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Spiroborate-Linked Ionic Covalent Adaptable Networks with Rapid Reprocessability and Closed-Loop Recyclability

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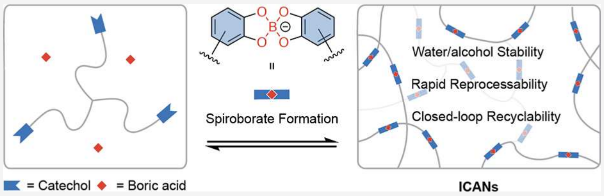
ABSTRACT: Covalent adaptable networks (CANs) represent a novel class of polymeric materials crosslinked by dynamic covalent bonds. Since their first discovery, CANs have attracted great attention due to their high mechanical strength and stability like conventional thermosets under service conditions and easy reprocessability like thermoplastics under certain external stimuli. Here, we report the first example of ionic covalent adaptable networks (ICANs), a type of crosslinked ionomers, consisting of negatively charged backbone structures. More specifically, two ICANs with different backbone compositions were prepared through spiroborate chemistry. Given the dynamic nature of the spiroborate linkages, the resulting ionomer thermosets display rapid reprocessability and closed-loop recyclability under mild conditions. The materials mechanically broken into smaller pieces can be reprocessed into coherent solids at 120 °C within only 1 min with nearly 100% recovery of the mechanical properties. Upon treating the ICANs with dilute hydrochloric acid at room temperature, the valuable monomers can be easily chemically recycled in almost quantitative yield. This work demonstrates the great potential of spiroborate bonds as a novel dynamic ionic linkage for development of new reprocessable and recyclable ionomer thermosets.



INTRODUCTION

The past decades have witnessed a dramatic increase in global usage of conventional polymers, which can be classified into thermoplastics and thermosets. Thermoplastics have weak intermolecular interactions between polymer chains and can be easily reprocessed and recycled. However, the weak non-covalent bonding interactions generally render thermoplastics inferior in mechanical performance, chemical resistance, and thermostability. In contrast, thermosets are network polymers crosslinked by strong covalent bonds. As a result, thermosets are widely used because of their outstanding dimensional stability, chemical inertness, and stiffness. However, on the other hand, the permanent crosslinking feature also critically limits the reprocessability and recyclability of thermosets at the end of their service lifetime.[1] Therefore, the development of novel polymeric materials that combine the easy malleability and recyclability of thermoplastics and the impressive chemical and mechanical properties of thermosets is highly desired,[2] which can reduce the ever-increasing polymer waste generation, and it has recently received great attention.

As one of the pioneering works, Scott et al.[3] reported a thermoset that can be reshaped through chain rearrangement enabled by photo-responsive sulfide bond exchange. The dynamic linkage undergoes addition-fragmentation reactions upon exposure to light irradiation, altering the network topology but leaving the chemical composition and cross-linking density unchanged. Since this work, the concept of incorporating dynamic linkages based on reversible reactions into thermosets has been applied to several materials, which were later commonly referred to as covalent adaptable networks (CANs).[4] Up to now, various dynamic covalent chemical reactions have been used to construct CANs, such as the Diels−Alder reaction,[5,6] urethane exchange,[7,8] carbonate exchange,[9] imine exchange,[10,11] vinylogous urethane transamination,[12] silyl ether exchange,[13−15] thiol−Michael reaction,[16,17] olefin metathesis,[18−20] transalkylation,[21,22] and boronic acid chemistry.[23−27] Most of these linkages have been applied to construct neutral CANs. Ionic covalent adaptable networks (ICANs) with permanently charged backbones would have interesting applications, which are similar to widely used thermoplastic ionomers (e.g., Nafion and Surlyn). Currently available ionomers typically consist of ionic groups as side chain pendants attached to less polar backbones.[28−30] To the best of our knowledge, crosslinked ionomers (i.e., ionomer thermoset) with negatively charged ionic backbones have not been reported. In this work, we

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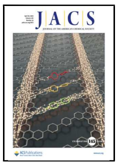

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report ICANs with crosslinked ionic backbones, which have excellent reprocessability and recyclability.

