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π -Conjugated Polyelectrolyte Ionic Assemblies with Self-Chaperoning Bolaamphiphiles
Nagarjuna Gavvalapalli, Department of Chemistry, Institute for Soft Matter Synthesis and Metrology,
Georgetown University

Research Impact: The Gavvalapalli research group has been working on developing π -conjugated polymers that are stretchable as well as self-healable for bioelectronics applications, including e-skin, artificial retinas, and soft robotics. π -Conjugated polymers inherently exhibit higher modulus, which limits their stretchable and self-healable nature. Moreover, the π -conjugated polymers, which already have high modulus, should be crosslinked with dynamic bonds to impart inherent self-healing capability to the polymers; the crosslinking may further increase the modulus of the polymer. This is one of the main reasons why reports on inherently self-healable π -conjugated polymers are scarce.

We proposed to use ionic crosslinking of π -conjugated polymers as a simple strategy to generate stretchable and self-healable π -conjugated polymer ionic networks (π -PINs). We have chosen ionic interactions because their interaction strength and network reversibility are controllable and tunable, which is necessary to control the mechanical and self-healable properties of the network. Thus, we have systematically varied the polymer and crosslinker ionic-head-group sizes and studied their effect on the network morphology, assembly, and thermal and optical properties. Since the dynamic properties of the network depend strongly on the charged ionic centers and less on the nature of the polymer repeat unit, this strategy is widely applicable to a plethora of π -conjugated polymers.

Results discussion: We have shown that poly [3-(6-carboxyhexyl)thiophene-2,5-diyl] (PTCOOH) generates ionic networks upon reacting with diamines in dimethylacetamide solvent (*Macromolecules*, **2017**, *50*, 7577). A proton transfer from the carboxylic acid of the PTCOOH to the amine generates a carboxylate polyanion and an ammonium dication crosslinker, thereby resulting in ionically crosslinked networks. The ionic interaction strength and hence the network strength is controlled by varying the alkyl group substituents length/size on the difunctional 2° and 3° amines. Lean amines generated insoluble networks, bulky amines resulted in soluble complexes, and intermediate amines generated gels. The storage modulus showed a clear dependence on the crosslinker ionic head group size and increased as the size of the ionic head group reduced. The G' and G'' values are reversible at the low and high strains for more than 5 cycles, thereby confirming that the proposed π -PINs are reversible and thixotropic. The low-angle and powder XRD spectra of all the dried π -PINs indicated lamellar assembly but with a higher d-spacing (Δd spacing = 0.4 nm) than the PTCOOH. The additional ~0.4 nm spacing corresponds to the amine crosslinker that is tilted between the polymer layers. Thus, the ionic crosslinking of the PTCOOH generates π -PINs with a lamellar assembly, which is advantageous for charge transport and hence the electronic applications.

Self-healing ability of the ionic networks generated above is determined by creating small cracks on ionic network thinfilms casted onto a glass slide. These films are slowly heated to higher temperatures (up to 80 °C) under optical microscopy to monitor the crack healing capability of the PINs. Unfortunately, none of the ionic networks showed self-healing capability. The networks showed reversible gel to sol transition but in the case of films the reversible nature of the network alone was not sufficient to generate self-healable networks. High glass transition temperature (T_g) of the π -PINs could be the main reason for the absence of self-healing capability.

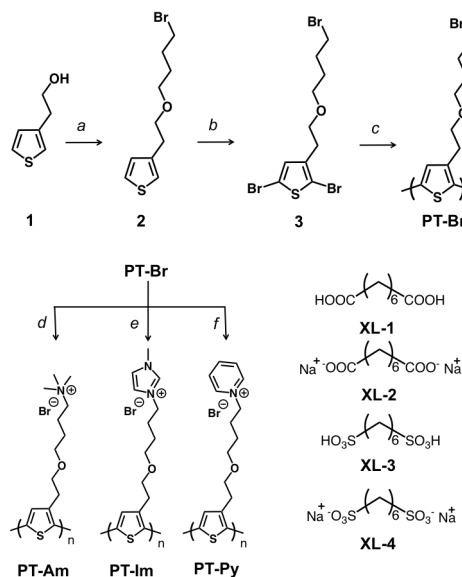


Figure 1: (top) Synthesis of three cationic polythiophene polymers; (bottom right) crosslinkers used for generating ionic networks of cationic polythiophene polymers.

