A review of semi-rigid, stilbene-containing alternating copolymers

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Abstract The synthesis and properties of sterically congested, stilbene-containing alternating copolymers are reviewed. Persistence lengths (2–6 nm) determined by size exclusion chromatography and small angle X-ray scattering techniques show that these are semi-rigid copolymers. Fully characterized polyanions and polyampholytes, prepared from organic-soluble precursors were studied, along with their respective salt and pH response behavior resulting from the semi-rigid polymer backbone. The solid-state characterization from these studies reveals a high degree of hindered rotation along the polymer backbone. The contorted structure and the hindered rotation of the polymer backbone generate inefficient chain packing, which leads to an increase of nanoporosity and higher surface areas. The semi-rigid stilbene-containing copolymers are a new class of copolymers where the increased polymer backbone rigidity leads to a wide range of polymer properties not attained with flexible polymers.

Keywords Stilbene · Alternating copolymers · Copolymerization · Maleic anhydride · Maleimides

Introduction

Substituted stilbenes (1,2-diphenylethylenes) are widely studied and used organic compounds for the optical properties arising from their conjugated ethylene structure, e.g. optical brighteners, dyes, etc. [1, 40]. Many applications of

stilbene derivatives have resulted in a large library of substituted stilbene small molecules and facile synthetic techniques to enable synthesis of a variety of derivatives many of which can serve as copolymerizable monomers. However, the addition polymerization and copolymerization of this family of 1,2-disubstituted olefins, like all 1,2-substituted ethylene structures, is difficult due to the steric constraints of the 1,2-structure. Homopolymerization of stilbene and substituted stilbenes to the corresponding poly (benzyl) backbone has not been achieved; however, alternating copolymerization of stilbene both anionically [48] and radically [44] is well documented. In alternating copolymerizations, the cross-propagation step is greatly favored since the steric interactions in the cross propagation step are depressed compared to those required for a successful self-propagation of the stilbene monomers. In addition the electronic effects resulting from electron rich and electron poor comonomers cross-propagating with an electron rich or electron poor terminal radical favor fast cross-propagation. Stilbene copolymers have been claimed in the patent literature to be useful in lubricants [37], lubricating oil additives [2, 31], thermal stability additives for photoresists [42], and improved stain resistant polyamide textiles [11], although successful commercialization of these potential applications is not known.

The radical alternating copolymerization of unsubstituted stilbene is the most studied stilbene polymerization [6, 16, 35]. It was found in 1930 that stilbene copolymerized with maleic anhydride [44]. Since neither monomer can undergo radical homopolymerization, these are strictly alternating copolymers with no stilbene–stilbene or maleic anhydride–maleic anhydride dyads present [21]. This study attracted many groups to study the comonomer reactivity ratios [21], monomer sequences [16], thermal stability [32], and copolymerization mechanism [9, 17, 34]. However,

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surprisingly limited solubilities and uninteresting brittle materials have slowed detailed investigations of the copolymerizations and the properties of the resulting copolymers [41].

N-substituted maleimides readily radically polymerize with stilbene into predominately alternating copolymer structures—maleimides can radically homopolymerize, so some maleimide–maleimide dyads can be present in these copolymers [19, 35, 46]. Many of these copolymers have limited solubilities in common organic solvents so solution studies are limited.

Our recent work involves the design and synthesis of new stilbene comonomers with specifically chosen functional groups for effecting the copolymerization with maleic anhydride or N-substituted maleimides. Radical polymerization processes are compatible with many functional groups [5] and the alternating nature of the copolymerization enables precise placement of functionality into the copolymer backbones for study of the structure/property relationships of these novel sterically congested backbone polymers in both solution and the solid state.

Monomer substituent effect on copolymerization

The type and position of substituents on the aromatic groups of stilbene were found to have a significant effect on both the overall copolymerization rates as well as the solubility of the copolymers [24]. Several methyl-substituted stilbene monomers were prepared by using the Wittig-Horner reaction and the resulting monomers were copolymerized with maleic anhydride. Feed ratio/composition studies and ^{13}C NMR confirmed the strictly

