

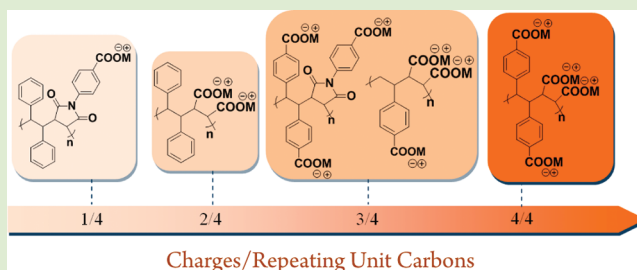
Sterically Crowded Anionic Polyelectrolytes with Tunable Charge Densities Based on Stilbene-Containing Copolymers

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Supporting Information

ABSTRACT: Anionic polyelectrolytes with various charge densities and a well-defined chain architecture have great industrial and fundamental importance. In this article, we describe the synthesis and characterization of new sterically crowded conformationally constrained anionic polyelectrolytes with tunable charge densities based on highly functionalized stilbene-maleic anhydride/maleimide comonomers. Polyelectrolyte precursors with *tert*-butyl carboxylate protecting groups are first prepared by radical polymerization and readily characterized by ^1H NMR, SEC, TGA, and DSC without the complications normally arising with charged macromolecules. The precursors are converted into their corresponding deblocked forms by simply reacting with trifluoroacetic acid to deprotect the *tert*-butyl group and then neutralized in basic aqueous solutions to yield anionic polyelectrolytes.



Polyelectrolytes, a group of polymers containing a high level of ionizable groups, exhibit electrostatic interactions and find applications in industrial processes and daily life, such as drug delivery,^{1–3} wastewater purification,⁴ surface modification for improved adhesion,⁵ and ionic conducting materials.⁶ Their properties depend on many variables, such as the nature of functionalities on the polymer backbone, charge densities along the polymer chain, and the backbone's intrinsic properties such as stiffness. Bowman et al. studied the complex formation between negatively charged polyelectrolytes and a net negatively charged polyampholyte due to the polarization-induced attraction.⁷ They concluded that the greater charge density of negatively charged polyelectrolytes increased the complex stability in solutions. It was reported by Arys et al. that with an “appropriate polyanion” a lyotropic ionene could form structured coatings.^{8–10} Later Koetse and co-workers studied cellulose sulfates as polyanions and found out the charge density of polyanions had a profound influence on coating properties, like the thickness and optical density.¹¹ A study of the impact of the charge density and hydrophobicity of polyanions on the stability of polyanion–protein complexes was carried out by Sedlak et al.¹² It was suggested that the charge density played a minor role on destabilization of the protein, while the hydrophobicity of polyanions was more responsible for perturbation of the protein structure. Poly(styrene-*alt*-maleic anhydride) derivatives were found by Fang et al. to be 100 times more potent than conventional antiviral microbicides and were considered as a new class of polyanionic microbicides.¹³ The study of negatively charged polyelectrolytes with tunable charge densities and a well-defined chain architecture continues to generate considerably fundamental and technological interest.

In this paper we report a simple and effective approach for synthesizing anionic polyelectrolytes with various charge densities via the design and synthesis of sterically crowded polymer backbones based on functionalized stilbenes and maleic anhydride/functionalized maleimides. Analogous styrenic copolymers, for direct comparison to the stilbene structures, have also been prepared. This approach permits the preparation of new anionic polyelectrolytes with tunable charge densities and adds to the diversity of well-defined polyelectrolyte structures available for study, in Figure 1.

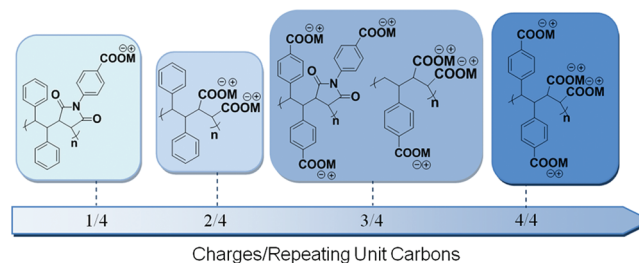


Figure 1. Polyelectrolytes with tunable charge densities.

