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Multicomponent Radziszewski Emulsion Polymerization toward Macroporous Poly(ionic liquid) Catalysts

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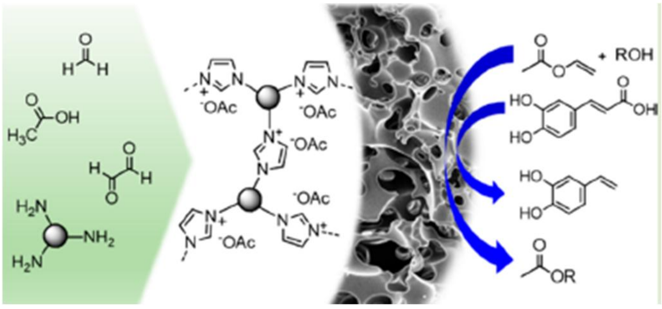
ABSTRACT

Interconnected macroporous imidazolium-based monoliths are produced via the modified Radziszewski multicomponent reaction (MCR) applied to triamines under high internal phase emulsion (HIPE) conditions. This straightforward one-pot synthesis combines the efficiency and versatility of MCRs with the ease of implementation of the emulsion templating polymerization process. The characterization of the chemical structure and morphology of the resulting materials confirms the formation of the expected macroporous poly(ionic liquid)s (PILs) networks. The promising catalytic activity and recyclability of these porous PIL monoliths are illustrated for the transesterification reaction and the decarboxylation of caffeic acid. In these cases, almost complete conversion is reached while benefiting from the advantages associated with a heterogeneous catalyst.



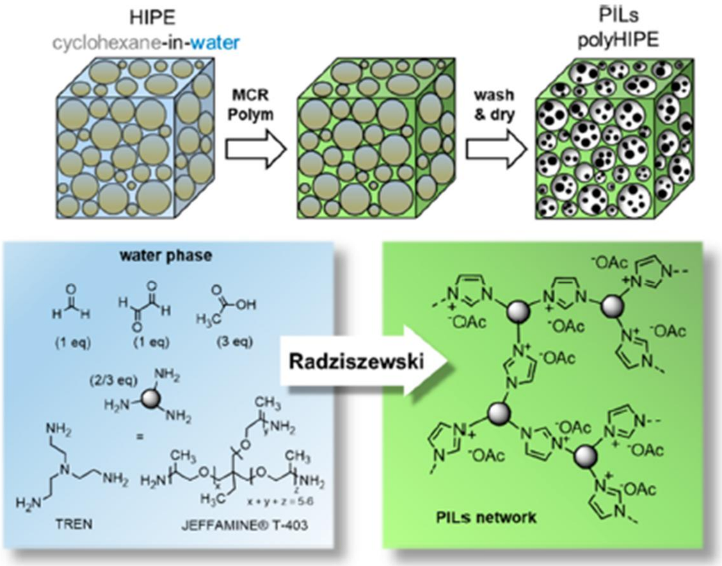
In the last years, multicomponent reactions (MCRs) have attracted a growing interest in the field of polymer chemistry and emerged as powerful macromolecular engineering methods due to their high efficiency, robustness, ease of implementation, and atom economy, as well as substrate versatility.[1-4] In these reactions, more than two compounds react in one pot and form a product featuring almost all atoms of the starting materials.[5] Some famous MCRs have already been exploited for designing functional polymers such as the Passerini,[6-11] Ugi,[12-24] Biginelli,[25-29] Kabachnick-fields,[30-32] and Hantzsch[29,33] reactions, to name a few. The modified Debus-Radziszewski MCR, which converts primary amines, aldehyde, and dicarbonyl compound into imidazolium derivatives under mild conditions, also proved its relevance in polymer synthesis, especially for the preparation of imidazolium-based poly(ionic liquid)s (PILs).[34] This reaction was used for the synthesis of ionic liquid building blocks,[35] as postpolymerization modification and cross-linking,[36-40] but also for the preparation of linear PILs containing imidazolium moieties in their backbone.[41-43]

The development of PILs is also a fast-growing research area because these materials combine some valuable features of ILs with the intrinsic characteristics of polymers. In particular, porous PILs[44,45] raise tremendous interest in gas cap- ture,[37,46-48] separation,[48-54] and catalysis[55-59] due to their enlarged surface area, high ionic density, spatial structuration, and the tunability of their properties via counterions exchange. Structuring PILs into porous materials was achieved by hard templating based on inorganic particles[47,53,54,60] and by soft templating involving self-assembled copolymers,[57] but also via template-free methods relying on porogenic solvents[59,61] or ionic complexations.[51,52,62,63] Some emulsion-templated radical polymerization methods also led to macroporous PILs.[64-66] Note that the porous PILs mentioned above were obtained via multistep approaches based on the polymerization of preformed IL monomers and cross-linkers or by post-modification of porous organic networks. Therefore, the search for a simpler and straightforward synthesis of interconnected porous PILs is highly relevant.

In the present work, we applied the modified Radziszewski multicomponent polymerization under high internal phase emulsion (HIPE) for the first time and produced interconnected macroporous imidazolium-based networks in one pot. To the best of our knowledge, it is the first example of emulsion multicomponent polymerization. This practical and straightforward approach combines the great availability of the starting reagents, the efficiency of one-pot MCRs, and the ease of implementation of emulsion templating polymerization.[67] The great potential of these interconnected macroporous PILs polyHIPEs as heterogeneous catalysts is highlighted for a model transesterification reaction and for the decarboxylation of renewable hydroxycinnamic acid derivatives.