In our previous study, we demonstrated the use of spiroborate as a dynamic linkage to construct ionic covalent organic frameworks.[31] More recently, the same linkage was applied to the synthesis of a single-crystal double-helix covalent polymer with high molecular weight and detailed structural information at the atomic level,[32,33] as well as a 3D covalent organic framework with a unique nbo topology.[34] Given the dynamic and robust nature of spiroborates, we envisioned that spiroborate chemistry could provide spiroborate-linked ICANs as a novel type of crosslinked ionomers with reprocessability. Such ICANs are water-resistant and thermostable, yet degradable under specific conditions and can be easily synthesized through the condensation between polyols and boric acid. We demonstrate these ICANs are rapidly reprocessable within 1 min under moderate heat and can be fully recycled at room temperature in a multiphase system. The findings here provide a new strategy for the design and synthesis of a novel class of crosslinked ionomers consisting of ionic backbone structures with excellent water resistance, rapid reprocessability, and closed-loop recyclability, which can potentially be applied to the development of membranes, actuators, electrolytes, and e-skins.

■ RESULTS AND DISCUSSION

Kinetics and Mechanism Study of the Spiroborate Exchange Reaction. Although spiroborate has been successfully applied in constructing multiple macromolecular and polymeric architectures, the kinetics data of this exchange reaction have not been fully investigated. To better understand the dynamic feature of the spiroborate linkage, two model compounds, diphenylene-spiroborate (DPSB) and dinaphthalene-spiroborate (DNSB) with 4-dimethylaminopyridinium as a counter-cation, were synthesized (see Supporting Information Section 2). At room temperature, a mixture of DPSB and DNSB with a molar ratio of 1:1 dissolved in DMSO-d_6 exhibited no bond exchange even after 48 h. However, upon heating at 60 °C overnight, a new species was observed in high-resolution mass spectroscopy (HR-MS). Its *m/z* value matched with the spiroborate anion consisting of one phenylene and one naphthalene moiety (Figure 1a,b, Supporting Information Section 2). When a freshly prepared mixture was injected into the MS instrument, only DPSB and DNSB anion signals were detected, thus further confirming that the new species was formed during the heating process instead of during the MS measurement. A more detailed ^{1}H-NMR study monitoring the exchange reaction was performed at 60 °C. At the very beginning, only two singlets from DPSB and DNSB were observed in the 6.25 to 7.05 ppm range. As the exchange proceeded with time, two additional peaks appeared with a slight change in the chemical shift due to the different electron-withdrawing effect of phenylene and naphthalene (Figure 1c). The intensity of the new peaks increased with time until the equilibrium was reached, where the molar ratio of DPSB and the newly formed hybrid PNSB and DNSB was found to be 1:2:1, indicating that the spiroborate exchange can be triggered solely by heat without additional catalyst. Similar ^{1}H-NMR experiments were carried out at 70, 90 ,and 100 °C to study the kinetics of spiroborate bond exchange (see Supporting Information Section 2). The exchange reaction was found to follow a second-order reversible reaction model. By fitting ln *k* vs 1000/*T* with the Arrhenius equation, a straight line was obtained, with the activation energy (E_a) calculated to be 132.0 kJ/mol. Although the E_a value was unexpectedly high, the absolute rate constant at elevated temperature was large (0.563 L mol^{-1} s^{-1} at 100 °C). As a matter of fact, the spiroborate exchange between DPSB and DNSB reached equilibrium within 5 min when the mixture was heated at 100 °C, indicating that it is possible to fabricate spiroborate-linked CANs that can be rapidly reprocessed under easily fulfilled conditions.

