

Electric Field-Induced Stretch of Pyrene-Labeled Diblock Weak Polyelectrolyte in Dilute Solution Monitored by Steady-State Fluorescence

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ABSTRACT: Pyrene-labeled diblock weak polyelectrolyte of poly (2-hydroxyethyl methacrylate)-*b*-poly (2-(dimethylamino) ethyl methacrylate) (Py-PHEMA-*b*-PDMAEMA) was successfully synthesized by atom transfer radical polymerization. The behavior of electric field induced diblock polyelectrolyte chain stretch in dilute solution was investigated by steady-state fluorescence spectroscopy. The effect of diblock polyelectrolyte concentration, pH value, salt concentration, and solvent viscosity on electric field-induced stretch was thoroughly investigated by the ratio (I_E/I_M) of excimer-to-monomer emission intensities obtained from the steady-state fluorescence spectroscopy. The results indicate that the weak diblock polyelectrolyte coil undergoes a stretching process in an external electric field, resulting in the electric field-induced stretch. An increasing polyelectrolyte concentration is advantageous to electric field-induced stretch. The degree of electric field-induced stretch is increased with the decrease of pH value by adding acid. In the presence of NaCl, the degree of electric field-induced stretch is increased with an increasing of salt concentration. However, an increase of solvent viscosity is disadvantageous to electric field-induced stretch. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 517–526, 2013

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INTRODUCTION

It is well known that polymer chains exhibit a first-order coil-stretch transition in certain flow fields and stretching along the shear direction.¹ Recent progresses in the stretch control of polymer chains using external fields, such as force fields, electric fields, and magnetic fields have been reviewed.² Molecular stretch can play a key role in estimating the certain crucial properties of functional materials in very broad and diverse areas, such as liquid-crystal display and nonlinear optical fields. In order to design and exploit such functional materials, a profound understanding of the stretch mechanism is vital to meeting current and future technological needs. It is well known that the stretch of polymer molecular chains in electric field arises from the torque produced by the permanent and induced dipole moments. Compared to uncharged polymers with mainly permanent dipole moment and/or comparatively weak induced moment, charged polymers can generate extra stretch torque because ion transport can significantly influence the electric field distribution.³ Therefore, the molecular chain stretch of charged polymers could be more easily induced in electric field

than uncharged ones. As one type of charged polymers, polyelectrolytes contain ionizable groups that can dissociate in polar solvents to create charged polymer chains as well as small mobile counterions that can escape into the bulk solution.⁴ The polyelectrolytes can be classified into strong polyelectrolytes and weak polyelectrolytes. For strong polyelectrolytes, the dissociation is independent on external conditions, and charges are generated by the dissociation of strong acidic and basic groups in aqueous solutions. Strong polyelectrolytes are also known as “quenched polyelectrolytes” by theoreticians due to “quenched” charge distribution on polymer chains. For weak polyelectrolytes, nevertheless, the dissociation is dependent on pH, ionic strength, and other parameters of the system. The charge distribution on such polymer chains is an “annealed variable” as charges generated by dissociation can be transient as a result of the pH-dependent dissociation of weak acidic or basic groups. Over the last few years, much interest has been devoted to the study of block weak polyelectrolytes. Block weak polyelectrolytes combining features from both block copolymers and weak polyelectrolytes have attracted considerable interest in experimental,

theoretical, and simulation fields for their special behavior.^{5,6} Efforts are mainly focused on structural and morphological transitions that occur in self-assembled aggregates as a response to varied environmental conditions (pH value, ionic strength and temperature in solution). For example, diblock weak polyelectrolyte with one weak polyelectrolyte block and one neutral block form micelles in solutions.^{5,7–11} The influence of uniform electric field on the dynamics and conformations of polyelectrolyte chains was also studied in a series of works.^{12–18} For instance, electric field effects on polyelectrolytes have been largely utilized to separate DNA by electrophoresis.¹⁸ Recently, Netz systematically investigated the stretch behavior of a single charged polymer in electric field using Brownian dynamics simulations and scaling arguments¹² and predicted that the single charged polymer chain will be unfolded with specific stretch along the field direction when the applied electric field slowly increases. Besides such theoretical investigations focusing on electric field-induced molecule chains alignment of homopolyelectrolytes rather than block polyelectrolytes, Park and Lee¹⁹ investigated electric field-induced self-assembly of strong polyelectrolyte containing ionic-*b*-neutral block copolymers micelles. However, the block polyelectrolyte molecular-level chain stretch induced by electric field is still an open question. A molecular-based understanding of electric field effect on block polyelectrolytes may provide a very rich area for technological exploitation which requires precise control over molecular stretch. This would have significant application value in studying nano-patterning of materials, nano-lithography, optical materials, storage devices, and biomimetic sensors.

