Synthesis of Dumbbell-Shaped Triblock Structures Containing Ferroelectric Polymers and Oligoanilines with High Dielectric Constants

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Electroactive polymers (EAP) that change shape in response to electric stimulation have emerged as highly promising candidates for advanced electromechanical applications, including transducers, actuators, sensors, artificial muscles, and microfluidic systems.[1] Poly(vinylidene fluoride) (PVDF) based ferroelectric polymers are a class of field-activated EAPs that possess a fast response time (typically on the order of milliseconds or below) and can be operated in air with no major constraints.[2] The electromechanical strain of the ferroelectric polymers is composed of the electrostatic force from the electrodes and the electrostrictive stress originating from the conformation changes in the polymer chains under an electric field.[3] Recent works have shown that this class of polymers can deliver large strain (~10%) and high elastic energy density (~1 J/cm^3), far above those from the conventional piezoelectric ceramics whose strains are typically less than 0.5% and elastic energy densities are below 0.1 J/cm^3.[4,5] However, the current field-driven EAPs usually require high electric fields (>100 MV/m) to realize a large electromechanical response, which severely limits their applications, especially in biomedical devices.

The required high operation field in the field-driven EAPs is a direct result of the low dielectric constant of the polymers. An important parameter for characterizing the electromechanical response of the materials is the electromechanical conversion efficiency, k, which is defined as[1b]

$$k^2 = \frac{\text{mechanical (electrical) energy converted into electrical (mechanical) energy}}{\text{input mechanical (electrical) energy}} \qquad (1)$$

For field-type EAPs that are usually assumed to be linear dielectric and elastic materials, k^2 is proportional to $K\varepsilon_0E^2/Y$, where K is the dielectric constant, ε_0 is the vacuum permittivity, E is the applied electric field, and Y is Young's modulus.[1b] The dielectric constant K of most polymers is rather low (<10) compared to those of piezoceramics which can reach more than thousands.[6] Consequently, a high field is required to make up for the low dielectric constant and to achieve high electromechanical efficiency. The composite approach where ceramic or metallic nanoparticles are doped into the polymer matrix has been developed to enhance the dielectric constant of the polymers.[7] However, high volume fractions of the inorganic dopants are generally needed for an appreciable increase in the dielectric constants of the resulting composites.[8] This would deteriorate the mechanical properties of the EAPs and result in loss of many attractive properties and characteristics including fracture tolerance and pliability. More recently, π-conjugated polymers have been utilized as the conductive fillers to improve the dielectric constants and electromechanical properties of the ferroelectric polymers while maintaining the flexibility of the polymer matrix.[9] The delocalized electrons from the conjugated π-bonds give rise to high interfacial polarization (Maxwell–Wagner effect) and large dielectric responses.[10] It has been shown that a strain of 1.5% can be induced under a field of 9.5 MV/m in a composite containing 23 vol % polyaniline, an 8-fold reduction in the field required for the same strain compared with the pristine polymer.[11] Nevertheless, this approach is plagued by difficulties in preparing the blends with uniform filler dispersion in these fluorinated polymers. The agglomeration of the conductive fillers and inevitable formation of voids lead to conduction loss and dielectric failure at much lower fields than the intrinsic breakdown field. In this Communication, we report the synthesis and characterization of monolithic dumbbell-shaped block structures with oligoanilines covalently grafted at the chain ends of the ferroelectric poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) [P(VDF–CTFE)].