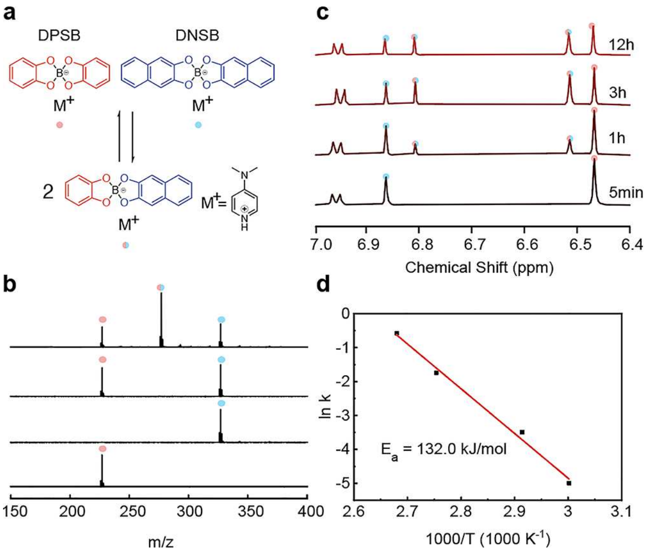

Figure 1. Small molecule model study of spiroborate exchange kinetics. (a) Model reaction between DPSB and DNSB. (b) HR-MS spectra (from top to bottom): mixture after heating; mixture before heating; DNSB; and DPSB. (c) ^{1}H-NMR spectra showing the benzylic protons on the aromatic rings next to the boron center. (d) Arrhenius plot with linear fitting.

In order to understand the spiroborate exchange mechanism, a series of DPSB and DNSB model compounds were synthesized by simply replacing the 4-dimethylaminopyridine (DMAP) with other cation sources. Interestingly, upon heating at 60 °C overnight, an exchange reaction was observed in all mixtures except for the one with sodium as the cation. Introducing water as a proton source into the DPSB-Na and DNSB-Na mixture failed to trigger the exchange. However, once 10 mol % of slightly acidic triethylammonium hydrochloride was added, the exchange reaction proceeded successfully. Furthermore, replacing triethylammonium hydrochloride with triethylmethylammonium iodide did not initiate the exchange, suggesting the acidic proton is necessary for this dynamic spiroborate system (see Supporting Information Section 2).

Synthesis of ICANs. Encouraged by the dynamic feature and fast exchange rate of small molecule spiroborates, we synthesized spiroborate-linked ICANs (Figure 2b). Two precursors C6-6OH and C10-6OH were prepared from pyrogallol and 1,1,1-tris(4-hydroxyphenyl)ethane and dibromo alkanes with high yields over three steps (Figure 2a and Supporting Information Section 3).

The spiroborate-linked ICANs were synthesized by reacting the polyol precursor (C6-6OH and C10-6OH) with boric acid in *N,N*-dimethylformamide (DMF) in the presence of DMAP. Gelation was observed within 1 min at room temperature. The viscous oligomer mixtures were heated at 80 °C for 12 h followed by curing at 120 °C for 6 h to completely remove