Here we focus on the question how the chain stretch of AB diblock weak polyelectrolyte containing ionic-*b*-neutral block is affected by external electric fields. The steady-state fluorescence spectroscopy with labels is often used to obtain a molecular-level information of macromolecular chains.²⁰ Traditionally, pyrene has been selected as a label because of its special photophysical properties and capacity of excimer formation.²¹ Obtained by applying a range of electric fields, the measurements of the ratio of pyrene excimer to monomer fluorescence emission intensities (I_E/I_M) principally lead to the quantitative interpretation of the secondary and higher order structures and the electric field-induced stretch properties. In order to achieve this goal, we have designed a pyrene-labeled AB diblock weak polyelectrolyte. More precisely, a model pyrene-poly (2-hydroxyethyl methacrylate)-*b*-poly (2-(dimethylamino) ethyl methacrylate) (Py-PHEMA-*b*-PDMAEMA) diblock weak polyelectrolyte was synthesized by atom transfer radical polymerization (ATRP). It is a coexistence of a pyrene-labeled neutral block (Py-PHEMA) and cationic weak polyelectrolyte block (PDMAEMA). The electric force pulls the cationic block along the electric field direction. However, the Py-PHEMA block adds a set of resistances (such as friction) to the motion of PDMAEMA block. The Py-PHEMA block is neutral, it has no innate mobility and the driving force relies entirely on the cationic block (PDMAEMA). The resistive drag of the Py-PHEMA block would pull back on the PDMAEMA block, resulting in stretching the molecule chain of block. The behavior of electric field-induced macromolecular chain stretch can be affected by

electric charge and the frictional drag-force. The steady-state fluorescence spectroscopy is used to obtain the molecular-level information of electric field-induced stretch.

EXPERIMENTAL

Materials

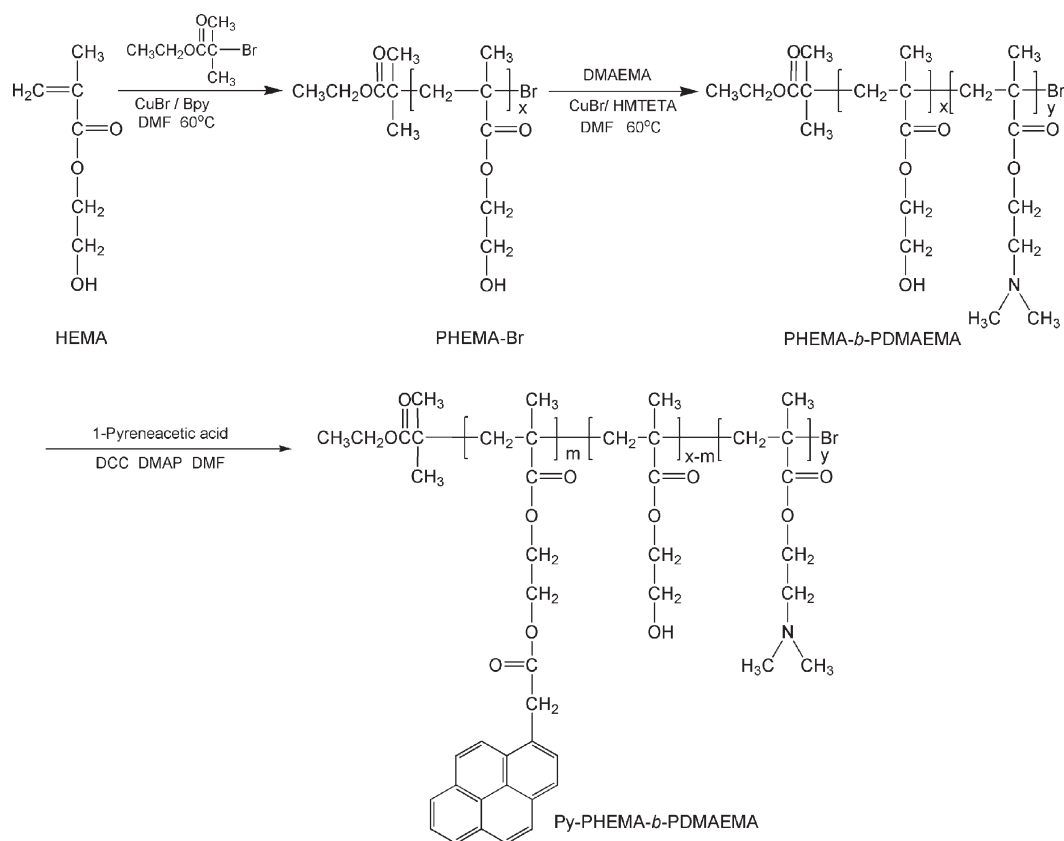
Dimethylformamide (DMF) was dried by anhydrous magnesium sulfate ($MgSO_4$) and then vacuum distilled over phosphorus pentoxide (P_2O_5) under nitrogen atmosphere. Water was twice distilled and passed through a Millipore apparatus. 2, 2'-bipyridine (Bipy), 1, 1, 4, 7, 10, 10-hexamethyltriethylenetetramine (HMTETA), 1, 3-dicyclohexylcarbodiimide (DCC), 4-Dimethylaminopyridine (DMAP), and ethyl alpha-bromoisobutyrate were purchased from Aldrich Chemical Co and used without further purification. 2-(Dimethylamino) ethyl methacrylate (DMAEMA) (Alfa Aesar 97%) and 2-hydroxyethyl methacrylate (98%, Aldrich) (HEMA) were passed through silica columns prior to polymerization. Copper (I) bromide (CuBr) was recrystallized from acetic acid. 1-Pyreneacetic acid was prepared by literature.²² All the other solvents and reagents were used without further purification, except as noted.