In light of its remarkably similar electronic and optical properties to those of polyaniline,[12] octaaniline, as a model compound of polyaniline, was incorporated into the ferroelectric P(VDF–CTFE)-based block structures. The preparation of the amine-capped octaaniline is outlined in Scheme 1. Oxidative dimerization of 4-aminodiphenylamine and reduction with hydrazine smoothly afforded amine-terminated tetramer **2**.[13] The primary amine in tetramer **2** was first condensed with benzophenone to form an imine, and the secondary amine was subsequently protected by a *tert*-butoxycarbonyl (BOC) group.[14] The introduced BOC groups not only prevent oxidation of the phenylenediamine units but also confer excellent solubility of the oligomers in common organic solvents. Selective removal of the diphenylmethylene group on the primary amine in compound **3** was achieved by catalyzed hydrogenation to provide compound **4**. Compound **5** was synthesized from 4-aminodiphenylamine by protection of the primary amine groups, bromination, and then protection of the second amine as its *tert*-butyl carbamate derivative. Employing Buchwald's conditions,[15] a palladium-catalyzed aromatic C–N coupling between the bromide groups in compound **4** and the primary amines in compound **5** furnished the protected hexamer **6**. Iteration of the sequence of BOC protection of the secondary amines and imine cleavage gave the amine-capped hexamer **7**. The octamer **8** with an amine terminal group was conveniently obtained from a palladium-catalyzed amination of compounds **7** with **5**, followed by BOC protection and recovery of the primary amino groups.

To integrate the oligoanilines into the ferroelectric polymers, telechelic polymers containing complementary carboxylic acid groups at chain ends were prepared using an approach developed in our laboratory.[16] As shown in Scheme 2, esterfication of terephthaloyl chloride (**9**) and partial hydrolysis provided terephthalic acid mono-*tert*-butyl ester (**10**), which was readily transformed into the benzoyl chloride and was further subject to acylation with lithium peroxide to afford *tert*-butyl ester benzoyl peroxide (**11**). The functional peroxide **11** was subsequently utilized as a free-radical initiator in the copolymerization of VDF and CTFE. It has been demonstrated that the termination of the growing fluoroalkyl chain in radical polymerization is essentially governed by the radical coupling reaction.[17] Accordingly, the *tert*-butyl ester groups were successfully transferred from the initiator to the chain ends of the polymer after

