Valorization of Plastic Wastes for the Synthesis of Imidazolium-Based Self-Supported Elastomeric Ionenes

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Imidazolium-based ionenes are known to be high-performance materials for a great variety of applications. The preparation of these polymers requires the use of bis-imidazole starting monomers, which are commonly prepared by using toxic chloride reagents. In this study, bis-imidazole monomers are synthesized by organocatalytic chemical recycling of discarded plastics through chemical depolymerization. By using poly(ethylene terephthalate) and bisphenol A polycarbonate as starting materials, different monomers containing amide or urea functionalities are prepared to produce high-molecular-weight ionic polymers. These novel ionenes show excellent elastomeric and self-healing behavior, serving as a promising means to expand the exploration of plastic wastes as a source of new materials.

Conventional plastics are designed to survive ambient attack from external forces such as light, water, and heat. As a result, plastic accumulation and pollution is severely affecting the environment. Landfill, incineration, and physical recycling are currently the three major processes utilized to address the disposal of excess plastic waste. The consequences of these methods have shown their limits in terms of sustainability.[1] Recently, chemical recycling whereby the polymer is used as a carbon source for the creation of high-purity monomers has emerged as a complementary sustainable alternative to physical recycling or incineration.[2] Among commodity plastics, poly(ethylene terephthalate) (PET) and bisphenol A polycarbonate (BPA-PC) are ideal candidates for chemical recycling because i) their scale of production is relatively high (together exceeds 30 Mt/y), ii) owing to the presence of carbonyl moieties in the polymer backbone, their chemical recycling is not as energetically disfavored as in the case of polyolefins, and iii) in comparison to other polymers bearing carbonyl groups in the polymer backbone, such as polyurethanes or polyamides, both plastics are composed of a single polymer, which facilitates sorting and classification.

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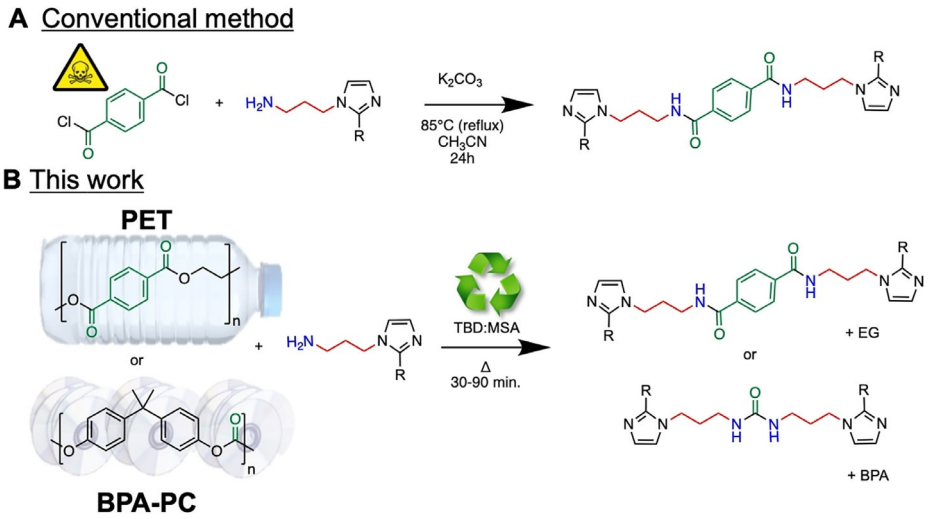
Specifically, the initial monomeric precursor could be obtained from chemical depolymerization then subsequently repolymerized to form a truly circular economy model, or innovative added-value building blocks could be obtained secondarily by synthetic modification to prepare more sophisticated polymers (commonly referred to as "upcycling"). The chemical recycling of PET and BPA-PC into their starting materials—dimethyl terephthalate (or derivatives) and bisphenol A (BPA), respectively—has been previously accomplished by using various catalysts.[3–10] The ultimate goal of these approaches is to design a cradle-to-cradle approach for the production of virgin-like PET or BPA-PC materials. Besides circular economy approaches, more recently PET and BPA-PC have been explored as alternative feedstocks to prepare high-added-value monomers.[11–20] In particular, the aminolysis process, which is more thermodynamically favorable, can provide a spectrum of new monomers that can be of great interest for the production of new polymers.[21–26] For instance, Hedrick and co-workers developed a class of terephthalamide monomers derived from chemical recycling of PET waste in high yields.[27] They demonstrated the upcycling of PET to materials with antifungal and antimicrobial character.[28–30] Earlier work by Bara and O'Harra introduced a new class of imide- and amide-functionalized bis-imidazole monomers, which were subsequently polymerized into high-performance imidazolium ionenes, which inspired this investigation probing similar greener synthetic routes toward ionic polymers for gas separation or 3D printing by upcycling.[31–36] Ionenes are ionic polymers that contain ionic moieties directly within the main chain, rather than as pendant groups (as in polyelectrolytes or ionomers).