Synthesis of PHEMA-Br Macroinitiator

All polymers were obtained by ATRP (see Scheme 1). A polymerization procedure was carried out as follows: Typically, HEMA (3.0 g, 23.05 mmol), ethyl alpha-bromoisobutyrate (0.0450 g, 0.23 mmol), CuBr (0.033 g, 0.23 mmol) and Bipy (0.0720 g, 0.46 mmol) and DMF (7.0 g) were transferred into a dry glass tube. Then degassing with three freeze-pump-thaw cycles was carried out, and the tube was sealed under vacuum. The tube was placed into a preheated oil bath at 60°C. At a certain time, the reaction solution was cooled to room temperature. The reaction mixture was diluted with acetone. Then, the solution was passed through neutral alumina column to remove the catalyst. The PHEMA-Br macroinitiator was isolated by precipitation from diethyl ether. ¹H NMR (dimethyl sulfoxide [$DMSO$]- d_6): δ 0.66–1.03 (m, $-CH_2-CH_3-O-$), 1.60–2.10 (m, $-CH_2-CH_3-O-$), 3.58 (s, $-OCH_2CH_2OH$), 3.89 (s, $-OCH_2CH_2OH$), 4.50–5.20 (m, $-CH_2OH$).

Synthesis of PHEMA-*b*-PDMAEMA

The PHEMA-Br macroinitiator (0.4567 g, 0.0326 mmol), DMAEMA (0.5121 g, 3.26 mmol), CuBr (4.6 mg, 0.0326 mmol), HMTETA (7.5 mg, 0.0326 mmol) and DMF (2 g) were added to a dry glass tube. After degassing with three freeze-pump-thaw cycles, the tube was sealed under vacuum. After the reaction was carried out at 60°C for 24 h, the tube was cooled to room temperature. The mixture was diluted with acetone and passed through neutral alumina column to remove the catalyst. The PHEMA-*b*-PDMAEMA diblock copolymer was isolated by repeated precipitation from DMF into a mixed solution of diethyl ether/sherwood oil (1/1 V/V). ¹H NMR ($DMSO$ - d_6): δ 0.59–1.33 (m, $-CH_2C(CH_3)COO$), 1.63–2.08 (m, $-CH_2C(CH_3)COO$), 2.22 (s, $-N(CH_3)_2$), 2.33 (s, $-CH_2N(CH_3)_2$), 3.58 (s, $-CH_2OH$), 3.90 (s, $-OCH_2CH_2OH$), 4.01 (s, $-CH_2CH_2N(CH_3)_2$), 4.80 (s, $-CH_2OH$).



Scheme 1. Synthesis route of the Py-PHEMA-*b*-PDMAEMA diblock polyelectrolyte.

