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Cationic Metallo-Polyelectrolytes for Robust Alkaline Anion-Exchange Membranes

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Abstract: Chemically inert, mechanically tough, cationic metallopolyelectrolytes were conceptualized and designed as durable anionexchange membranes (AEMs). Ring-opening metathesis polymerization (ROMP) of cobaltocenium-containing cyclooctene with triazole as the only linker group, followed by backbone hydrogenation, led to a new class of AEMs with a polyethylene-like framework and alkaline-stable cobaltocenium cation for ion transport. These AEMs exhibited excellent thermal, chemical and mechanical stability, as well as high ion conductivity.

Polyelectrolytes have vast applications ranging from coating to biomedical materials.^[1] Among them, cationic polyelectrolytes are widely pursued as anion-exchange membranes (AEMs) in alkaline fuel cells for converting fuels into electricity,^[2] which can be operated below 100 °C and thus are more attractive as energy conversion devices for electric vehicles and powering portable devices.

Commonly, AEMs are copolymers containing cations that are covalently linked to hydrophobic polymer backbones.^[2a, b, m, 3] The most popular approach is the use of quaternary ammonium cation (QAC)-containing polymers. However, QACs are prone to degradation through Hofmann elimination (E2) or nucleophilic substitution (S_N2) under highly basic conditions. Over the past few years, several strategies have been adopted to improve the alkaline stability of AEM backbones: (i) protect ammonium cations using steric protection, conformational restrictions or inductive effects;^[4] (ii) explore alternative stable cations such as benzyl quaternary guanidinium,^[5] imidazolium,^[6] and phosphonium^[7] to slow down degradation. However, these methods have either

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sacrificed ion conductivity or still faced challenges on achieving long-term stability.

Of equal importance, other components of polyelectrolytes as AEMs are also required to be stable for withstanding harsh chemical environments. A degradation or deterioration of chemical compositions of polyelectrolytes would have a catastrophic impact on membrane performance. It is essential to design novel cationic polyelectrolytes with high cation stability and superior chemical durability of the polymer framework.

Herein we report a new class of robust AEMs based on cobaltocenium-containing polyelectrolytes that bear promising hydroxide conductivity as well as mechanical, thermal and chemical stability. These novel membranes exhibited long-term stability that is unprecedented over many reported polymeric systems. Specifically, we developed side-chain cobaltoceniumcontaining vinyl polymers, which have non-hydrolysable hydrocarbon backbones and extraordinarily stable side chains, yet with high modulus and toughness.

We along with others have discovered that cationic cobaltocenium exhibits good stability toward harsh chemical environments in both strong acidic and basic conditions.^[8] As shown in Figure S1, there is negligible change in characteristic UV absorption corresponding to cobaltocenium after it was dissolved in a solution of NaOH (pH = 14) or HCI (pH = 1.5) for two weeks. Moreover, published work by Yan^[9] and Zhu^[10] both demonstrated that cobaltocenium cations with substituent group in Cp ring had superior thermal and chemical stability over other reported cations. Such extraordinary stability of cationic cobaltocenium motivated us to design ultra-stable polyelectrolytes in both cations and other compositions of frameworks for AEMs. To construct the new polymeric systems, we need to avoid the integration of functional groups (e.g. ester, amide, anhydride, carbonate, etc.) and linkers that are susceptible to degradation under strong basic conditions for a prolonged period of time. Due to the instabilities of ester or imide group, most cobaltocenium polymers reported in literature could not be used as stable AEMs directly.[11]

To place our work in context, metal cations have been used for AEMs. Hickner and Tew reported the synthesis of AEMs functionalized with bis(terpyridine)-ruthenium(II) complexes.^[2I] These membranes exhibited good ion conductivity and mechanical properties. However, the decline of conductivity in alkaline condition over a long term was a concern. Yan and coworkers reported permethyl cobaltocenium-containing