The imidazolium units of our PIL networks were formed via Radziszewski reaction, which consists of coupling two amino groups with glyoxal and formaldehyde in the presence of acetic acid. Two commercially available triamines, namely, tris(2-aminoethyl)amine (TREN) and Jeffamine-T403 (JEFF), composed of short polypropylene oxide (PPO) sequences, were considered as reactants to ensure the cross-linking of the final materials (Scheme 1). In order to create an interconnected porosity within these PILs, the polymerization was carried out in the external aqueous phase of a cyclohexanein-water HIPE emulsion whose organic dispersed phase represents more than 74% of the emulsion volume. After the curing step, cyclohexane was removed, leading to a typical polyHIPE structure composed of cavities connected to each other by pores. In practice, cyclohexane (75 v%) was added dropwise under stirring to an aqueous solution (25 v%) containing formaldehyde (1 equiv), glyoxal (1 equiv), triamine (TREN or JEFF, 2/3 equiv), acetic acid (3 equiv), and PEO- PPO-PEO pluronics F68 (4 wt % of the aq phase) used as a surfactant.

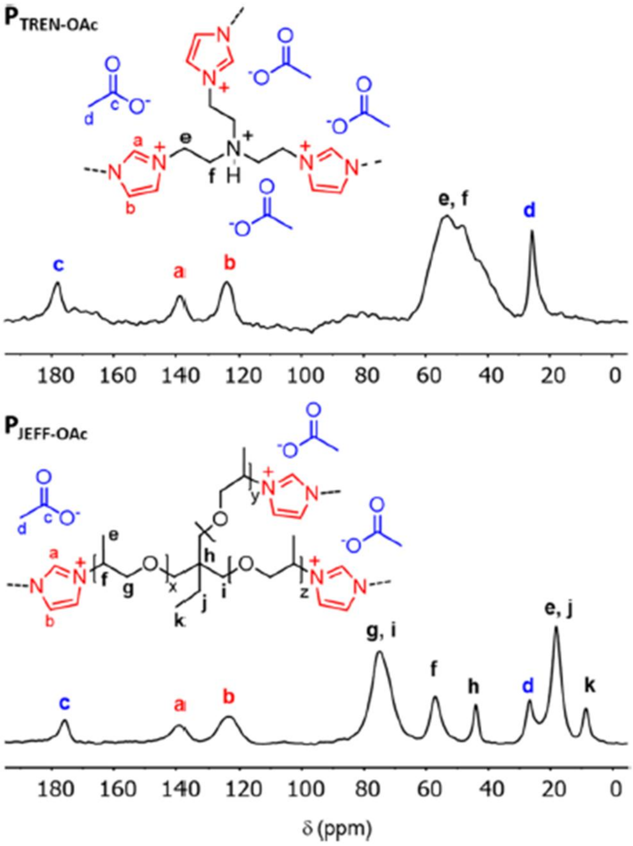
Scheme 1. General Strategy for the Synthesis of Interconnected Macroporous PILs via Emulsion Templating Radziszewski Polymerization



The resulting mixtures were simply casted in a mold and cured at room temperature for 3 days. No demixing of the emulsions was observed during the polymerization, and monoliths were collected accordingly. The latter are designated as P_{TREN} and P_{JEFF} throughout the text in reference to the triamines that compose them. After washing and drying under vacuum, P_{TREN} and P_{JEFF} were characterized by ^{13}C solid state NMR to ascertain their chemical structure (Figure 1). The formation of the imidazolium moieties is evidenced by peaks (a and b) at 125 and 140 ppm corresponding to the carbons of the heterocycles. The acetate counterions also feature peaks at 177 and 26 ppm assigned to the carbonyl c and the methyl group d, respectively. Expectedly, the ^{13}C spectra of $P_{TREN-OAc}$ and $P_{JEFF-OAc}$ only differ by signals corresponding to the spacers between the IL units (e-k). IR analyses further confirmed the formation of the PIL materials based on peaks at 1573 and 1381 cm^{-1} attributed to the C⊠O stretching of the acetate group and signals at 1150 and 1060 cm^{-1} assigned to the stretching vibrations of the imidazolium ring (Figures S1 and S2).[68]

After confirming the chemical structures of the PIL materials, we addressed their macroscopic behaviors and porous architectures. The morphology of $P_{TREN-OAc}$ and $P_{JEFF-OAc}$ was tentatively investigated by conventional scanning electron microscopy (SEM). However, significant shrinkage of the samples occurred upon drying, especially for $P_{JEFF-OAc}$. The volumes of $P_{TREN-OAc}$ and $P_{JEFF-OAc}$ are reduced by a factor 2 and 10, respectively, compared to the crude materials, as displayed in Figures S3A-F. In spite of this phenomenon, SEM images of $P_{TREN-OAc}$ show the typical open-porous structure of polyHIPEs (Figure S3G).

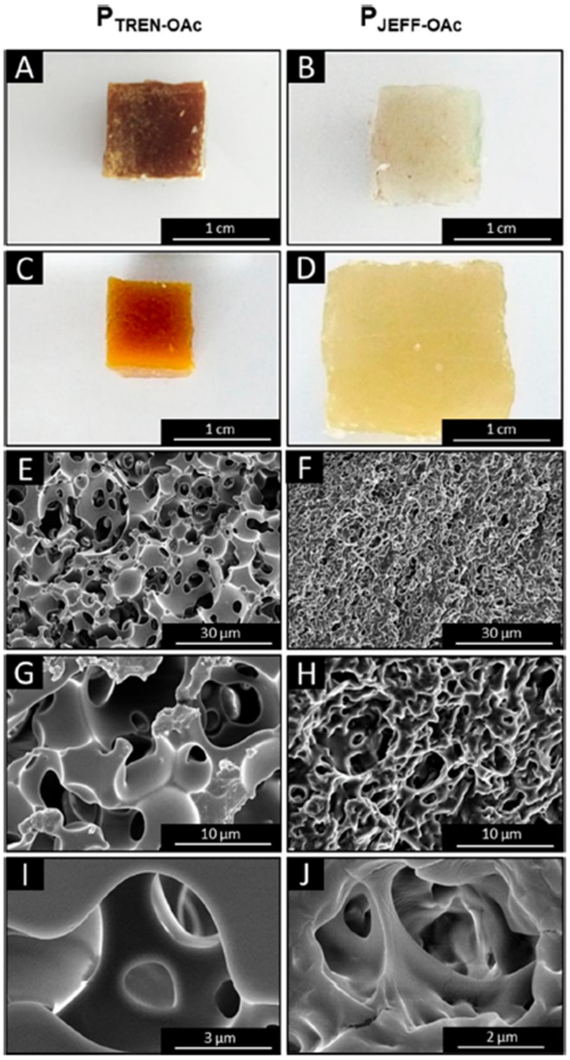
Figure 1. ^{13}C solid state NMR spectra of $P_{TREN-OAc}$ and $P_{JEFF-OAc}$.