Reaction conditions: a) i) NaH, THF, 0 °C, ii) dibromobutane, 2 days, 65 °C; b) NBS, DMF, rt; c) i) *t*BuMgCl, THF; ii) Ni(dppp)Cl₂; d) trimethylamine, DMF, MeOH, 40 °C; e) 1-methylimidazole, DMF, 70 °C; f) Pyridine, MeOH, 50 °C.

To reduce the T_g of the ionic networks we have followed two approaches: i) reducing the ionic interaction strength; and ii) using ionic crosslinkers that also act as additives and reduce T_g . To further reduce the ionic interaction strength, three polythiophene (PT) based pi-conjugated polymers containing different cationic groups (PT-Am, PT-Im and PT-Py) are synthesized (Figure 1). These polymers are generated from a precursor PT-Br polymer, which was synthesized from dibromothiophene ethanol in four steps as shown in Figure 1. The precursor polymer was reacted with trimethylamine, imidazole and pyridine to generate three ammonium polymers. These polymers are reacted with four different crosslinkers alkyldicarboxylic acid, alkyldisulfonic acid and the corresponding sodium salts. The PT-Am polymer with alkyldisulfonic acid resulted in a gel after few days and rest of the samples resulted in soluble ionic complexes (Table 1). These results clearly indicate that the ammonium ionic head groups generate weaker ionic complexes than the polythiophene carboxylate complexes. All the ionic complexes showed a shift in the UV-vis absorption maximum compared to the polymer alone indicating that the complexation has occurred.

Polymer	XL-1	XL-2	XL-3	XL-4
PT-Am	Homogenous complex	Homogenous complex	Gel	Homogenous complex
PT-Im	Homogenous complex	Homogenous complex	Homogenous complex	Homogenous complex
PT-Py	Homogenous complex	Homogenous complex	Homogenous complex	Homogenous complex

Table 1: Morphology of ionic networks of crosslinked cationic polymers.

The soluble complexes were precipitated in a bad solvent (diethyl ether or acetone) and the resultant samples were characterized using ATR-IR, TGA, and DSC. For alkyldicarboxylic acid and the corresponding sodium salt the trend in thermal transition is PTPy > PTIm > PTAm. Whereas for the alkyldisulfonic acid and the corresponding sodium salt the trend in thermal transition is PTAm > PTIm > PTPy. A higher thermal transition indicates stronger ionic interactions within the networks. Therefore by varying the ionic head groups the ionic interaction strength can be varied dramatically.

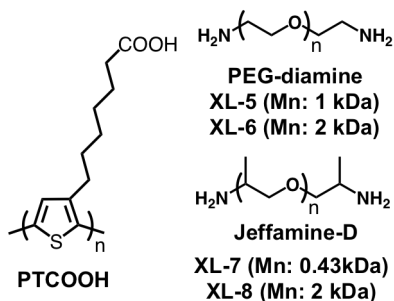


Figure 2: Chemical structures of PTCOOH and polyetheramine crosslinkers used in this study.

In order to further reduce the glass transition temperature, PTCOOH was complexed with PEG-diamine (MW: 1.0 kDa and 2.0 kDa) and Jeffamine-D (MW: 0.43 kDa, and 2.0 kDa) (Figure 2). These polyetheramines (PEAs) not only act as ionic crosslinkers but also as additives and reduce the T_g of the network. Ionic network morphology showed dependency on the PEA molecular weight. High molecular weight PEAs generated viscous homogeneous complexes whereas the low molecular weight PEAs generated gels. Higher weight percentage of high molecular weight PEAs resulted in weak complexes. Thus, varying the PEA molecular weight is another strategy to controlling the ionic network strength and therefore the T_g of the network. Interestingly, the T_g of these ionic networks is lower than the polythiophene ammonium based networks discussed above. The lower T_g values are expected to reduce the network modulus and therefore enhance the self-healing

capability. The mechanical and self-healing properties of all the networks are currently being investigated.

During the first term of the funding period, Prof. Nagarjuna Gavvalapalli presented 5 seminars at various institutes and conferences. All of those presentations included results from this work. A graduate student from the PI's research group presented this work at the ionic liquids Gordon Research Conference. This work helped one postdoctoral scholar, one grad student, and a visiting scholar to gain experience in small molecule and polymer synthesis, and their characterization. The postdoctoral scholar and grad student also learned various characterization techniques that are required for this work.

Polymer	XL-5	XL-6	XL-7	XL-8
PTCOOH	Gel	Viscous homogenous complex	Gel	Viscous homogenous complex

Table 2: Morphology of PTCOOH ionically crosslinked with polyetheramines.