycling of polymer waste.
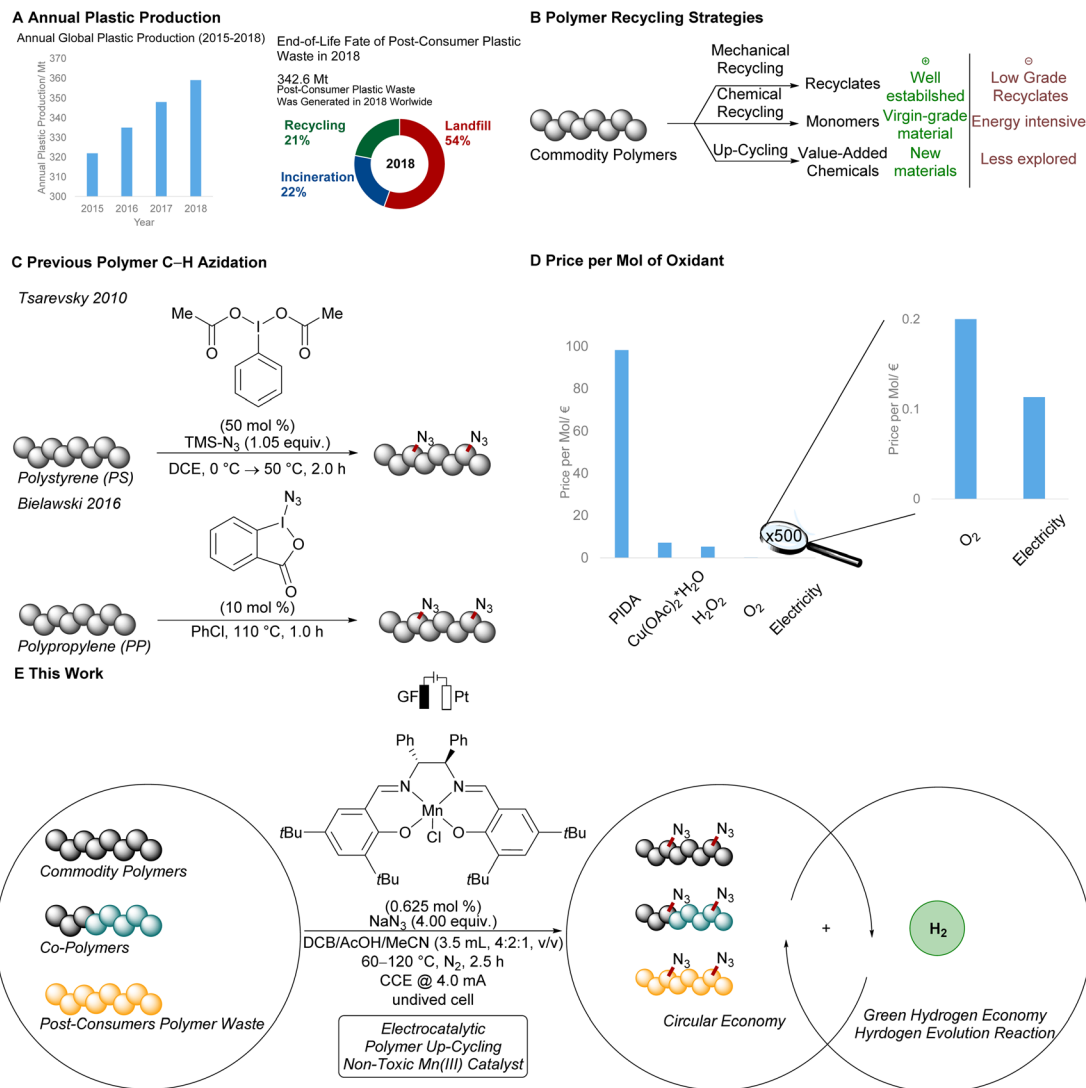
Fig. 1 (A) Annual global plastic production and the waste treatment in the EU in 2018, (B) different approaches to deal with post-consumer polymer waste, (C) previous polymer C–H azidation mediated by hypervalent iodine(III), (D) price per mol in € for various oxidants and (E) this work using electricity as the terminal oxidant.

