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Chemical valorization of waste polyacrylonitrile polymers via shuttle catalysis

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Acrylonitrile-based polymers are widely used in industrial and consumer settings, contributing to the growing amount of plastic waste. Yet, their chemical recycling has largely been neglected, partly due to the potential release of harmful gases such as HCN and NOx. Herein, we report a catalytic process that enables valorization of the polymer's N- and C-content, without releasing harmful nitrogen gases. Our strategy uses Pd-based shuttle catalysis to transfer HCN units from the polymer's backbone to an olefin acceptor molecule, generating a carbonaceous polyolefin residue amenable to further upcycling, alongside a useful nitrile building block. The protocol can be optimized in two ways: to efficiently functionalize olefins and produce nitriles in up to quantitative yields as a safe, cost-effective alternative to commonly employed nitrile synthesis methods, and to fully dehydrocyanate polymers using ethylene as HCN acceptor. Furthermore, we demonstrate the applicability of our strategy for the upcycling of commercial polyacrylonitrile materials.

To date, plastic recycling has largely focused on mechanical recycling, which often needs a pretreatment step, and has the downside of degrading the plastic material quality. To improve the currently low recycling rates of plastic waste streams, innovations in chemical recycling methods are necessary. Extensive research has been conducted on commodity plastics such as polyethylene and polyvinyl chloride, typically aiming at pyrolysis and preceding heteroatom removal[1–3]. Conversely, although of increasing importance e.g., in the automotive and electronics industry, the chemical recycling of acrylonitrile-based copolymers has largely stayed out of the limelight. With an estimated production of 14.22 Mt in 2022 and an expected production of almost 20 Mt in 2027 for poly(styrene-co-acrylonitrile) (SAN) and poly(acrylonitrile-butadiene-styrene) (ABS)[4] (Fig. 1), the quest for new and efficient chemical recycling methods for these polymers is pertinent, especially given that state-of-the-art valorization of SAN and ABS remains dependent on pyrolysis and gasification methods[5,6]. These processes hardly fit in a sustainable closed-loop framework, as they require a (very) high energy input and generate gaseous nitrogenous pollutants, including ammonia and organic compounds such as hydrogen cyanide, 4-phenylbutyronitrile, and phenylacetonitrile, which cause environmental risks and reduce the value of the liquid residue as a fuel[7–9]. Thus, contingent removal of the N content from these polymers is a condition sine qua non in their valorization.

Current denitrogenation methods include catalytic denitrogenation of pyrolysis oil[10], hydrothermal denitrogenation of pyrolysis oil[11] and polyethylene glycol-enhanced alkaline denitrogenation[12]. Although some of these methods are efficient, harsh conditions are applied and the valuable nitrogen content is lost in the exhaust gas stream. It would be a big leap forward if the efficient removal of the N content could be coupled with a synthesis procedure that keeps the reduced nitrogen in the loop, e.g., as organic N-based building blocks.

From this perspective, SAN and ABS waste could be seen as solid reactants releasing their N content on demand, for example as HCN.

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While HCN is a highly versatile N-synthon, its in situ release would cause severe safety concerns. Hence, we conjectured that a shuttling manifold[13] in which HCN is transferred from the polymer backbone to an unsaturated acceptor compound would serve as an operationally safe and highly attractive entry point for the molecular and chemical valorization of (end-of-life) polyacrylonitrile waste polymers. This process would generate a highly versatile nitrile synthon and a residual (partly) unsaturated N-free polymer backbone, which can be further valorized to hydrocarbon feedstock via e.g., ethenolysis[14], pyrolysis and oxidative degradation. As such, both the N and C content of the original polyacrylonitrile polymer can be reintroduced into the chemical supply chain in a highly modular fashion, as our proposed reaction allows for the polymer to be controllably manipulated and deconstructed at a molecular level.

In this work, we demonstrate the feasibility of this approach by subjecting waste SAN and ABS polymers to a transfer hydrocyanation reaction manifold that operates under Pd(Xantphos)/$AlMe_2Cl$ catalysis, in the guise of previously established HCN shuttling reactions[13,15]. We show that the polymers can be used in excess as a cheap and benign HCN donor to generate synthetically useful nitrile compounds from valuable olefins in quantitative yields. Further manipulation of the nitrile products and the unsaturated polymer backbone could lead to N- and C-containing platform chemicals. Conversely, we show that practically 100% dehydrocyanation can be achieved by the net transfer of HCN from the polymer backbone to an excess of unsaturated acceptor compound, including feedstock alkenes like ethylene.

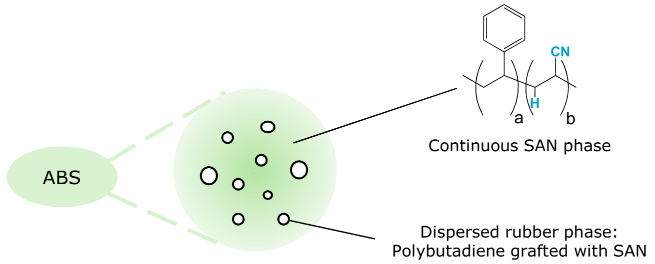


Fig. 1 | General structure of ABS polymers. ABS polymers consist of a dispersed rubber phase (white circles) in a continuous SAN phase (green area)[18,19].

Results

Model transfer hydrocyanation reaction

At first, a model transfer hydrocyanation reaction between equimolar amounts of SAN or ABS polymer as HCN donor and 4-*tert*-butylstyrene (4-TBS) as HCN acceptor was selected (Fig. 2). We initiated our attempts with the catalytic system reported in Morandi's seminal transfer hydrocyanation[13], i.e., Ni/DPEphos/$AlMe_2Cl$, which proved to be rather unfruitful (Tables S6, 7). Subsequently, we found that upon switching to Pd-catalysis, for example as reported by Dallenes et al.[15], yields of nitrile **1** as high as 59% (using SAN) or 57% (using ABS) could be achieved in a 6 h reaction at 120 °C, with Xantphos being the most competent ligand (Table 1 & Tables S6–8). The influence of polymer molecular weight was investigated by comparing two different molecular weights (M_n) of SAN, viz. SAN_{43} ($M_n = 43{,}000\ g.mol^{-1}$) and SAN_{75} ($M_n = 75{,}000\ g.mol^{-1}$). The use of lower molecular weight SAN_{43} slightly improved the product yield from 59% to 65% (Table 1).

