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Simple amination of polystyrene *via* radical sp^3 C–H imination†

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We report the mild functionalization of polystyrene with primary amines and other nitrogen groups through sp^3 C–H imination. This process significantly increases hydrophilicity without deterioration of molecular weight or thermal properties, and provides a handle for further covalent modification. This work will enable the upcycling and diversification of commodity polyolefins.

Introduction

Polyolefins constitute the most prolific family of synthetic polymers, accounting for over half of global polymer production annually.[1] The commercial success of polyolefins can be attributed to their attractive mechanical and processing properties, as well as low production cost. However, adapting polyolefins to new applications remains challenging due to their hydrophobicity and chemical inertness. As nonpolar hydrocarbons, polyolefins suffer poor biocompatibility, adhesion, and blending,[2] properties essential for many applications and for the recycling of polymer mixtures.[3] Likewise, polyolefins lack functional groups for covalent modification and reactive extrusion.[4]

These limitations can be significantly ameliorated by incorporating polar substituents through copolymerization and end-group functionalization.[5] However, incorporating polar functional groups by postpolymerization modification offers two principal advantages. First, *de novo* polymer production is rarely economical because commercial polymerization is a capital-intensive process that favours economies of scale.[6] Second, the goal of upcycling polyolefins requires the ability to modify polymers that are already in widespread use.[7]

For these reasons, sp^3 C–H functionalization of polyolefins has attracted academic interest,[8] and produced commercially important products.[9] However, radical methods for polymer modification often suffer extensive chain cleavage and crosslinking.[10] These side reactions damage the polymer's mechanical properties and limit the scope of functional groups that can be installed this way.[11]

These challenges have made the simple amination of polyolefins to generate primary amines (–NH$_2$) an elusive goal, despite the attractiveness of this functional group for polymer modification. Primary amines represent versatile functional handles for both covalent modification[12] and reactive extrusion.[13] Furthermore, amine-containing polymers can be more biocompatible[14] and microbe resistant[15] than polyolefins. Likewise, amine polymers[16] serve a variety of biomedical roles including tissue adhesion,[17] gene transfection,[18] preservation,[19] and biomolecule immobilization.[20]

Yet the simple sp^3 C–H amination of polyolefins remains limited. Direct methods involving harsh and nonselective conditions such as ammonia plasma[21] and chromic acid treatment[22] result in extensive chain-cleavage and crosslinking. Likewise, sp^3 C–H functionalization of polyolefins with azides,[23] has been reported with extensive chain cleavage and crosslinking. By contrast, hydrazines[24] and arylsulfonylamides[25] have been appended to polyolefins by sp^3 C–H functionalization with higher chain integrity. In a major advance, the Hartwig lab recently reported the copper-catalysed sp^3 C–H amidation of polyethylenes without noticeable crosslinking or chain cleavage.[26]

Herein, we describe the mild and selective simple amination of polystyrene by radical sp^3 C–H imination without chain cleavage or crosslinking. We modified our recently reported sp^3 C–H imination of small molecules[27] to make it more appropriate for polystyrene. Our method incorporates primary amines (–NH$_2$, **1**), primary ammonium salts (–NH$_3$Cl, **1**·HCl), and benzophenone imines (–N=CPh$_2$, **3**) without noticeable chain cleavage or crosslinking. Amination considerably improves the hydrophilicity of polystyrene without degrading its mechanical or thermal properties.

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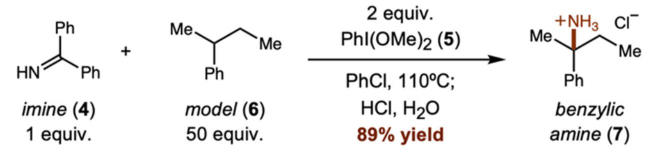
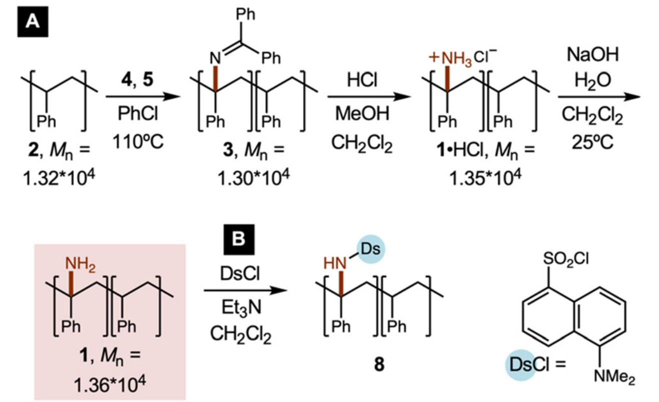
Results and discussion

We first had to address the moderate solubility of polystyrene under our published protocol, which involved high concentrations of the C–H donor at moderate temperatures.[27] Thus, we performed imination on a mixture of benzophenone imine (**4**), $PhI(OMe)_2$ (**5**), and *s*-butylbenzene (**6**) in chlorobenzene at 110 °C (Scheme 1), as a model for conditions under which polystyrene is soluble. This reaction gave us hydrochloride salt **7** in 89% isolated yield after acidic hydrolysis, promising for polystyrene and for high selectivity toward the benzylic C–H bond. Along these lines, we estimated that the bond dissociation free energy was 12.1 kcal mol^{-1} lower for the benzylic C–H bond in **6** than the secondary C–H bond by density functional theory modelling (section S5.1†).