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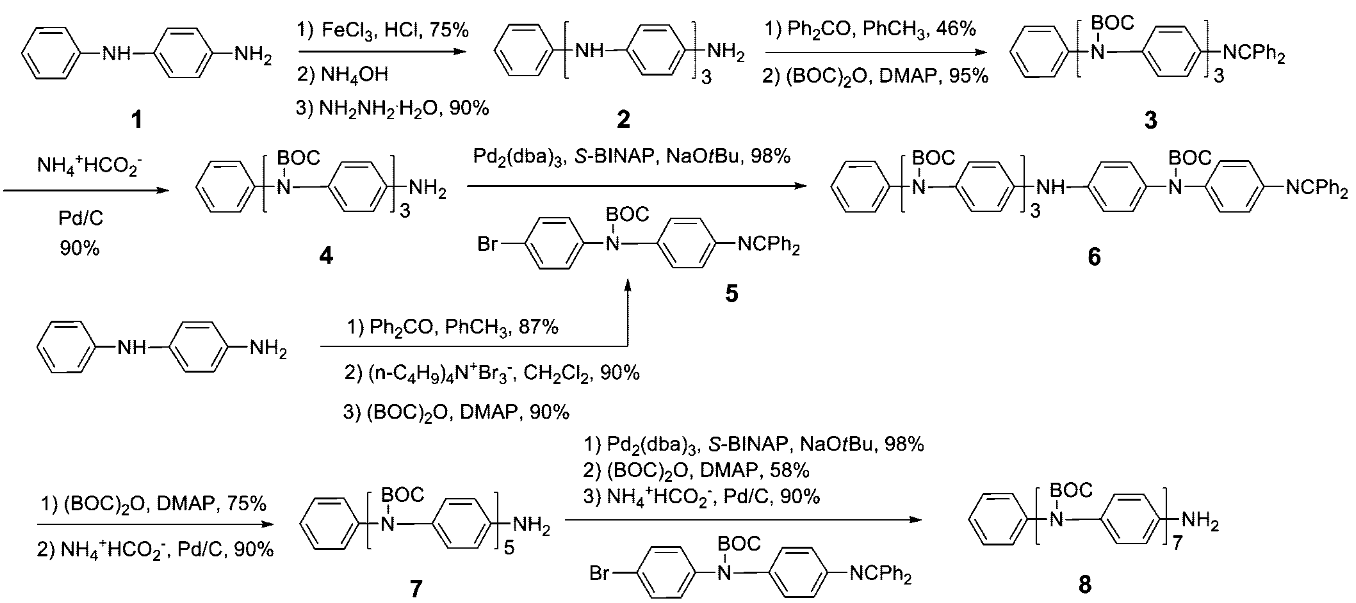
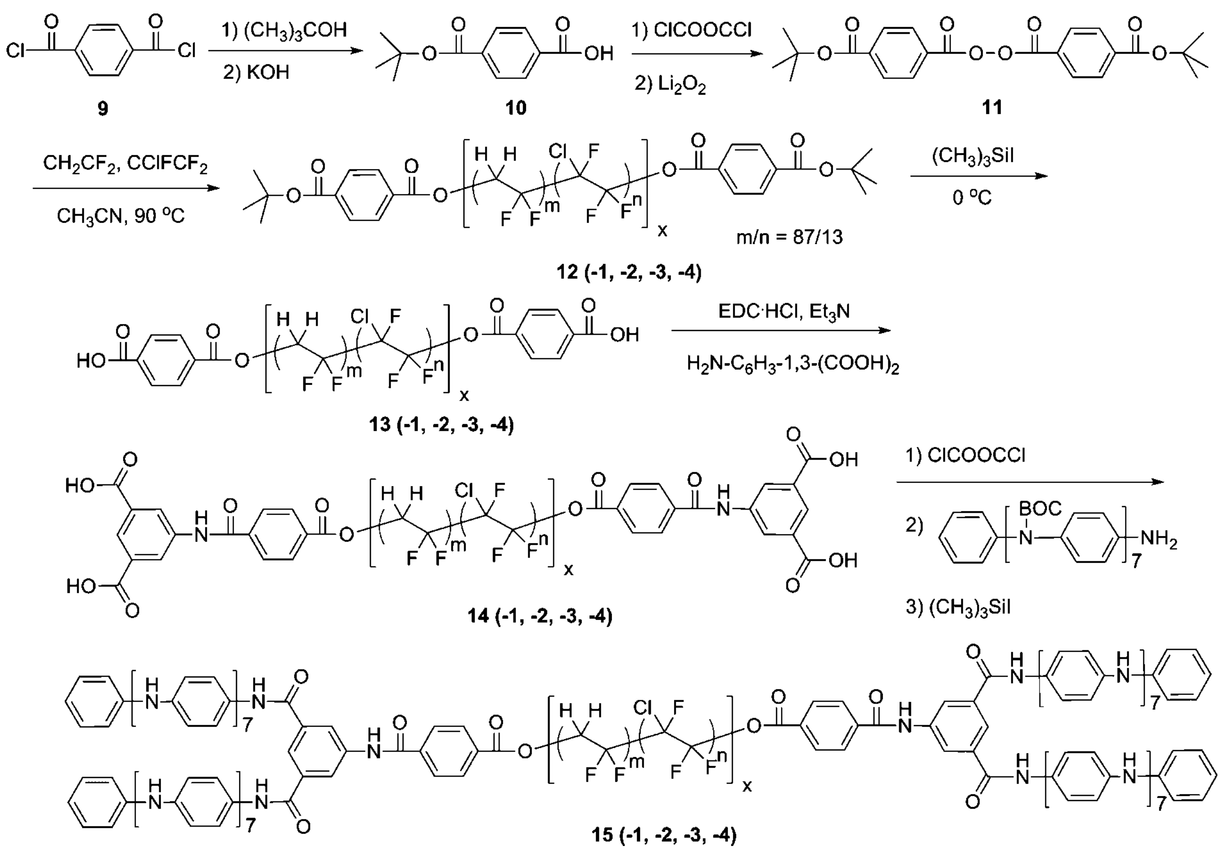
Scheme 1. Synthesis of Octaaniline with Amine Terminal Groups