Taking advantage of the structural diversity in plastic waste, in this study PET and BPA-PC were used as precursors to produce bis-imidazole monomers for the preparation of high-added-value ionenes. Ionenes built from bis-imidazole monomers by the Menshutkin reaction were efficiently synthesized in our previous work.[31] Ionenes have recently received increasing attention from the scientific community, notably for their diverse processability and compatibility with various functional groups. They can exhibit interesting properties depending upon sequencing and functionality, including gelation behavior (hydrogels and ionogels), self-healing and shape-memory character, and performance as membranes for separation processes.[36,37] Owing to the large variety and synthetic versatility of imidazole derivatives, this building block is suitable for the development of diverse imidazolium-based ionenes as promising, robust materials.

Recently, we reported that the combination of ionenes and polyamides is applicable to formation for free-standing membranes, fibers for additive manufacture, or for the treatment of

microbial infections.[28–36,38] H-bonding provided by the amide functionality and ionic interactions between imidazolium moieties were both factors contributing to the thermal and mechanical stabilities of the membranes.[35,36,38] Nevertheless, the conventional synthesis requires terephthaloyl chloride, which is a hazardous compound both for environment and for health (Scheme 1 A). That said, the aminolysis leading to bis-imidazoles featuring terephthalamide or urea moieties from PET and BPA-PC, respectively, offers excellent promise and product potential for the preparation of imidazolium-mediated ionenes. Several organic catalysts have been successfully employed for the depolymerization of BPA-PC and PET. We selected a catalyst made from an ionic protic salt composed of triazabicyclodecene (TBD) and methanesulfonic acid (MSA; Scheme 1 B), denoted as TBD:MSA, which has excellent thermal stability, recyclability, and the ability to efficiently mediate the glycolysis of poly(ethylene terephthalate) and BPA-PC.[39–41]

We investigated two imidazole–amine compounds used to chemically recycle these two types of plastic waste (Table 1). Based on previous results, 1-(3-aminopropyl)imidazole (API) was primarily used with PET samples and 0.1 equivalents of TBD:MSA at 180 °C and enabled the formation of [(1*H*-imidazol-1-yl)propyl]terephthalamide (TA API). Depolymerization reactions were performed until PET had completely disappeared. After 90 min, an 87% yield of TA API was obtained (Table 1, entry 1). Similarly, 1-(3-aminopropyl)-2-methyl-1*H*-imidazole (2Me-API; see the Supporting Information, Figure S1 for ^{1}H NMR spectrum) selectively depolymerized PET into [(2-



Scheme 1. Formation of bis-imidazole monomers for ionene formation: A) Reported strategy using terephthaloyl chloride.[38] B) Organocatalytic depolymerization of PET and BPA-PC.

Table 1. Organocatalytic depolymerization of PET and BPA-PC using aminopropylimidazole compounds.

Entry	Recycled polymer	Imidazole–amine	Bis-imidazole Product	Depolymerization time [min]	Yield [%][a]
1[b]	PET	API (R = H)	TA API	90	87
2[b]	PET	2Me-API (R = CH_3)	TA 2Me-API	90	80
3[c]	BPA-PC	API (R = H)	U API	40	50
4[c]	BPA-PC	2Me-API (R = CH_3)	U 2Me-API	60	59

[a] Isolated product. [b] Reaction conditions: [Imid-NH_2]/[PET]/[TBD:MSA] = 5:1:0.1, 180 °C, 500 rpm. [c] Reaction conditions: [Imid-NH_2]/[BPA-PC]/[TBD:MSA] = 4:1:0.15, 130 °C, 500 rpm.

methyl-1*H*-imidazol-1-yl)propyl]terephthalamide (denoted as TA 2Me-API) with 80% yield after 90 min (Table 1, entry 2). These TA-containing imidazole compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S2–S5).

