Reversible Anion-Induced Cross-Linking of Well-Defined Calix[4]pyrrole-Containing Copolymers

Eric S. Silver, Brett M. Rambo, Christopher W. Bielawski,* and Jonathan L. Sessler*

Department of Chemistry, 105 East 24th Street, Stop A5300, The University of Texas at Austin, Austin, Texas 78712, United States

S *Supporting Information*

ABSTRACT: Reversible addition/fragmentation chain-transfer polymerization is used to generate a calix[4]-pyrrole methacrylate-derived copolymer. The material is found to undergo supramolecular cross-linking upon exposure to select dianionic species (e.g., pyrophosphate and terephthalate salts), altering the viscoelastic properties of the copolymer in solution and in the solid state. The copolymeric material is also used for selective differentiation of mono- and bis-anions under conditions of liquid/liquid extraction.

The field of supramolecular polymers has witnessed explosive growth over the past 20 years. Its influence is now manifest in a number of important application areas, including sensor design,[1] self-healing materials,[2] and controlled delivery systems.[3] The ability to assemble and cross-link polymeric structures through multiple weak non-covalent interactions can endow a macromolecular system with a number of unique properties, such as the ability to respond on a molecular level to external stimuli.[4] To date, a number of strategies have been successfully used to create controlled responses in both supramolecular and covalent polymers. These include exploiting light-induced rearrangements,[5] pH-sensitive moieties,[6] H-bonding motifs,[7] hydrophobic effects,[8] charge-transfer interactions,[9] cation complexation,[10] and thermally sensitive polymer backbones.[11] However, one approach that, to our knowledge, has yet to be explored involves anion binding. It is our belief that bis-anionic species could be used not only to induce supramolecular cross-linking but also to provide a means for selective extraction and removal of targeted dianionic species from aqueous environments.[12] Further, such systems could prove useful in advanced applications, including as scaffolds for biomineralization (calcium carbonate and calcium phosphate being key targets)[13] or as charge-neutral alternatives to cationic materials for transporting anionic payloads.[14]

A number of dianions have biological features that make them of specific interest. For instance, pyrophosphate plays a central role in DNA synthesis and is the product of ATP hydrolysis. It is also a key component of teeth and bones.[15] Various dicarboxylates are involved in the citric acid and glyoxylate cycles,[16] while glutamate is a recognized neurotransmitter.[17] Our own group found that terephthalate in its mono- and bisanionic forms can be used to control the self-assembly of cationic "boxes".[18] One approach to achieving selective recognition of these and other targeted species is through the use of polymeric systems that undergo supramolecular cross-linking in the presence of dianions but not in the presence of ostensibly similar monoanions.

In previous studies, Huang et al. employed bis-ammonium cations to cross-link polymers bearing pendant dibenzo[28]-crown-8-ether groups, resulting in reversible self-healing gel formation.[19] Separately, Meijer et al. exploited the recognition features of 2-ureidopyrimidinone incorporated into poly-(norbornene) to force the collapse of individual polymer chains through intrachain H-bonding interactions.[20] A number of other systems that exploit inter alia cation complexation,[21] H-bonding,[22] and hydrophobic[23] interactions to effect cross-linking have also been reported.[24] Here we report a complementary approach to achieving supramolecular control over polymer function. Specifically, we detail a poly(calix[4]pyrrole ethyl methacrylate-*co*-methyl methacrylate) copolymer (**4**) that undergoes supramolecular cross-linking upon exposure to selected bis-anionic species. The resulting supramolecular cross-linking is found to induce reversible changes in the viscoeleastic properties of the polymeric system, as inferred from viscometry measurements, ^{1}H NMR spectroscopy, and dynamic mechanical analysis (DMA). Moreover, it is found that **4** can be used to extract the terephthalate dianion (as the tetrabutylammonium (TBA) salt) from aqueous environments with concurrent formation of an organic gel. These findings lead us to suggest that systems such as **4** could find utility in the extraction and separation of dianions from aqueous media.