As a result, we report on the hypervalent iodine-free mangana-electrocatalyzed post-synthetic azidation on a variety of polymers (Fig. 1E). Notably, the electrocatalytic C–H nitrogenation proved scalable and is operative *via* cathodic hydrogen evolution reaction (HER), hence featuring a unique potential for scalable anodic oxidation for a green future hydrogen economy.

Results and discussion

Optimization of the reaction conditions

We commenced our studies by evaluating the choice of the metal catalyst under electrochemical conditions using a platinum (Pt) cathode, graphite felt (GF) anode, and polystyrene **1** as the substrate, and sodium azide **2** as being a more readily accessible azide source than previously used TMS-N$_3$ (Table 1). To evaluate the efficiency of the C(sp^3)–H azidation two parameters were identified as being of primary relevance. First,

the retention of the mass average molar mass (M_w-retention) was considered. Second, the level of functionalization was determined. Thus, a high M_w-retention and high level of functionalization were focused on during the optimization study. The variation of different 3d metal catalysts showed the superior role of manganese complexes as compared to its congeners. The C–H azidation using [**Mn1**] furnished a modified polystyrene material with a 48% retained mass average molar mass and 1.6 mol% azidation (entry 1–4), the catalytic efficiency being slightly compromised as compared to the C(sp^3)–H functionalization of small molecules. Although the level of functionalization was rather promising, the mass average molar mass retention was significantly lower compared to the other 3d metal complexes indicating an accompanied β-scission pathway of the radical intermediate.[56]

We hypothesized whether the deleterious side reaction could be prevented by varying the ligand motif, to thereby achieve

Table 1 Electrochemical azidation of polystyrene **1**[a]

Entry	[ML]	Level of functionalization[b]/(mol%)	M_w-retention[c]/%	$Đ$[c]	Catalyst efficiency[d]
1	[Co1]	0.8	77	2.79	0.64
2	[Ni1]	0.8	66	2.88	0.64
3	[Cu1]	1.1	66	3.11	0.88
4	[Mn1]	1.6	48	2.37	1.28
5	[Mn2]	0.8	45	2.41	0.64
6	[Mn3]	1.9	65	2.65	1.52
7	[Mn4]	1.4	69	2.68	1.12

[a] Reaction conditions: **1** (1.0 mmol monomer unit), **2** (1.0 equiv.), [ML] (1.25 mol%), LiClO$_4$ (0.17 M), 1,2-DCB (4.0 mL), MeCN (1.0 mL), AcOH (1.0 mL), CCE @ 2.0 mA at 60 °C under N$_2$ for 5.0 h. 1,2-DCB = 1,2-dichlorobenzene, CCE = Constant Current Electrolysis. [b] Determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol%, R^2 = 0.9942). Relative IR intensities were determined by the ratio of the N$_3$-band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [c] The mass average molar mass and dispersity ($Đ$) were determined by analytical GPC against narrow-disperse polystyrene standards using THF as eluent at 30 °C and are reported as mass average molar mass retention of the parent polymer. [d] Catalyst efficiency = [level of functionalization (mol%)/catalyst loading (mol%)].

a higher M_w-retention, while preserving the remarkable C(sp^3)–H functionalization efficiency. Indeed, the substitution pattern exhibited a considerable influence on the M_w-retention (entries 4–7). Notably, high catalytic efficiency in the electrochemical azidation was observed for sterically demanding complex [Mn4] and manganese salen [Mn3]. While the structural simplicity of [Mn3] represents an advantage, we selected [Mn4] for further studies as the chemo-selectivity in terms of suppression of polymer degradation was improved. Furthermore, various metal salts have been probed in the electrochemical up-cycling and confirmed the superior nature of the manganese catalysts (see ESI Table S6†).