We next investigated these conditions on polystyrene (**2**) prepared by atom-transfer radical polymerization ($M_n = 1.32 \times 10^4$, $Đ = 1.06$),[28] to facilitate analysis of crosslinking or chain cleavage by gel-permeation chromatography (GPC). We used the same reagents, ratios, and concentration as in Scheme 1, specifically a 50 : 2 : 1 ratio of polystyrene[29] : iodane **5** : imine **4**. Polymeric intermediates were isolated in a stepwise fashion for characterization (Scheme 2A). Thus, we prepared first iminylpolystyrene **3** by C–H imination, then hydrochloride salt **1**·HCl by acidic hydrolysis, and finally primary amine **1** by base treatment. No chain cleavage or crosslinking was observed by GPC analysis, as evidenced by the consistent number-average molecular weights (M_n) and dispersities ($Đ$) and by visual comparison of the RI traces for all of these intermediates (Fig. S3.5†). GPC with UV detection gave a significant absorption at $\lambda = 300$ nm only for **3** (Fig. S3.1–4†), consistent with the incorporation and then removal of the benzophenone imine functional group. Indeed, full UV/Vis spectra showed two absorbance features at roughly 285 and 320 nm in iminyl polymer **3** and in imine **4**, but not in polymers **2**, **1**·HCl or **1** (Fig. S3.8–9†). Furthermore, infrared spectroscopy analysis of **2**, **3**, and **1** revealed a peak at 1650 cm^{-1} only for **3** (section S3.2†), which we assign to the $\nu(C{=}N)$ stretching mode of the imine.



Scheme 1 Model for polymer amination with *s*-butylbenzene.



Scheme 2 (A) Stepwise modification of polystyrene. (B) Dansyl tagging of amine **1**. M_n values are in Daltons.

To confirm the presence of the primary amine in **1**, we performed a Dansyl tagging experiment (section S2.7†),[30] providing Dansylamide polymer **8** (Scheme 2B). We characterized Dansyl tagging by fluorimetry, using cumylamine-derived model Dansylamide **S1**. Next, we quantified the amine loading in **1** by preparing a triflic acid salt (**1**·HOTf) and analysing by ^{19}F-NMR with a fluorine internal standard (section S2.6†). We thereby obtained an amine loading of 0.27% per styrene unit.

To evaluate the influence of functionalization on physical properties, we next analysed **2**, **3**, **1**·HCl, and **1** by both Sessile drop test and by differential scanning calorimetry (DSC, Table 1, sections S3.3 and 5†). We found that the water contact angles decrease significantly from 108° to 85° in the order **2**, **3**, **1**, and **1**·HCl, consistent with the increasing polarity of those functional groups. Iminyl polymer **3** showed the greatest decrease in glass transition temperature (T_g), whereas **2**, **1**·HCl, and **1** had more similar glass transition temperatures. These results are significant for the upcycling applications because our method significantly increases hydrophilicity without a significant change in molecular weight or processing temperatures.

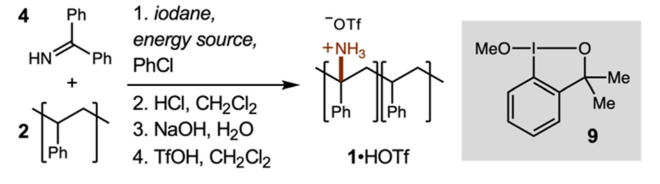
We next used this quantification method to compare polymer imination under different conditions (section S2.6.4†). In this study we cascaded the imination, hydrolysis, free-basing steps, and triflic acid treatment to isolate **1**·HOTf for ^{19}F-NMR assay. Table 2 lists the amine loading and % yields for the amination performed with varying reagent ratios, the energy source, and iodane, variables significant in the optimization of our small molecule method.[27] Decreasing the ratio of polystyrene to imine from 100 : 1 to 12.5 : 1 lead to a consistent increase in amine loading from 0.17% to 0.43%, but also a consistent decrease in yield from 17% to 5.4% (entries 1–4). Using a 2 : 1 ratio of iodane **5** to imine **4** proved optimal; decreasing the iodane loading to 1 : 1 resulted in

Table 1 Parameters from Sessile drop test and DSC

Entry	Sample	Nitrogen loading[c]	Water contact angle[d]	T_g [e]
1[a]	**2**	0%	108°	86 °C
2[a]	**3**	0.27%	98°	77 °C
3[a]	**1**·HCl	0.27%	85°	90 °C
4[a]	**1**	0.27%	87°	89 °C
5[b]	**1**	0.52%	51°	74 °C

[a] The same samples were used as in Scheme 2A. [b] The sample from Table 2 entry 9. [c] Fraction of monomer units bearing an C–N bond. [d] Determined by the Sessile drop test. [e] By DSC.