Although some remnants of the cavities of $P_{JEFF-OAc}$ seem to appear on the SEM pictures, no conclusion can be drawn on their porosity, which collapsed upon drying (Figure S3H). Such a discrepancy between these materials might be due to the lower intrinsic cross-linking density of $P_{JEFF-OAc}$ produced from a triamine with longer arms. In order to overcome the shrinkage issue, the polyHIPEs were dried using a procedure based on the critical point drying and analyzed by FESEM (Figure 2). First, the crude $P_{TREN-OAc}$ and $P_{JEFF-OAc}$ (Figure 2A,B) were washed by prolonged immersion in DMSO (Figure 2C,D). The comparison of Figure 2C and D clearly suggests a higher solvent uptake (SU) in DMSO for P_{JEFF} compared to P_{TREN} (SU $P_{TREN-OAc}$ = 2000 wt %

and $P_{JEFF\text{-}OAc}$ = 4200 wt %). The higher swelling of the latter can be ascribed to the affinity of its PPO sequences for DMSO and to its lower cross-linking density previously mentioned. Then, DMSO contained in the polyHIPEs was exchanged for water prior to drying via the critical point method. As expected, the FESEM images clearly highlight the open structure of both polyHIPEs (Figure 2E-J). In the case of $P_{TREN\text{-}OAc}$, the cavities vary in size from 5 to 30 µm with an average diameter of 9 µm, whereas the pore sizes are around 2-5 µm (Figure 2E-H). Because FESEM pictures do not display defined spherical voids for $P_{JEFF\text{-}OAc}$, it is difficult to evaluate properly the average size of its cavities. Nevertheless, the presence of an interconnected porosity is undeniable, especially at the highest magnification (Figure 2J), and the pores of $P_{JEFF\text{-}OAc}$ and $P_{TREN\text{-}OAc}$ seem to be in the same range, that is, 2-5 µm (compare Figure 2I and J).

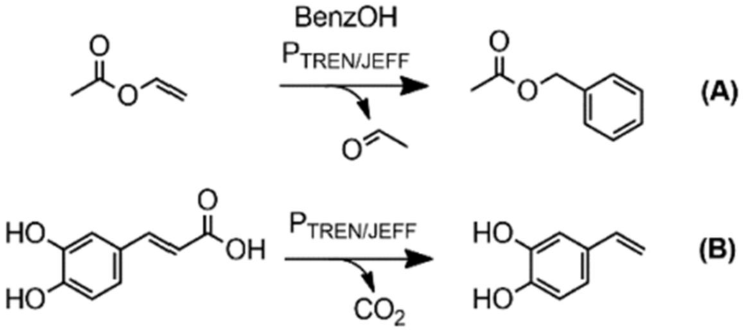
Figure 2. Pictures of $P_{TREN\text{-}OAc}$ (A, C) and $P_{JEFF\text{-}OAc}$ (B, D) before (A, B) and after (C, D) immersion in DMSO. FESEM pictures of $P_{TREN\text{-}OAc}$ (E, G, I) and $P_{JEFF\text{-}OAc}$ (F, H, J).



Before considering any application of these macroporous PILs, we studied their thermal properties and swelling in order to identify their potential operating conditions and also their ability to undergo counterion exchange reactions, because the properties of PILs highly depend on this parameter.69 Such ion exchange reactions were thus applied to the imidazolium-based polyHIPEs composed of acetate anions originating from the acetic acid used in the Radziszewski reaction. As illustrated above, such a polar anion favors the swelling of the porous PILs in polar solvents like water, DMSO, and MeOH. The acetate anions of PTREN-OAc and PJEFF-OAc were then exchanged for bromide (Br−) and bis(trifluoromethanesulfonyl)imide (TFSI) in MeOH using an excess of NaBr and LiTFSI salts. Note that the macroporosity of the polyHIPEs facilitates the diffusion of the anions in the heart of the monoliths. IR (Figures S1 and S2) and solid-state NMR (Figures S4 and S5) analyses confirmed the successful ion-exchange via the disappearance of signals characteristic of the carbonyl of the acetate. As anticipated, changing the counterion of the polyHIPEs significantly affected their swelling. Indeed, when immersed in the NaBr or LiTFSI solutions, PTREN and PJEFF gradually shrank until there was a complete exchange (Figure S6). Like linear PILs,69 the thermal properties of the PIL polyHIPEs, in particular, P_{JEFF}, are also influenced by the nature of anions (Table S1). For example, P_{JEFF}, with different anions is ranked in the following order of increasing glass transition temperature (T_g): $P_{JEFF-TFSI}$ (-5 °C) < $P_{JEFF-OAc}$ (27 °C) < $P_{JEFF-Br}$ (61 °C). The onset degradation temperatures (TOD) followed a different order, that is, $P_{JEFF-OAc}$ (172 °C) < $P_{JEFF-Br}$ (300 °C) < $P_{JEFF-TFSI}$ (347 °C). The same trend was observed for the TOD of the P_{TREN} derivatives, which exhibit lower thermal stabilities compared to their P_{JEFF} counterparts (151 °C < TOD < 274 °C, Table S1). Overall, these ion property dependences emphasize that the imidazolium-based polyHIPEs possess the intrinsic characteristics of PILs materials.