Previously, our group reported a poly(methyl methacrylate) (PMMA) that contained pendant calix[4]pyrrole[25] groups.[26] The innate ability of calix[4]pyrrole to bind the fluoride and chloride anions in solution and when incorporated into this polymer provided a means of extracting negatively charged substrates (as the corresponding TBA salts) from aqueous solutions. Further, when the starting calix[4]pyrrole methacrylate monomer was copolymerized with a benzo-15-crown-5-ether methacrylate derivative, a copolymer was produced that was capable of extracting relatively hard halide salts (e.g., KF and KCl) from an aqueous environment into an organic phase.[27] Subsequently, Sada et al. reported a covalently cross-linked polymer system with thiourea-based anion receptors, which when swelled in organic solvents was capable of recognizing fluoride and acetate anions.[28] In early seminal work, Sun,[29] Anzenbacher,[30] and Steed[31a] prepared polymers with anion recognition properties. Steed also reported an organic gel.[31b] However, no evidence of anion-based cross-linking was disclosed in any of these systems. In an effort to address the challenge of achieving a

macromolecular system capable of anion-induced cross-linking, we synthesized the calixpyrrole-containing copolymer **4** and exposed it to dianionic species.

To prepare the aforementioned copolymer, we synthesized the requisite methacrylate-derived calix[4]pyrrole monomer **2** in two steps from commercially available starting materials (Scheme 1).

Scheme 1. Syntheses of (a) Calix[4]pyrrole Methacrylate Monomer (2) and (b) Poly(calix[4]pyrrole ethyl methacrylate-*co*-methyl methacrylate) (4)
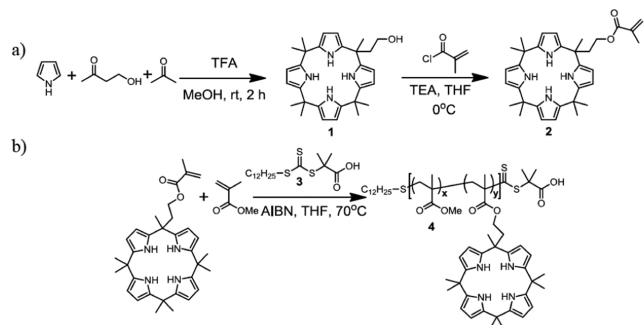
First, a catalytic amount of trifluoroacetic acid (TFA) was added to a dilute methanol solution of a 4:1:3 molar ratio of pyrrole, 4-hydroxy-2-butanone, and acetone under an inert atmosphere. Filtration of the ensuing precipitate and subsequent purification by column chromatography gave ethyl hydroxycalix[4]pyrrole (**1**) as a solid white powder in 10% yield.[32] Compound **1** was then esterified with methacryloyl chloride in dry tetrahydrofuran (THF) in the presence of triethylamine (TEA) at 0 °C to produce the **2** in 65% yield as a fluffy white solid. With monomer **2** in hand, conventional reversible addition/fragmentation chain-transfer polymerization (RAFT) methods were used to generate copolymer **4**. Briefly, **2**, methyl methacrylate, 5 mol% of a chain-transfer agent (**3**),[33] and 1 mol% of azobisisobutyronitrile (AIBN) were dissolved in dry THF and subjected to three freeze/pump/thaw cycles. The reaction mixture was then heated to 70 °C, stirred overnight, and finally precipitated from a large excess of cold methanol to yield **4** as a slightly off-white powder. GPC analysis revealed that the resulting polymer had an average molecular weight of 26.2 kDa and a molar mass dispersity of 1.41. Furthermore, ^{1}H NMR spectroscopy revealed **4** to be a random copolymer comprised of a 1:14 molar ratio of **2** to MMA.

To investigate the ability of **4** to recognize mono- and dianionic species in organic media, ^{1}H NMR analyses were carried out. Initially, the interactions of **4** with monoanionic species were investigated. In these studies, TBA fluoride (TBAF), TBA benzoate, and 1-butyl-3-methylimidazolium bromide were added separately as 0.1 M solutions to CD$_2$Cl$_2$ solutions of **4** (cf. Figure 1). Upon addition of the monoanionic species, downfield shifts in the signals corresponding to the pyrrolic NH protons were observed. Typically, these signals were shifted from their initial value of ~7.2 ppm to between 10 and 11 ppm. In addition, the NMR signal for the β-pyrrolic protons exhibited an upfield shift from ~5.9 to ~5.5 ppm. These shifts are consistent with previous binding studies involving octamethylcalix[4]pyrrole.[34] Thus, the NMR data were taken as initial evidence for the presence of H-bonding interactions between the pyrrole moieties of the calix[4]pyrrole receptor and the monoanionic species.