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polysulfone as AEMs that exhibited extraordinary stability of cations and chemical stability of polymers.^[9] The ion conductivity was mediocre, partially due to the steric hindrance for the pentamethyl group. These polymers were quite brittle with elongation at break only about 10%. Later Zhu and coworkers synthesized polybenzimidazole polymers with cobaltocenium cations in the main-chain.^[10] These membranes showed improved thermal stability and ion-exchange capacity, but the mechanical and alkaline stability of these AEMs were inferior because of the poor stability of linkage groups and the rigid polymer backbones. Both approaches adopted condensation polymerization to prepare rigid polymers with relatively limited molecular weight. In addition, the synthesis was particularly laborious with low yields. In this work, we followed three design principles: (1) eliminate any hydrolysable functionalities; (2) maximize the content of hydrocarbon in the compositions; (3) enable polymers with controlled molecular weight. Specifically, we used highly efficient click chemistry to attach cobaltocenium onto a cyclic vinyl monomer, which was executed for ring-opening metathesis polymerization (ROMP).^[12] The resultant polymer has only one triazole group as a linker between cobaltocenium and the polymer backbone. This powerful synthetic tool allows the preparation of high molecular weight toward mechanically flexible and tough polymers. In addition, these polymers have a polyethylene-like backbone to warrant mechanical integrity and chemical stability under harsh basic conditions.

Scheme 1. (a) Synthesis of cobaltocenium monomer 2, copolymer 3 and hydrogenated polymer 4 as AEMs; (b) Images of transparent and flexible cobaltocenium AEMs; (c) Proposed structures of cobaltocenium-containing AEMs in a hydroxide solution.



We prepared cobaltocenium-containing cyclooctene that was subject to ROMP, as illustrated in Scheme 1. 5-Bromocyclooct-1ene was derived from cyclooctadiene,^[7d] and then converted to 5azidocyclooct-1-ene (1). A copper-catalyzed click reaction

between **1** and ethynylcobaltocenium hexafluorophosphate yielded cobaltocenium cyclooctene with a triazole as the linker (**2**), which was subsequently carried out for ROMP with cyclooctene as a co-monomer with the aid of Grubbs II catalyst to get a copolymer **3**. The molecular weight was well controlled by adjusting the molar ratio of monomers to catalysts. In this study, we chose a polymer with molecular weight at 80,000 g/mol (Table S1), which is sufficiently high to warrant the formation of flexible membranes. The cobaltocenium monomer and cationic copolymers in hexafluorophosphate form were characterized by ¹H NMR spectroscopy (Figure 1), which unambiguously confirmed their structures with specific assignments to each proton.



Figure 1. ¹H NMR spectra of cobaltocenium monomer 2 (top), copolymer 3 (middle) and hydrogenated polymer 4 (bottom).

The presence of unsaturated bonds in the backbone of polymer 3 could be a concern on the long-term stability in alkaline conditions. The alkaline stability of this copolymer was improved by hydrogenation of the backbone. The reduction of double bonds could be confirmed with ¹H NMR (Figure 1) and disappearance of characteristic absorption in the range of 1686~1796 cm⁻¹ in FTIR spectrum (Figure S2). These hydrogenated copolymers were subsequently carried out ion-exchange from hexafluorophosphate (PF_6^-) to chloride (CI^-) and then to hydroxide (OH⁻) ion, and further fabricated to form anion exchange membranes H-AEM_x-OH (5) (x represents the molar fraction of cobaltocenium units in a polymer composition). Cobaltocenium monomer 2 with Cl⁻ anion was evaluated for its alkaline stability by UV-vis spectroscopy, as cobaltocenium has a characteristic UV absorption at ~ 282 nm (Figure S3c).^[8a, b] The monomer was dissolved in 1 M NaOH at 80 °C and then collected for time-dependent UV-vis spectra. Two representative absorption peaks appeared at 282 nm and 346 nm, characteristically originated from the cobaltocenium and triazole groups respectively. The absorption spectrum obtained after 10 days perfectly overlapped with the initial one. Both peaks maintained nearly 100% of initial intensity even after 10 d, unambiguously indicating excellent alkaline stability of cobaltocenium and triazole at elevated pH and temperatures. Furthermore, the stability of cobaltocenium monomer 2 was confirmed by ¹H NMR (Figure S4a) and mass spectrum (Figure S4b) after exposure in alkaline conditions. We noticed that protondeuterium exchange occurred on protons from both aromatic

COMMUNICATION

rings and alkenes in the monomer structure, while no signals indicated any degraded products. As investigated recently by the Patric group,^[13] this kind of proton-deuterium exchange is reversible and does not lead to any structural degradation. All above stability tests suggested cobaltocenium is a stable cation suitable for AEM applications.