Synthesis of Pyrene-Labeled Polymer Py-PHEMA-*b*-PDMAEMA

Pyrene was labeled at the terminal of the PHEMA block by DCC condensation reaction. To a stirred solution of PHEMA-*b*-PDMAEMA (0.284 g) and 1-pyreneacetic acid (0.104 g, 0.40 mmol) in dry DMF (4.0 mL) was added a solution of DCC (0.2063 g, 1 mmol) and DMAP (0.0244 g, 0.2 mmol) in DMF (2.0 mL). The reaction mixture was stirred at room temperature for 48 h. The PHEMA-Py-*b*-PDMAEMA diblock copolymer was isolated by repeated precipitation from DMF into a mixed solution of diethyl ether/etherwood oil (1/1 V/V). ^1H NMR ($\text{DMSO}-d_6$): δ 0.70–1.11 (m, $-\text{CH}_2\text{C}(\text{CH}_3)\text{COO}$), 1.60–2.10 (m, $-\text{CH}_2\text{C}(\text{CH}_3)\text{COO}$), 2.23 (s, $-\text{N}(\text{CH}_3)_2$), 2.53–2.60 (m, $-\text{CH}_2-\text{N}(\text{CH}_3)_2$), 3.93–4.12 (m, $-\text{COOCH}_2\text{CH}_2\text{OOC}-$), 4.20–4.54 (m, $-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)_2$), 4.78 (s, $-\text{CH}_2\text{OH}$), 7.86–8.16 (m, pyrenyl protons).

Instruments and Measurements

^1H NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature, using deuterated DMSO as the solvent and tetramethylsilane as the internal standard.

The number-average molecular weights and molecular weight distribution of the polyelectrolyte was determined by DMF gel permeation chromatography (GPC) at 80°C. The GPC setup comprised three Polymer Laboratories PL gel 5 μL MIXED-D columns (300 \times 7.5 mm) in series with a Viscotek TriSEC model 302 refractive detector. The flow rate was 1.0 mL/min, and the mobile phase contained 10 mmol LiBr. Five near-monodisperse polystyrene standards ($M_n = 0.2\text{--}400.0$ kg

mol^{-1}) were used for calibration. Data were analyzed using Viscotek TriSEC 3.0 software.

Pyrene fluorescence spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer and emission spectra were recorded on a Perkin-Elmer LS-55 luminescence spectrometer. For the measurement of pyrene emission spectra, emission and excitation bandwidths were both set at 10 nm. The excitation wavelength was 347 nm, and the pyrene emission was recorded in the wavelength range 350–600 nm. The spectra were accumulated with an integration of 10 s/nm. Polymer dilute solutions examined here were prepared in methanol-water mixture solvent. All measurements were carried out at 20°C, unless otherwise stated. The electric field of the sample was adjusted by a DC power supply (ZhongCe NingBo DF1761SL3A) which was connected on the sample cell (a distance of 1.0 cm between the two electrodes) with thin bow-shaped brass wires as electrode. Each electric pressure was kept for 10 min before measurement.

The viscosities of binary mixtures of water and ethylene glycol were measured using a rotary viscometer (Brookfield DV-C).

In all cases, the samples were prepared from the Methanol solvent of the weak polyelectrolytic diblock copolymer Py-PHEMA-*b*-PDMAEMA, and the polyelectrolyte solutions of suitable concentration were prepared by dilution of a polyelectrolyte stock solution (0.76 mg/mL). For fluorescence measurements, 5 μL of diblock polyelectrolyte Py-PHEMA-*b*-PDMAEMA stock solution was dissolved in 2 mL duplicate