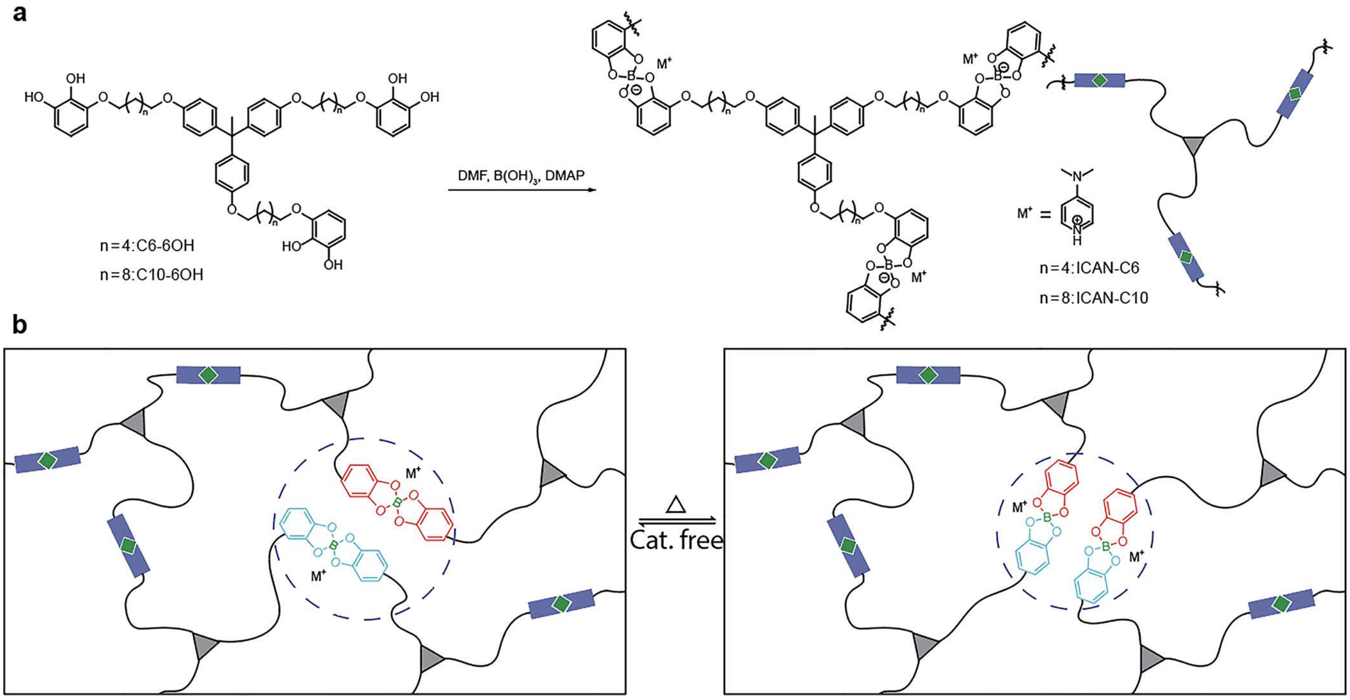

Figure 2. Preparation of ICANs. (a) Synthesis of ICAN-C6 and ICAN-C10. (b) Catalyst-free spiroborate exchange reaction in ICANs.

DMF. Finally, the ICAN-C6 and ICAN-C10 were obtained as slightly colored transparent membranes.

Characterizations and Mechanical Properties of ICANs. Fourier-transform infrared (FTIR) of fully cured ICAN-C6 displayed a weak N−H vibration signal from DMAPH$^+$ counterion above 3000 cm^{-1}, while the strong O−H stretching around 3500 cm^{-1} from polyol and boric acid disappeared, indicating that the pyridinium was incorporated into the material during polymerization, and the free OH groups were fully reacted (Figure 3a). The typical intense broad peak of B−O vibration was observed at 1000 cm^{-1} as well. Differential scanning calorimetry (DSC) measurement of ICAN-C6 showed a slight drop at 114 °C, which is attributed to the glass transition temperature (T_g) of the material (Figure 3b). A similar trend was also observed in ICAN-C10, although the T_g was reduced to 87 °C due to the higher elastic composition of longer flexible chains (Figure 3b). Solid-state polarization magic angle spinning (CP-MAS) NMR spectra of both ICANs were collected and compared with ^{13}C-NMR of precursors and model compound DPSB (see Supporting Information Section 4). For ICAN-C6, the peaks close to 150 and 40 ppm aligned perfectly with those in DPSB, confirming the successful incorporation of DMAPH$^+$ ions. Meanwhile, the peaks in the 25−70 ppm range matched well with precursor C6-6OH aliphatic backbones. The signals in the aromatic region also matched well with the signals of the other aromatic carbons of DPSB. Despite the high solubility of small molecule spiroborates, the crosslinked ICANs remained insoluble and unswollen in most organic solvents and water (Figure 3c and Supporting Information Section 4). Thermogravimetric analysis (TGA) shows less than 5 wt % of mass loss below 300 °C, indicating good thermal stability of the network (see Supporting Information Section 4). To measure the mechanical properties of the new materials, ICAN films were cut into rectangular strips and tested using the uniaxial tensile method (Figure 3d). At a 5%/min strain rate, Young's modulus, the ultimate tensile stress, and the strain at break of ICAN-C6 were measured to be 1.51 GPa, 35.5 MPa, and 3.8%, respectively. Such mechanical properties are similar to those polyimine CANs[10] that we previously reported, which have been utilized in the preparation of carbon fiber reinforced composites, wearable electronics, aerogels, etc. When four more methylenes were installed on each flexible hydrocarbon tether, the ICAN-C10 became more ductile with a lower modulus of 1.13 GPa, an ultimate tensile stress of 32.0 MPa, and a strain at break of 5.4%. The lower T_g of ICAN-C10 can be attributed to the higher chain mobility as well.