For cobaltocenium-containing polymers, direct anion exchange from hydrophobic PF_6^- to hydrophilic OH^- was challenging.^[2I, 9] We resolved this problem by first exchange to CI^- in 2 M aqueous solution of NH_4CI at 60 °C. Then, exchange from CI^- to OH^- was carried out by immersing polymer membranes into 1 M NaOH solution. Complete ion-exchange was confirmed by ion exchange capacity (IEC) titration (Table 1) and Energy Dispersive X-ray (EDX) characterization (Figure S5). These membranes were in yellow color, flexible and transparent (Scheme 1b). All membranes after anion exchange were not soluble in water or other polar aprotic solvents like dimethylacetamide and acetonitrile.

The thermal stability of cobaltocenium-containing polymers was studied by thermogravimetric analysis (TGA) (Figure 2a). The decomposition of hydrogenated H-AEM_x-OH membranes under N₂ atmosphere consisted of two different stages and occurred only well above 300 °C. The 5% weight-loss decomposition temperature (*T_d*) of H-AEM₄₀-OH and H-AEM₅₀-OH were 347 °C and 328 °C, respectively. In comparison, many reported AEMs with ammonium or imidazole cations have much lower decomposition temperature for their cations (< 200 °C).^[14] Our results suggested both cobaltocenium cations and the hydrocarbon backbone have excellent thermal stability.

Mechanical properties of AEMs are largely dependent on the choice of polymer backbones. For well-studied poly(p-phenylene oxide), polybenzimidazole, and polystyrene based AEMs, the tensile strain at break is usually lower than 80% due to their rigid aromatic backbones. While for flexible poly(4-methyl-1-pentene) based films,^[15] the tensile strength is relatively low. We intended cobaltocenium polymers to be tough: flexible and strong. Mechanical properties of cobaltocenium AEMs were characterized at 80% RH and under ambient temperature (Figure S6). Both H-AEM₄₀-OH and H-AEM₅₀-OH retained tensile strain over 120% attributed to the existence of a highly flexible backbone. These cobaltocenium membranes were expected to have phase separation due to immiscibility of the hydrophobic backbone and hydrophilic side chain in the copolymers. Small-angle X-ray scattering (SAXS) was used to investigate the morphology of cobaltocenium membranes (Figure 2b). Both of the membranes exhibited a broad primary scattering peak around $q^* = 1.28$ and 1.54 nm⁻¹ with a *d* spacing $(2\pi/q^*)$ of 4.9 and 4.1 nm. The lack of higher orders of scattering peaks implied that the phase separation is probably short-range correlated,^[16] which is reasonable given the membranes are not block copolymers. Atomic force microscopy (AFM) images also confirmed the microphase separation between hydrophilic and hydrophobic domains under spin casting conditions (Figure S7). The dark areas represent the soft matrix from polyethylene backbone, whereas the brighter ones represent hard domains from cobaltocenium side chains. Such phase-separated morphology is essential for anion exchange materials with desirable properties. The hydrophobic backbone provided mechanically flexible and chemically stable scaffold, whereas the hydrophilic side-chains facilitated ion transport through connected ionic channels.

Table 1. Properties of cobaltocenium AEMs

Sample	X ^[a]	y ^[a]	IEC _{theo} (mmol/g)	IEC _{titr} (mmol/g)	λ
H-AEM ₄₀ -OH	40	60	1.81	1.53	11.2
H-AEM50-OH	50	50	2.02	1.86	11.6

[a] x and y represent molar fractions of cobaltocenium and cyclooctene units respectively (Scheme 1a).

Figures S8 show the water uptake and swelling ratio of hydrogenated membranes in DI water at different temperature. Even under high cation loading, side-chain cobaltocenium AEMs still exhibited relatively low water uptake and swelling ratio especially at room temperature, which can be explained by the hydrophobic nature of polyethylene-like backbone. Furthermore, the number of absorbed water molecules per cobaltocenium cation was calculated to be in the range of 11.2 to 11.6, and showed a tendency of slight increase with higher IEC (Table S1). Hence, both cobaltocenium copolymers showed good resistance to water uptake at various temperature. Such water management property could play a critical role in forming ion conducting pathways (Scheme 1c) and ensure the membranes to be dimensionally stable over a long term. While for many quaternary ammonium or phosphonium polymers, high cation loading for better electrical property makes them much more hydrophilic and absorbs excess water, which in turn sacrifices the overall stability.^[7d, 14a, 17] Our study on cobaltocenium AEMs indicated the possibility of simultaneously making high IEC and having good water management property.