Scheme 2. Synthesis of the P(VDF−CTFE)-Based Block Structures with Octaaniline at Chain Ends



the polymerization. The presence of *tert*-butyl ester terminal groups in polymer **12** was verified in the NMR spectrum (Figure S1, Supporting Information), and the average degree of functionality was found to be ~1.9, close to the theoretic value of 2.[16a] By varying the initiator concentration and polymerization time, polymers **12** with four different molecular weights were obtained. The gel permeation chromatography (GPC) measurement, using THF as the eluent and polystyrene as the standard, revealed number-average molecular weights of 59, 45, 32, and 17 kg/mol with polydispersity indexes ranging from 1.43 to 1.50 for polymers **12-1**, **12-2**, **12-3**, and **12-4**. Removal of the *tert*-butyl groups in polymers **12** was achieved upon treatment with iodotrimethylsilane, evidenced by complete disappearance of the peaks from *tert*-butyl protons at 1.58 ppm and the change from doublets to a singlet peak for the aromatic protons in the ^{1}H NMR spectra (Figure S2). With the purpose of increasing the concentration of oligoanilines in the ferroelectric polymers, polymers **13** reacted with 5-aminoisophthalic acid to provide polymers **14**, which is confirmed by the emergence of a signal at 10.8 ppm corresponding to the secondary amine in the ^{1}H NMR spectrum (Figure S3). The carboxylic acid groups in polymers **14** were further activated to acyl chloride followed

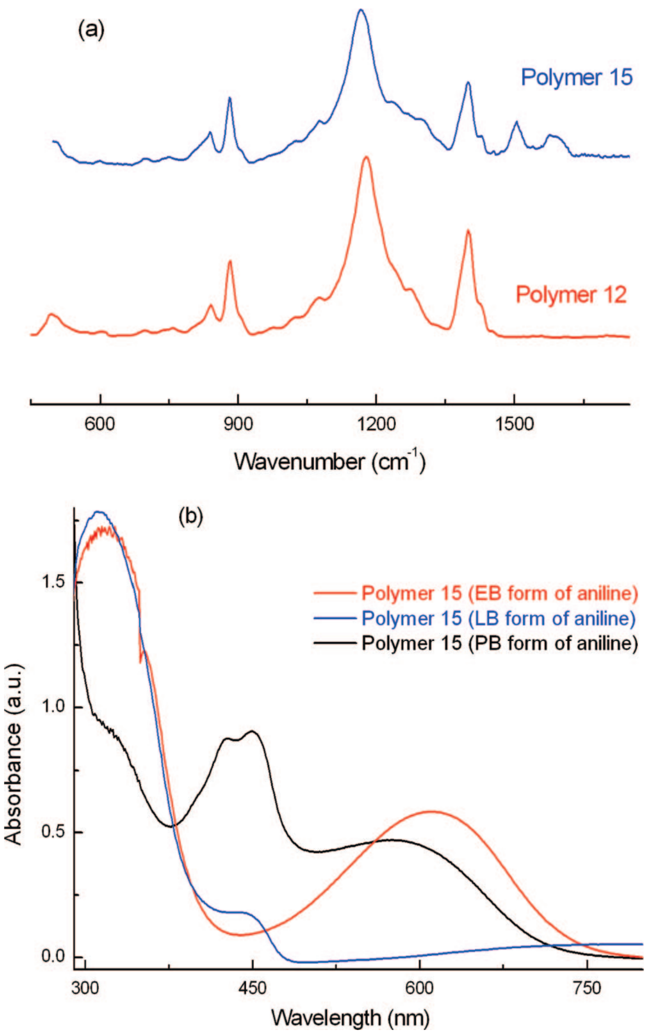


Figure 1. (a) FTIR spectra of polymers **12** and **15**. (b) UV/vis absorption spectra of polymer **15** containing oligoanilines with different oxidation states.

by amidation with amine-capped oligoanilines to furnish the dumbbell-shaped triblock structures **15**, where the BOC protecting groups in the oligoanilines were facilely removed in the presence of iodotrimethylsilane. The deprotection was verified by the appearance of the peak at 3390 cm^{-1} assigned to the N−H stretching of the diphenylamine moiety and the absence of carbonyl stretching resonance from *tert*-butyl carbamate groups at 1710 cm^{-1} in the FTIR spectra.