Reaction thermodynamics

In principle, the transfer hydrocyanation reaction, and in general any isofunctional shuttle reaction, is an equilibrium reaction due to its near-ergoneutrality ($\Delta_r G^0 \sim 0$) and its microscopically reversible nature[13,16,17]. To verify the reversibility of the transfer hydrocyanation reaction with polymeric HCN donors, the forward reaction between SAN_{43} and styrene on one hand, and the reverse reaction between $dSAN_{43}$ and 3-phenylpropionitrile on the other hand were compared (Fig. 3; the prefix 'd' indicates a defunctionalized polymer). Starting from an equimolar amount of nitriles on the SAN_{43}-backbone and styrene, a phenylpropionitrile yield of 60% (l:b = 78:22) was obtained. Conversely, starting from an equimolar amount of 3-phenylpropionitrile and double bonds on the SAN_{43}-backbone, a styrene yield of 34% was obtained (Fig. 3). Thus, within experimental error, the same distribution of nitrile groups over polymer and phenylpropionitriles is reached, which clearly proves the reversibility of the transfer hydrocyanation reaction with polymeric HCN donors. Per conventional equilibrium-shifting principles, highly energetic HCN acceptors like norbornene (NBE) and ethylene (C_2H_4) shift the equilibrium completely to the right side, as does an excess of polyacrylonitrile HCN donor (Table 2). The difference in calculated standard Gibbs free energy for the hydrocyanation reactions of styrene, ethylene and norbornene reflects the different capabilities

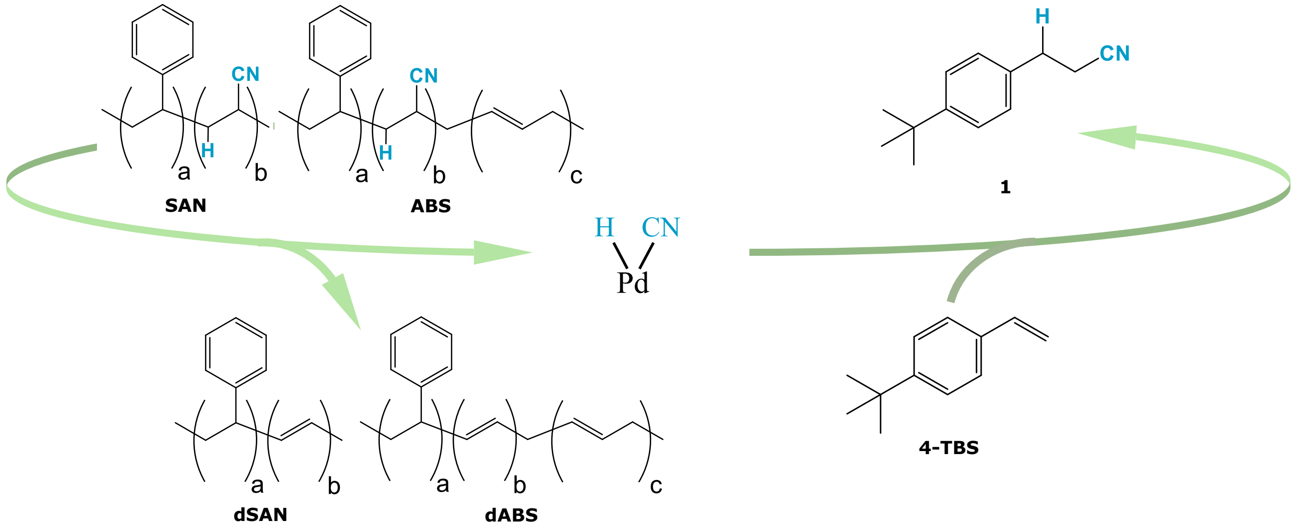
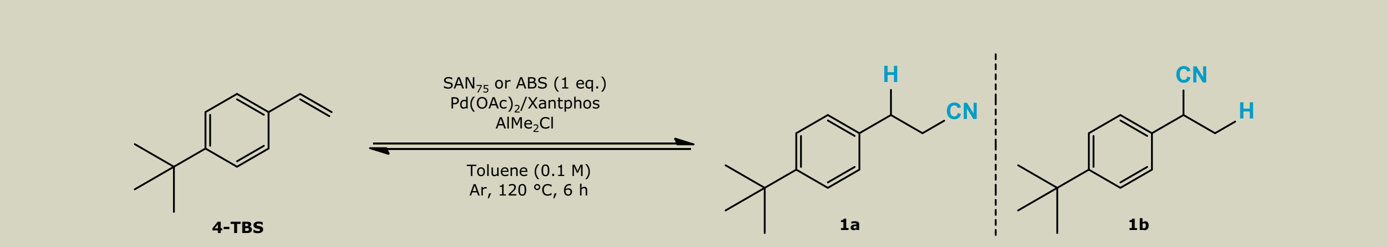


Fig. 2 | Scheme for model transfer hydrocyanation reaction. SAN or ABS ($M_n = 45{,}000\ g.mol^{-1}$), serving as HCN donors, are defunctionalized to yield dSAN or dABS. In contrast, 4-TBS, acting as the HCN acceptor, is functionalized to produce the linear and branched nitrile products (for simplicity, only the linear product is shown here). Pd(Xantphos) functions as a shuttle catalyst, transferring the HCN moiety from the polymer to 4-TBS.

Table 1 | Model reaction with reaction screening conditions



Entry	Polymer	Pd/Xantphos/AlMe$_2$Cl (mol%)	Yield of 1
1	SAN$_{75}$	5/20/40	20%
2	SAN$_{75}$	5/5/40	59%
3	SAN$_{75}$	5/5/20	59%
4	ABS	5/5/20	58%
5	SAN$_{43}$	5/5/20	65%

Summary of results showing the best catalyst conditions for all tested polymers. L:B ratios for 5/5/20 reactions: 76:24.