Next, using an experimental protocol analogous to that described above, **4** was treated with several dianionic species of interest, viz. tris(TBA) hydrogen pyrophosphate
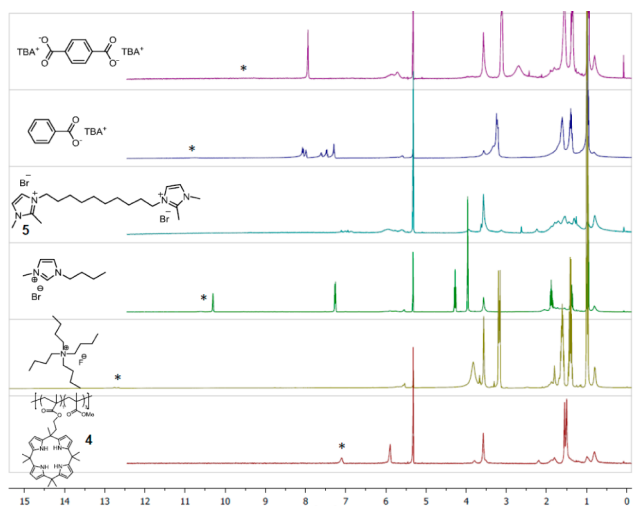

Figure 1. ^{1}H NMR spectra of **4** in CD$_2$Cl$_2$ recorded before and after addition of TBA fluoride, 1-butyl-3-methylimidazolium bromide, bis(imidazolium) dibromide **5**, TBA benzoate, and bis(TBA) terephthalate. All ionic species were added as 0.1 M solutions in CD$_2$Cl$_2$.

((TBA)$_3$HP$_2$O$_7$), bis(TBA) terephthalate ((TBA)$_2$TPA, a model dicarboxylate), and the bis(imidazolium) dibromide **5** shown in Figure 1.[35] Again, distinct shifts in the ^{1}H NMR features ascribable to **4**, observed upon addition of the dianionic species, were taken as evidence for H-bond-mediated anion binding.

With the above predictive studies complete, we sought to determine whether the inferred anion/polymer interactions could be used to induce control over the bulk material properties of **4**. Toward this end, an Ubbelohde tube viscometer was used to monitor the changes, if any, in viscosity upon exposure to mono- and dianionic species. For these studies, solutions of **4** (25 mg/mL in dry CHCl$_3$) were separated into two fractions: (A) containing only polymer and (B) with **4** and 10 equiv of a TBA salt (with the stoichiometry based on the number of calix[4]-pyrrole repeat units in **4**). Fraction B was then titrated into Fraction A. The kinematic viscosity, measured prior to the first addition and after each additional aliquot, was converted to specific viscosity, and the log of specific viscosity was subsequently plotted against the log of the salt concentration. From these plots, the critical cross-linking concentrations (determined from the observed inflection point in the slope) upon exposure of **4** to (TBA)$_3$HP$_2$O$_7$, (TBA)$_2$TPA, and **5** were determined to be 0.02, 0.025, and 0.01 M, respectively (Figure 2). (TBA)$_2$TPA resulted in the largest observable induced cross-
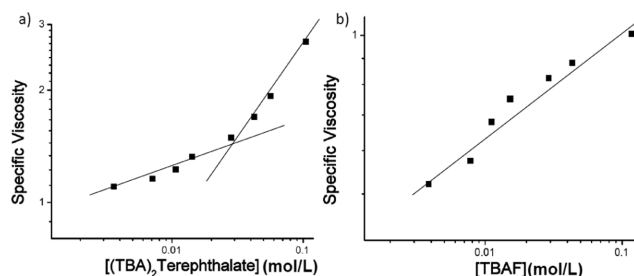

Figure 2. Double logarithmic plots of specific viscosity vs salt concentration for CHCl$_3$ solutions of copolymer **4** titrated with increasing concentrations of (a) (TBA)$_2$TPA and (b) TBAF. Note the change in slope of (a) from 0.15 to 0.93 at the critical cross-linking concentration, 0.02 M.

linking, as inferred from these measurements. Specifically, a change in slope from 0.15 to 0.93 was observed, consistent with polymer entanglement induced by the bisanion. In contrast, a control study with monoanion TBAF exhibited no significant change in slope (0.16) as the number of equivalents of fluoride was increased. Based on these observations, we suggest that the differing behavior seen with monoanions vs dianions reflects not only binding of the dianion to **4** in chloroform solution but also the fact that binding of an appropriately selected bis-anionic substrate gives rise to changes in viscosity as the result of supramolecular polymer cross-linking under the conditions of the experiment.