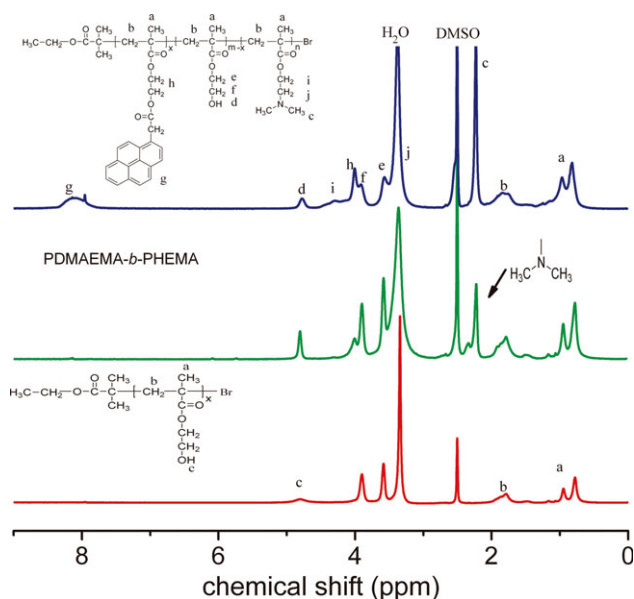


Figure 1. ^1H NMR spectra recorded for the PHEMA-Br (in DMSO), the PDMAEMA-*b*-PHEMA diblock precursor (in DMSO), and the final Pyrene-Labeled Py-PHEMA-*b*-PDMAEMA diblock polyelectrolyte (in DMSO). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mixture of H_2O -Methanol (1:1, v/v), and the solution was allowed to stabilize at room temperature for 30 min before further use. The pH value of all solutions was set to the desired value by dropwise addition of aqueous HCl (0.20 mg/mL), and the ionic strength of the sample solution was adjusted by NaCl (11.72 mg/mL). The fluorescence intensity as a function of temperature or pH value or NaCl concentration of the polyelectrolyte solutions was determined at the fixed excitation wavelength 347 nm with a circulating water bath and external electric field equipment. The concentration of the diblock polyelectrolyte was kept at 0.0019 mg/mL in mixed solution, and the pyrene group concentration was 1.6×10^{-6} mol/L. The solutions were equilibrated for 30 min before measurement.

RESULTS AND DISCUSSION

Synthesis of Py-PHEMA-*b*-PDMAEMA

A multistep synthetic procedure was followed to prepare the Py-PHEMA-*b*-PDMAEMA diblock copolymer by ATRP (Scheme 1). Basically, the diblock copolymer synthesis was based on a two-step controlled living radical polymerization. Pyrene moieties were labeled at the terminal of the PHEMA block. The two blocks show different nature in aqueous media, such as, a weak cationic PDMAEMA block and a hydrophilic

Table I. Characteristic of PHEMA-Br and PHEMA-*b*-PDMAEMA^a

Sample	Polymers	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	PDI
1	PHEMA-Br	4.60	5.38	1.17
2	PHEMA- <i>b</i> -PDMAEMA	5.52	6.51	1.18

^aMeasured by GPC using PS standards and DMF as solvent.

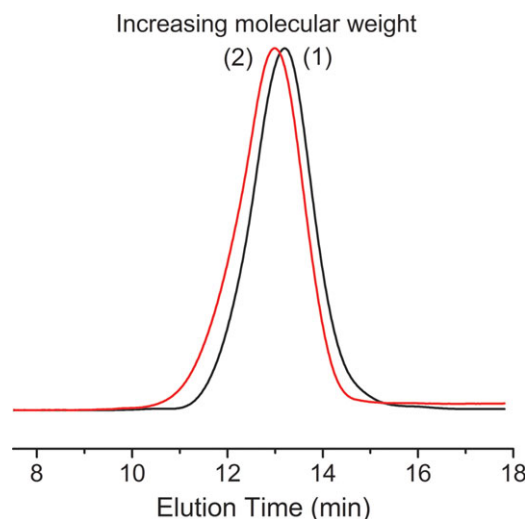


Figure 2. Gel permeation chromatograms of (1) the PHEMA-Br, (2) the PHEMA-*b*-PDMAEMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

neutral PHEMA block. The block composition of the diblock copolymer was determined by ^1H NMR (Figure 1). The weight-average molecular weights (M_w), number-average molecular weights (M_n) and the polydispersity index (PDI) of relevant block copolymer were determined by GPC (Table I). Figure 2 shows the typical evolution of the GPC chromatograms during the syntheses of PHEMA-*b*-PDMAEMA diblock copolymer using the ethyl alpha-bromoisobutyrate as initiator. The macroinitiator (PHEMA-Br) exhibited a narrow GPC trace with polydispersity of 1.17 ($M_w/M_n = 1.17$) (Table I). These indicate that ethyl alpha-bromoisobutyrate was involved efficiently in initiating ATRP of HEMA, that the ATRP of HEMA was well-controlled. The diblock copolymer exhibited a narrow GPC trace with polydispersity of 1.18 (Table I). These data indicate that the ATRP of DMAEMA monomers was well-controlled. By the analysis of the ^1H NMR spectrum (in Experimental Section), pyrene labeling was successfully performed by a DCC-mediated coupling reaction between the hydroxyl end group of the PHEMA block and the carboxyl group of 1-pyreneacetic acid. Thus, the Py-PHEMA-*b*-PDMAEMA diblock copolymer was successfully prepared. The weak cationic block (PDMAEMA) charges can be controlled by the protonation/ionization in methanol-water mixture.