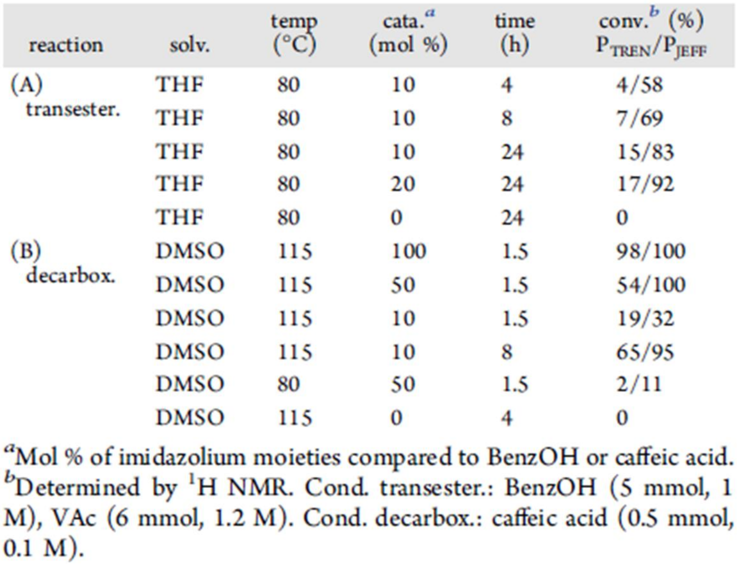
Finally, we explored the potential of P_{TREN} and P_{JEFF} macroporous PILs in catalysis, especially for transesterification and decarboxylation reactions known to be catalyzed in the presence of imidazolium acetate derivatives.[70,71] For example, Taton et al. catalyzed transesterifications with styrene/vinyl imidazolium acetate-based copolymers.[70] In the case of the transesterification between vinyl acetate and benzyl alcohol, the conversion reached 97% after 2 h at 80 °C in THF. Recently, Singh et al. described the use of 1-ethyl-3-methyl imidazolium acetate for catalyzing the decarboxylation of hydroxycinnamic acid derivatives, which are naturally abundant in plants, leading to vinyl catechol.[71] In this case, the self-deprotonation of the imidazolium moieties produced in situ N- heterocyclic carbenes (NHCs), which catalyzed the decarboxylation of the hydroxycinnamic acid compounds.[71] The organocatalyst was recycled via extraction using a biphasic reaction system. Considering the excellent flow through properties and the substantial surface area associated with macroporous materials, the imidazolium-based polyHIPEs developed in this work appear as very promising supports for catalysis notably in terms of accessibility to the catalytic site and recyclability. For this reason, we tested $P_{TREN-OAc}$ and $P_{JEFF-OAc}$ as catalysts for the decarboxylation of cinnamic acid derivatives and transesterification of vinyl esters (Scheme 2 and Table 1).

Scheme 2. Porous PILs-Catalyzed Transesterification and Decarboxylation



The catalytic efficiencies of $P_{\text{TREN-OAC}}$ and $P_{\text{JEFF-OAc}}$ were first assessed for the transformation of vinyl acetate (VAc) into benzyl acetate (BenzOAc) in the presence of benzyl alcohol (Table 1, part A). This model transesterification reaction was performed in THF at 80 °C using 10 mol % of imidazolium moieties, as described elsewhere,[70] and the conversion was monitored by ^{1}H NMR (Figure S7). After 4 h, the conversion reached 58% for P_{JEFF} and only 4% for P_{TREN}. Such a discrepancy most probably accounts for the lower swelling of P_{TREN} in THF compared to P_{JEFF}, which limits the access of the substrates to the catalytic moieties located in the polyHIPE walls. Longer reaction time, for example, 24 h, improved the conversion (15 and 83% for P_{TREN} and P_{JEFF}, respectively). Finally, a conversion as high as 92% was achieved when doubling the catalyst load for P_{JEFF}.

Table 1. Transesterification and Decarboxylation Reactions Catalyzed by $P_{\text{JEFF-OAc}}$ and $P_{\text{TREN-OAc}}$



reaction	solv.	temp (°C)	cata.[a] (mol %)	time (h)	conv.[b] (%) $P_{\text{TREN}}/P_{\text{JEFF}}$
(A) transester.	THF	80	10	4	4/58
	THF	80	10	8	7/69
	THF	80	10	24	15/83
	THF	80	20	24	17/92
	THF	80	0	24	0
(B) decarbox.	DMSO	115	100	1.5	98/100
	DMSO	115	50	1.5	54/100
	DMSO	115	10	1.5	19/32
	DMSO	115	10	8	65/95
	DMSO	80	50	1.5	2/11
	DMSO	115	0	4	0

[a] Mol % of imidazolium moieties compared to BenzOH or caffeic acid. [b] Determined by ^{1}H NMR. Cond. transester.: BenzOH (5 mmol, 1 M), VAc (6 mmol, 1.2 M). Cond. decarbox.: caffeic acid (0.5 mmol, 0.1 M).

Inspired by Singh et al. who reported the complete decarboxylation of caffeic acid into 4-vinyl catechol after 1 h at 120 °C in the presence of 100 mol % of 1-ethyl-3-methyl imidazolium acetate,[71] we tested $P_{\text{TREN-OAc}}$

and $P_{JEFF-OAc}$ as catalysts of this reaction under similar conditions (115 °C, 100 mol % of imidazolium functions; Table 1, part B). Note that the temperature was lowered to 115 °C in order to prevent any degradation of $P_{TREN-OAc}$, which exhibits the lowest TOD, as mentioned earlier. Under these conditions, near quantitative formation of vinyl catechol (determined by ^{1}H NMR, Figure S8) was achieved after 90 min with both polyHIPEs, which is quite similar to the performances reported for the free imidazolium acetate catalysts.[71] Hence, lower catalyst loadings were considered. These experiments underlined the higher catalytic efficiency of $P_{JEFF-OAc}$. The conversion reached 100% and 54% in the presence of 50 mol % of P_{JEFF} and P_{TREN}, respectively. High conversion (95%) can also be achieved after 8 h with 10 mol % of P_{JEFF}, which represents a 10-fold decrease of the catalyst loading compared to the initial report involving free ILs.[71] Decreasing the temperature to 80 °C almost inhibits the decarboxylation reaction (Table 1). Overall, P_{JEFF} appears as the most promising catalyst for both types of reactions.