Enhanced cross-linking induced by the terephthalate and pyrophosphate salts, as compared to the bisimidazolium dibromide salt, can be rationalized on the basis of previous binding studies conducted with octamethylcalix[4]pyrrole and the benzoate, phosphate, and bromide anions (as their TBA salts). In those studies, benzoate was found to display a higher affinity than bromide ($K_a = 1.4 \times 10^5$ vs 3.4×10^3 M^{-1}, respectively), as determined by isothermal calorimetry measurements carried out in acetonitrile.[34] Likewise, as inferred from early ^{1}H NMR analyses, calix[4]pyrrole binds the dihydrogen phosphate anion more strongly than the bromide anion ($K_a = 97$ vs 10 M^{-1} in CD_2Cl_2 as the TBA salts, respectively).[36]

To investigate further how (if at all) supramolecular cross-linking influences the solid-state properties (i.e., the loss and storage moduli and the tan delta) of **4**, films of **4** were cast in the absence and presence of dianionic salts. While **4** could be cast from 1,2-dichloroethane or chloroform solutions, the resulting films were brittle and lacked mechanical robustness. However, when the polymer was combined with salts in a chloroform solution, the drop-cast films were viscoelastic.

The properties of the solid-state polymers were investigated by DMA. Specifically, we studied the storage and loss moduli, as well as the tan delta, of pure **4**, pure PMMA, and composites of **4** with various salts using a dual-cantilever setup and ramping the temperature from −80 to 150 °C while keeping the frequency constant (Figures S8−S13). Notably, **4** and the PMMA samples did not exhibit substantial thermal features, as gleaned from the plot of the loss modulus vs temperature. In contrast, composites of **4** with $(TBA)_3HP_2O_7$, $TBAH_2PO_4$, $(TBA)_2TPA$, and TBAF exhibited β-transitions at −17.7 °C, −57.3 and 13.6 °C, −43.8 and 10.5 °C, and −44.5 °C, respectively. Furthermore, a shift in the glass transition temperature (T_g) was observed for all four salt composites at 56.5, 80.5, 84.3, and 52.9 °C, respectively (cf. Figure 3). These results reflect a clear change in the ordering and crystallinity of the polymers in the presence of appropriately chosen anions, a result we interpret in terms of specific polymer/anion interactions.

In purely operational terms, it is important to note that the polymer/anion composites were more flexible and produced more malleable films than those derived from the pure copolymer **4**. We attribute this observation to two competing factors: (1) the large, flexible TBA cations disrupt the packing of the polymer chains, which leads to lower crystallinity and, as a result, more flexible films; and (2) the anion binding of the bisanions to the calix[4]pyrrole units counteracts the disruptive force of the large cations by bringing the polymer chains together. As inferred from the viscosity studies (cf. Figure S1), the most effective dianion was $(TBA)_2TPA$, as it gave the copolymer/salt system with the highest T_g. Similarly, the use of $(TBA)_3HP_2O_7$ led to cross-linking and gave rise to a distinctly lowered T_g (changes in T_g were confirmed independently using differential scanning
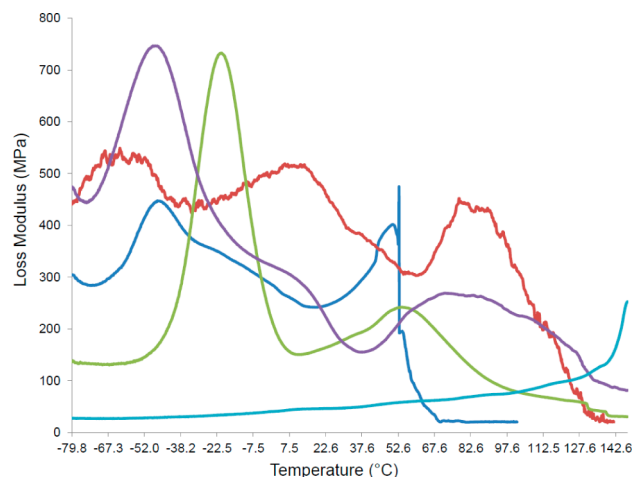