With [Mn4] identified as being the optimal catalyst, we probed further reaction parameters (Table S3 and S4†). An excess of sodium azide proved essential to obtain a high M_w-retention (Table S4†). We were delighted to find reaction conditions for high M_w-retention along with a level of functionalization of 1.9 mol% (Table 2, entry 1). Other solvents, such as 1,2-dichloroethane (DCE) or tetrahydrofuran (THF), did not improve the outcome as the increased polymer dispersity $Đ$ indicated masked degradation (entry 2 and 3). Control experiments reflected the essential role of the electricity (entry 4). Thus, the azidation was completely shut down without electricity. Notably, complex [Co1] proved less efficient in the electrochemical C(sp^3)–H azidation. Submitting polystyrene to reported electrophotocatalytic small molecule azidation,[57] resulted in a high azide incorporation accompanied by

significant polymer degradation. Thus, in contrast to the mangana-electrocatalyzed azidation, a very low mass average molar mass retention was observed (entry 7).

Electrode material

Next, we probed the impact of the electrode on the polymer modification (Fig. 2), by examining the optimized mangana-electrocatalyzed polymer up-grading with various carbon-based electrode materials. Reducing the surface area diminished the level of functionalization (Fig. 2). Reticulated vitreous carbon (RVC) – a porous electrode material[58] – gave slightly lower levels of functionalization and comparable M_w-retention. We attribute this trend of comparable functionalization to the high specific surface area of the RVC anode. For graphite (G), a lower level of functionalization was observed, mirroring the requirement of a large surface area for efficient C–H azidation. The geometry of the electrode did not significantly alter the outcome, as was demonstrated when using a graphite rod (GR) as anode material. Also, glassy carbon (GC) as well as boron-doped-diamond (BDD) fell short in improving the mangana-electrocatalyzed C(sp^3)–H azidation on polystyrene. Control experiments using a glassy carbon (GC) anode at prolonged electrolysis time gave a comparable level of functionalization of 1.5 mol% and M_w-retention of 81% (Table S5, entry 6†). Based on orienting studies and previous findings on mangana-electrocatalyzed small molecule C(sp^3)–H azidation,[55] we

Table 2 Optimized reaction conditions for the mangana-electrocatalyzed polystyrene 1 azidation[a]

Entry	Deviation from above	Level of functionalization[b]/(mol%)	M_w-retention[c]/%	$Đ^c$	Catalyst efficiency[d]
1	None	1.9	84	2.72	3.04
2	DCE instead of DCB	2.3	81	3.37	3.68
3	THF instead of DCB	0.3	96	3.34	0.48
4	No electricity	n.o.	100	2.34	—
5	[Co1] instead of [Mn4]	0.7	95	2.42	1.12
6[e]	Electrophoto-catalytic conditions	11.6	15	4.44	1.16

[a] Reaction conditions: 1 (1.0 mmol monomer unit), 2 (4.0 equiv.), [Mn4] (0.625 mol%), LiClO$_4$ (0.17 M), 1,2-DCB (2.0 mL), AcOH (1.0 mL), MeCN (0.5 mL), CCE @ 4.0 mA at 60 °C under N$_2$ for 2.5 h. 1,2-DCB = 1,2-dichlorobenzene, CCE = Constant Current Electrolysis. [b] Determined by an IR-^{1}H NMR correlation curve (m = 2.7051 mol%, R^2 = 0.9942). Relative IR intensities were determined by the ratio of the N$_3$-band (2106 cm^{-1}) to the benzylic C–H band (3026 cm^{-1}). [c] The mass average molar mass and dispersity ($Đ$) were determined by analytical GPC against narrow-disperse polystyrene standards using THF as eluent at 30 °C and are reported as mass average molar mass retention of the parent polymer. [d] Catalyst efficiency = [level of functionalization (mol%)/catalyst loading (mol%)]. [e] See ESI for details, n.o. = not observed.
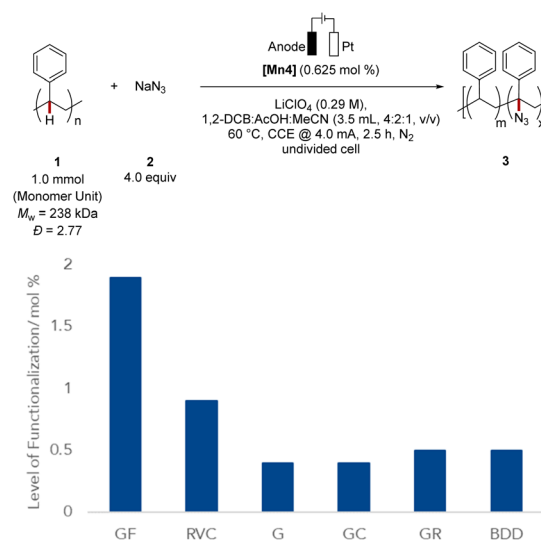