BPA-PC was similarly depolymerized with 4 equivalents of API or 2Me-API at 130 °C in the presence of 0.15 equivalents of TBD:MSA catalyst. Both imidazole–amine compounds led to the formation of the desired products and bisphenol A (BPA) as side-product. From aminolysis of BPA-PC by API, 1,3-bis[3-(1*H*-imidazol-1-yl)propyl]urea (U API) was obtained after 40 min with 50% yield after purification. Lower monomer yields were obtained for BPA-PC depolymerization, as column chromatography was required for purification. 2Me-API was then used as an aminolysis agent to convert the carbonate moiety of BPA-PC polymers into 1,3-bis[3-(2-methyl-1*H*-imidazol-1-yl)propyl]-urea (U 2Me-API) after 60 min with a 59% yield of the isolated product. The chemical structures of these novel urea-containing monomers were verified by ^{1}H and ^{13}C NMR spectroscopy (Figures S6–S9) and mechanisms have been proposed for both BPA-PC and PET depolymerization (Scheme S1).

Once isolated, the bis-imidazole monomers were quaternized by using α,α′-dichloro-*p*-xylene (pX) via step-growth polymerization, proceeding by the Menshutkin reaction at 150 °C in *N*-methyl-2-pyrrolidone (NMP) for 24 h (Figure 1 A). Anion exchange from the chloride (Cl^-) salt to the bis(trifluoromethanesulfonyl)imide (NTf_2^-) salt was promoted by pouring the crude reaction mixture into aqueous $LiNTf_2$ (2.5 equiv.) at room temperature. It should be noted that the Cl^- forms of the ionenes are fully water soluble, but the corresponding NTf_2^- forms are hydrophobic and readily precipitate. After drying, the resultant ionenes were all rubbery materials. ^{1}H NMR spectroscopy was used to verify the formation of ionenes. Structural evidence of the quaternization occurring during the polymerization was provided in TA API pX and U API pX derivatives by the characteristic downfield shift (≈1.7 ppm, C–H at the 2-position) of the imidazolium protons, which is indicative of the change from the neutral imidazole to the charged imidazolium form. Additionally, chemical shifts corresponding to the incorporation of the xylyl linkage were observed in all spectra: CH_2 groups close to the ammonium group (signal *i*) were detected at $\delta = 5.45$ ppm and 5.43 ppm, for TA API pX and TA 2Me-API pX, respectively, and aromatic protons (signal *h*) were detected at $\delta = 7.5$ ppm and 7.39 ppm, for TA API pX and TA 2Me-API pX, respectively (Figures S10 and S11). Similarly, the formation of U-based ionenes was verified by ^{1}H NMR spectroscopy, with chemical shifts corresponding to the addition of the xylyl linkage (signals *h* and *i*, Figures S12 and S13). All four ionenes achieved high molecular weights, yielding M_n values of 55–84 kDa (measure by MALDI-TOF mass spectrometry), corresponding to X_n values of 56–87 repeat units (Figure 1 B, left). Although dispersity is less controlled in step-growth mechanisms, the Carothers' equation and end-group analysis by ^{1} H NMR spectroscopy support conversions of greater than 98.2%. Two endotherms were observed from differential scanning calorimetry analysis, including a subtle relaxation below 0 °C followed by a more pronounced glass tran-