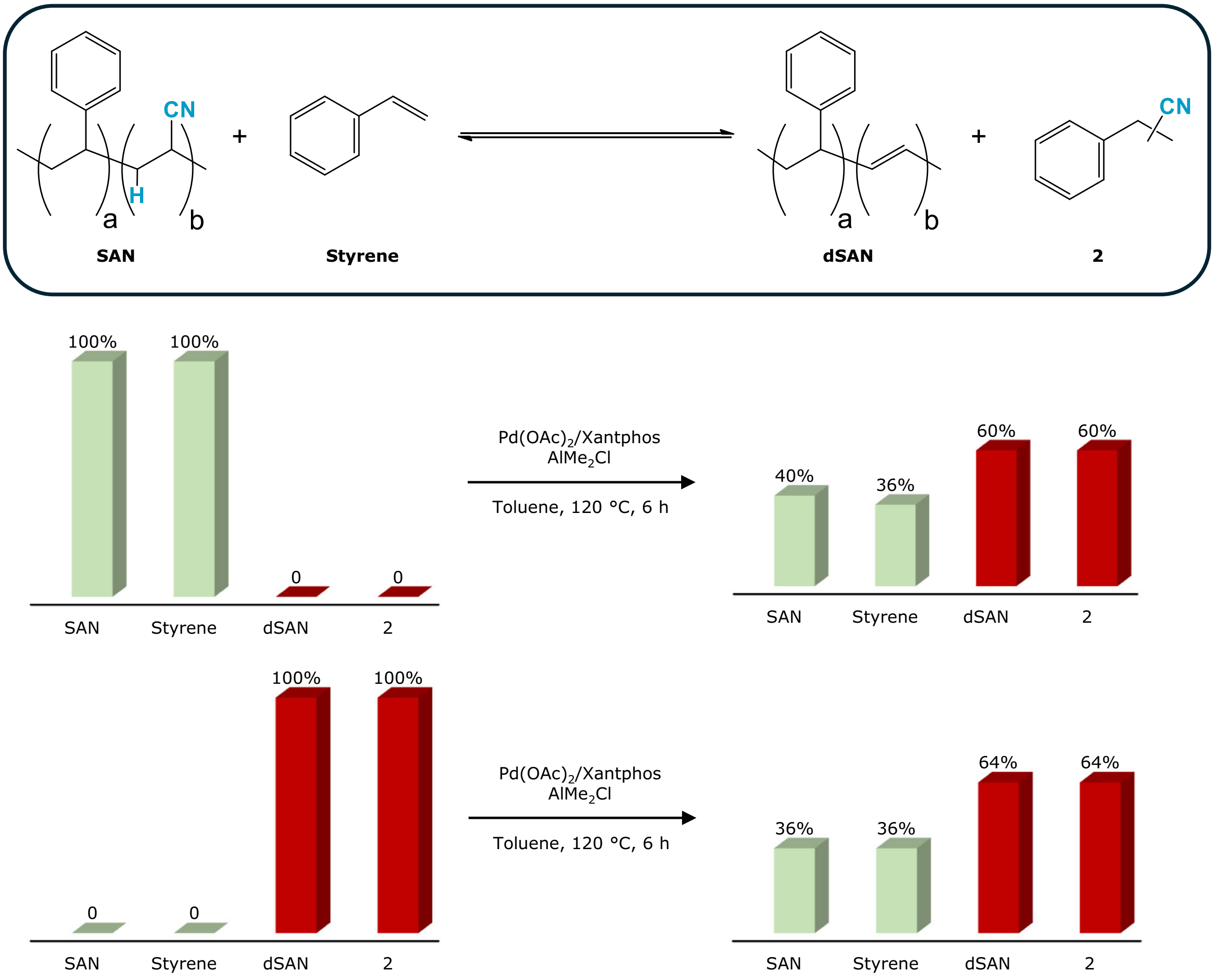


Fig. 3 | Reversibility of the transfer hydrocyanation reaction with polymeric reagents. 0.1 M reagents in toluene (ratio 1:1). Pd(OAc)$_2$/Xantphos/AlMe$_2$Cl = 5/5/20 mol%.

of these alkenes to dehydrocyanate the polymers (Supplementary Table 9). When increasing the amount of polymer in the reaction mixture relative to styrene, a strongly increased yield of **2** was observed, from 60% to 95% when using a 5-fold excess of polymer.

Polyacrylonitrile polymers as user friendly HCN donors

The potential use of polyacrylonitrile polymers as cheap, benign and easy-to-handle HCN donors prompted us to investigate the synthetic scope of our polymer-based HCN transfer manifold. With the model

Table 2 | Shifting equilibrium with excess of polyacrylonitrile donor (Entry 2) or using highly energetic HCN acceptors (Entry 3 & 4)

Entry	HCN acceptor	HCN donor	Ratio	Temperature (°C)	Time (h)	Yield of nitrile products
1	Styrene	SAN_{43}	1:1	120	6	60%
2	Styrene	SAN_{43}	1:5	120	18	95%
3	NBE	SAN_{43}	1:1	120	6	91%
4	C_2H_4	SAN_{43}	/	130	18	96%

$Pd(OAc)_2$/Xantphos/$AlMe_2Cl$ = 5/5/20 mol%.

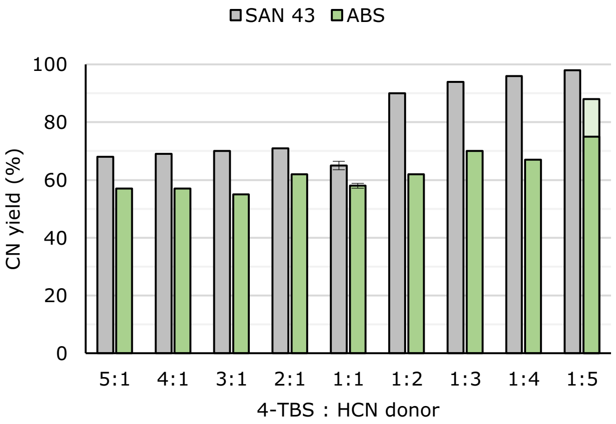


Fig. 4 | Yields of 1 for reactions with different ratios of 4-TBS and SAN_{43} or ABS and $Pd(OAc)_2$/Xantphos/$AlMe_2Cl$ = 5/5/20 mol% or 10/10/40 mol% (light green). Reaction time = 6 h or 18 h (light green). Error bars correspond to the standard deviation of three independent measurements.

reaction between SAN or ABS and 4-TBS, the influence of using different excesses of polyacrylonitrile HCN donor was investigated. As shown in Fig. 4, near-quantitative yields of hydrocyanated styrene **1** could be achieved with a 5-fold excess of SAN_{43} as HCN donor. Comparatively, ABS resulted in lower yields (<75%), possibly explained by (1) the presence of double bonds on the polymer backbone of ABS, and (2) the microstructure of ABS, which contains a dispersed rubber phase in a continuous SAN phase[18,19]. This can result in a lower solubility and decreased accessibility of the nitrile groups. When using more catalyst (10/10/40 mol%) and extending the reaction time to 18 h, the yield increased from 75% to 88% even when using the less reactive ABS (Fig. 4).