Figure 2. Cobaltocenium AEMs: (a) TGA and DTG curves; (b) SAXS profiles; (c) Hydroxide conductivity of membranes as a function of temperature in fully hydrated condition; (d) Room temperature conductivity as a function of immersion time of membranes in 1 M NaOH solution at 80°C.

The hydroxide conductivity of membranes with different loading of cobaltocenium cation as a function of temperature is shown in Figure 2c. Both membranes showed steadily increased conductivity at elevated temperature likely due to higher water uptake and faster ion migration. The hydroxide conductivity of H- AEM_{40} -OH and H- AEM_{50} -OH reached pretty high value at 90 °C:

COMMUNICATION

72 and 90 mS/cm, respectively. Considering the processability and durability of membranes, we only incorporated up to 50 mol% cobaltocenium in copolymers at this stage. It could be possible to achieve even higher hydroxide conductivity by increasing the IEC and optimizing the compositions of copolymers. Moreover, the hydroxide conductivity at different temperature generally followed an Arrhenius relationship (Figure S8). The activation energy for ion transport was calculated to be 19.2 to 20.2 kJ/mol.

The alkaline stability at high operating temperature has always been a key concern for AEMs. For polymers prepared via ROMP, the unsaturated double bond in repeating units is considered to not only limit the chain flexibility, but also make membranes less stable in harsh basic conditions. We employed direct hydrogenation to reduce the double bonds in the polymer backbone. In addition, polymers with polyethylene-like backbone exhibited improved durability and ductility. H-AEM₅₀-OH was chosen for the long-term stability test because of its higher ion capacity and hydroxide conductivity. FTIR spectra (Figure S9) showed that all chemical structures of membranes remained almost unchanged before and after the test. Moreover, initial hydroxide conductivity of hydrated membranes was maintained over 95% after soaking in 1 M NaOH at 80 °C for one month (Table S3), indicating their superior chemical and mechanical stability.

In summary, a new design for anion-exchange membranes was achieved using metallo-polyelectrolytes containing cationic cobaltocenium with a polyethylene-like backbone and a nonhydrolysable linker. These copolymers were prepared via ROMP in conjunction with hydrogenation of polymer backbones. These membranes exhibited long-term durability with excellent mechanical toughness and flexibility, great chemical stability of cations and other polymer compositions, as well as good ion work demonstrated conductivity. This that side-chain cobaltocenium polymers can be used as a candidate for newgeneration anion-exchange membrane materials in fuel cell applications.

Experimental Section

Experimental details and complete characterization data are provided in supporting information.

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Keywords: cobaltocenium polyelectrolytes • anion-exchange membranes • ion conductivity • ROMP • microphase separation

- a) L. Zhai, F. Ç. Cebeci, R. E. Cohen, M. F. Rubner, *Nano Lett.* 2004, *4*, 1349-1353; b) D. W. Pack, A. S. Hoffman, S. Pun, P. S. Stayton, *Nat. Rev. Drug Discov.* 2005, *4*, 581-593.
- [2] a) J. R. Varcoe, R. C. T. Slade, *Fuel Cells* 2005, *5*, 187-200; b) M. A. Hickner, A. M. Herring, E. B. Coughlin, *J. Polym. Sci., Part B: Polym. Phys.* 2013, *51*, 1727-1735; c) G. Merle, M. Wessling, K. Nijmeijer, *J. Membr. Sci.* 2011, *377*, 1-35; d) G. Couture, A. Alaaeddine, F. Boschet, B. Ameduri, *Prog. Polym. Sci.* 2011, *36*, 1521-1557; e) N. J. Robertson, H. A. Kostalik, T. J. Clark, P. F. Mutolo, H. D. Abruña, G. W. Coates, *J. Am. Chem. Soc.* 2010, *132*, 3400-3404; f) J. John, K. M. Hugar, J.