Figure 3. Plots of loss modulus as a function of temperature from −80 to 150 °C for copolymer **4** (light blue), **4** + $(TBA)_2TPA$ (purple), **4** + $(TBA)_3HP_2O_7$ (green), **4** + $TBAH_2PO_4$ (red), and **4** + TBAF (dark blue). Note the glass transition temperatures of the polymer/salt composites at 84.3, 56.5, 80.5, and 52.9 °C, respectively.

calorimetry; see the Supporting Information). In contrast, the monoanions tested did not induce cross-linking in the viscosity studies. They also resulted in materials that adopted relatively disordered morphologies in the solid state. Presumably, this reflects the fact that, in this case, it was the large cations that dominated the observed physical properties.

The effects of anion addition to **4** were also apparent under conditions of bulk analysis. For instance, when **4** (40 mg) was dissolved in a minimum quantity of CH_2Cl_2, the free-flowing solution gelled upon the addition of $(TBA)_2TPA$ (15 mg), a process that was found to be reversible. For example, the addition of a competitive monoanion (i.e., TBAF) to the gel led to its breakup (cf. Figure 4). Similarly, heating the gel system also led to
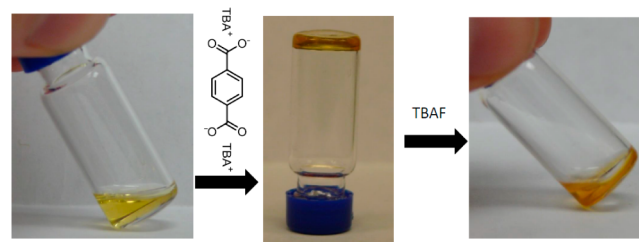

Figure 4. Photographs of (left to right) 40 mg of **4** dissolved in CH_2Cl_2 (0.15 mL), gel formed after addition of $(TBA)_2TPA$ (15 mg), and breakup of the gel after addition of excess TBAF.

a disruption in gelation (cf. Figure S14). The de-gelling phenomenon was ascribed to competitive binding of the fluoride anion to the calix[4]pyrrole sites and hence a severing of the dianion-induced supramolecular polymer cross-linking process.

The above findings led us to propose that **4** could be applied to the extraction and separation of dianions from aqueous environments. To test this possibility, we mixed a solution of **4** in CH_2Cl_2 with an aqueous solution of $(TBA)_2TPA$. After 12 h, the organic layer underwent gelation, which was ascribed to extraction of the dianion from the water layer and subsequent cross-linking of **4** (see Figure S15). The two layers were then separated by decanting the aqueous layer and collecting the organic gel via filtration. The presence of the dianion in the gel

was later confirmed by removing the excess solvent and analyzing the resulting material by ^{1}H NMR spectroscopg.

Analogous studies carried out with $(TBA)_3HP_2O_7$ also facilitated extraction followed by gelation. However, in this case, the gelation process took considerably longer (3 days). Likewise, **4** showed a lower extraction efficiency for $(TBA)_3HP_2O_7$ (10%) than for $(TBA)_2TPA$ (13%) (cf. Table S1). This trend is in accord with the Hofmeister bias, as terephthalate is more hydrophobic than pyrophosphate.

In summary, we have synthesized a copolymer of methyl methacrylate and calix[4]pyrrole through controlled RAFT methods and demonstrated that this material undergoes cross-linking upon the addition of appropriately chosen dianions. DMA studies of the polymer/salt composite films revealed changes in the structural ordering of the copolymer as a result of interactions with the dianions. Moreover, gel-like materials were obtained by dissolving copolymer **4** in a minimum amount of CH_2Cl_2 and then adding $(TBA)_2TPA$. Gel formation was reversed by adding TBAF (a source of a competitive monoanion) and/or applying heat. This ability to form gels allows for extraction and separation of dianions from aqueous media under conditions of liquid/liquid extraction. Taken in concert, the present findings lead us to suggest that anion-induced cross-linking may be used to influence the physical and material properties of polymeric species and to produce materials that have potential utility in recognition and selective separation of a broad range of dianions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
bielawski@cm.utexas.edu; sessler@cm.utexas.edu
Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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