Using either SAN_{43} or ABS, a variety of nitrile products could be obtained in high yields (up to 100%) and with good regioselectivities (Fig. 5). Relevant functional handles like -F, -Cl, -CN, -$SiMe_3$ and -OR on the aromatic ring were well tolerated (**4-10**), leading to medicinally relevant building blocks. For instance, compound **13** is a precursor for nabumetone, a nonsteroidal anti-inflammatory drug. Non-activated cyclic and terminal olefins (**14-17**) were fruitful, generating multipurpose building blocks. Controlling the amount of the $AlMe_2Cl$ cocatalyst is key in achieving the equilibrium product ratios. Low $AlMe_2Cl$ availability erodes the l:b ratio (viz. **4** & **7**), instigating increased amounts of the kinetically favored branched products[20].

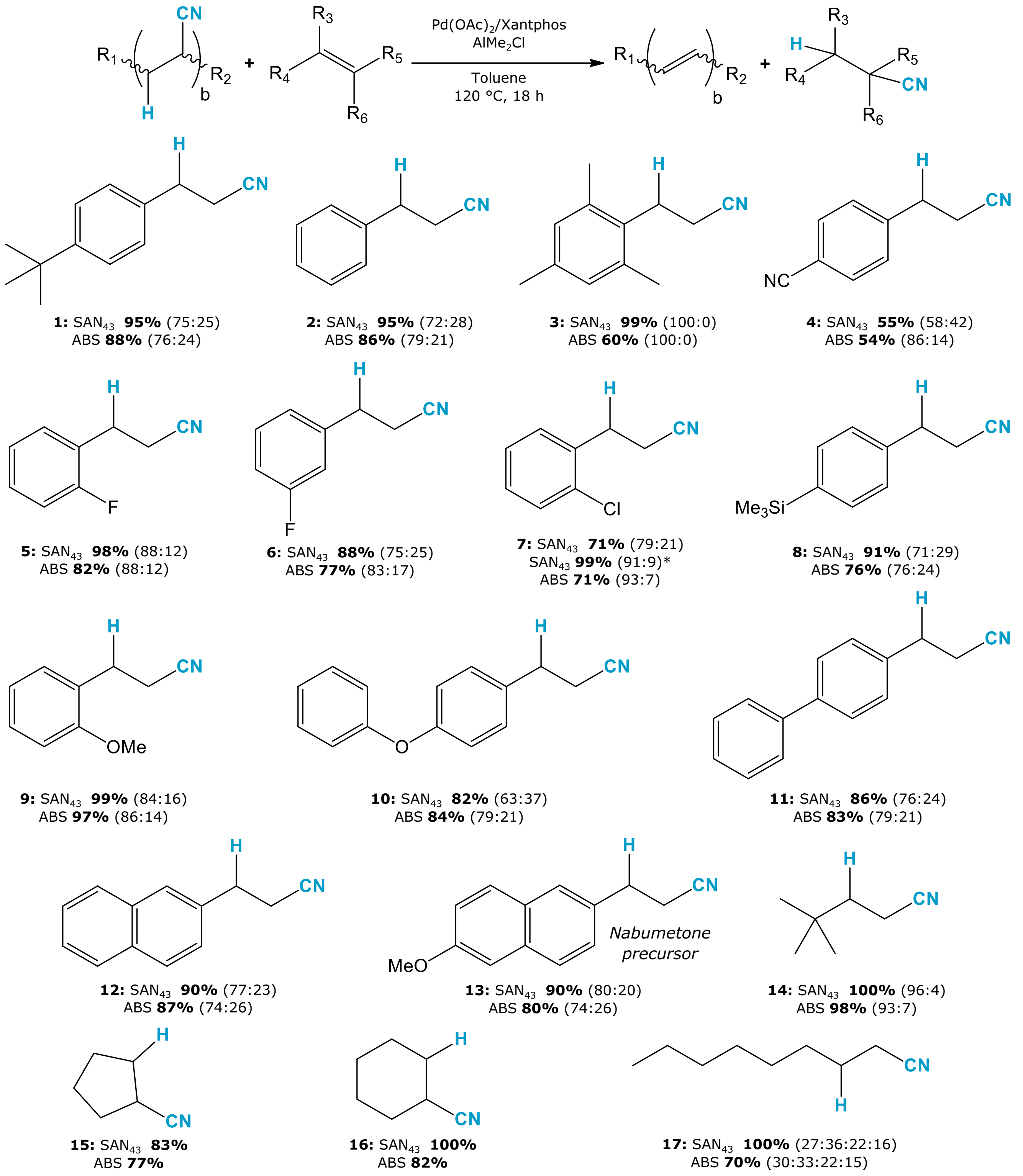
Dehydrocyanation of polymer backbone and scale-up

Exploring the HCN transfer reaction's efficiency in terms of the polymer dehydrocyanation degree requires one to reverse the reactant ratios, now using the polymer as limiting reagent. The HCN acceptor and its amount relative to the polymer were optimized with the goal of obtaining full polymer dehydrocyanation. Styrene acceptors were not effective in achieving full dehydrocyanation, with values being capped at 71% (Fig. 4). Switching to the more suitable NBE (vide supra), the shuttling equilibrium is driven toward (nearly) full dehydrocyanation of the polymer (100% and 97% for SAN and ABS, respectively) (Table 3, entry 4 & 5). Presumably, a fraction of the polymer chain (~30%) contains nitrile motifs that are somewhat harder to remove (thermodynamically and kinetically), engendering the need for an effective HCN trapping agent like NBE. Nonetheless, the NBE-derived nitrile does not have immediate synthetic usefulness, thwarting our envisioned polymeric-to-useful-organic building block N-to-N transfer premise. Therefore, we set out to optimize the dehydrocyanation system with ethylene as a feedstock acceptor, generating propionitrile as a multi-purpose organic platform molecule (used e.g. as solvent[21] and amine precursor[22]). Conspicuously, propionitrile can be converted to acrylonitrile via dehydrogenation[23], effectively regenerating the original nitrile monomer. A dehydrocyanation degree of 96% for SAN_{43} and 91% for ABS was obtained when performing the reaction with 8 bar N_2 and 4 bar ethylene in a homemade stainless steel 10 ml reactor (Table 3, entry 6 & 8). Moreover, when upscaling the dehydrocyanation reaction with ethylene to 7.5 mmol scale in a 60 mL reactor, a similar degree of dehydrocyanation (94%) could be achieved (Table 3, Entry 7).