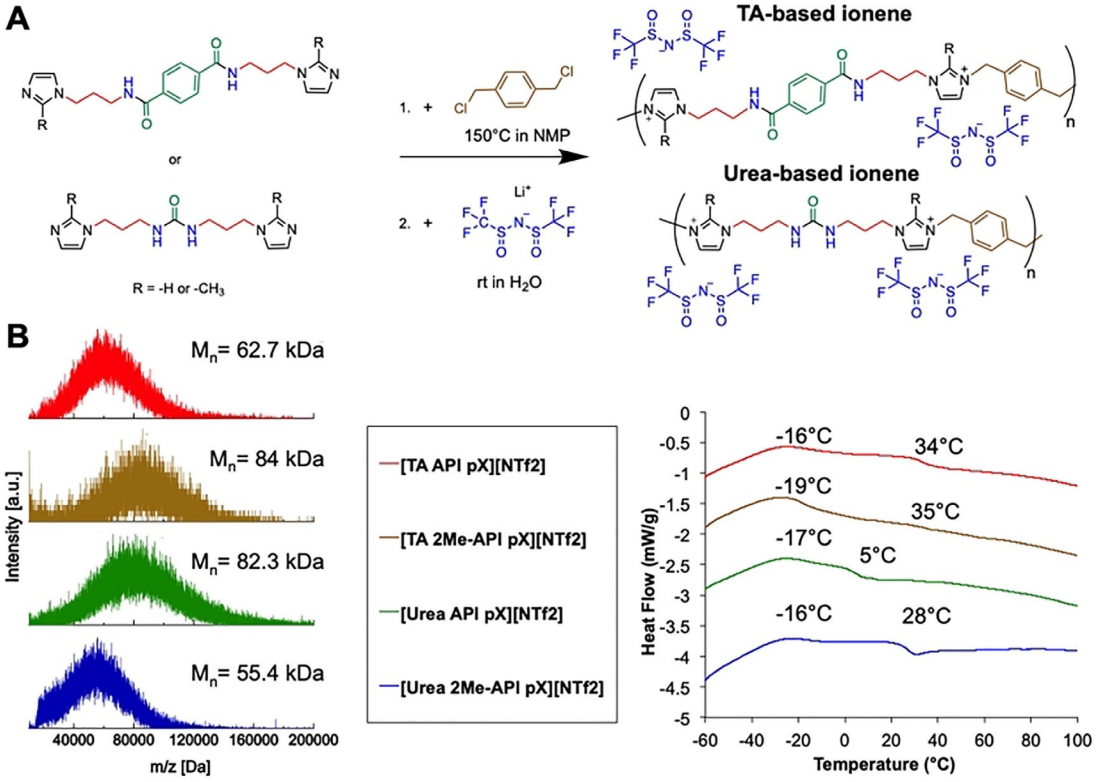


Figure 1. A) Formation of terephthalamide (TA)-based and urea (U)-based ionenes. B) MALDI-TOF mass spectra and differential scanning calorimetry profiles of the corresponding ionenes.

sition indicative of chain mobility (Figure 1 B, right). The intermolecular interactions in these materials are complex, with contributions from H-bonding, ionic, and π–π or π–cation interactions impacting the organization of domains and entanglement of chains. The existence of two distinct glass transition temperatures (T_g) has been shown for various polyamides and polyureas. The typical T_g representative of the motion of molecular segments is evident, but another T_g is sometimes considered a form of relaxation. A broad melting temperature (T_m) endotherm is also observed above 160 °C.

These materials are diversely processable, which lends them to several potential uses including membranes, adhesives, coatings, or elastomeric fibers. They may also be candidates for 3 D printing applications. Although [TA API pX][Cl] has demonstrated utility as an antimicrobial coating and all derivatives introduced herein were fully water soluble in the halide form, previous work has shown that more robust and hydrophobic imidazolium ionenes with improved thermal and mechanical stabilities are obtained when the anion is exchanged from a halide to a fluorinated group (e.g., Tf_2N, OTf).[1] Whereas comparable membranes comprised of the synthetically derived [TA API pX][NTf_2] did not yield high gas-permeation results, this derivative yielded high CO_2 selectivity versus H_2 and CH_4 and demonstrated that the material is suitable for solution casting into very thin films or coatings (Figure 2 A).[36] Thin films were prepared by solvent casting from a dilute solution of ionene (100 mg) in acetone (10 mL) poured into a PTFE mold with shallow wells (d = 60 mm), which was slowly heated in a vacuum oven to remove the solvent (30–70 °C, 48 h).