Fig. 2 Variation of carbon-based anode material. Level of functionalization for Graphite Felt (GF), Reticulated Vitreous Carbon (RVC), Glassy Carbon (GC), Graphite (G), Graphite Rod (GR), Boron Doped Diamond (BDD).

propose the formation of a manganese(IV) diazido species (Fig. 3) through anodic oxidation, along with subsequent hydrogen atom transfer (HAT) and azide transfer, thereby also rationalizing the preferential functionalization at benzylic positions of polystyrene (*vide supra*). At the cathode, molecular hydrogen is formed through HER.

Electrocatalysis robustness

With the optimized reaction conditions in hand, we examined the versatility of the mangana-electrocatalyzed C–H azidation

(Scheme 1). First, we probed whether chain scission was hidden by the large polymer dispersity. Thus, we performed the C–H azidation on a narrow-disperse polystyrene (4). Here, we could observe complete M_w-retention (100%) with virtually no change in $Đ$ and comparable high functionalization of 2.1 mol%.

Prolonging the electrolysis time furnished polystyrene material with an increased level of functionalization of 6.8 mol% and a M_w-retention of 100%. However, extending the electrolysis further led to a significant increase of $Đ$ through a competing chain–chain coupling pathway (see Fig. S29 in ESI†). A polystyrene with medium M_w (5) was also efficiently up-cycled and gave a very high M_w-retention of 95% and a similar level of functionalization. To our delight, the electrochemical polymer up-cycling proceeded with a higher efficiency and at the same time a comparable retention of the mass average molar mass in comparison to previously reported hypervalent

Fig. 3 Proposed mechanism for mangana-electrocatalyzed C–H azidation of commodity polymers.

Scheme 1 Scope of the mangana-electrocatalyzed azidation. Standard reaction conditions: **1** (1.0 mmol, 1.0 equiv.), **2** (4.0 mmol, 4.0 equiv.), [Mn4] (6.25 μmol), $LiClO_4$ (0.29 M), 1,2-DCB (2.0 mL), AcOH (1.0 mL), MeCN (0.5 mL), CCE @ 4.0 mA at 60 °C under N_2 for 2.5 h. The mass average molar mass and dispersity (*Đ*) were determined by GPC against narrow-disperse polystyrene standards using THF as eluent at 30 °C and were reported as the molar weight retention of the parent polymer. *Reaction performed at 80 °C. **Reaction performed at 120 °C. [a]The level of functionalization was estimated using an IR-^{1}H NMR correlation curve ($m = 2.7051$ mol%, $R^2 = 0.9942$) and the relative IR intensity of the N_3-band (2106 cm^{-1}) to the benzylic C−H band (3026 cm^{-1}) of the polystyrene sample. [b]Results are reported as average over three runs. [c]The level of functionalization was determined by elemental analysis. [d]The level of functionalization was determined by ^{1}H NMR analysis of the 1,3-cycloaddition product with methyl propiolate. [e]For details on selectivity, see the ESI.† [f]The level of functionalization refers to α and β (1.0 : 1.5) in total. [g]The level of functionalization was estimated by ^{1}H NMR analysis of the 1,3-cycloaddition product with dimethyl acetylenedicarboxylate.