Finally, the excellent recyclability of the macroporous PIL catalysts was demonstrated for the decarboxylation reaction. P_{JEFF} and P_{TREN} were used five times without drastic deactivation or formation of side products (Figure S9). Note that the recycling procedure is very easy to implement. For the sake of the accuracy of the study, polyHIPEs were immersed in DMSO between each recycling, but in practice, this step is not mandatory: new portions of reactants can be added to the porous PILs after simple removal of the reaction supernatant.

In conclusion, we implemented a multicomponent polymerization under emulsion conditions for the first time and developed a unique and straightforward platform for the synthesis of macroporous imidazolium-based networks. This one-pot approach combining the Radziszewski MCR and the emulsion templating polymerization process satisfies several criteria for widespread use in practical applications, including great availability of the reactants, high atom economy, metalfree, room temperature, and nonsensitivity to moisture or air. The resulting porous PIL monoliths were shown to be very efficient catalysts for transesterification and decarboxylation reactions. They were also easily recycled, and no loss of activity was detected after several recycling steps. Given the excellent flow-through properties associated with macroporous poly- HIPEs, their use as supported catalysts in continuous flow chemistry is promising and is under current investigation. In this study, the imidazolium acetate-based polyHIPEs were selected to illustrate the potential of such materials, but we also demonstrated the possibility of exchanging their counterions and tuning their properties. This feature allows to consider numerous other catalytic reactions and to considerably broaden the scope of their use, especially for separation and gas capture applications.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.9b00942.

Detailed experimental procedures, TGA and DSC data, infrared, NMR spectra of the networks, and NMR spectra of the catalyzed reactions, as well as recyclability tests (PDF available at http://pubs.acs.org/doi/suppl/10.1021/acsmacrolett.9b00942/suppl_file/mz9b00942_si_001.pdf)

The authors declare no competing financial interest.

Author Contributions

All authors have given approval to the final version of the manuscript.

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Bibliography

(1) *Kakuchi, R. Multicomponent Reactions in Polymer Synthesis. Angew. Chem., Int. Ed. 2014, 53 (1), 46-48.*

(2) *Yang, B.; Zhao, Y.; Wei, Y.; Fu, C.; Tao, L. The Ugi Reaction in Polymer Chemistry: Syntheses, Applications and Perspectives. Polym. Chem. 2015, 6 (48), 8233-8239.*

(3) *Rudick, J. G. Innovative Macromolecular Syntheses via Isocyanide Multicomponent Reactions. J. Polym. Sci., Part A: Polym. Chem. 2013, 51 (19), 3985-3991.*

(4) *Theato, P. Multi-Component and Sequential Reactions in Polymer Synthesis; Springer International Publishing: Hamburg, 2015.*

(5) *Dömling, A.; Wang, W.; Wang, K. Chemistry and Biology Of Multicomponent Reactions. Chem. Rev. 2012, 112 (6), 3083-3135.*

(6) *Zhang, J.; Wu, Y.-H.; Wang, J.-C.; Du, F.-S.; Li, Z.-C. Functional Poly(Ester-Amide)s with Tertiary Ester Linkages via the Passerini Multicomponent Polymerization of a Dicarboxylic Acid and a Diisocyanide with Different Electron-Deficient Ketones. Macromolecules 2018, 51 (15), 5842-5851.*

(7) *Cui, Y.; Zhang, M.; Du, F.-S.; Li, Z.-C. Facile Synthesis of H2O2-Cleavable Poly(Ester-Amide)s by Passerini Multicomponent Polymerization. ACS Macro Lett. 2017, 6 (1), 11-15.*

(8) *Zhang, J.; Zhang, M.; Du, F.-S.; Li, Z.-C. Synthesis of Functional Polycaprolactones via Passerini Multicomponent Polymerization of 6- Oxohexanoic Acid and Isocyanides. Macromolecules 2016, 49 (7), 2592-2600.*

(9) *Sehlinger, A.; Schneider, R.; Meier, M. A. R. Passerini Addition Polymerization of an AB-Type Monomer - A Convenient Route to Versatile Polyesters. Eur. Polym. J. 2014, 50, 150-157.*

(10) *Wang, Y.-Z.; Deng, X.-X.; Li, L.; Li, Z.-L.; Du, F.-S.; Li, Z.-C. One-Pot Synthesis of Polyamides with Various Functional Side Groups via Passerini Reaction. Polym. Chem. 2013, 4 (3), 444-448.*

(11) Deng, X.-X.; Li, L.; Li, Z.-L.; Lv, A.; Du, F.-S.; Li, Z.-C. Sequence Regulated Poly(Ester-Amide)s Based on Passerini Reaction. ACS Macro Lett. 2012, 1 (11), 1300-1303.

(12) Stiernet, P.; Lecomte, P.; De Winter, J.; Debuigne, A. Ugi Three-Component Polymerization Toward Poly(α-Amino Amide)S. ACS Macro Lett. 2019, 8 (4), 427-434.

(13) Tao, Y.; Wang, Z.; Tao, Y. Polypeptoids Synthesis Based on Ugi Reaction: Advances and Perspectives. Biopolymers 2019, 110 (6), 1-11.