These films were then peeled from the mold to yield unsupported, neat films. The [U 2Me-API pX][NTf_2] derivative is shown overlaid over text and a ruler to depict its transparency. If the polymers are melt-pressed into films, the membranes are opaque. SEM images show measured film thicknesses of approximately 23 μm for the urea ionene shown in Figure 2 and approximately 13 μm for the [TA 2Me-API pX][NTf_2] ionene film (Figures S14 and S15). These elastomers, as shown by the pulled fiber (Figure 2 B), may also demonstrate utility when aligned as fibers for a 3 D printing feed. A video demonstration of the self-healing and elastomeric behavior is included in the Supporting Information.

In conclusion, we have demonstrated the possibility to convert commodity polymers, such as PET and BPA-PC wastes, into functional monomers for the formation of polyamide and polyurea ionenes. Aminolytic depolymerization by using imidazole–amines and TBD:MSA ionic salt was very efficient (isolated in 50–87 % yield) in short reaction times (45–90 min). The resulting terephthalamide- and urea-based bis-imidazole products were then used as starting materials for step-growth polymerizations, proceeding by the Menshutkin reaction with *p*-xylene. Following anion exchange to the robust, hydrophobic NTf_2^- form, high molecular weights of 55–84 kDa were achieved and the thermal properties of these ionenes were analyzed (Figure 1 and Figure S17). The applicability of these terephthalamide- and urea-based ionenes was demonstrated by processing into solvent-cast films as thin as approximately 13 μm, which were transparent when solvent cast but opaque if melt pressed (Figures S15 and S16). Finally, these polymers demon-

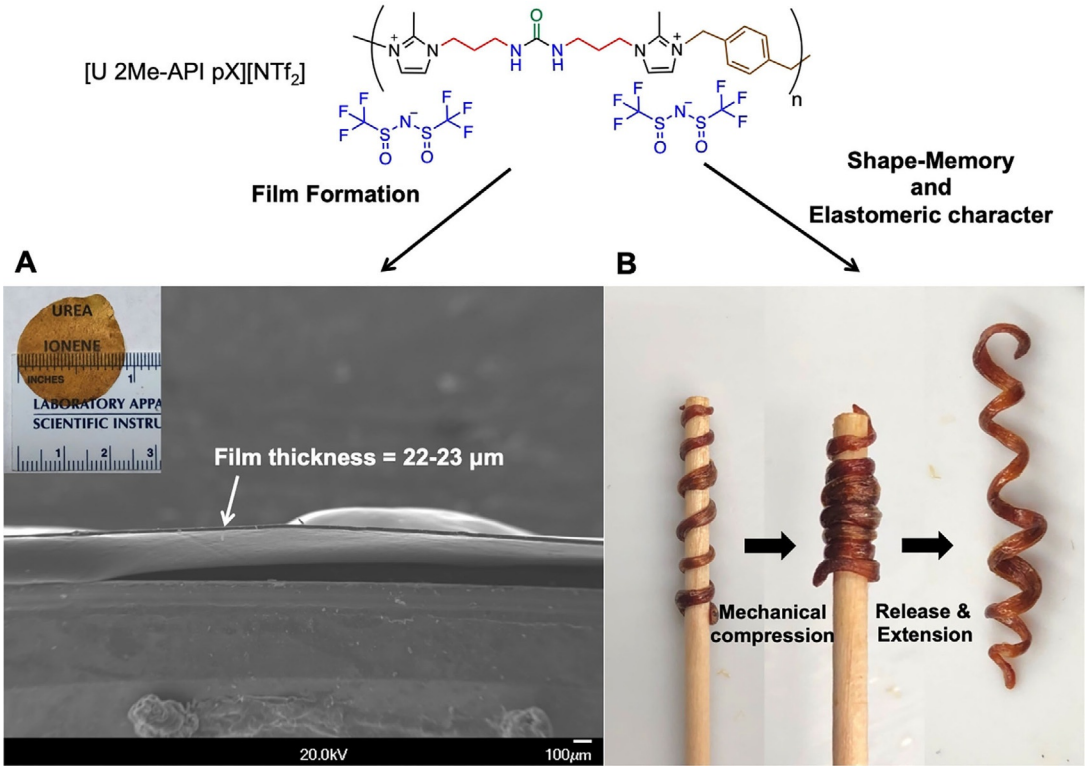


Figure 2. Processing of [U 2Me-API pX][NTf_2] ionene: A) Photograph of thin film overlaid on a ruler, alongside SEM picture of the membrane cross-section (scale bar = 100 μm). B) Images demonstrating the elastomeric character of the polymer wound on a wooden dowel.

