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Synthesis and characterization of highly functionalized polymers based on N,N,N',N'-tetraalkyl-4,4′-diaminostilbene and maleic anhydride

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Abstract

Novel, highly functionalized rod-like copolymers have been synthesized by alternating copolymerization of N,N,N',N'-tetraalkyl-4,4′-diaminostilbenes (TDASs) with maleic anhydride. These unique copolymers have been characterized by SEC, DSC and TGA. The solubility of these copolymers in organic solvents is strongly dependent on the length of the alkyl chains on the amino groups and the solubility in aqueous media is pH dependent. Light scattering studies indicate that the conformation of the polymer backbone does not change upon increasing temperature or introducing charges to the amino groups. High chain rigidity is further corroborated by the high T_g of the polymers. There is no observed glass transition below 280 °C. The light scattering and thermal results are indicative of a rod-like backbone structure.

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1. Introduction

Synthetic macromolecules containing functional groups pendant to the polymer backbone enable an expanding number of important applications including drug delivery [1], waste water purification [2], stabilization of micro- and nanoparticles [3], surface modification for improved adhesion [4], etc. Because of the tolerance of free radical polymerization processes to functional groups, free radical polymerization is the most highly used process for preparing functional polymers. In addition to the type of functional group, molecular weight control, and polymer architecture, the density of functional groups and stiffness of the polymer chain can be an important parameter for imparting specific properties. 1,2-Disubstituted monomers have the potential to raise the functionality density along the backbone and thus to increase the functional group concentration as well as impact the chain stiffness.

Although 1,2-disubstituted monomers can be problematic in polymerizations there are several examples of very interesting polymers that are prepared from 1,2-disubstituted monomers. One important family of 1,2-substituted polymer backbone polymers is based on fumarate esters. Fumarate esters have been found to be readily polymerizable to poly(substituted methylenes) and these polymers and polymerizations have been the subject of several studies [5,6]. Cyclic 1,2-monomers, in particular *N*-substituted maleimides, have been studied as monomers for homopolymerizations via free radical and anionic processes [7–10]. The resulting homopolymers are reported to have stiff chains predominately formed by *trans* addition of the double bonds of the maleimides and consequently these polymers have very high glass transition temperatures.

The incorporation of *N*-substituted maleimides in free radically prepared copolymers has been an extensively studied area. Because of the strong electronegativity of the maleimide double bond, maleimide copolymers have a strong propensity to be alternating. The ease of preparing *N*-functionalized maleimides has resulted in the preparation of various functionalized alternating copolymers where the fundamental physical

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properties have been studied. The fundamental studies with these polymers have subsequently led to the design and synthesis of specific structures and functionality for candidates in a large variety of potential applications [11–16]. The combination of high levels of functionality that can be readily and precisely modified and the stiffness of the chain imparted by 1,2-disubstituted monomers continue to be an area of high scientific output as well as offers the possibility of obtaining novel polymers with a wide range of potentially useful properties as specific structure property relationships are understood.

trans-Stilbene or 1,2-diphenylethylene is another 1,2-disubstituted monomer that can be readily functionalized and that can be anticipated to have a significant impact on chain dimensions due to an expected predominant *trans* enchainment mode of the monomer and steric repulsion of the pendant aromatic substituents along the chain. Unlike the fumarates and *N*-substituted maleimides, stilbene and its derivatives are electron rich or donor 1,2-monomers. Stilbene has been found to form alternating copolymers with maleic anhydride and this system has been studied as a classical donor/acceptor comonomer system [17–21]. Maleimide, *N*-ethylmaleimide, and *N*-phenylmaleimide were found to form alternating copolymers with stilbene [22]. As an example of a functionalized maleimide stilbene copolymer poly(*N*-(*p*-acetoxyphenylmaleimide)-*alt*-stilbene) was found to be readily prepared and readily deprotected to the phenolic copolymer. This copolymer showed miscibility with novolac resins and was developed as a T_g enhancer for positive photoresists [23–25].