iodine-mediated azidation on polystyrene[27] with stoichiometric chemical oxidants (see Fig. S18 in ESI†). When we subjected a derivative of polystyrene, namely poly(2-vinylnaphthalene), to the mangana-electro C–H azidation, the azidation took site-selectively place at the benzylic C–H bond and furnished **6** with a very high M_w-retention (93%) and high azidation of

2.6 mol%. To our delight, also poly(4-methylstyrene) proved compatible with our strategy, furnishing material **7** with a remarkably high level of functionalization (5.0 mol%).

Here, chain–chain coupling led to an increased mass average molar mass and *Đ* being indicative of the formation of cross-linked material. The C–H azidation occurred preferentially on

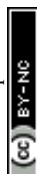**Table 3** T_g and T_{deg} of polymer **4** and **15**

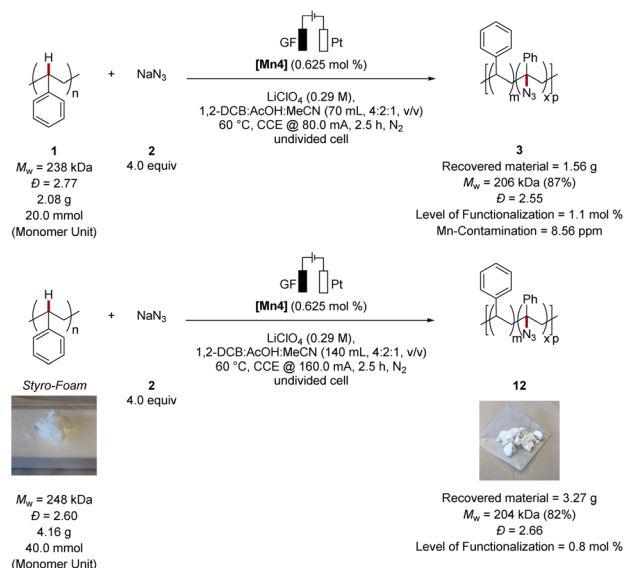| Entry	M_w^a/kDa	Level of functionalization^b/(mol%)	T_g^c/°C	T_{deg}^d/°C
1^e	16.7	0.0	101.1	410.2
2	16.9	2.4	98.6	382.2
3	16.7	6.8	104.1	339.7
4^f	16.8	6.9^g	120.3	346.5

^{a} Determined by GPC against narrow-disperse polystyrene standards.
^{b} Determined by IR-^{1}H NMR correlation curve. ^{c} Determined by DSC.
^{d} Determined by TGA. ^{e} Parent polymer. ^{f} Results for polymer **15**.
^{g} Determined by ^{1}H NMR analysis.

Fig. 4 Scale-up of the C–H azidation on polystyrene. See ESI† for details.

the more readily accessible benzylic methyl moiety of the pendant group rather than at the benzylic C–H of the polymer backbone.[59] A styrene-containing copolymer was tolerated in the electrocatalyzed C(sp^3)–H functionalization likewise. The mangana-electrocatalyzed C–H azidation of polystyrene-*b*-polyisoprene-*b*-polystyrene triblock copolymer delivered the modified polymer **8** with a very high level of functionalization of 14.0 mol%. The azidation of the triblock copolymer preferentially took place on the allylic position of the unsaturated moieties at the polyisoprene block.[60] Although the M_w was efficiently retained, an increased Đ indicated accompanied radical–radical recombination. It is particularly noteworthy that our strategy was not limited to polystyrenes, but also challenging polyethylene and polypropylene were functionalized with high efficiency. We were delighted to observe no loss in reactivity furnishing azidated polyethylene **9** (ref. 61) and polypropylene **10**.[61] The challenging nature of polyethylene[25] and polypropylene[28] azidation is mirrored in thus far reported catalyst efficiencies of 0.40 and 0.38, respectively. In stark contrast, the mangana-electrocatalyzed C–H nitrogenation proved remarkably efficient for polyethylene and polypropylene azidation with a catalyst efficiency of 1.60 and 4.16, respectively.