strated very promising characteristics as elastomeric self-healing materials, which are flexible yet robust, owing to the combined effects of intermolecular interactions. This work highlights the viability of efficient upcycling of plastic waste into building blocks for high-performance ionic polymers, which can be tailored by the use of other linkages, and introduces methods that can be expanded upon to explore alternative functionalities or charged features.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ionenes · organocatalysis · plastics · recycling · waste valorization

[1] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.
[2] J. B. Williamson, S. E. Lewis, R. R. I. I. I. Johnson, I. M. Manning, F. A. Leibfarth, *Angew. Chem. Int. Ed.* **2019**, *58*, 8654 – 8668; *Angew. Chem.* **2019**, *131*, 8746 – 8761.
[3] F. Iannone, M. Casiello, A. Monopoli, P. Cotugno, M. C. Sportelli, R. A. Picca, N. Cioffi, M. M. Dell'Anna, A. Nacci, *J. Mol. Catal. A* **2017**, *426*, 107 – 116.
[4] L. Li, F. Liu, Z. Li, X. Song, S. Yu, S. Liu, *Fibers Polym.* **2013**, *14*, 365 – 368.
[5] E. Quaranta, *Appl. Catal. B* **2017**, *206*, 233 – 241.
[6] G. P. Tsintzou, D. S. Achilias, *Waste Biomass Valorization* **2013**, *4*, 3 – 7.
[7] C. Alberti, S. Eckelt, S. Enthaler, *ChemistrySelect* **2019**, *4*, 12268 – 12271.
[8] E. Quaranta, D. Sgherza, G. Tartaro, *Green Chem.* **2017**, *19*, 5422 – 5434.
[9] C. Alberti, S. Enthaler, *Waste Biomass Valorization* **2019**, https://doi.org/10.1007/s12649-019-00794-8.
[10] F. Liu, J. Guo, P. Zhao, M. Jia, M. Liu, J. Gao, *Polym. Degrad. Stab.* **2019**, *169*, 108996.
[11] E. Bergin, *Nat. Catal.* **2019**, *2*, 945 – 946.
[12] D. K. Schneiderman, M. A. Hillmyer, *Macromolecules* **2017**, *50*, 3733 – 3749.
[13] M. Hong, E. Y.-X. Chen, *Green Chem.* **2017**, *19*, 3692 – 3706.
[14] T. Do, E. R. Baral, J. G. Kim, *Polymer* **2018**, *143*, 106 – 114.
[15] E. Quaranta, C. C. Minischetti, G. Tartaro, *ACS Omega* **2018**, *3*, 7261 – 7268.
[16] G. Grause, N. Tsukada, W. J. Hall, T. Kameda, P. T. Williams, T. Yoshioka, *Polym. J.* **2010**, *42*, 438 – 442.
[17] C.-H. Lin, H.-Y. Lin, W.-Z. Liao, S. A. Dai, *Green Chem.* **2007**, *9*, 38 – 43.
[18] D. Kim, B. Kim, Y. Cho, M. Han, B.-S. Kim, *Ind. Eng. Chem. Res.* **2009**, *48*, 685 – 691.
[19] S. Hata, H. Goto, E. Yamada, A. Oku, *Polymer* **2002**, *43*, 2109 – 2116.
[20] S. Hata, H. Goto, S. Tanaka, A. Oku, *J. Appl. Polym. Sci.* **2003**, *90*, 2959 – 2968.
[21] R. Shamsi, M. Abdouss, G. M. M. Sadeghi, F. A. Taromi, *Polym. Int.* **2009**, *58*, 22 – 30.
[22] M. M. Aslzadeh, G. M. M. Sadeghi, M. Abdouss, *Materialwiss. Werkstofftech.* **2010**, *41*, 682 – 688.