Other than thermal studies and our previous work on blends for photoresists, to the best of our knowledge, there has been no work on preparation of functional stilbene alternating copolymers and characterization of the properties of these novel structures. These novel rigid alternating copolymers contain groups that can be converted to ionic groups to promote water solubility. Therefore we have prepared *N*,*N*,*N*′,*N*′-tetraalkyl-4,4′-diaminostilbenes (TDASs) based on the well developed synthetic routes of substituted stilbenes [26] and studied their copolymerization with maleic anhydride. Such copolymers can be the basis of novel rigid polyelectrolytes and strictly alternating polyampholytes which potentially will possess unique solution and other physical characteristics.

2. Experimental section

2.1. General considerations

All reagents were purchased from Aldrich and were used as received. ^{1}H NMR spectra were determined at 25 °C in $CDCl_3$ at 400 MHz with a Varian Unity spectrometer. IR spectra were recorded with a MIDAC M2004 FT-IR spectrophotometer in the reflection mode. Melting points of monomers were measured on BUCHI Melting Point B-540 instrument. The elemental analysis was done by Atlantic Microlab, Inc. (Norcross, Georgia).

Thermogravimetric analysis (TGA) was conducted under nitrogen, from 25 °C to 600 °C at a heating rate of 10 °C/min using a TA Instrument TGA 295. Glass transition temperatures were determined using a Perkin–Elmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Molecular weights of the synthesized polymers were determined using size exclusion chromatography (SEC) using a Waters 717 Autosampler equipped with three in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. The d*n*/d*c* values were determined on-line using the calibration constant for the RI detector and for the mass of the polymer sample. SEC measurements were performed at 40 °C in tetrahydrofuran at a flow rate of 1.0 ml/min. For all samples, it was assumed that 100% of the polymer was eluted from the column during the measurement.

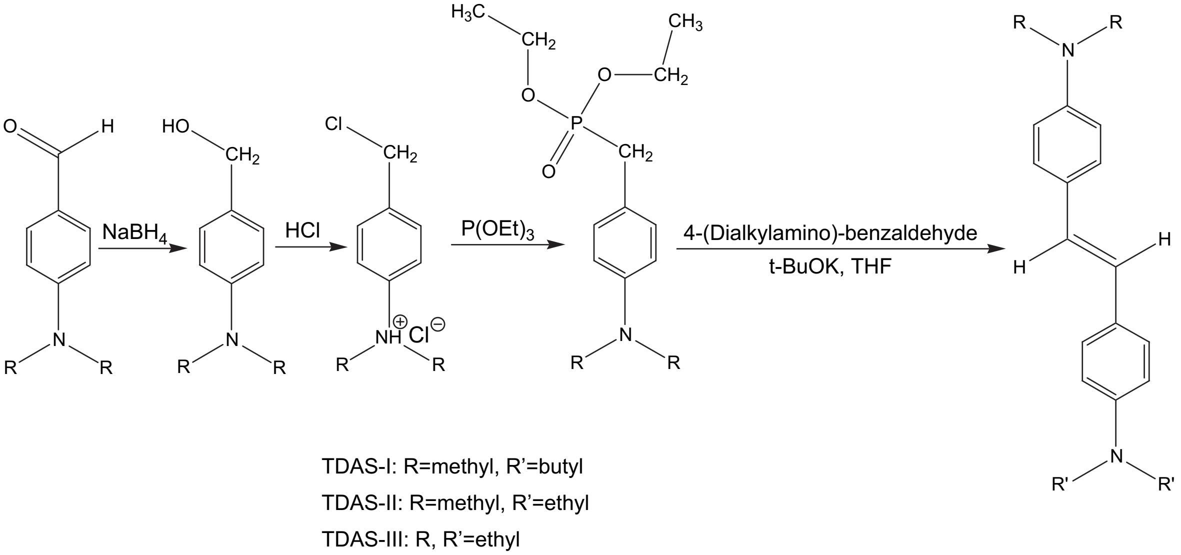
Dynamic light scattering measurements were performed using a Malvern CGS-3 light scattering instrument with a He–Ne laser ($\lambda = 632.8$ nm) as the incident source. The sample chamber was thermostated and could be controlled to within 0.1 °C. The intensity–intensity time correlation functions were analyzed by means of CONTIN method.