(14) Schade, O. R.; Dannecker, P.-K.; Kalz, K. F.; Steinbach, D.; Meier, M. A. R.; Grunwaldt, J.-D. Direct Catalytic Route to Biomass- Derived 2,5-Furandicarboxylic Acid and Its Use as Monomer in a Multicomponent Polymerization. ACS Omega 2019, 4 (16), 1697216979.

(15) Hartweg, M.; Edwards-Gayle, C. J. C.; Radvar, E.; Collis, D.; Reza, M.; Kaupp, M.; Steinkoenig, J.; Ruokolainen, J.; Rambo, R.; Barner-Kowollik, C.; Hamley, I. W.; Azevedo, H. S.; Becer, C. R. Ugi Multicomponent Reaction to Prepare Peptide-Peptoid Hybrid Structures with Diverse Chemical Functionalities. Polym. Chem. 2018, 9 (4), 482-489.

(16) Koyama, Y.; Ihsan, A. B.; Taira, T.; Imura, T. Fluorinated Polymer Surfactants Bearing an Alternating Peptide Skeleton Prepared by Three-Component Polycondensation. RSC Adv. 2018, 8 (14), 7509-7513.

(17) Tao, Y.; Wang, S.; Zhang, X.; Wang, Z.; Tao, Y.; Wang, X. Synthesis and Properties of Alternating Polypeptoids and Polyampholytes as Protein-Resistant Polymers. Biomacromolecules 2018, 19 (3), 936-942.

(18) Al Samad, A.; De Winter, J.; Gerbaux, P.; Jeŕ ôme, C.; Debuigne, A. Unique Alternating Peptide-Peptoid Copolymers from Dipeptides via a Ugi Reaction in Water. Chem. Commun. 2017, 53 (90), 1224012243.

(19) Koyama, Y.; Gudeangadi, P. G. One-Pot Synthesis of Alternating Peptides Exploiting a New Polymerization Technique Based on Ugi's 4CC Reaction. Chem. Commun. 2017, 53 (27), 38463849.

(20) Hartweg, M.; Becer, C. R. Direct Polymerization of Levulinic Acid via Ugi Multicomponent Reaction. Green Chem. 2016, 18 (11), 3272-3277.

(21) Zhang, X.; Wang, S.; Liu, J.; Xie, Z.; Luan, S.; Xiao, C.; Tao, Y.; Wang, X. Ugi Reaction of Natural Amino Acids: A General Route toward Facile Synthesis of Polypeptoids for Bioapplications. ACS Macro Lett. 2016, 5 (9), 1049-1054.

(22) Gangloff, N.; Nahm, D.; Döring, L.; Kuckling, D.; Luxenhofer, R. Polymerization via the Ugi-Reaction Using Aromatic Monomers. J. Polym. Sci., Part A: Polym. Chem. 2015, 53 (14), 1680-1686.

(23) Sehlinger, A.; Dannecker, P.-K.; Kreye, O.; Meier, M. A. R. Diversely Substituted Polyamides: Macromolecular Design Using the Ugi Four-Component Reaction. Macromolecules 2014, 47 (9), 27742783.

(24) Sehlinger, A.; Schneider, R.; Meier, M. A. R. Ugi Reactions with CO2: Access to Functionalized Polyurethanes, Polycarbonates, Polyamides, and Polyhydantoins. Macromol. Rapid Commun. 2014, 35 (21), 1866-1871.

(25) Boukis, A. C.; Llevot, A.; Meier, M. A. R. High Glass Transition Temperature Renewable Polymers via Biginelli Multicomponent Polymerization. Macromol. Rapid Commun. 2016, 37 (7), 643-649.

(26) Zhao, Y.; Wu, H.; Wang, Z.; Wei, Y.; Wang, Z.; Tao, L. Training the Old Dog New Tricks: The Applications of the Biginelli Reaction in Polymer Chemistry. Sci. China: Chem. 2016, 59 (12), 1541-1547.

(27) Zhao, Y.; Yu, Y.; Zhang, Y.; Wang, X.; Yang, B.; Zhang, Y.; Zhang, Q.; Fu, C.; Wei, Y.; Tao, L. From Drug to Adhesive: A New Application of Poly(Dihydropyrimidin-2(1H)-One)s via the Biginelli Polycondensation. Polym. Chem. 2015, 6 (27), 4940-4945.

(28) *Zhao, Y.; Wu, H.; Zhang, Y.; Wang, X.; Yang, B.; Zhang, Q.; Ren, X.; Fu, C.; Wei, Y.; Wang, Z.; Wang, Y.; Tao, L. Postpolymerization Modification of Poly(Dihydropyrimidin-2(1H)- Thione)s via the Thiourea-Haloalkane Reaction to Prepare Functional Polymers. ACS Macro Lett. 2015, 4 (8), 843-847.*

(29) *Wu, H.; Fu, C.; Zhao, Y.; Yang, B.; Wei, Y.; Wang, Z.; Tao, L. Multicomponent Copolycondensates via the Simultaneous Hantzsch and Biginelli Reactions. ACS Macro Lett. 2015, 4 (11), 1189-1193.*

(30) *Moldenhauer, F.; Kakuchi, R.; Theato, P. Synthesis of Polymers via Kabachnik-Fields Polycondensation. ACS Macro Lett. 2016, 5 (1), 10-13.*

(31) *Bachler, P. R.; Schulz, M. D.; Sparks, C. A.; Wagener, K. B.; Sumerlin, B. S. Aminobisphosphonate Polymers via RAFT and a Multicomponent Kabachnik-Fields Reaction. Macromol. Rapid Commun. 2015, 36 (9), 828-833.*

(32) *Zhang, Y.; Zhao, Y.; Yang, B.; Zhu, C.; Wei, Y.; Tao, L. 'One Pot' Synthesis of Well-Defined Poly(Aminophosphonate)s: Time for the Kabachnik-Fields Reaction on the Stage of Polymer Chemistry. Polym. Chem. 2014, 5 (6), 1857-1862.*