The block copolymers **15** show chemical shifts at 2.9 and 2.3 ppm associated with VDF unit with a head-to-tail (H−T) $(-CF_2-CH_2-CF_2-CH_2-)$ and a head-to-head (T−T) $(-CF_2-CH_2-CH_2-CF_2-)$ sequences, respectively, and a broad peak centered at 7 ppm attributed to oligoaniline segments in the ^{1}H NMR spectra (Figure S3). Although noticeable changes in the GPC traces from polymers **12** to **15** were not observed, polymers **15** display strong responses under both refractive index (RI) and UV/vis detectors, whereas polymers **12** show weak RI signals and are UV/vis inactive. The presence of oligoanilines in polymers **15** was further manifested by FTIR spectroscopy. In addition to the absorption bands from P(VDF−CTFE) at around 850 and 880 cm^{-1} (symmetric stretching and rocking modes of C−F), 1180 cm^{-1} (antisymmetric stretching of C−F), and 1400 cm^{-1} (bending and wagging modes of C−H), Figure 1a also displays the characteristics of aromatic chains in the oligoaniline at ca. 1590 and 1510 cm^{-1} originating from the typical benzenoid and quinoid ring stretching as well as broad bands at ca. 3300 cm^{-1} due to the vibration of N−H. The UV/vis spectrum (Figure 1b) of the block copolymers **15** containing the reduced leucoemeradine (LB) form of octaaniline in THF shows a prominent absorption peak at 315 nm associated with $\pi-\pi^*$ transition in the benzene unit and a shoulder band at 445 nm which is presumably due to the polaron transition.[15] The aniline octamers in block copolymers **15** can be easily oxidized to the emeraldine (EB) state upon exposure to air, resulting in a purple solution with a sharp peak a 320 nm and a broad absorption band at 620 nm. The first peak was attributed to the $\pi-\pi^*$ transition in the benzenoid ring, and the second one was ascribed to exciton-type transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring.[14] The aniline octamers in block copolymers **15** can be further oxidized by silver(II) oxide, which is evidenced by a blue shift of the excitonic transition from 620 to 450 nm. This strong blue shift indicates the decreased charge-transfer absorption in the pernigraniline (PB) form of the oligoanilines.[15] Differential scanning calorimetry (DSC) measurements were carried out to examine the thermal transitions of the block copolymers. The melting temperature and heat of fusion decrease from 91.5 °C and 13.8 J/g in P(VDF−CTFE) (**12-1**) to 82.2 °C and 11.8 J/g in the block copolymer **15-1**, respectively. This is in accordance with the shift of the crystallization temperature from 44.8 °C in P(VDF−CTFE) (**12-1**) to 36.4 °C in the block copolymer **15-1**, suggesting that the existence of oligoaniline segment hinders the crystallization of P(VDF−CTFE).

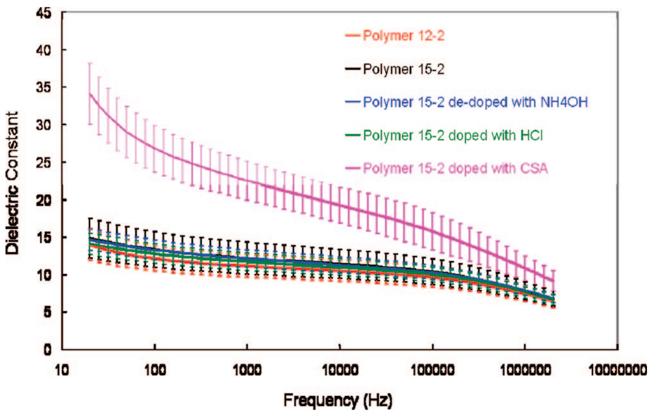


Figure 2. Dependence of the dielectric constant of the polymers on frequency at room temperature.