2.2. Synthesis of *N*,*N*,*N*′,*N*′-tetraalkyl-4,4′-diaminostilbenes (TDASs)

Horner–Emmons condensation of an aldehyde with a phosphonate is employed to synthesize these TDASs [27] (Scheme 1). 4-*N*,*N*-Dibutylaminobenzyl phosphonate and 4-*N*,*N*-diethylaminobenzyl phosphonate were prepared following a previously published procedure [28].

A typical procedure to prepare *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-4,4′-diaminostilbene (TDAS-I) is as follows: to a solution of 4-*N*,*N*-dibutylaminobenzyl phosphonate (2.61 g, 7.35 mmol) and 4-*N*,*N*-dimethylaminobenzaldehyde (1.10 g, 7.35 mmol) in dry THF (15 ml) cooled in a ice-water bath was added KO^{t}Bu (1.0 M in THF, 12 ml) slowly over 10 min. The solution was stirred at room temperature for 3 h. After that, the reaction mixture was poured into 100 ml water. The product precipitated out from the solution was collected by filtration. The crude product was purified by recrystallization from methanol. Yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.32 (m, 4H, Ar-H), 6.82 (s, 2H, vinyl), 6.70 (m, 4H, Ar-H), 3.25 (m, 4H, NCH_2), 2.95 (s, 6H, NCH_3), 1.60 (m, 4H, CH_2), 1.40–1.30 (m, 4H, CH_2), 0.95 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm: 149.3, 147.2, 127.1, 126.8, 125.4, 124.9, 123.9, 112.7, 111.7, 50.8, 40.6, 29.4, 20.3, 14.0. Elemental analysis: calculated C, 82.23; H, 9.78; N, 7.99. Found: C, 82.12; H, 9.90; N, 7.91. Mp: 87.1–87.4 °C.

N,*N*-Dimethyl-*N*′,*N*′-diethyl-4,4′-diaminostilbene (TDAS-II) was synthesized via the condensation of 4-*N*,*N*-diethylaminobenzyl phosphonate with *N*,*N*-dimethylaminobenzaldehyde. The crude product was purified by recrystallization from acetone. Yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm: 7.34 (m, 4H, Ar-H), 6.82 (s, 2H, vinyl), 6.65 (m, 4H, Ar-H), 3.32 (q, 4H, NCH_2), 2.92 (s, 6H, NCH_3), 1.12 (t, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm: 149.5, 146.7, 127.2, 127.0, 126.9, 125.7, 124.9, 124.1, 112.7, 111.9, 44.4, 40.6, 12.7.



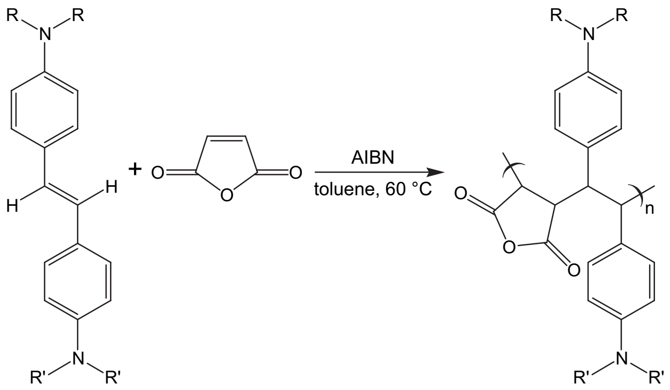
Scheme 1. Synthesis of *N,N,N',N'*-tetraalkyl-4,4'-diaminostilbenes.

Elemental analysis: calculated C, 81.59; H, 8.90; N, 9.51. Found: C, 81.52; H, 9.14; N, 9.48. Mp: 155.4–155.8 °C.