(33) *Wu, H.; Wang, Z.; Tao, L. The Hantzsch Reaction in Polymer Chemistry: Synthesis and Tentative Application. Polym. Chem. 2017, 8 (47), 7290-7296.*

(34) *Saxer, S.; Marestin, C.; Mercier, R.; Dupuy, J. The Multicomponent Debus-Radziszewski Reaction in Macromolecular Chemistry. Polym. Chem. 2018, 9 (15), 1927-1933.*

(35) *Esposito, D.; Kirchhecker, S.; Antonietti, M. A Sustainable Route towards Imidazolium Building Blocks Based on Biomass Molecules. Chem. - Eur. J. 2013, 19 (45), 15097-15100.*

(36) *Zhao, X.; Guo, S.; Li, H.; Liu, J.; Liu, X.; Song, H. In Situ Synthesis of Imidazolium-Crosslinked Ionogels via Debus-Radzis- zewski Reaction Based on PAMAM Dendrimers in Imidazolium Ionic Liquid. Macromol. Rapid Commun. 2017, 38 (21), 1700415.*

(37) *Dani, A.; Crocella,`V.; Magistris, C.; Santoro, V.; Yuan, J.; Bordiga, S. Click-Based Porous Cationic Polymers for Enhanced Carbon Dioxide Capture. J. Mater. Chem. A 2017, 5 (1), 372-383.*

(38) *Sirviö, J. A.; Visanko, M.; Liimatainen, H. Synthesis of Imidazolium-Crosslinked Chitosan Aerogel and Its Prospect as a Dye Removing Adsorbent. RSC Adv. 2016, 6 (61), 56544-56548.*

(39) *Talapaneni, S. N.; Buyukcakir, O.; Je, S. H.; Srinivasan, S.; Seo, Y.; Polychronopoulou, K.; Coskun, A. Nanoporous Polymers Incorporating Sterically Confined N-Heterocyclic Carbenes for Simultaneous CO2 Capture and Conversion at Ambient Pressure. Chem. Mater. 2015, 27 (19), 6818-6826.*

(40) *Krannig, K.-S.; Esposito, D.; Antonietti, M. Highly Efficient Transfer of Amino Groups to Imidazolium Entities for Polymer Coupling and Cross-Linking. Macromolecules 2014, 47 (7), 23502353.*

(41) *Grygiel, K.; Kirchhecker, S.; Gong, J.; Antonietti, M.; Esposito, D.; Yuan, J. Main-Chain Polyimidazolium Polymers by One-Pot Synthesis and Application as Nitrogen-Doped Carbon Precursors. Macromol. Chem. Phys. 2017, 218 (18), 1600586.*

(42) *Lindner, J.-P. Imidazolium-Based Polymers via the Poly- Radziszewski Reaction. Macromolecules 2016, 49 (6), 2046-2053.*

(43) *Castro-Grijalba, A.; Reyes-Gallardo, E. M.; Wuilloud, R. G.; Lucena, R.; Caŕdenas, S. Synthesis of Magnetic Polymeric Ionic Liquid Nanocomposites by the Radziszewski Reaction. RSC Adv. 2017, 7 (68), 42979-42985.*

(44) *Zhang, W.; Zhao, Q.; Yuan, J. Porous Polyelectrolytes: The Interplay of Charge and Pores for New Functionalities.*

Angew. Chem., Int. Ed. 2018, 57 (23), 6754-6773.

(45) Zhang, S.; Dokko, K.; Watanabe, M. Porous Ionic Liquids: Synthesis and Application. Chem. Sci. 2015, 6 (7), 3684-3691.

(46) Soll, S.; Zhao, Q.; Weber, J.; Yuan, J. Activated CO2 Sorption in Mesoporous Imidazolium-Type Poly(Ionic Liquid)-Based Polyampholytes. Chem. Mater. 2013, 25 (15), 3003-3010.

(47) Wilke, A.; Yuan, J.; Antonietti, M.; Weber, J. Enhanced Carbon Dioxide Adsorption by a Mesoporous Poly(Ionic Liquid). ACS Macro Lett. 2012, 1 (8), 1028-1031.

(48) Zulfiqar, S.; Sarwar, M. I.; Mecerreyes, D. Polymeric Ionic Liquids for CO2 Capture and Separation: Potential, Progress and Challenges. Polym. Chem. 2015, 6 (36), 6435-6451.

(49) Li, Y.; Qi, L.; Shen, Y.; Zhang, H.; Ma, H. Facile Fabrication of Polymeric Ionic Liquid Grafted Porous Polymer Monolith for Mixed Mode High Performance Liquid Chromatography. Chin. J. Chem. 2014, 32 (7), 619-625.

(50) Yin, M.-J.; Zhao, Q.; Wu, J.; Seefeldt, K.; Yuan, J. Precise Micropatterning of a Porous Poly(Ionic Liquid) via Maskless Photolithography for High-Performance Nonenzymatic H2O2 Sensing. ACS Nano 2018, 12 (12), 12551-12557.

(51) Lin, H.; Gong, J.; Miao, H.; Guterman, R.; Song, H.; Zhao, Q.; Dunlop, J. W. C.; Yuan, J. Flexible and Actuating Nanoporous Poly(Ionic Liquid)-Paper-Based Hybrid Membranes. ACS Appl. Mater. Interfaces 2017, 9 (17), 15148-15155.

(52) Zhao, Q.; Yin, M.; Zhang, A. P.; Prescher, S.; Antonietti, M.; Yuan, J. Hierarchically Structured Nanoporous Poly(Ionic Liquid) Membranes: Facile Preparation and Application in Fiber-Optic PH Sensing. J. Am. Chem. Soc. 2013, 135 (15), 5549-5552.