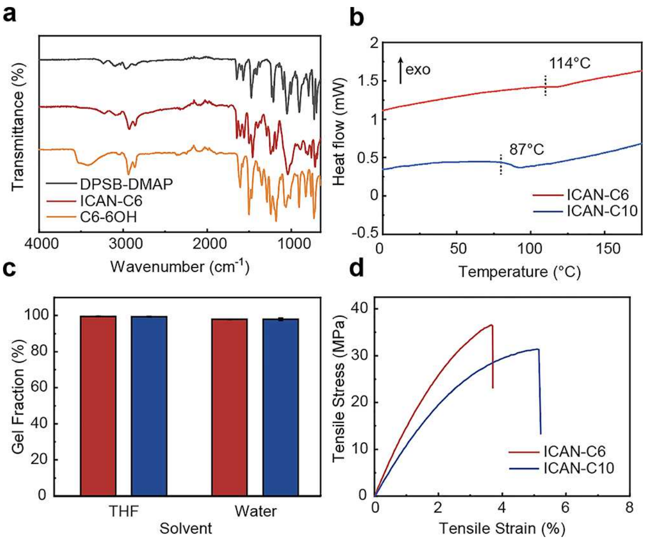

Figure 3. Characterization of ICANs. (a) FTIR spectra of DPSB, C6-6OH monomer, and ICAN-C6. (b) DSC traces of ICAN-C6 and ICAN-C10. (c) Gel fraction of ICANs in water and THF. Red: ICAN-C6. Blue: ICAN-C10. (d) Representative strain−stress curves of ICANs.

Water and Alcohol Resistance of ICANs. It has been recognized that one challenge of CANs linked by boronic acid derivatives is their compatibility with moisture and alcohol solvents. Boronic ester and boroxine can be decomposed in the presence of water and alcohol at room temperature, and heating can facilitate such hydrolysis/alcoholysis. Although recent works have shown the synthesized materials can survive water/alcohol treatment under ambient conditions, their long-time stability remained unclear. In 2020, Zhang et al. reported a new type of boronic ester CAN with an internal boron−nitrogen coordination to improve its stability. Despite the fast hydrolysis of the small molecule model compound, the polymeric material exposed to 40% relative humidity at 30 °C for 4 weeks still retained its original mechanical performance.[35] However, its stability under elevated temperatures is unknown. Inspired by the water stability of spiroborate-linked helical polymer reported in 2021,[32] we first tested water and alcohol stability of the model compound DPSB by treating it with 4 equiv deionized water or methanol in DMSO-d_6 at 100 and 60 °C. To our delight, no reaction was observed even after 24 h of heating (see Supporting Information Section 5). Such enhanced stability in a small molecule can be attributed to the strong chelating effect of the catechol moieties.