Moreover, ketone functionalized polyethylene was also suitable in this transformation providing access to the azide functionalized polyethylene **11** with a total functionalization of 2.3 mol% (3°:2° = 3.6 : 1.0) (Scheme 1).[61]

With the scope of well-defined polymer sources being established, we investigated challenging post-consumer polystyrene materials containing unknown additives and pigments. Here, additives in styrofoam as well as pigments of a polystyrene-based bowl did not suppress the reactivity and gave functionalized polystyrene materials **12** and **13**, highlighting the applicability for polymer up-cycling.

Thermal and mechanical properties

To determine the impact of the C(sp^3)–H functionalization on the physical properties of the thus obtained polymeric material, we performed differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 3). While only minor changes of the glass transition temperature (T_g) was observed for azidated polymers (Table 3, entries 1 to 3), the incorporation of a triazole moiety increased the T_g (entry 4), thus, highlighting the potential of the azide moiety as synthetic handle for late-stage diversification. Interestingly, an initial weight loss at 250 °C, accounting for a loss of the azide was observed for polymer **4** (see ESI† for details). The mechanical properties were not significantly altered through azidation as was shown in a static material testing, with a modulus of 1014 MPa for **12** compared to 1122 MPa of the parent polymer. Overall, the azide functionalized polymers showed comparable mechanical stability as the parent material, enabling late-stage diversification with azides as synthetically useful handle. Furthermore, the lower degradation temperature (T_{deg}) of the azidated polymer will allow easier degradation after the end use of this material.

Scale-up and click-diversification

Next, we became intrigued by scaling-up the electrocatalytic polymer C–H functionalization to highlight the unique potential of polymer up-grading for a HER-based green hydrogen economy (Fig. 4). Here, we obtained the modified polymer within 2.5 h in high M_w-retention (87%) and a level of functionalization of 1.1 mol%. The trace metal impurity analysis by ICP-MS of the obtained material showed only a minor contamination of 8.56 ppm manganese in the thus obtained material. Notably, the scaling-up was successfully achieved likewise with styrofoam as the polymer source. Thus, the desired functionalized polymer was obtained in high M_w-retention (82%) and a level of functionalization of 0.8 mol%. It is noteworthy, that *in situ* formed catalysts proved active as well, with MnBr$_2$ and 1,10-phenanthroline, which gave comparable results as the well-defined catalyst **[Mn4]** (see ESI Table S6†).