Fluorescence Spectra of Py-PHEMA-*b*-PDMAEMA Dilute Solution

The dilute solution of the Py-PHEMA-*b*-PDMAEMA diblock weak polyelectrolyte prepared in methanol-water mixture was used to avoid intermolecular interactions in solution. Figure 3 shows the fluorescence spectra of the Py-PHEMA-*b*-PDMAEMA diblock weak polyelectrolyte in methanol-water mixture by excitation at 347 nm. Typical pyrene monomer emission peaks are observed at 383 nm and 397 nm. The excimer emission is broad and structureless with a maximum peak at 470 nm. The excimer emission is attributed to the emission of preassociated pyrene dimers.²¹ According to the excimer-monomer kinetics predicted by Birks, the ratio of excimer to monomer fluorescence intensities is proportional to $(k_1)/(k_{-1} + 1/\tau_E)$,²³ where k_1 is the

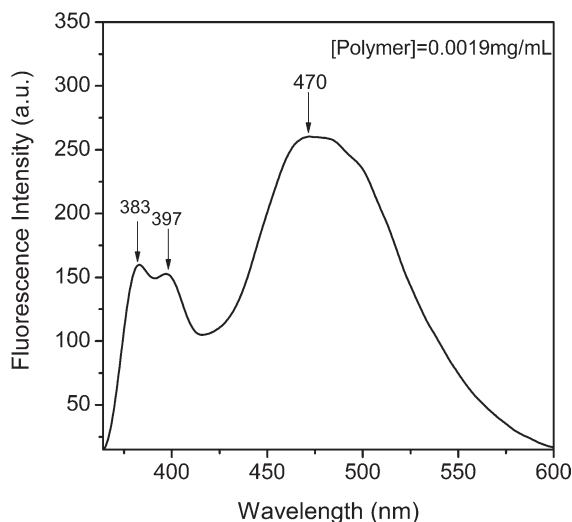


Figure 3. The fluorescence spectra of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA diblock polyelectrolyte solution at 20°C (in methanol-water mixture).

average rate constant of excimer formation, k_{-1} is the dissociation rate constant of excimer, and τ_E is excimer lifetime (does not change much with temperature).²⁴ At low temperatures the excimer dissociation k_{-1} is negligible ($k_{-1} < 1/\tau_E$). Hence, at room temperature, the I_E/I_M ratio is expected to be proportional to $(k_1)/(1/\tau_E)$. Since k_1 depends on the distance between the monomers, the I_E/I_M ratio yields information about the macromolecular chain configuration. Therefore, the ratio I_E/I_M can be taken as a measure of the intramolecular rate of excimer formation, showing the information of chain lengths between two pyrenes.²⁴ The I_E/I_M ratio is reduced if the distance between adjacent pyrene groups is increased. Cuniberti and Perico used steady-state I_E/I_M values for pyrene-end-capped poly (ethylene oxide) to study the polymer cyclization dynamics.²⁵ They adopted the excimer emission maximum peak at 480 nm and the monomer emission peak at 396 nm to calculate the ratio I_E/I_M . According to fluorescence spectra of Py-PHEMA-*b*-PDMAEMA in dilute solution (Figure 3), to calculate the ratio I_E/I_M in this work, we adopted the excimer emission maximum peak at 470 nm and the monomer emission peak at 397 nm.

Diblock Polyelectrolyte Concentration Dependence of Electric Field-Induced Stretch

Figure 4 shows the effect of diblock polyelectrolyte concentration on the I_E/I_M ratio of Py-PHEMA-*b*-PDMAEMA solution under zero field strength at 20°C. The concentration dependences of I_E/I_M ratio are complicated. The I_E/I_M ratio at low polyelectrolyte concentration shows only a small concentration dependence, signifying little or no change in the pyrene environment and therefore in polymer conformation. However, the I_E/I_M ratio increases obviously at polyelectrolyte concentrations above ca. 0.02 mg/mL, indicating that the pyrene groups are in an increasingly hydrophobic environment presumably caused by increasing intermolecular hydrophobic associations.²⁶ In fact, if the increase in association was only intramolecular, an increase in the I_E/I_M ratio with polymer concentration would not be observed.²⁷

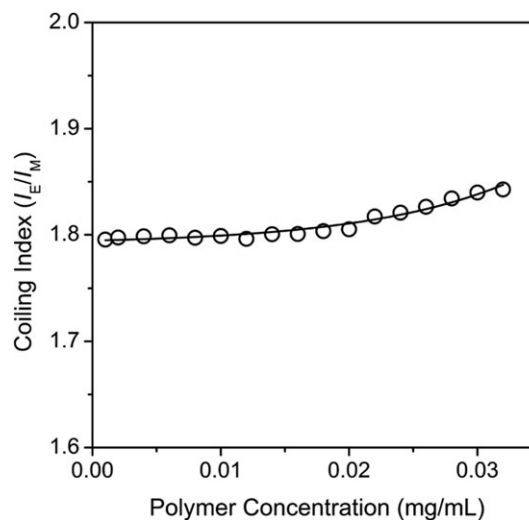


Figure 4. The effect of diblock polyelectrolyte concentration on the I_E/I_M ratio of Py-PHEMA-*b*-PDMAEMA solution under zero field strength at 20°C.