N,N,N',N'-Tetraethyl-4,4'-diaminostilbene (TDAS-III) was synthesized via the condensation of 4-*N,N*-diethylaminobenzyl phosphonate with *N,N*-diethylaminobenzaldehyde. The crude product was purified by recrystallization from acetone. Yield: 68%. ^{1}H NMR (CDCl$_3$, 400 MHz) δ ppm: 7.30 (m, 4H, Ar-H), 6.80 (s, 2H, vinyl), 6.62 (m, 4H, Ar-H), 3.32 (q, 4H, NCH$_2$), 1.12 (t, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, 400 MHz) δ ppm: 146.7, 127.1, 125.8, 124.2, 111.9, 44.4, 12.6. Elemental analysis: calculated: C, 81.94; H, 9.38; N, 8.69. Found: C, 81.94; H, 9.38; N, 8.53. Mp: 136.3–136.9 °C.

2.3. Polymerization

The TDAS, maleic anhydride, and toluene were added together with an initiator [2,2'-azobisisobutyronitrile (AIBN)] in a 50-ml, septum sealed glass bottle equipped with a magnetic stirrer. All of the copolymers contained an equal molar ratio of TDAS and maleic anhydride. The initiator concentration varied from 0.1 wt% to 1 wt%. The mixture was degassed by purging with argon for 20 min and polymerized at 60 °C for 24 h (Scheme 2). The copolymers were then isolated by precipitating into hexane. The collected crude products were re-dissolved into chloroform and precipitated in hexane. The cycle was done for three times to remove the unreacted monomers. The copolymer formed by TDAS-II and maleic anhydride is insoluble in all solvents and was freed from monomers by repeated rinsing with chloroform. All polymers were dried in the vacuum oven at 60 °C overnight before characterization. Two peaks associated with the anhydride groups of the copolymers (1841 cm^{-1} and 1772 cm^{-1}) were clearly observed in the IR spectrum, and the peak from the free carboxylic acid groups was absent.



Scheme 2. Alternating copolymerization of *N,N,N',N'*-tetraalkyl-4,4'-diaminostilbenes with maleic anhydride.

3. Results and discussions

Free radical alternating copolymerization of electron rich and electron poor monomers is a well-documented polymerization process for enabling the copolymerization of monomers that do not homopolymerize under free radical conditions. The stilbene maleic anhydride comonomer pair and the vinyl ether maleic anhydride comonomer pair are classical examples of this phenomenon since neither stilbene, vinyl ethers, nor maleic anhydride homopolymerize in a radical process, yet the alternating copolymerization of these comonomer pairs readily yields high molecular weight copolymer [29–31].

Since amino groups are very strong electron-donating groups, TDASs readily copolymerize with maleic anhydride to yield high molecular weight soluble alternating copolymers with almost 100% conversion. After TDASs were mixed with maleic anhydride, the solutions turned dark red immediately, which may be due to the formation of donor–acceptor complexes. The color of the solutions disappeared after about

2 h. This polymerization process is not spontaneous. Without the addition of initiator, the color did not fade and on precipitation no polymer was isolated. Unlike the stilbene maleic anhydride copolymer, these copolymers are soluble in organic solvents. The solubility and molecular weight data are shown in Table 1.

As shown in Table 1, the solubility characteristics of these polymers in organic solvents are dependent on the length of the *N*-alkyl substituents. Long alkyl chains on the amino groups, acting as the solvating segments, significantly increase the solubility of these polymers in organic solvents. Water solubility of these copolymers is pH dependent. They are highly soluble in dilute aqueous hydrochloric acid solution. After the pH of the solution is increased to 4.9, the polymers precipitate out. Further raising pH to 12 yields a slightly turbid solution. The low solubility of these polymers in basic aqueous solution can be accredited to the hydrophobic amine-substituted phenyl groups.