Finally, we directly used sunlight as a renewable energy source, highlighting the potential of our mangana-electrocatalyzed C(sp^3)–H nitrogenation for a future decentralized sustainable hydrogen economy. Thus, applying a commercially available photovoltaic panel, furnished the desired
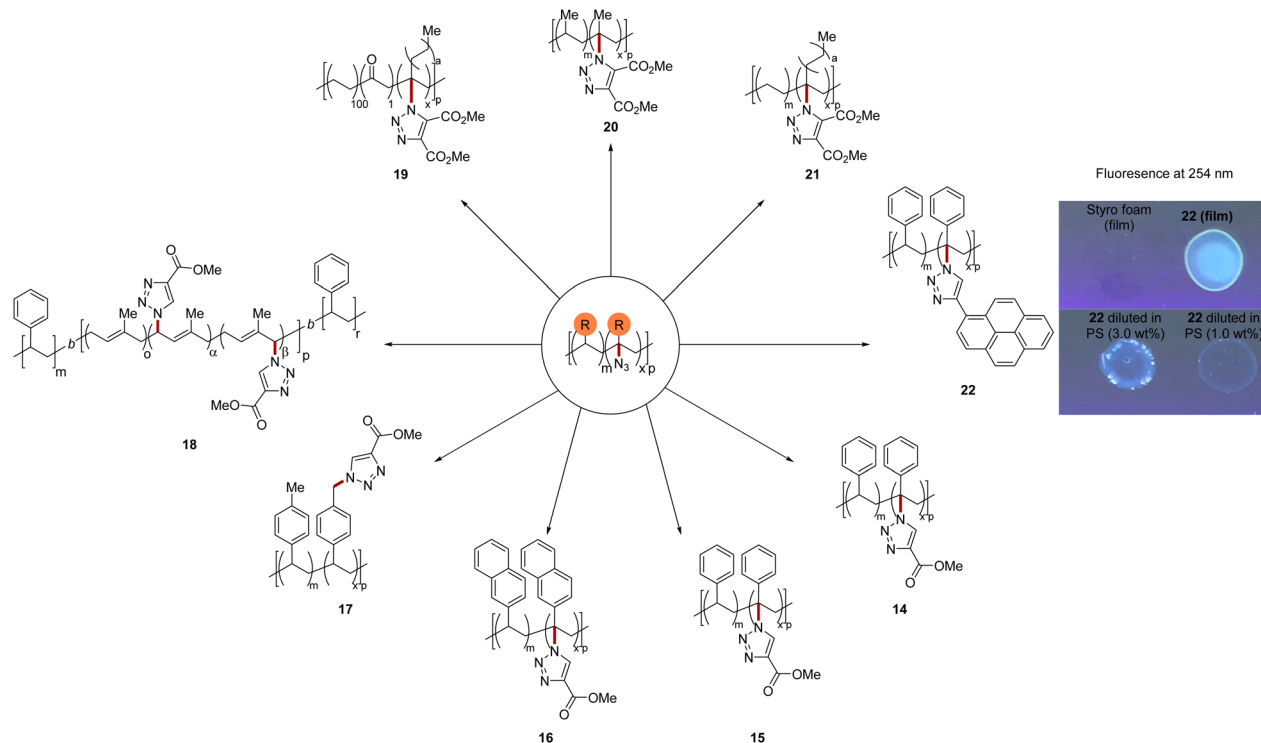
Fig. 5 Product derivatization and fluorescence study. See ESI† for details.

functionalized polymer in high M_w-retention and high level of functionalization (see ESI† for details).

To further demonstrate the applicability of this method, we exploited the azide moiety as synthetic handle for the copper(I)-catalyzed azide–alkyne cycloaddition (Fig. 5). Fluorescence labeling was performed on polystyrene exploiting ethynyl pyrene, demonstrating the power of the azidation for polymer sorting. Indeed, adding 3 wt% of the fluorescent tagged polymer **22** to a solution of styrofoam provided a fluorescent film. Fluorescence was still observable in a mixture of only 1 wt% **22** in styrofoam. Thus, the up-cycled polymers could reenter the in-use cycle as an additives to facilitate polymer sorting in a tracer-based sorting approach.[62]

Conclusions

In summary, we have reported on an efficient mangana-electrocatalysis strategy for the up-grading of polymers by undirected $C(sp^3)$–H alkane nitrogenation. A wide array of polystyrene-derived polymers as well as challenging poly-ethylene and polypropylene polymers were altered by syntheti-cally useful azido groups in a sustainable manner. The modification proceeded without significant polymer chain degradation. The electrocatalytic oxidation avoided the use of stoichiometric chemical oxidants, such as iodine(III) reagents. The mangana-electrocatalysis proved broadly applicable and featured ease of scale-up. The functionalized azido-modifications proved to be useful linchpin diversification points for further late-stage click-transformations. On a conceptual level, the merger of this synthetically useful anodic scalable polymer up-grading with the cathodic hydrogen evolution reaction (HER) highlights an outstanding potential for a decentralized green hydrogen economy.

Data availability

The data supporting this article have been uploaded as part of the ESI.†

Author contributions

Conflicts of interest

There are no conflicts to declare.

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