Encouraged by the small molecule experiment, we further sought out to test the stability of the polymer networks. Both ICAN films were treated in room-temperature water, boiling water, and methanol for 1 week, 24 h, and 48 h, respectively. To our delight, the samples immersed in water at room temperature displayed no shape change. Samples treated with methanol became slightly softer, but the absorbed methanol can be easily removed by a simple heat press to re-generate the material with the original shape. Materials kept in boiling water exhibit deformation as a result of high temperature and water vapor bubbling disturbance. The original rectangular film can be reproduced by heat pressing the deformed samples in a PTFE mold. After removing the solvent, only a trace amount of mass loss (<4.5%) was observed for all materials (Figure 4c). FTIR spectra did not show OH vibration peak, indicating the ICANs are stable against hydrolysis (Figure 4a,b). To confirm the retention of mechanical performance, the uniaxial tensile test was applied to all processed samples. As expected, Young's modulus, ultimate tensile stress, and strain at break remained nearly the same (Figure 4d). Such a high water/alcohol stability makes ICANs suitable materials for many applications that involve long-term exposure to moisture and/or alcohol vapor, particularly at elevated temperatures.

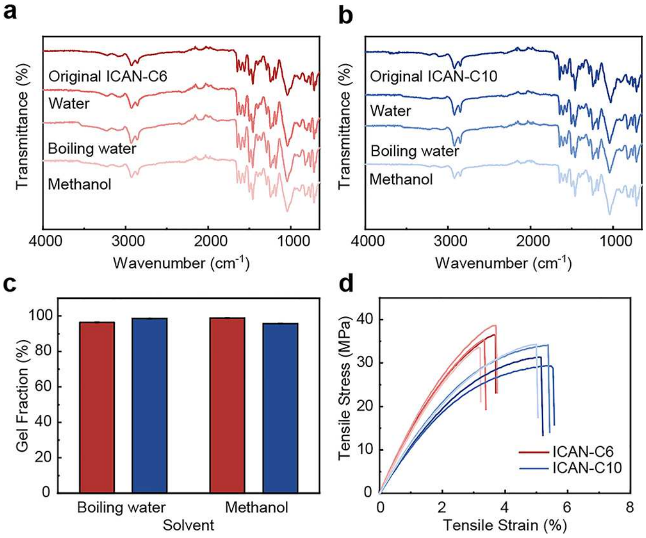

Figure 4. Water and alcohol resistance tests of ICANs. (a) FTIR spectra of the original ICAN-C6, treated with water, boiling water, and methanol. (b) FTIR spectra of the original ICAN-C10, treated with water, boiling water, and methanol. (c) Gel fraction of ICANs in boiling water and methanol. Red: ICAN-C6. Blue: ICAN-C10. (d) Representative strain−stress curves of original and treated ICANs. From the darkest to the lightest colored curves: original sample, soaked in room temperature water for 1 week, soaked in boiling water for 24 h, and soaked in methanol for 48 h.

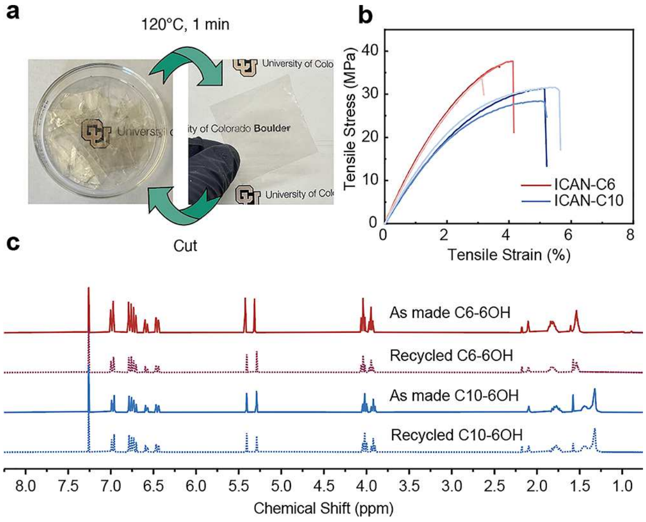

Figure 5. Reprocessability and recyclability of ICANs. (a) Images of cut and reprocessed ICAN-C10. (b) Representative strain−stress curves of original and reprocessed ICANs. From the darkest to the lightest colored curves: original sample, reprocessed once sample, and reprocessed twice sample. (c) ^{1}H NMR spectra of as made and recycled monomers.