The polymers are thermally stable up to 300 °C (measured by TGA). Similar to polyfumarates, there is no observed glass transition for these polymers up to 280 °C, which indicates very stiff polymer backbones. Moreover, in the 400 MHz ^{1}H NMR spectrum of the TDAS-I maleic anhydride alternating copolymer, the aromatic hydrogen atoms show very broad peaks, and the peaks of the hydrogen atoms on the polymer backbone are almost invisible. Similar phenomenon is also observed for TDAS-III maleic anhydride alternating copolymer. Such highly broadened peaks are consistent with severely restricted rotation of the polymer backbones, indicating very rigid polymer chains.

The backbone rigidity of these TDAS maleic anhydride copolymers is further corroborated by the dynamic light scattering measurements. The hydrodynamic radius (R_h) of the TDAS-I maleic anhydride alternating copolymer chains in THF was monitored as a function of temperature (Fig. 1). At the temperature range from 10 °C to 40 °C, the copolymer has almost the same R_h, around 10 nm. If the polymer chains adopt a coil conformation in the solution, their size will vary with the change of the temperature, unless THF is an extremely good solvent for this alternating copolymer so the polymer chains already are highly extended at the low temperature.

Table 1
Solubility of *N*,*N*,*N*′,*N*′-tetraalkyl-4,4′-diaminostilbene polymers in common solvents

Polymer	Water	Methanol	THF	Chloroform	Toluene	Hexane
R = methyl, R′ = ethyl	−	−	−	−+	−	−
R,R′ = ethyl	−	−	−+	+	−+	−
R = methyl, R′ = butyl	−	−	+[a]	+	+	−

−, insoluble; −+, slightly soluble; +, soluble.

[a] MALLS–SEC: $[\bar{M}_n] = 94{,}600$ g/mol; $[\bar{M}_w] = 164{,}600$ g/mol; $\bar{M}_w/\bar{M}_n = 1.74$.

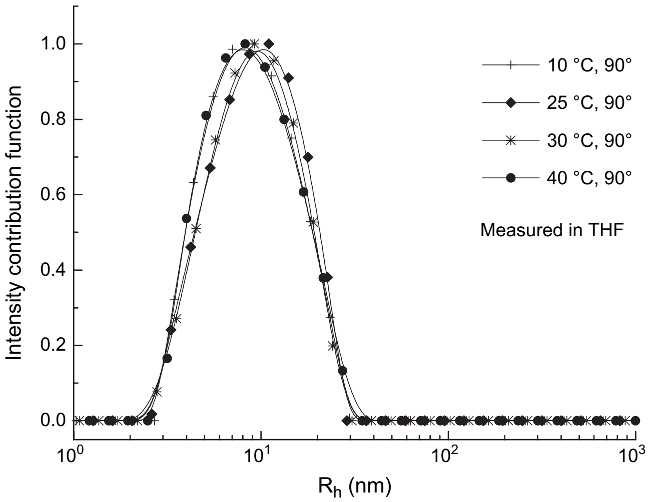
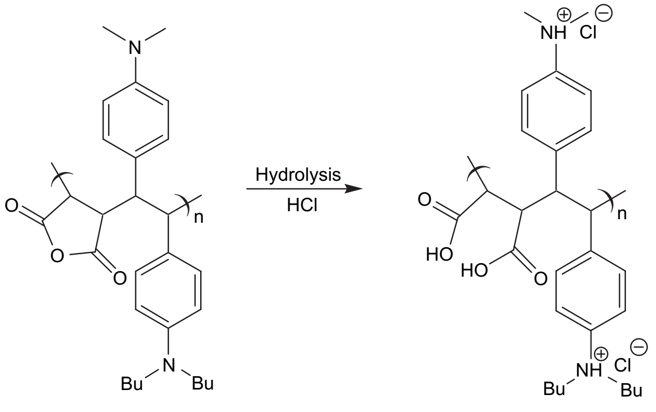


Fig. 1. Hydrodynamic radius of the *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-4,4′-diaminostilbene maleic anhydride alternating copolymer in THF at different temperatures.