Rivera-Meléndez, H. A. Kostalik, E. D. Rus, H. Wang, G. W. Coates, H.
D. Abruña, J. Am. Chem. Soc. 2014, 136, 5309-5322; g) T. J. Clark, N.
J. Robertson, H. A. Kostalik Iv, E. B. Lobkovsky, P. F. Mutolo, H. D.
Abruña, G. W. Coates, J. Am. Chem. Soc. 2009, 131, 12888-12889; h)
M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H.
Tanaka, B. Bae, K. Miyatake, M. Watanabe, J. Am. Chem. Soc. 2011, 133, 10646-10654; i) O. D. Thomas, K. J. W. Y. Soo, T. J. Peckham, M.
P. Kulkarni, S. Holdcroft, J. Am. Chem. Soc. 2012, 134, 10753-10756; j)
C. Chen, Y.-L. S. Tse, G. E. Lindberg, C. Knight, G. A. Voth, J. Am. Chem. Soc. 2016, 138, 991-1000; k) N. Li, Y. Leng, M. A. Hickner, C.-Y. Wang, J. Am. Chem. Soc. 2013, 135, 10124-10133; l) Y. Zha, M. L. Disabb-Miller, Z. D. Johnson, M. A. Hickner, G. N. Tew, J. Am. Chem. Soc. 2012, 134, 4493-4496; m) D. W. Shin, M. D. Guiver, Y. M. Lee, Chem. Rev. 2017, 117, 4759-4805.

- [3] J. Pan, C. Chen, L. Zhuang, J. Lu, Acc. Chem. Res. 2012, 45, 473-481.
- [4] a) A. D. Mohanty, C. Bae, J. Mater. Chem. A 2014, 2, 17314-17320; b)
 M. G. Marino, K. D. Kreuer, ChemSusChem 2015, 8, 513-523; c) T. H.
 Pham, P. Jannasch, ACS Macro Lett. 2015, 4, 1370-1375; d) H.-S. Dang,
 P. Jannasch, J. Mater. Chem. A 2016, 4, 11924-11938; e) Z. Yang, R.
 Guo, R. Malpass-Evans, M. Carta, N. B. McKeown, M. D. Guiver, L. Wu,
 T. Xu, Angew. Chem. 2016, 128, 11671-11674; f) W.-H. Lee, Y. S. Kim,
 C. Bae, ACS Macro Lett. 2015, 4, 814-818; g) Z. Yang, J. Zhou, S. Wang,
 J. Hou, L. Wu, T. Xu, J. Mater. Chem. A 2015, 3, 15015-15019; h) Y. Liu,
 B. Zhang, C. L. Kinsinger, Y. Yang, S. Seifert, Y. Yan, C. Mark Maupin,
 M. W. Liberatore, A. M. Herring, J. Membr. Sci. 2016, 506, 50-59; i) H.-S.
 S. Dang, E. A. Weiber, P. Jannasch, J. Mater. Chem. A 2015, 3, 5280-5284.
- a) D. Chen, M. A. Hickner, ACS Appl. Mater. Interfaces 2012, 4, 5775-5781; b) D. S. Kim, A. Labouriau, M. D. Guiver, Y. S. Kim, Chem. Mater. 2011, 23, 3795-3797.
- [6] a) K. M. Hugar, H. A. Kostalik, G. W. Coates, *J. Am. Chem. Soc.* 2015, 137, 8730-8737; b) B. S. Aitken, C. F. Buitrago, J. D. Heffley, M. Lee, H. W. Gibson, K. I. Winey, K. B. Wagener, *Macromolecules* 2012, 45, 681-687; c) B. Lin, H. Dong, Y. Li, Z. Si, F. Gu, F. Yan, *Chem. Mater.* 2013, 25, 1858-1867.
- [7] a) S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, *Angew. Chem. Int. Ed.* 2009, *48*, 6499-6502; b) S. Gu, R. Cai, T. Luo, K. Jensen, C. Contreras, Y. Yan, *ChemSusChem* 2010, *3*, 555-558; c) S. Gu, R. Cai, Y. Yan, *Chem. Commun.* 2011, *47*, 2856-2858; d) K. J. T. Noonan, K. M. Hugar, H. A. Kostalik, E. B. Lobkovsky, H. D. Abruña, G. W. Coates, *J. Am. Chem. Soc.* 2012, *134*, 18161-18164.
 [8] a) C. G. Hardy, J. Zhang, Y. Yan, L. Ren, C. Tang, *Prog. Polym. Sci.*

a) C. G. Hardy, J. Zhang, Y. Yan, L. Ren, C. Tang, *Prog. Polym. Sci.* 2014, 39, 1742-1796; b) Y. Yan, P. Pageni, M. P. Kabir, C. Tang, *Synlett* 2016, 27, 984-1005; c) C. Ornelas, J. Ruiz, D. Astruc, *Organometallics* 2009, 28, 276-2723; d) J. E. Sheats, M. D. Rausch, *J. Org. Chem.* 1970, 35, 3245-3249; e) G. Wilkinson, *J. Am. Chem. Soc.* 1952, 74, 6148-6149; f) L. Zhao, X. Liu, L. Zhang, G. Qiu, D. Astruc, H. Gu, *Coord. Chem. Rev.* 2017, 337, 34-79; g) H. Gu, R. Ciganda, P. Castel, J. Ruiz, D. Astruc, *Macromolecules* 2016, *49*, 4763-4773.