alternating sequences in the backbone [24]. The methyl-substitution increased the solubility of the copolymers in organic solvents by disrupting copolymer aggregation. This allowed for thorough characterization of these copolymers via SEC, NMR and DLS (dynamic light scattering). We note that with unsubstituted stilbene and maleic anhydride copolymers, strong aggregation in DLS was observed which likely accounts for the “insolubility” of these copolymers as reported in the literature. The location of the methyl groups on the phenyl rings was found to have a strong influence on the overall rate of copolymerization. Methyl groups in the para position led to increase copolymerization rates due to the inductively electron donating characteristics which lead to a more reactive stilbene radical to cross propagate with the electron deficient double bond of maleic anhydride. The ortho-methyl stilbene monomers were found to copolymerize at significantly slower rates due to the loss of conjugation of the aromatic groups with the radical due to steric interactions of the methyl groups forcing the phenyl groups out-of-plane (Fig. 1). DLS measurements showed that the para-substituted stilbene copolymers formed higher molecular weight aggregates in solution, where little aggregation was observed in the ortho substituted samples [24].

Strong electron donating groups, such as dialkyl amino substituents in the para position of stilbene showed extremely high copolymerization rates [29]. Unsymmetrical alkyl substituents on the stilbene comonomers were employed to obtain soluble copolymers. For all of the stilbene copolymers thermal analyses by DSC showed no observable T_g at temperatures $<250^\circ\text{C}$ [29].

With the goal of synthesizing a family of precisely functionalized polyanions, both styrene and stilbene

Fig. 1 Structures of organic-soluble, main-chain stilbene-containing copolymer precursors. **a** poly((*E*)-2-methylstilbene-*alt*-maleic anhydride) (2MeSti-*alt*-MAn) [24], **b** poly(*N,N,N',N'*-tetraalkyl-4,4'-diaminostilbene-*alt*-maleic anhydride) (TADASTi-*alt*-MAn) [29],

c poly((*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate-*alt*-maleic anhydride) (DTBCSti-*alt*-MAn) [22], and **d** poly((*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate-*alt*-*tert*-butyl 4-maleimidobenzoate) (DTBCSti-*alt*-TBCPMI) [22]

monomers were synthesized with *tert*-butyl ester groups in the para positions [22]. Higher temperatures were required to obtain efficient copolymerizations because of the electron withdrawing nature of the para ester groups. The use of the *tert*-butyl ester copolymers, as precursors to the polyanions, enabled the accurate determination of the molar mass and molar mass distributions by SEC avoiding the known SEC analysis problems of polyelectrolytes. The *tert*-butyl ester groups were found to cleanly thermally decompose as determined by the expected weight loss for extrusion of isobutylene in thermal gravimetric analyses [22]. For study of the polyanions, deprotection with trifluoroacetic acid followed by neutralization with base and dialysis yielded the pure, well-characterized polyanions. The solution properties of the precursor *tert*-butyl ester copolymers and the polyanions were studied in detail [23].

Polymer rigidity

The early investigation of main-chain stilbene copolymers suggested that they possessed characteristics consistent with rigid rod-like structures. This led to further investigation into the chain stiffness of the copolymer backbone [28–30]. When examining the ^1H NMR spectra of any of these copolymers, the backbone and aromatic peaks

appeared very broad [24]. When associated with rigid polymers and high molecular weight materials, broad peaks develop due to strong homonuclear dipolar couplings and slow ^1H relaxation rates [45]. With no observed T_g below 250 °C, evidence of hindered rotation and limited movement of the polymer backbone pointed to a more rigid polymer backbone with a sterically crowded configuration. In the case of poly (*N,N,N',N'*-tetraethyl-4,4'-diaminostilbene-*alt*-maleic anhydride) (TEDAS*ti-alt*-MAN), the copolymer backbone likely conformed into a contorted, sterically crowded conformation with the maleic anhydride units existing predominately in the *cis* configuration [28] (Fig. 1b).

To confirm the rigidity or chain stiffness of the stilbene alternating copolymers, SEC and SAXS were used to directly measure the chain stiffness (persistence length, l_p) [25]. Defined as a measure of chain stiffness or rigidity, persistence lengths provide a direct comparison of intrinsic polymer chain stiffness with other flexible and rigid polymers. (*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate and the styrene analog (*tert*-butyl 4-vinyl benzoate) were copolymerized with MAN and *tert*-butyl 4-maleimidobenzoate, respectively. This copolymer series was studied to investigate the effects of the added extra phenyl ring of stilbene monomer and cyclic monomer structure (MAN versus maleimide) on the persistence lengths [22, 25]. Based on