Polymer characterization

To monitor the transfer reaction from the polymer's side, defunctionalized SAN (dSAN) and ABS (dABS) were isolated and characterized after reaction. FTIR-ATR was the first characterization technique that was used to get insight in the removal of the nitriles (with a characteristic peak at 2238 cm^{-1} corresponding to the $C\equiv N$ stretching vibration) and the appearance of $C=C$ double bonds (with a characteristic peak at 967 cm^{-1} corresponding to the C = **C-H** deformation vibration of *trans*-alkenes) (Fig. 6c)[24].

NMR analysis confirmed these observations, with the nitrile ($\delta = 26.0–28.9$ ppm & $\delta = 118.2–122.5$ ppm (^{13}C)) and backbone methylene -CH_2- ($\delta = 1.1–2$ ppm (^1H)) signals of the polyacrylonitrile substrates making place for olefinic signals ($\delta = 4.7–6.3$ ppm (^1H) and $\delta = 125.5–129.6$ ppm (^{13}C)) and methylene signals corresponding to allylic -CH_2- groups ($\delta = 2-2.4$ ppm (^1H)) (Fig. 6a, b). Moreover, we were able to accurately depict these changes on the level of the polymer's microstructure (i.e., the monomer distribution and arrangement). The acrylonitrile units in the SAN_{43} starting polymer are mainly comprised of SAS triads (i.e. sequence of three adjacent structural units; S = styrene monomer, A = acrylonitrile monomer), with SAA (or AAS) triads being much less abundant and AAA triads not being detected (Fig. 6b & Supplementary Fig. 18). For the styrene units, it was clear that SSA (or ASS) as well as ASA triads were common structures, whereas SSS triads were less abundant. This analysis shows that the distribution of the monomers can mostly be described as alternating. However, some SS as well as AA dyads (i.e., sequence of two adjacent structural units) are present. Dehydrocyanation of these latter is expected to result in conjugated double bonds. Indeed, the olefinic peak in the ^1H-NMR spectrum consists of two peaks, with the minor downfield peak ($\delta = 5.7–6.3$ ppm) being assigned to conjugated double bonds resulting from the dehydrocyanation of two adjacent acrylonitrile units (i.e., AA dyads). The peak at $\delta = 2.7–3.6$ ppm appearing after defunctionalization was confirmed to correspond to methine groups in between double bonds and phenyl side groups. Moreover, the peaks



1: SAN$_{43}$ **95%** (75:25)
ABS **88%** (76:24)

2: SAN$_{43}$ **95%** (72:28)
ABS **86%** (79:21)

3: SAN$_{43}$ **99%** (100:0)
ABS **60%** (100:0)

4: SAN$_{43}$ **55%** (58:42)
ABS **54%** (86:14)

5: SAN$_{43}$ **98%** (88:12)
ABS **82%** (88:12)

6: SAN$_{43}$ **88%** (75:25)
ABS **77%** (83:17)

7: SAN$_{43}$ **71%** (79:21)
SAN$_{43}$ **99%** (91:9)*
ABS **71%** (93:7)

8: SAN$_{43}$ **91%** (71:29)
ABS **76%** (76:24)

9: SAN$_{43}$ **99%** (84:16)
ABS **97%** (86:14)

10: SAN$_{43}$ **82%** (63:37)
ABS **84%** (79:21)

11: SAN$_{43}$ **86%** (76:24)
ABS **83%** (79:21)

12: SAN$_{43}$ **90%** (77:23)
ABS **87%** (74:26)

13: SAN$_{43}$ **90%** (80:20)
ABS **80%** (74:26)

14: SAN$_{43}$ **100%** (96:4)
ABS **98%** (93:7)

15: SAN$_{43}$ **83%**
ABS **77%**

16: SAN$_{43}$ **100%**
ABS **82%**

17: SAN$_{43}$ **100%** (27:36:22:16)
ABS **70%** (30:33:22:15)

Fig. 5 | Substrate scope of the transfer hydrocyanation reaction with 5 equivalents nitrile donor. Pd(OAc)$_2$/Xantphos/AlMe$_2$Cl = 5/5/20 mol% (* = 5/5/40 mol%) for reactions with SAN$_{43}$ and 10/10/40 mol% for reactions with ABS.

corresponding to SSA, ASS and ASA triads disappeared, while the peaks corresponding to SSS triads remained present (δ = 138.6–146.1 ppm). This again confirms the complete removal of nitriles from the polymer backbone. NMR peaks were assigned based on literature[25,26], DEPT-NMR experiments, 2D-NMR experiments and DFT calculations (see Supp. Note 8).

Ultimately, GPC analysis was performed to check the change in molecular weight before and after dehydrocyanation reaction (Fig. 6d). We detected a decrease in molecular weight of almost 50%, (M_n decreased from 43,000 g.mol^{-1} to 23,000 g.mol^{-1}) while the weight loss due to HCN removal was only 15%. We believe that this can be explained by the differences in coiling and dimensions between starting and product polymer chains, resulting in a lower observed molecular weight. A detailed discussion hereof is provided in the Supplementary Note 8. For completely dehydrocyanated ABS (dABS), the analysis results closely resembled those for dSAN$_{43}$ (see Supp. Note 8).

Table 3 | Comparison of transfer hydrocyanation reactions with 4-TBS and NBE as HCN acceptor and Pd/Xantphos/$AlMe_2Cl$ amounts of 5/5/20 mol%

Entry	HCN acceptor	HCN donor	Ratio	Temperature (°C)	Time (h)	Degree of dehydrocyanation
1	4-TBS	SAN_{43}	1:1	120	6	65%
2	NBE	SAN_{43}	1:1	120	6	91%
3	4-TBS	SAN_{43}	5:1	120	18	74%
4	NBE	SAN_{43}	2:1	120	18	100%
5	NBE	ABS	2:1	120	18	97%
6	C_2H_4	SAN_{43}	/	130	18	96%
7[a]	C_2H_4	SAN_{43}	/	130	18	94%
8	C_2H_4	ABS	/	120	18	91%

[a] 7.5 mmol scale.