Table 2 Amine loading resulting from various imination conditions



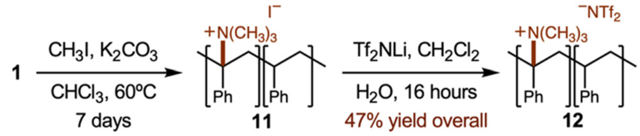
Entry	Iodane	Ratio of 2 : iodane : 4	Energy source	Yield[a]	Amine loading[b]
1[d]	**5**	100 : 2 : 1	110 °C	17%	0.17%
2[d]	**5**	50 : 2 : 1	110 °C	13%	0.26%
3[d]	**5**	25 : 2 : 1	110 °C	8.5%	0.34%
4[d]	**5**	12.5 : 2 : 1	110 °C	5.4%	0.43%
5[d]	**5**	50 : 1 : 1	110 °C	8.0%	0.16%
6[d]	**5**	50 : 2 : 1	Blue LED[c]	7.0%	0.14%
7[d]	**9**	50 : 2 : 1	110 °C	19%	0.38%
8[d]	**9**	12.5 : 2 : 1	110 °C	5.5%	0.44%
9[e]	**5**	12.5 : 2 : 1	110 °C	6.6%	0.52%

[a] Yield with respect to **4**. [b] $-NH_2$ loading per polystyrene unit, as determined by ^{19}F-NMR. [c] λ = 450 nm. [d] At a concentration of 0.5 g mL^{-1}. [e] At a concentration of 1 g mL^{-1}.

lower yield and amine loading (entry 5 *versus* entry 2). Performing the imination at room temperature with blue LEDs also resulted in decreased yield and amine loading (entry 6 *versus* entry 2). By contrast, using cyclic iodane **9** instead of $PhI(OMe)_2$ (**5**) resulted in a modest increase in yield and amine loading but did not significantly increase our highest loading (entries 7 and 8 *versus* entries 3 and 4). The oxidative dimer of **4** ($Ph_2C{=}N{-}N{=}CPh_2$, **10**) was observed in the C–H imination step (Fig. S2.15†), accounting for the low yield with respect to the imine **4**. In our previous work,[27] we showed that low concentration or omission of the C–H donor lead to predominant N–N coupling and the formation of dimer **10**. This is the reason why our polymer imination requires such a high concentration of polystyrene (0.5 g mL^{-1}). Along these lines, doubling the concentration of polymer to 1.0 g mL^{-1} did increase the overall loading to 0.52%. Sessile drop analysis of this sample with higher loading resulted in a water contact angle of 51°, a decrease of 57° from unmodified polystyrene **2**.

We next performed the imination protocol on polystyrene isolated from a commercial disposable cup at a 50 : 2 : 1 ratio of polystyrene to $PhI(OMe)_2$ (**5**) to imine **4** (section S2.9†). We obtained a $-NH_2$ loading of 0.42% without a significant change in molecular weight distribution (Fig. S3.7†).

Finally, to show the utility of the amino group in **1** toward further covalent elaboration, we prepared a tetraalkylammonium polymer by exhaustive methylation (Scheme 3, section S2.8†). Tetraalkylammonium-functionalized polymers are versatile ionomers, and they have often been prepared by alkylation of naturally occurring amine polymers.[31] Thus, heating amino-polymer **1** with CH_3I and K_2CO_3 gave putative trimethylammonium salt **11**. Ion exchange with Tf_2NLi (Tf_2N^- = $(CF_3SO_2)_2N^-$) gave ionomer **12**, from which we measured a 47% overall yield by ^{19}F-NMR. We also repeated the synthesis with $^{13}CH_3I$, to confirm the formation of a trimethylammonium group by ^{13}C-NMR (Fig. S2.10†). Again, GPC comparison of **1**, **11**, and **12** shows no significant impact of these reactions on the molecular weight distribution (Fig. S3.6†).



Scheme 3 Ionomer synthesis by exhaustive alkylation of **1**.

Conclusions

We have demonstrated that sp^3 C–H imination is a mild method to endow polystyrene with nitrogen functional groups. Even at modest loadings (up to 0.52%), amino-functionalization significantly increases the hydrophilicity of the material without noticeable change to the T_g or the molecular weight distribution. Significantly, the reactions work well both on synthetic polystyrene and on material isolated from a consumer product. Moreover, the amino group ($-NH_2$) in **1** undergoes covalent modification by Dansyl tagging and by exhaustive alkylation. These results illustrate the versatility of imination for the synthesis of more elaborate specialty polymers from mass-produced polyolefins.

Author contributions

Mengnan Hu: investigation, methodology, writing–review & editing. Lizhe He: investigation, validation, writing–review & editing. Robert J. Comito: conceptualization, funding acquisition, methodology, project administration, resources, supervision, visualization, writing–original draft, writing–review & editing.

Data availability

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

Conflicts of interest

There are no conflicts to declare.

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