Due to the polyelectrolyte effect the charges on the polymer chains will expand the backbones from the electrostatic repulsion between the charged groups. As stated before, these TDAS maleic anhydride copolymers are soluble in dilute aqueous hydrochloric acid solution and turn into cationic polyelectrolytes. If the chains of these alternating copolymers in neutral form are coils, then the introduced charges on the polymer chains would stretch the coils into rods. The TDAS-I maleic anhydride alternating copolymer was dissolved in dilute aqueous hydrochloric acid, subsequently it was hydrolyzed and highly charged (Scheme 3). The hydrolyzed and positively charged polymer was isolated by precipitating into THF and dried in vacuum oven at 70 °C overnight. Besides the disappearance of the peaks from the anhydride groups (1841 cm^{-1} and 1772 cm^{-1}), a strong absorption peak associated with the free carboxylic acid (1721 cm^{-1}) was observed in the IR spectrum, indicating the complete hydrolysis of the anhydride groups. The hydrodynamic radius of the copolymer in neutral form dissolved in chloroform was identical to the R_h of the hydrolyzed, highly charged form of the polymers dissolved in acidic water (Fig. 2), suggesting that the neutral



Scheme 3. Hydrolysis of *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-4,4′-diaminostilbene maleic anhydride alternating copolymer in dilute aqueous hydrochloric acid solution.

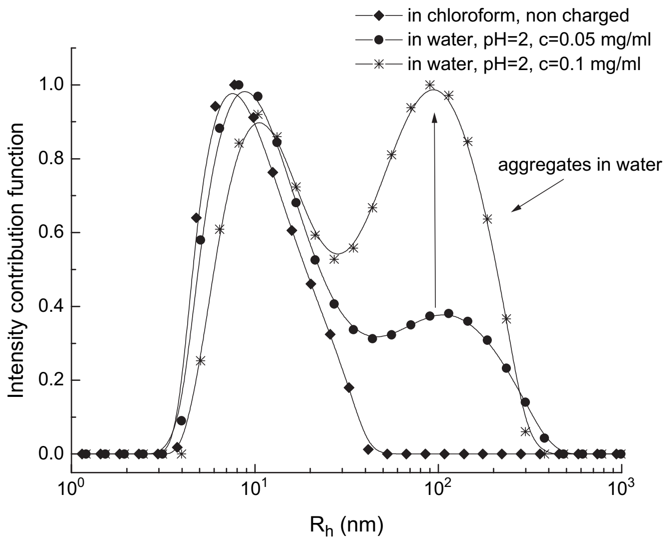


Fig. 2. Hydrodynamic radius of the neutral and charged forms of the *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-4,4′-diaminostilbene maleic anhydride alternating copolymer.

initial chain is rigid. Due to the hydrophobic butyl chains on the amino groups, the copolymer in dilute aqueous hydrochloric acid solution is a partially hydrophobic polyelectrolyte which forms large aggregates. The nature of such aggregates has not been studied.

4. Summary

In summary we have synthesized a series of novel, highly functionalized rod-like copolymers by the alternating copolymerization of TDAS with maleic anhydride and characterized some of their properties. These alternating copolymers possess some unusual and fundamentally interesting solution properties. Increasing the length of alkyl chains on the amino group significantly enhances the solubility of these alternating copolymers in organic solvents. Depending on solution pH, the alternating copolymers can be converted into strictly alternating polyampholytes, cationic or anionic polyelectrolytes with different solubilities in aqueous solution. The hydrodynamic radius (R_h) of these alternating copolymers does not change upon increasing temperature or introducing charges to the amino groups, indicating the presence of very rigid polymer backbones. There is no observed glass transition below 280 °C which corroborates the chain rigidity. These results indicate that a wide variety of responsive rod-like copolymers are readily accessible using substituted stilbene monomers. We are currently investigating the solution properties of these novel alternating copolymers and rod–coil block copolymers using the substituted stilbene maleic anhydride alternating copolymer as a responsive rod segment. We will report the results of these studies in the future.

Acknowledgments

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