- [9] S. Gu, J. Wang, R. B. Kaspar, Q. Fang, B. Zhang, E. Bryan Coughlin, Y. Yan, *Sci. Rep.* 2015, *5*, 11668.
- [10] N. Chen, H. Zhu, Y. Chu, R. Li, Y. Liu, F. Wang, Polym. Chem. 2017, 8, 1381-1392.
- [11] a) L. Ren, C. G. Hardy, C. Tang, J. Am. Chem. Soc. 2010, 132, 8874-8875; b) L. Ren, C. G. Hardy, S. Tang, D. B. Doxie, N. Hamidi, C. Tang, Macromolecules 2010, 43, 9304-9310; c) L. Ren, J. Zhang, X. Bai, C. G. Hardy, K. D. Shimizu, C. Tang, Chem. Sci. 2012, 3, 580-583; d) J. Zhang, Y. P. Chen, K. P. Miller, M. S. Ganewatta, M. Bam, Y. Yan, M. Nagarkatti, A. W. Decho, C. Tang, J. Am. Chem. Soc. 2014, 136, 4873-4876; e) J. B. Gilroy, S. K. Patra, J. M. Mitchels, M. A. Winnik, I. Manners, Angew. Chem. Int. Ed. 2011, 50, 5851-5855; f) U. F. J. Mayer, J. B. Gilroy, D. O'Hare, I. Manners, J. Am. Chem. Soc. 2009, 131, 10382-10383; g) Y. Yan, J. Zhang, L. Ren, C. Tang, Chem. Soc. Rev. 2016, 45, 5232-5263; h) R. Ciganda, H. Gu, P. Castel, P. Zhao, J. Ruiz, R. Hernández, D. Astruc, Macromol. Rapid Commun. 2016, 37, 105-111; i) H. Gu, R. Ciganda, R. Hernandez, P. Castel, P. Zhao, J. Ruiz, D. Astruc, Macromol. Rapid Commun. 2016, 37, 630-636.

COMMUNICATION

- [12] a) J. Zhang, Y. Yan, M. W. Chance, J. Chen, J. Hayat, S. Ma, C. Tang, *Angew. Chem. Int. Ed.* **2013**, *52*, 13387-13391; b) J. Wei, L. Ren, C. Tang, Z. Su, *Polym. Chem.* **2014**, *5*, 6480-6488.
- [13] T. H. Pham, J. S. Olsson, P. Jannasch, J. Am. Chem. Soc. 2017, 139, 2888-2891.
- [14] a) D. Guo, A. N. Lai, C. X. Lin, Q. G. Zhang, A. M. Zhu, Q. L. Liu, ACS Appl. Mater. Interfaces **2016**, *8*, 25279-25288; b) H. Wu, W. Jia, Y. Liu, Journal of Materials Science **2017**, *52*, 1704-1716; c) Q. Ge, J. Ran, J. Miao, Z. Yang, T. Xu, ACS Appl. Mater. Interfaces **2015**, *7*, 28545-28553.
- [15] M. Zhang, C. Shan, L. Liu, J. Liao, Q. Chen, M. Zhu, Y. Wang, L. An, N. Li, ACS Appl. Mater. Interfaces 2016, 8, 23321-23330.
- a) N. Li, L. Wang, M. Hickner, *Chem. Commun.* 2014, *50*, 4092-4095; b)
 T.-H. Tsai, S. P. Ertem, A. M. Maes, S. Seifert, A. M. Herring, E. B. Coughlin, *Macromolecules* 2015, *48*, 655-662.
- [17] a) X. Ren, S. C. Price, A. C. Jackson, N. Pomerantz, F. L. Beyer, ACS Appl. Mater. Interfaces **2014**, *6*, 13330-13333; b) J. Pan, S. Lu, Y. Li, A. Huang, L. Zhuang, J. Lu, Adv. Funct. Mater. **2010**, *20*, 312-319.

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