Reprocessing and Closed-Loop Recycling of ICANs. Although the ICANs are highly crosslinked with robust mechanical performance, they were found to be highly malleable. To test its reprocessability, an ICAN-C10 sample was manually cut into small pieces and heat pressed at 120 °C under 5 MPa. A uniform transparent membrane without surface defects was successfully obtained within 1 min (Figure 5a). The rapid reprocessability is consistent with the stress relaxation experiment results observed at elevated temperatures (see Supporting Information Section 4). The applied stress was quickly relaxed even when the experimental temperature was slightly below the glass transition temperature. After reprocessing, no degradation or oxidation was observed in FTIR for both ICANs (see Supporting Information Section 6). The rapid spiroborate exchange facilitated the inter-chain rearrangement and interfacial bond exchange between the contacting surfaces. Such a reprocessing mechanism also matches with the second-order kinetic model of small molecule spiroborates. To our delight, even after two cycles of rapid reprocessing, both ICANs did not show any noticeable degradation of the mechanical properties (Figure 5b, see Supporting Information Section 6 for the summarized table). The fast rehealing within a minute with nearly 100% healing efficiency is superior to many recently reported representative CANs[10,12,14,25,36−39] with different types of dynamic linkages (see Supporting Information Section 6 for the summarized comparison table). The reprocessing conditions of ICANs are overall much milder and no catalyst is needed, which could minimize thermal degradation during reprocessing and also avoid small molecule leaching.

Conventional thermosets can hardly be degraded and are not recyclable and reprocessable, thus causing significant environment concerns. In great contrast, linked by cleavable dynamic linkages, most CANs can be easily depolymerized into small molecules and/or oligomers. However, in many cases, it is difficult to isolate original monomers, which can be easily reused for their original purposes. Closed-loop recycling enables the reuse of all valuable components and has been actively pursued in the development of new CANs. To demonstrate the closed-loop recyclability of ICANs, an ICAN-C6 film was soaked in a mixture of aqueous 2 M hydrochloric acid solution and ethyl acetate. At room temperature, the film was completely depolymerized within 2 h under gentle stirring. By simply extracting the aqueous phase with ethyl acetate and removing the solvent, the valuable C6-6OH monomer was recycled with over 95% recovery. The ^{1}H-NMR spectrum of the recovered C6-6OH was nearly identical to that of the as-synthesized monomer, showing clean recovery of the monomer in a high yield and purity (Figure 5c). When ICAN-C10 was treated by the same method, the C10-6OH monomer can also be recycled with an excellent yield (Figure 5c). By titrating the aqueous phase with sodium hydroxide, 4-dimethylaminopyridinium can also be recovered as neutral DMAP and the boron species can be converted as sodium borate salts, which are widely used in the chemical industry. The closed-loop recycling of ICANs can be easily performed under moderate conditions within hours and the separation of valuable monomers is straightforward.

CONCLUSIONS

In conclusion, for the first time, we have introduced spiroborate as an ionic dynamic linkage into CANs to form an ionomer version of CANs (ICANs). The resulting networks are mechanically strong, water/alcohol stable, rapidly reprocessable, and closed-loop recyclable under mild conditions with a simple setup. The ICANs are prepared via a simple polyol and boric acid condensation. The monomers can be easily synthesized, and the length of flexible tethers can be tuned. Since they are highly crosslinked, the ICANs are insoluble in common organic solvents. The ICANs also showed high resistance toward hydrolysis and alcoholysis. Moreover, while exhibiting high Young's modulus and ultimate tensile stress, both ICANs can be rapidly reprocessed within a minute under moderate heat and press. Finally, ICANs can also be closed-loop recycled to reproduce valuable monomers under acidic conditions. We envision that this type of ICANs with charged backbone structures could provide a new platform for the development of ionomer networks with good mechanical properties, reprocessability, and recyclability, which could be highly complementary to the existing industry benchmarks, Nafion and Surlyn ionomers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c00774.

Synthetic methods, kinetics and mechanism studies, NMR, FTIR, TGA, stress relaxation, and tensile testing data (PDF)

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Notes

The authors declare no competing financial interest.

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