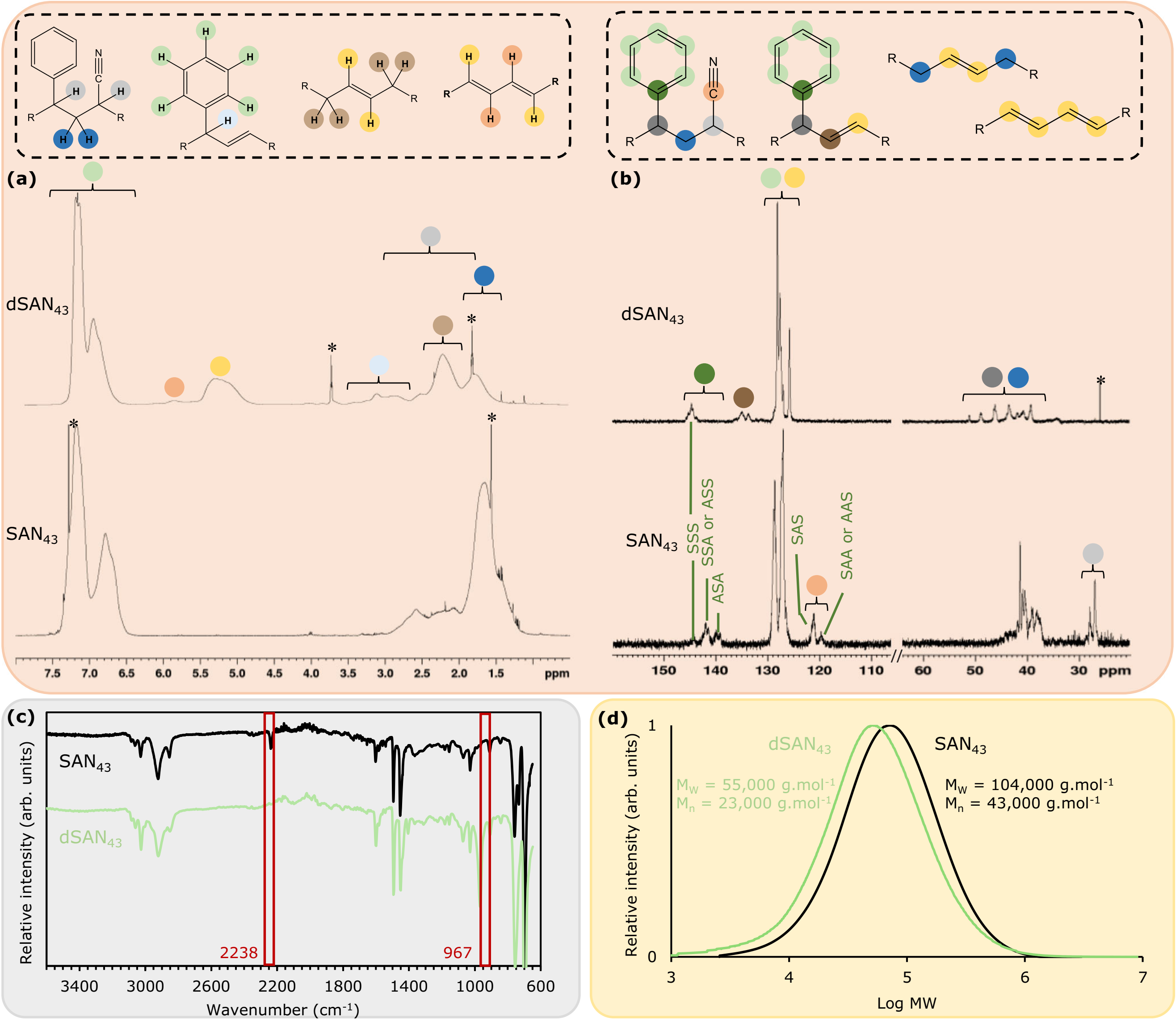


Fig. 6 | Characterization of SAN before (SAN_{43}) and after complete dehydrocyanation ($dSAN_{43}$). a ^1H-NMR spectra and corresponding chemical structures of different units. Non-polymer peaks are indicated with * and correspond to impurities ($\delta = 7.26$ ppm = $CHCl_3$, $\delta = 3.76$ & 1.85 ppm = THF, $\delta = 1.56$ ppm = H_2O), **b** ^{13}C-NMR spectra and corresponding chemical structures of different units. Non-polymer peaks are indicated with * and correspond to THF ($\delta = 25.7$ ppm), **c** FTIR-ATR spectra with characteristic peaks for nitrile groups (2238 cm^{-1}) and C = C double bonds (967 cm^{-1}). The spectra are offset for clarity, **d** GPC chromatograms with M_W and M_n values. The molecular weight distributions are offset for clarity.