(53) Huang, J.; Tao, C.; An, Q.; Lin, C.; Li, X.; Xu, D.; Wu, Y.; Li, X.; Shen, D.; Li, G. Visual Indication of Enviromental Humidity by Using Poly(Ionic Liquid) Photonic Crystals. Chem. Commun. 2010, 46 (23), 4103-4105.

(54) Hu, X.; Huang, J.; Zhang, W.; Li, M.; Tao, C.; Li, G. Photonic Ionic Liquids Polymer for Naked-Eye Detection of Anions. Adv. Mater. 2008, 20 (21), 4074-4078.

(55) Guo, Z.; Jiang, Q.; Shi, Y.; Li, J.; Yang, X.; Hou, W.; Zhou, Y.; Wang, J. Tethering Dual Hydroxyls into Mesoporous Poly(Ionic Liquid)s for Chemical Fixation of CO2 at Ambient Conditions: A Combined Experimental and Theoretical Study. ACS Catal. 2017, 7 (10), 6770-6780.

(56) Wang, Q.; Hou, W.; Li, S.; Xie, J.; Li, J.; Zhou, Y.; Wang, J. Hydrophilic Mesoporous Poly(Ionic Liquid)-Supported Au-Pd Alloy Nanoparticles towards Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid under Mild Conditions. Green Chem. 2017, 19 (16), 3820-3830.

(57) Gao, C.; Chen, G.; Wang, X.; Li, J.; Zhou, Y.; Wang, J. A Hierarchical Meso-Macroporous Poly(Ionic Liquid) Monolith Derived from a Single Soft Template. Chem. Commun. 2015, 51 (24), 4969-4972.

(58) Wang, X.; Zhou, Y.; Guo, Z.; Chen, G.; Li, J.; Shi, Y.; Liu, Y.; Wang, J. Heterogeneous Conversion of CO2 into Cyclic Carbonates at Ambient Pressure Catalyzed by Ionothermal-Derived Meso- Macroporous Hierarchical Poly(Ionic Liquid)S. Chem. Sci. 2015, 6 (12), 6916-6924.

(59) Kuzmicz, D.; Coupillaud, P.; Men, Y.; Vignolle, J.; Vendraminetto, G.; Ambrogi, M.; Taton, D.; Yuan, J. Functional Mesoporous Poly(Ionic Liquid)-Based Copolymer Monoliths: From Synthesis to Catalysis and Microporous Carbon Production. Polymer 2014, 55 (16), 3423-3430.

(60) Huang, J.; Tao, C.; An, Q.; Zhang, W.; Wu, Y.; Li, X.; Shen, D.; Li, G. 3D-Ordered Macroporous Poly(Ionic Liquid) Films

as Multifunctional Materials. Chem. Commun. 2010, 46 (6), 967-969.

(61) Zhang, H.; Bai, L.; Wei, Z.; Liu, S.; Liu, H.; Yan, H. Fabrication of an Ionic Liquid-Based Macroporous Polymer Monolithic Column via Atom Transfer Radical Polymerization for the Separation of Small Molecules. Talanta 2016, 149, 62-68.

(62) Taü ber, K.; Zhao, Q.; Antonietti, M.; Yuan, J. Tuning the Pore Size in Gradient Poly(Ionic Liquid) Membranes by Small Organic Acids. ACS Macro Lett. 2015, 4 (1), 39-42.

(63) Zhao, Q.; Zhang, P.; Antonietti, M.; Yuan, J. Poly(Ionic Liquid) Complex with Spontaneous Micro-/Mesoporosity: TemplateFree Synthesis and Application as Catalyst Support. J. Am. Chem. Soc. 2012, 134 (29), 11852-11855.

(64) Mathieu, K.; Jeŕ ôme, C.; Debuigne, A. Macroporous Poly(Ionic Liquid)/Ionic Liquid Gels via CO2-Based Emulsion-Templating Polymerization. Polym. Chem. 2018, 9 (4), 428-437.

(65) Boyeȑ e, C.; Favrelle, A.; Leó nard, A. F.; Boury, F.; Jeŕ ôme, C.; Debuigne, A. Macroporous Poly(Ionic Liquid) and Poly(Acrylamide) Monoliths from CO2-in-Water Emulsion Templates Stabilized by Sugar-Based Surfactants. J. Mater. Chem. A 2013, 1 (29), 8479-8487.

(66) Yan, F.; Texter, J. Surfactant Ionic Liquid-Based Microemulsions for Polymerization. Chem. Commun. 2006, 25, 2696-2698.

(67) Zhang, T.; Sanguramath, R. A.; Israel, S.; Silverstein, M. S. Emulsion Templating: Porous Polymers and Beyond. Macromolecules 2019, 52 (15), 5445-5479.

(68) Kiefer, J.; Fries, J.; Leipertz, A. Experimental Vibrational Study of Imidazolium-Based Ionic Liquids: Raman and Infrared Spectra of 1-Ethyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide and 1-Ethyl-3-Methylimidazolium Ethylsulfate. Appl. Spectrosc. 2007, 61 (12), 1306-1311.

(69) Qian, W.; Texter, J.; Yan, F. Frontiers in Poly(Ionic Liquid)s: Syntheses and Applications. Chem. Soc. Rev. 2017, 46 (4), 11241159.

(70) Lambert, R.; Coupillaud, P.; Wirotius, A.-L.; Vignolle, J.; Taton, D. Imidazolium-Based Poly(Ionic Liquid)s Featuring Acetate Counter Anions: Thermally Latent and Recyclable Precursors of Polymer- Supported N-Heterocyclic Carbenes for Organocatalysis. Macromol. Rapid Commun. 2016, 37 (14), 1143-1149.

(71) Liu, D.; Sun, J.; Simmons, B. A.; Singh, S. N-Heterocyclic Carbene Promoted Decarboxylation of Lignin-Derived Aromatic Acids. ACS Sustainable Chem. Eng. 2018, 6 (6), 7232-7238.