The dielectric properties of the polymers were characterized by an Agilent multifrequency LCR meter. Free-standing films of the block copolymers **15** were prepared by doping with NH_4OH, HCl, and camphorsulfonic acid (CSA) and casting from solution in DMF. Typical sample thicknesses were about 20 μm. Presented in Figure 2 is the dielectric constant of the polymers as a function of frequency measured at room temperature. Compared with the P(VDF−CTFE) (**12-2**), which has a dielectric constant of 12 at 1 kHz, the dielectric constant was raised to 23 in the block copolymer **15-2** doped with CSA. On the other hand, the dielectric constants of the NH_4OH and HCl doped block structures remain largely unchanged. This result is directly correlated with the significantly greater improvement in delocalized charge density and electrical conductivity of the CSA-doped polyanilines over those in the HCl-doped samples and electrical insulation of the polyanilines dedoped by NH_4OH.[18,19] Moreover, the CSA-treated polymer displays a notable decrease of dielectric constant with the increase of frequency, which indicates the existence of strong interfacial

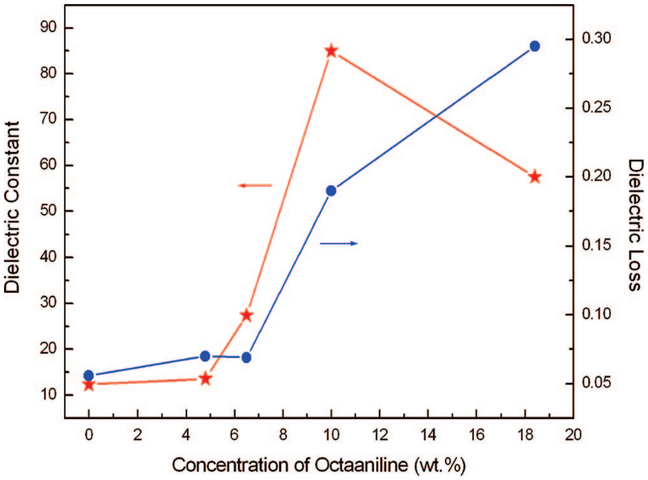


Figure 3. Evolution of the dielectric constant and loss measured at 1 kHz as a function of the octaaniline concentration at room temperature.

polarization.[20] A strong dependence of dielectric properties of the CSA-doped block copolymers **15** on the concentration of octaaniline is described in Figure 3. The weight percentages of aniline octamers in the copolymer **15** were estimated on the basis of the intensity ratios of the characteristic resonances assigned to the aromatic protons in octaanilines to those of methylene protons in P(VDF−CTFE) in the ^{1}H NMR spectra. The dielectric constant rapidly increases from 12 to 85 when the content of octaaniline reaches 10 wt %. A further increase of the octaaniline concentration results in a decreased dielectric constant, presumably reaching to the point of percolation for electron conduction. Meanwhile, the dielectric loss monotonically increases with the increase of the octaaniline content. The postulated percolation threshold at around 10 wt % for the CSA-doped triblock copolymers is close to the value (∼14 wt %) predicted for a perfectly random three-dimensional percolative system,[21] implying a homogeneous distribution of octaaniline segments in the P(VDF−CTFE) matrix.

In conclusion, we have successfully grafted octaanilines onto the chain ends of the ferroelectric P(VDF−CTFE). Covalent assembly of multiple electroactive components is expected to offer long-term stability, improved electrical strength, and synthetic tailorability and control. The prepared dumbbell-shaped block structures have demonstrated a large enhancement in the dielectric constants in comparison to the neat ferroelectric polymers and a strong frequency dependence of the dielectric properties associated with the interfacial polarization.

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Supporting Information Available: Experimental details for the synthesis and characterization. This material is available free of charge via the Internet at http://pub.acs.org.

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