Many reports on stilbene containing copolymers suggest that these copolymers have properties consistent with a nonflexible backbone.^{14–24} The pendant phenyl ring from stilbene unit can add potential rigidity into the polymer backbone due to its steric hindrance effect. In addition the rich chemistry available

Received: September 11, 2011

Accepted: December 27, 2011

Published: January 10, 2012

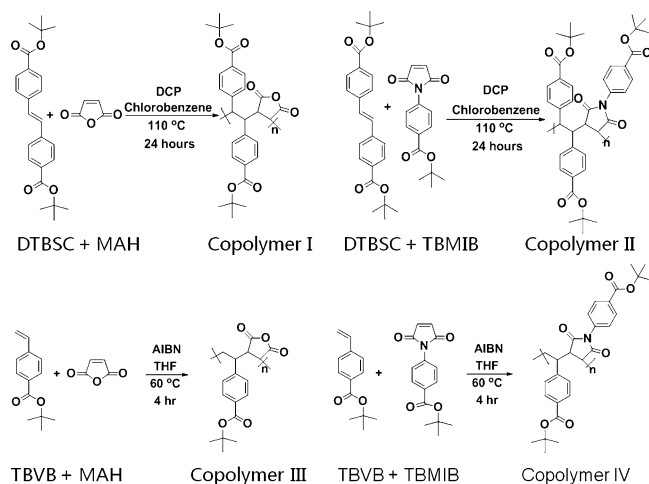
for stilbenes makes the preparation of a variety of functional stilbene derivatives possible, which opens up interesting families of new polyelectrolytes for study. Our previous studies showed that from the solid-state NMR torsional angle measurement maleic anhydride units of *N,N,N',N'*-tetraethyl-4,4'-diaminostilbene (TDAS) maleic anhydride (MAH) alternating copolymer were enchain in a predominately *cis* configuration causing a highly contoured chain.¹⁴ It was also observed that from DLS results the hydrodynamic radius (R_h) of this TDAS–MAH alternating copolymer did not change upon increasing temperature or introducing charges to the amino groups.¹⁵ In addition we observed that a block copolymer containing a polyampholyte based on TDAS–MAH comonomer and a poly(methoxy-capped oligo(ethylene glycol)methacrylate) block exhibited polyion complexes with unusual pH and salt responsive properties similar to like-charge attraction effects in rigid polyelectrolytes.¹⁶ It is our goal to take advantage of the rich stilbene chemistry and prepare and study new stilbene based polyelectrolytes. To avoid the problems in direct characterization of polyelectrolytes as to the determination of molecular weight, molecular weight distributions, and etc., a two-step blocked ionic group approach is taken as the synthetic strategy. Polyelectrolyte precursors are first prepared by radical polymerization due to its good tolerance to various functionalities.²⁵ The blocked polyelectrolyte precursors are then readily characterized by ¹H NMR, SEC, TGA, and DSC without the complications arising with charged macromolecules. The deprotection reactions are followed by neutralization in basic solution to obtain polyanions.²⁶ The advantage of this two-step blocked ionic group approach is that the charges of polyelectrolytes regularly positioned from carbon atoms of the polymer backbone are obtained by mild deblocking reaction. The functional groups along the polymer chain are easily converted to their charged analogous polyelectrolytes with defined molecular weight and molecular weight distribution. The copolymers based on functionalized stilbenes were prepared at 110 °C with dicumyl peroxide (DCP) as initiator and chlorobenzene as solvent while the copolymers based on functionalized styrene were prepared at 60 °C with AIBN as initiator and THF as solvent. These copolymerizations are shown in Scheme 1. All of the copolymerization experiments contained an equimolar ratio of