Figure 5 shows plots of the I_E/I_M ratio of the diblock Polyelectrolyte Py-PHEMA-*b*-PDMAEMA dilute solution as a function of electric field at different polyelectrolyte concentration (in methanol-water mixture) at 20°C. All the curves exhibit a general trend for the value of I_E/I_M ratio to decrease with the increase of field strength. The onset of the change in I_E/I_M is a steep decrease. With further increase of field strength, the change of the I_E/I_M ratio is smooth. Compared with the change of I_E/I_M ratio at various polyelectrolyte concentrations, the decreasing degree of I_E/I_M ratio is larger with increasing polyelectrolyte concentration (compare 0.0019 mg/mL with 0.010 mg/mL), whereas the change of the I_E/I_M ratio is smooth in higher field strength. The trends for the I_E/I_M ratio can be easily

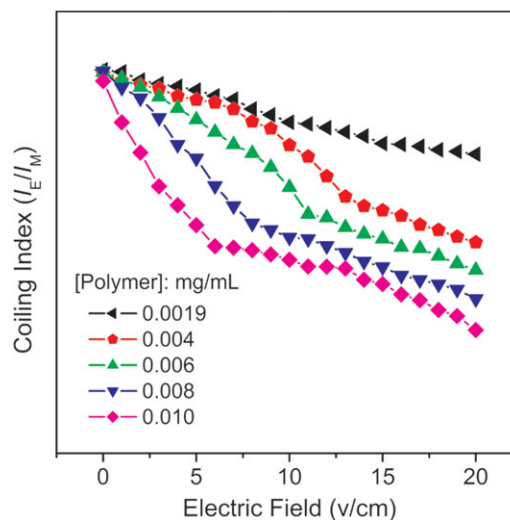


Figure 5. Plots of the I_E/I_M ratio of the diblock Polyelectrolyte Py-PHEMA-*b*-PDMAEMA dilute solution as a function of electric field at different polyelectrolyte concentration (in methanol-water mixture) at 20°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

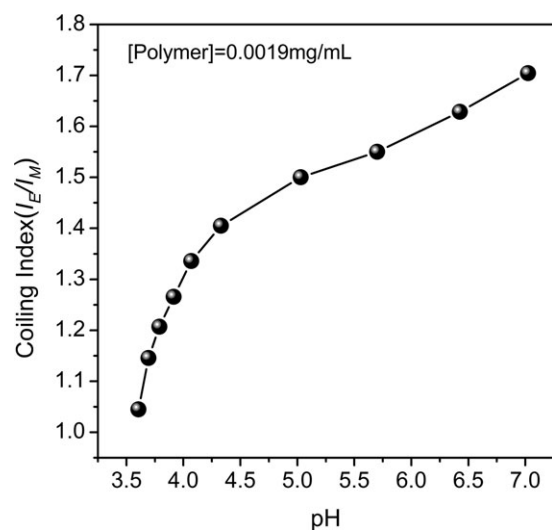


Figure 6. The effect of pH on the I_E/I_M ratio of Py-PHEMA-*b*-PDMAEMA solution (0.0019 mg/mL) at 20°C.

rationalized by the electric field-induced stretch of polyelectrolyte macromolecular chain. In methanol-water mixture, the PDMAEMA block is protonated and bears positive charge. The electric force pulls the charged block PDMAEMA along the electric field direction. However the neutral Py-PHEMA slows down this motion. So the Py-PHEMA-*b*-PDMAEMA macromolecular chain is stretched along the field direction, leading to a stretching molecular chain conformation and an increased distance between adjacent pyrene groups. All curves (see Figure 5) show a decreasing trend for the I_E/I_M ratio, and the reduced value of the I_E/I_M ratio indicates that the degree of electric field-induced stretch increases with the increase of field strength. In the same electric field gradient region, it is surprising that the degree of the I_E/I_M ratio decrease is increased with the increase of polyelectrolyte concentration in diluted solution. The most reasonable explanation of this behavior is that the increase of polyelectrolyte concentration in diluted solution may be favorable to the electric field-induced stretch. As the polyelectrolyte concentration is increased, the protonation degree of the PDMAEMA block is increased. Consequently, the net positive charge of PDMAEMA block is increased with the increasing polyelectrolyte concentration. In the conditions, the electric force is increased. As a result, the diblock weak polyelectrolyte macromolecular chain exhibits a further stretch along the field direction at the same condition, resulting in fewer pyrene excimers. Therefore, the reduced I_E/I_M ratio is a sharp decrease at high concentration (see [polymer] = 0.010 mg/mL in Figure 5), and the degree of electric field-induced stretch is higher. When the polyelectrolyte chain is stretched to a certain level, the conformational entropy of polyelectrolyte plays a leading role, and macromolecular chains is difficult to extend. Thus the change of I_E/I_M ratio is smooth in higher field strength.