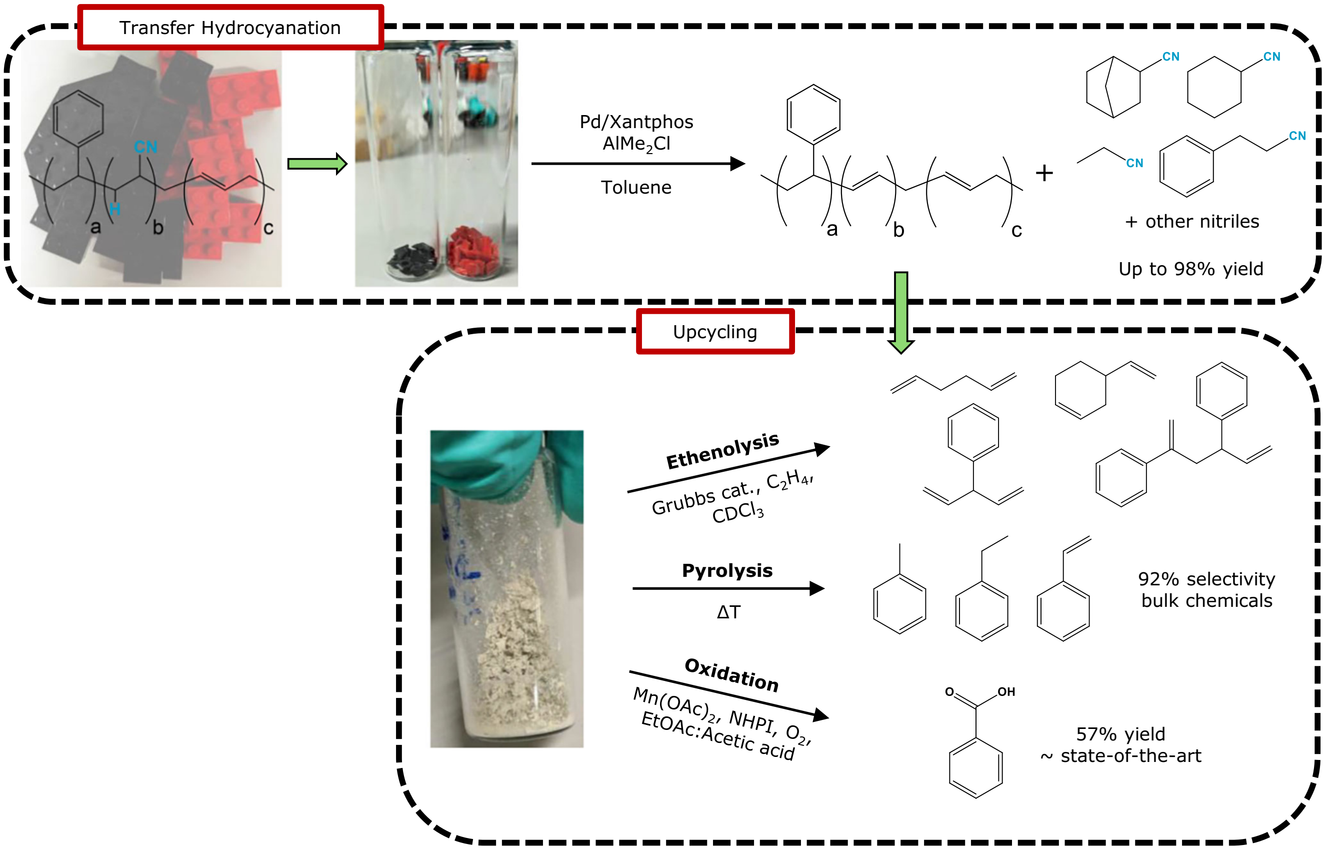


Fig. 7 | Scheme for the complete valorization of a commercial ABS commodity, LEGO®. First, LEGO® is defunctionalized under optimized conditions to yield dABS. Several alkenes or styrene derivatives can be used as HCN acceptors. The resulting defunctionalized polymer, dABS, can subsequently be upcycled through various methods. Ethenolysis affords a mixture of linear α,ω-dienes, cyclic alkenes and phenyl-containing α,ω-dienes. Pyrolysis produces a mixture of bulk chemicals, with the highest selectivity toward toluene, ethylbenzene and styrene. Oxidation reactions yield benzoic acid in high yields.

Commercial ABS commodity and upcycling of product polymer

A well-known application of ABS is found in the toy industry, where LEGO® uses ABS polymer as main material for their LEGO® cubes. We therefore investigated whether this transfer hydrocyanation approach can also be used with consumer LEGO® cubes. Firstly, the composition of the LEGO® cubes was verified to be (mainly) ABS polymer by ^{1}H-NMR analysis (Supplementary Fig. 23) and the M_n of the LEGO® ABS polymer was determined to be 49,000 g.mol^{-1} (Supplementary Table 1). To focus on the recycling aspect of this research, dehydrocyanation of LEGO® with both norbornene and ethylene as HCN acceptor was investigated. The defunctionalization degree of LEGO® was similar to that of pure ABS, namely 97% with norbornene and 87% with ethylene. These results suggest that commercial ABS waste can be used as HCN source without any pretreatment.

To illustrate the amenability of our dehydrocyanated polymer toward downstream valorization, an exemplary ethenolysis reaction was performed on dABS using 8 bars of ethylene and 1 mol% of Grubbs catalyst® M220. GC analysis confirmed the formation of linear α,ω-dienes and cyclic alkenes (e.g., 1,5-hexadiene, 4-vinylcyclohexene) derived from the polybutadiene backbone as well as mono- and diphenyl-containing α,ω-dienes derived from the SAN phase (Fig. 7, Supplementary Figs. 24–26 and Supplementary Table 14). Moreover, we expanded the chemical upcycling toolbox for dABS with pyrolysis as a more straightforward method. The application of the transfer hydrocyanation procedure as a pretreatment step prior to pyrolysis proved effective in producing a mixture of pyrolysis products composed exclusively of hydrocarbon compounds, with no harmful and value-reducing N-containing compounds being detected (Supplementary Table 15). Although the high selectivity (~92%) toward bulk chemicals is promising, the pyrolysis of dABS faces challenges due to solid residue formation, likely resulting from the presence of unsaturated carbon-carbon bonds (Fig. 7 & Supplementary Table 15). Another promising upcycling approach for styrene-based polymers involves their oxidative degradation into benzoic acid (BA) and other aromatic acids. Benzoic acid is extensively utilized across multiple industries, including the food, chemical, polymer and agricultural sectors. Recent advancements in the oxidative conversion of styrene-based polymers include a Mn-catalyzed oxidation of pure PS (64% BA yield)[27] and a Mn/Co-catalyzed system that oxidizes a mixture of PS and HDPE (71% BA yield)[28]. Application of the Mn-catalyzed oxidation protocol to dABS resulted in a BA yield of 57% (Supplementary Figs. 27–29), which is comparable to previously reported state-of-the-art systems. These results underpin the feasibility of using our polymer-based HCN transfer manifold to completely and catalytically convert nitrile polymers to core N- and C-based feedstock chemicals. An overview of the conversion of ABS to a selection of feedstock chemicals is provided in Fig. 7.

Discussion

In summary, we report the development of a catalytic polyacrylonitrile valorization method via a Pd-catalyzed HCN shuttling approach. A model shuttle reaction with commercial poly(styrene-co-acrylonitrile) and poly(acrylonitrile-butadiene-styrene) polymers highlights the importance of the reaction thermodynamics, showing that the equilibrium can be effected by carefully adjusting the ratio and nature of the reactants. Using excess polymer enables olefin transfer hydrocyanations to proceed in high yields, while a slight excess of a reactive olefin acceptor unlocks full polymer dehydrocyanation. The dehydrocyanated polymers were thoroughly characterized and shown to be amenable toward further valorization, paving the way for a circular polyacrylonitrile chemistry.