comonomers except for copolymerization of *tert*-butyl 4-vinyl benzoate (TBVB) with maleic anhydride (MAH) (TBVB:MAH = 1:2 mol/mol) in order to optimize the formation of the alternating copolymer because of TBVB's tendency to undergo homopolymerization. All of the copolymerizations were conducted for 24 h except for copolymerization of *tert*-butyl 4-vinyl benzoate (TBVB) with maleic anhydride (MAH) which was run for only 4 h to minimize any homopolymerization of TBVB. The initiator concentration was 1.0 wt % based on the monomers. The monomer concentration was 20 wt % based on the solution. The initiator and monomer concentrations may vary for different targeted molecular weight copolymers. For example, a mixture of (*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate (DTBSC) (3.80 g 10.00 mmol), MAH (0.98 g, 10.00 mmol), chlorobenzene (17.2 mL, 20 wt %), DCP (0.0478 g, 1.0 wt %) was sealed in a 50 mL, septum-sealed glass bottle equipped with a magnetic stirrer and was degassed by purging with argon for 20 min and polymerized for 24 h. Copolymers were recovered by precipitating into hexanes twice and then Soxhlet extracted with hexanes to remove the residual monomers and dried under vacuum at 60 °C overnight before characterization. Two peaks associated with the anhydride groups of the copolymers (1847 and 1777 cm^{-1}) were clearly observed in the IR spectrum (Figure S1, Supporting Information). The 1:1 structures of the copolymers were confirmed by the elemental analysis and TGA analysis. In TGA analysis, compositions of copolymers were identified by comparing a mass loss of isobutylene caused by the cleavage of thermally unstable *t*-butyl groups to the theoretical mass loss assuming the strictly alternating structure, shown in Figure S2, Supporting Information. The elemental analysis and TGA analysis results are shown in Table S1, Supporting Information, and in Table 1, respectively. For copolymer II, found nitrogen percentage in

Table 1. Calculated and Found Mass Loss of Copolymers I, II, III, and IV

	calculated isobutylene loss (%)	found isobutylene loss (%)
copolymer I	23.4	23.2
copolymer II	25.7	24.9
copolymer III	18.6	19.6
copolymer IV	23.4	22.0

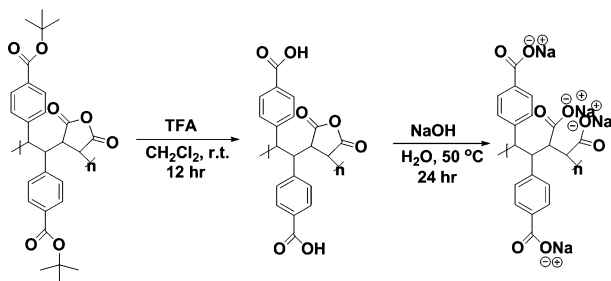
Scheme 1. Synthetic Scheme for Stilbene and Styrene Alternating Copolymers



the elemental analysis is a little higher than the theoretical percentage. This can be attributed to maleimide's tendency to form *tert*-butyl 4-maleimidobenzoate (TBMIB–TBMIB) sequences in the polymer backbone. For copolymer III, calculated isobutylene elimination is about 18.6% which is a little less than the found mass loss of 19.6%. This indicates that the styrene copolymer is not strictly alternating and its backbone may contain some TBVB–TBVB sequences.

tert-Butyl carboxylate protecting groups were deblocked from the copolymer backbones by reacting with trifluoroacetic acid (TFA) and then the resulting polymers with carboxylic acid groups and anhydride groups along the backbone were dissolved in NaOH solutions to form polyanions, shown in Scheme 2. For example, copolymer I (0.80 g, 3.34 mmol of *tert*-butyl carboxylate group) was mixed with TFA (0.84 g, 7.35 mmol) and CH_2Cl_2 (0.45 mL, 7.35 mmol) for 12 h at room temperature. The excess of TFA and CH_2Cl_2 were stripped off in a stream of argon and the polymer was dried in vacuum oven for 24 h at 60 °C. The resulting copolymer (0.61 g) was then

Scheme 2. Conversion of *tert*-Butyl Carboxylate Protecting Copolymer I into its Corresponding Poly-anion



readily dissolved in stoichiometric NaOH aqueous solution (0.27 g of NaOH) with pH = 10. The poly-anion solutions were frozen by immersion of sample vials in liquid nitrogen. The frozen samples were freeze-dried for 24 h on a Virtis lyophilizer. The conversion was confirmed by IR spectrum shown in Figure 2. After the cleavage of the *tert*-butyl ester groups, the

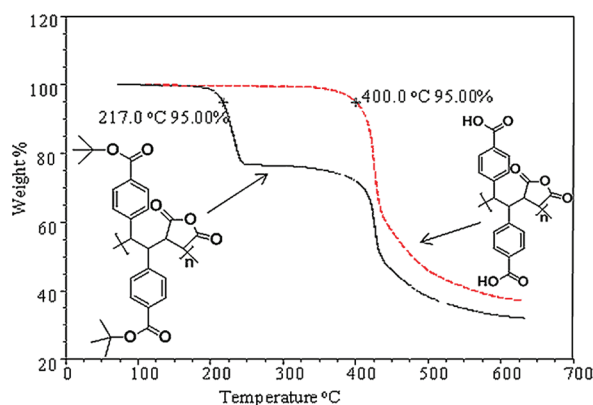


Figure 2. TGA curves for copolymer I. Solid line is for copolymer I; dashed line is for copolymer I after deblocking the *tert*-butyl groups.

anhydride groups remained intact. The adsorption peaks from the anhydride groups disappeared with the subsequent hydrolysis (Figure S1, Supporting Information).