[23] A. C. Fonseca, M. H. Gil, P. N. Simoes, *Prog. Polym. Sci.* **2014**, *39*, 1291 – 1311.
[24] V. Jamdar, M. Kathalewar, A. Sabnis, *J. Polym. Environ.* **2018**, *26*, 2601 – 2618.
[25] J. Natarajan, G. Madras, K. Chatterjee, *ACS Appl. Mater. Interfaces* **2017**, *9*, 28281 – 28297.
[26] S. M. Elsaeed, R. K. Farag, *J. Appl. Polym. Sci.* **2009**, *112*, 3327 – 3336.
[27] K. Fukushima, J. M. Lecuyer, D. S. Wei, H. W. Horn, G. O. Jones, H. A. Al-Megren, A. M. Alabdulrahman, F. D. Alsewailem, M. A. McNeil, J. E. Rice, J. L. Hedrick, *Polym. Chem.* **2013**, *4*, 1610 – 1616.
[28] J. Hedrick, M. Fevre, N. Park, V. Piunova, Y. Y. Yang, P. K. J. Tan, C. Yang (International Business Machines Corporation, Armonk, NY), WO2019116160A1, **2019**.
[29] K. Fukushima, S. Liu, H. Wu, A. C. Engler, D. J. Coady, H. Maune, J. Pitera, A. Nelson, N. Wiradharma, S. Venkataraman, Y. Huang, W. M. Fan, J. Y. Ying, Y. Y. Yang, J. L. Hedrick, *Nat. Commun.* **2013**, *4*, 3861.
[30] J. P. K. Tan, J. Tan, N. Park, K. Xu, E. D. Chan, C. Yang, V. A. Piunova, Z. Ji, A. Lim, J. Shao, A. Bai, X. Y. Bai, D. Mantione, H. Sardon, Y. Y. Yang, J. L. Hedrick, *Macromolecules* **2019**, *52*, 7878 – 7885.
[31] K. E. O'Harra, I. Kammakakam, J. E. Bara, E. M. Jackson, *Polym. Int.* **2019**, *68*, 1547 – 1556.
[32] K. E. O'Harra, I. Kammakakam, E. M. Devriese, D. M. Noll, J. E. Bara, E. M. Jackson, *Membranes* **2019**, *9*, 79.
[33] I. Kammakakam, K. E. OHarra, J. E. Bara, E. M. Jackson, *ACS Omega* **2019**, *4*, 3439 – 3448.
[34] M. S. Mittenthal, B. S. Flowers, J. E. Bara, J. W. Whitley, S. K. Spear, J. D. Roveda, D. A. Wallace, M. S. Shannon, R. Holler, R. Martens, D. T. Daly, *Ind. Eng. Chem. Res.* **2017**, *56*, 5055 – 5069.
[35] E. K. O'Harra, I. Kammakakam, M. D. Noll, M. E. Turflinger, P. G. Dennis, M. E. Jackson, E. J. Bara, *Membranes* **2020**, *10*, 51.
[36] I. Kammakakam, K. E. O'Harra, G. P. Dennis, E. M. Jackson, J. E. Bara, *Polym. Int.* **2019**, *68*, 1123 – 1129.
[37] J. E. Bara, K. E. O'Harra, *Macromol. Chem. Phys.* **2019**, *220*, 1900078.
[38] J. E. Bara, K. E. O'Harra, M. M. Durbin, G. P. Dennis, E. M. Jackson, B. Thomas, J. A. Odutola, *MRS Adv.* **2018**, *3*, 3091 – 3102.
[39] C. Jehanno, I. Flores, A. P. Dove, A. Muller, F. Ruiperez, H. Sardon, *Green Chem.* **2018**, *20*, 1205 – 1212.
[40] A. Basterretxea, C. Jehanno, D. Mecerreyes, H. Sardon, *ACS Macro Lett.* **2019**, *8*, 1055 – 1062.
[41] C. Jehanno, J. Demarteau, D. Mantione, M. C. Arno, F. Ruiperez, J. L. Hedrick, A. P. Dove, H. Sardon, *ACS Macro Lett.* **2020**, *9*, 443 – 447.

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