Methods

HCN transfer reaction procedure with liquid HCN acceptors

In general, 45.09 mg SAN_{75} or 50.89 mg SAN_{43} (0.25 mmol CN), 2.81 mg of $Pd(OAc)_2$ (0.0125 mmol) and 7.23 mg Xantphos (0.0125 mmol) were added to a 10 mL glass vial. The vial was then capped and subsequently purged with argon. Subsequently, 2.5 mL dry toluene, 0.25 mmol of an olefin substrate and 19.5 µL *n*-decane (0.1 mmol, internal standard) were added. Finally, 55 µL of 0.9 M $AlMe_2Cl$ in heptanes (0.05 mmol) was injected. The vial was then placed in a preheated aluminum heating block set to 120 °C. After 6 h, the vial was allowed to cool to room temperature, and two drops of methanol were added to quench residual Lewis acid. Following centrifugation of the reaction mixture, the resulting liquid was analyzed. Reactions employing ABS as the HCN donor were carried out in an analogous manner. Alternatively, reactions were conducted using varying concentrations of HCN donor, HCN acceptor, or catalyst, with equivalents always based on 0.25 mmol of the limiting reagent.

HCN transfer reaction procedure with ethylene gas

In general, 50.89 mg SAN_{43} or 60.30 mg ABS (0.25 mmol CN), 2.81 mg of $Pd(OAc)_2$ (0.0125 mmol) and 7.23 mg Xantphos (0.0125 mmol) were added to a 8 mL glass liner and put in a 12 mL stainless steel pressure reactor. After closing and purging the reactor with argon, following liquids were injected sequentially with the help of a dip tube: 2 mL dry toluene, 19.5 µL *n*-decane (0.1 mmol) and 55 µL of 0.9 M $AlMe_2Cl$ in heptanes (0.05 mmol). The reactor was then pressurized with ethylene and nitrogen gas and heated to 130 °C for 18 h. Hereafter, the reactor was cooled down to room temperature and depressurized after which two drops of methanol were added to quench residual Lewis acid. Following centrifugation of the reaction mixture, the resulting liquid was analyzed.

Reaction analysis

Quantification of the products was performed on a Shimadzu CP-Sil 5 CB column (Shimadzu GC-2010) equipped with a FID using *n*-decane as an internal standard. Reaction yield, selectivities and conversions were calculated based on the effective carbon number method. Automated injection was done with a volume of 1 µL in split mode. The standard temperature program was 50 °C (5 min hold time), 12 °C min^{-1} to 200 °C, 15 °C min^{-1} to 320 °C (3 min hold time). For identification of the different products, an Agilent 6890 gas chromatograph equipped with an HP-1MS ultrainert capillary column and an Agilent 6973 MSD mass spectrometer was used.

Polymer purification

Defunctionalized polymers were isolated after reaction as follows: after centrifugation of the reaction mixture, the liquid phase was added dropwise into a mixture of 7.5 mL methanol and 0.75 mL H_2O while stirring to precipitate the polymer. The polymer was then collected by centrifugation and redissolved in 2 mL THF. The solution was added dropwise into a mixture of 7.5 mL methanol and 0.75 mL H_2O while stirring, again. The redissolution and precipitation steps were repeated one more time. Finally, the polymer was collected by centrifugation and dried overnight under vacuum.

Fourier-transformed infrared spectroscopy

FTIR spectra were obtained using an Agilent Cary 630 FTIR Spectrometer using the attenuated total reflectance accessory.

NMR characterization

NMR spectra were recorded using a Bruker Avance III HD 400 spectrometer with $CDCl_3$ as the solvent at room temperature and the data were analyzed using the Bruker Topspin 4.0.9 software.

Gel permeation chromatography

The molecular weight of the polymers was determined by comparison with Agilent InfinityLab EasiVial PS-M polystyrene standards (162–364,000 Da) in THF on a Agilent 1260 Infinity II GPC/SEC instrument equipped with a PL143-6500 column and analyzed with Agilent GPC/SEC Software Version 2.2.

Ethenolysis

14.1 mg dABS (0.1 mmol double bonds), 0.88 mg Grubbs catalyst M220 (0.001 mmol), 8.12 µL *n*-octane and 1 mL $CDCl_3$ were added to a 5 mL glass liner and put in a 12 mL stainless steel pressure reactor. The reactor was pressurized with 8 bar ethylene and heated to 100 °C for 3 h. Hereafter, the reactor was cooled down to room temperature and depressurized after which the reaction mixture was purged with argon to remove remaining ethylene. The yield of the ethenolysis products was measured by GC-FID analysis whereas the conversion of the double bonds on the polymer backbone was measured by ^{1}H-NMR analysis.

Oxidation

100 mg dABS, 60 mg NHPI and 4 mg $Mn(OAc)_2$ were added to a 5 mL glass liner and put in a 12 mL stainless steel pressure reactor. Next, a mixture of EtOAc:acetic acid (2:1 mL) was added and the contents of the reactor were stirred for 5 min. The reactor was then pressurized with 18 bar O_2 and heated to 150 °C for 12 h. After completion, the reactor was cooled down to room temperatures and depressurized after which the reaction mixture was transferred into a round bottom flask. The leftovers in the liner were washed two times with MeOH and transferred into the round bottom flask. Volatiles including MeOH, EtOAc and acetic acid were removed employing rotary evaporation and the mixture was dispersed in 5 mL 1 M NaOH aqueous solution. Insoluble particles were removed using a 0.2 µm syringe PTFE filter. HCL 37% was added dropwise until the pH of the filtrate was 1. Next, the mixture was extracted with EtOAc (5 × 7 mL) and the combined organic aliquots were dried over $MgSO_4$. Afterwards, 50 mg (0.3 mmol) 1,3,5-trimethoxybenzene was added as an internal standard and the organic extract was condensed using rotary evaporation. The mixture was dissolved in DMSO-d_6 and analyzed via ^{1}H-NMR to calculate the amounts of the isolated acids.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and supplementary information. All other data are available from the authors upon request.

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Author contributions

Experiments were devised by J.L., J.D., and D.D.V. Transfer hydrocyanation reactions were carried out by J.L. and T.V.G. Polymer characterization was conducted by J.L. Ethenolysis of (d)ABS was performed by T.V.G.; Pyrolysis and oxidation of (d)ABS were carried out by N.G. L.C.A. analysis was conducted by A.S. and S.D.M.

Competing interests

The authors declare no competing interests.

Additional information

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