Fig. 2 A series of *tert*-butyl protected stilbene and styrene containing alternating copolymer precursors in order of increasing rigidity (increases left to right). **a** poly(*tert*-butyl 4-vinyl benzoate-*alt*-maleic anhydride) (CSty-*alt*-MAN), **b** poly((*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate-*alt*-

maleic anhydride) (DTBCSti-*alt*-MAN), **c** poly(*tert*-butyl 4-vinyl benzoate-*alt*-*tert*-butyl 4-maleimidobenzoate) (CSty-*alt*-TBCPMI) and **d** poly((*E*)-di-*tert*-butyl 4,4'-stilbenedicarboxylate-*alt*-*tert*-butyl 4-maleimidobenzoate) (DTBCSti-*alt*-TBCPMI) [25]

Fig. 3 Structures of carboxylated stilbene-containing polyanions: poly(stilbene-*alt*-maleic acid) (Sti-*alt*-MA), poly((4,4'-stilbenedicarboxylate)-*alt*-maleic acid) (DCSti-*alt*-MA), and poly((4-vinyl benzoic acid)-*alt*-maleic acid) (CSty-*alt*-MA) [23]

SEC and SAXS methods [3, 4, 38, 39], this copolymers series exhibited the persistence lengths between 2 and 6 nm. From this direct comparison and measurement, stilbene alternating copolymers are classified as semi-rigid polymers (Fig. 2). For example, a typical flexible copolymer, polystyrene, exhibits a persistence length of 0.9 nm [10] and a rigid copolymer, polyphenylene with sulfonate ester side groups exhibits a persistence length of 13 nm [14, 43]. Accordingly, the stilbene-containing copolymers appear 20 % more rigid than the styrene analogs and the maleimide-containing copolymers appear 50 % more rigid than MAn-containing copolymers of the same comonomer. The polymer physical properties that arise from these semi-rigid and sterically crowded copolymers involve unique solution and solid-state properties.

Solution properties

Using the same deprotection strategy above, a family of polyanion and polyampholyte copolymers were prepared with stilbene comonomers and the solution properties arising from the semi-rigid copolymer backbone were studied [22, 23, 30].

Polyanions

As mentioned above, carboxylated polyanions [22, 25] were synthesized from the deprotection of the precursor copolymers, and fully characterized with respect to molar mass, composition, and intrinsic polymer rigidity. Further physical aqueous solution properties evaluated using steady-state solution shear rheology, dynamic light scattering (DLS), and titration studies proved critical to understanding effects of polymer rigidity and conformation in aqueous solutions [23].

Using steady-state solution shear rheology, reduced viscosity plotted against polymer concentration revealed a

Fig. 4 Polyampholyte structure of poly(oligo-(ethylene glycol)methacrylate)-*b*-((*N,N,N',N'*-tetraethyl-4,4'-diaminostilbene)-*alt*-maleic acid)) (OEGMA-*b*-(TADASTi-*alt*-MA))) [30]

prominent polyelectrolyte effect in deionized water for DCSti-*alt*-MA, CSty-*alt*-MA, and Sti-*alt*-MA shown in Fig. 3 [23]. Increasing the sodium chloride (NaCl) concentration suppressed the polyelectrolyte effect by decreasing the Debye Length and electrostatic repulsions as the polymer concentration decreased. These results were consistent with semi-rigid polymers.

The statistical segment length (L_k) for each copolymer with or without NaCl was measured by adding the intrinsic statistical segment length (L_0) to the electrostatic statistical segment length (L_e) [7, 8, 47]. In deionized water, the carboxylated copolymers behaved like rigid-rods due to strong electrostatic repulsions and the statistical segment lengths decreased as NaCl concentration increased. Thus, the polyanions behaved like semi-rigid copolymers in NaCl solutions and followed the same rigidity trends established for the intrinsic statistical segment lengths above [25].

To further characterize the polymer properties in aqueous solutions, pH titration was used to evaluate the dissociation behavior of the polyanions. Titration results revealed multiple inflection points arising from the two vicinal carboxylic acid groups. Due to the close proximity of the diacids, each carboxylic acid has a distinct pKa and dissociates at different pH. This is consistent with poly(styrene-*alt*-maleic acid) (Sty-*alt*-MA) titration results [12].