The influence of the copolymerization conditions (i.e., solvent, initiator, reaction temperature) on the rate of copolymerization and molecular weight of copolymers was observed (Table S2, Supporting Information). Under condition A (chlorobenzene–DCP–110 °C), all the copolymers had 2–3 times higher yields than under condition B (THF–AIBN–60 °C). This may be partially due to DCP being more effective than AIBN as an initiator for the polymerization involving stilbene. This explanation is supported by Bevington et al. that stilbene is very reactive toward an oxygen-centered radical such as the benzoyloxy radical from benzoyl peroxide (BPO); and it remained unreactive toward carbon-centered radicals like 1-cyano-1-methylethyl radical derived from AIBN.^{27,28} An analogous experiment was carried out to synthesize copolymer I with BPO as the initiator at 70 °C and resulted in a 60% yield which is consistent with Bevington's hypothesis. It was also observed that the condition A resulted in higher molecular weights compared to the condition B for all three stilbene copolymers. This is probably because the steric hindrance in the transition state for cross propagation is overcome at higher temperature. It was concluded that condition A has a synergistic effect on stilbene copolymerization yields and the

corresponding molecular weights and thus is used in stilbene copolymerization as an optimized condition. The typical yields and molecular weight information of copolymers I, II, and III are shown in Table 2.

Table 2. Typical Yields and Molecular Weights of Copolymers under Optimized Copolymerization Conditions

	condition	reaction duration (h)	yield (%)	M_n (kg/mol)	M_w/M_n
copolymer I	A	24	85	28.6	1.87
copolymer II	A	24	77	7.00	1.68
copolymer III	B	4	65	17.7	1.54
copolymer IV	B	4	41	19.7	1.89

The aromatic hydrogen atoms and hydrogen atoms on the polymer backbone exhibited very broad peaks in the ¹H NMR spectrum which is consistent with the lack of mobility in the polymer chains (Figure S3, Supporting Information). This observation is consistent with previously reported functionalized stilbene copolymers.^{14–17} There was no glass transition temperature (T_g) or crystalline melting temperature (T_m) observed in DSC analysis for copolymer I, II, III, and IV under their corresponding degradation temperatures (Figure S4, Supporting Information). The cleavage of the *tert*-butyl groups occurs at around 200 °C as shown in Figure 2. After deprotection, the 5% weight loss degradation temperature was shifted to 400 °C. It is noted that T_g and T_m were still not observed in DSC curve after the cleavage, shown in Figure S4, Supporting Information. This is indicative of a structure with restricted chain motion, which is consistent with the extremely broad ¹H NMR results.

In summary, a new series of polyelectrolyte precursors with tunable charge densities were synthesized and characterized under optimized conditions with a two-step synthetic strategy. The steric crowding, arising from pendent phenyl groups along the polymer backbone, resulted in the broad peaks of ¹H NMR spectrum as well as the absence of thermal transitions below the elevated degradation temperature at around 400 °C. Polyelectrolyte precursors were then readily converted into their corresponding anionic new polyelectrolytes with new stilbene comonomers that have various types and amounts of ionic precursor groups. We are examining the steric crowding effect imparted to the chain by the stilbene comonomers by determination of persistence length and other solution measurements.²⁹ We anticipate that the synthetic versatility, provided by this strategy, will enable systematic variation of the type of ionic functionality with precisely placed charges with varying charge densities along the polymer backbone. These new polyelectrolytes could provide unique solution properties and other properties involved with polyion complexation.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section, synthesis schemes, IR, DSC and ¹H NMR spectra, and tables giving elemental analysis results and a comparison of yields and molecular weights. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the donors of the American Chemical Society Petroleum Research Fund, the National Science Foundation under Grant No. DMR-0905-231 and a teaching assistantship from the Department of Chemistry at Virginia Tech. We thank Professor Timothy Long's group and Professor Judy Riffle's group for the help on the SEC, TGA, and DSC measurements.

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