Polyampholytes

The first stilbene-containing polyampholyte diblock copolymers were prepared using RAFT (reversible addition fragmentation chain transfer) polymerization techniques [30]. The diblock copolymer, poly(OEGMA-*b*-(TADASTi-*alt*-MA)), consisted of a polymerized methoxy-capped

Fig. 5 Structures of maleimide copolymers with stilbene and styrene analogs. **a** poly(styrene-*alt*-*N*-(2-methylphenyl) maleimide) (Sty-*alt*-2MePMI); **b** poly(stilbene-*alt*-*N*-phenyl maleimide) (Sti-*alt*-NPMI); **c** poly(stilbene-*alt*-*N*-(2-methylphenyl) maleimide) (Sti-*alt*-2MePMI) [27]

oligo-(ethylene glycol)methacrylate) (OEGMA) block chain extended with *N,N,N',N'*-tetraethyl-4,4'-diaminostilbene and MAN [30]. After molar mass determination in organic solvent, the block copolymer converted to its subsequent polyampholyte (Fig. 4) via simple acid hydrolysis. The resulting water-soluble polyampholyte ((OEGMA-*b*-(TADASTi-*alt*-MA))) formed polyion complexes (PICs) and exhibited a pH and salt responsiveness atypical of polyampholytes.

To evaluate the PIC aggregate response to pH and salt concentration, DLS was used to monitor the aggregate size. The aggregate size increased as the pH approached the isoelectric point (IEP) of the polyampholyte. For more flexible and non-flexible polyampholytes, as the pH neared the IEP, the copolymer chains expand as the electrostatic attractive forces decrease [13, 26]. Atypical for polyampholytes, adding NaCl to the [(OEGMA-*b*-(TADASTi-*alt*-MA))] copolymer solution increased the PIC size even as the electrostatic repulsions decrease. The “like-charge” attraction of the polymer chains causes polymer chains to aggregate and increase PIC size [15, 18, 20]. The semi-rigid polymer backbone of the TADASTi-*alt*-MA block facilitated dipole–dipole interactions of condensed counter-ions and induced the “like-charge” attraction [18, 20]. Ongoing work involves investigating the effects of charge density, molar mass, and linear, water-soluble homopolymer blocks [36].

Solid-state properties

Forming brittle films when cast from solution, the semi-rigid copolymers offer unique solid-state properties like birefringence and nanoporosity as a result of the sterically crowded copolymer backbones. Hindered rotations and inefficient chain packing of the copolymer backbone significantly affects and enhances the solid-state properties.

A series of methyl-substituted maleimide copolymers with stilbene and styrene analog films exhibited large negative birefringence up to 0.02 for Sti-*alt*-2MePMI (Fig. 5) [27]. During casting of the film, the ortho-methyl forced the phenyl groups to align normal to the imide

plane. Due to the anisotropy of the benzene ring, the alignment of the phenyl rings, and the restricted rotation induced a negative birefringence [33]. The same effect did not appear in Sti-*alt*-NPMI (Fig. 5b) without the ortho-methyl substituent; thus, the phenyl rings freely rotated. The less sterically crowded Sty-*alt*-2MePMI (Fig. 5a) showed a low negative birefringence of 0.002 which indicated that the sterically crowded polymer backbone influences the free rotation of the phenyl rings.

The nanoporous characteristics of the same series of *tert*-butyl carboxylate functionalized alternating copolymers using nitrogen adsorption/desorption isotherms and atomistic molecular simulations were studied (Fig. 2) [49]. These alternating copolymers showed a nanoporosity with Brunauer-Emmett-Teller (BET) surface area of 20–40 m²/g. This is likely due to the insufficient chain packing of these semi-rigid polymer chains and the increase in the internal free volume leads to an increased surface area. Also, as the chain rigidity increased, then the BET surface areas increased for this copolymer series [49].

Conclusions

This review highlights the synthesis and properties of sterically crowded stilbene-containing copolymers. The alternating copolymerization gives precise control over monomer sequence, which affords precise placement of functional groups along the polymer backbone. With precise control over monomer sequence, stilbene-containing alternating copolymers afford semi-rigid copolymers. Both the solution and solid-state properties confirm the semi-rigid nature of the backbone. Continued research on stilbene-containing copolymers and block copolymers is focused on new polymeric derivatives to explore the wide range of solid state and solution properties that result from the semi-rigid backbone characteristics.

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