The pH Value Dependence of Electric Field-Induced Stretch

The Py-PHEMA-*b*-PDMAEMA is a typical diblock weak polyelectrolyte with pH sensitivity because the PDMAEMA is a pH-dependent positively charged block. The charge of the weakly basic groups (DMAEMA) of the diblock polyelectrolyte varies with the pH. The effect of pH on the electric field-induced

stretch behavior of Py-PHEMA-*b*-PDMAEMA is expected. Here, the pH value is controlled by hydrochloric acid. First of all, we investigated the behavior of Py-PHEMA-*b*-PDMAEMA chain conformation with different pH value under zero electric field. Figure 6 shows the effect of pH on the I_E/I_M (measured 470 and 397 nm, respectively) ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA dilute solution under zero field strength at 20°C. The general tendency of the value of I_E/I_M ratio is reduced with decreasing pH value. The most reasonable explanation of this behavior is that the protonation of DMAEMA block. The degree of protonation of DMAEMA block increases and the net positive charge is enhanced with decreasing pH value. The strong electrostatic interactions within the bulk block results in an extended chain conformation. Hence, a decreasing pH value of the solution by adding acid results in an extended chain conformation of Py-PHEMA-*b*-PDMAEMA, and the I_E/I_M ratio decreases with decreasing pH (Figure 6). When an electric field (E) is applied to the Py-PHEMA-*b*-PDMAEMA solution, it can be seen that the forces acting on the Py-PHEMA-*b*-PDMAEMA. Based on the theory of Slater and coworkers for the electrophoresis of polyelectrolytes,^{28,29} the following forces act on Py-PHEMA-*b*-PDMAEMA chain in the electric field: the first force is electric force F_{ED} ($F_{ED} = QE$, Q is the effective charge of the PDMAEMA, E is the electric field strength) due to the electric field; the second force is the entropic force (F_S), is used to maintain the random coil conformation; The third force is the friction of Py-PHEMA-*b*-PDMAEMA (f_{H-D}), which defines the hydrodynamic interaction of the diblock polyelectrolyte with solvent, summarizes the combined effect of interaction of the polyelectrolyte and the surrounding ions with the solvent. If the positive direction is chosen to that of the PDMAEMA motion such that the nonelectric forces is negative. The net force acting on the Py-PHEMA-*b*-PDMAEMA is following (since there is no acceleration, the sum must be equal to zero):

$$F_{ED} - F_S - f_{H-D} = 0$$

Due to the charge difference of PDMAEMA block with different pH, the electric force F_{ED} ($F_{ED} = QE$) can be obviously affected by solution pH. The electric force F_{ED} obviously affects the stretching behavior of Py-PHEMA-*b*-PDMAEMA chain. Thus, the electric field-induced stretch behavior of Py-PHEMA-*b*-PDMAEMA can be obviously affected by solution pH. Figure 7 shows plots of the I_E/I_M ratio of the diblock weak polyelectrolyte as a function of electric field with different pH at 20°C. All of curves of I_E/I_M ratio exhibit a general trend to decrease with increasing field strength, whereas the reduced I_E/I_M ratio is a sharp decrease at lower pH value (see pH = 3.91 in Figure 7). As for the observed phenomena, the reasonable explanation of this behavior is the conformation change of Py-PHEMA-*b*-PDMAEMA chain by electric field inducing. First of all, the Py-PHEMA-*b*-PDMAEMA chain should form a single random coil in dilute solution (methanol-water mixture solvent). When an electric field (E) is applied to the Py-PHEMA-*b*-PDMAEMA solution, electric force F_{ED} ($F_{ED} = QE$) acts on the cationic block PDMAEMA due to the electric field. The electric field force pulls the PDMAEMA block along the electric field direction. However, the Py-PHEMA block is neutral, it has no innate

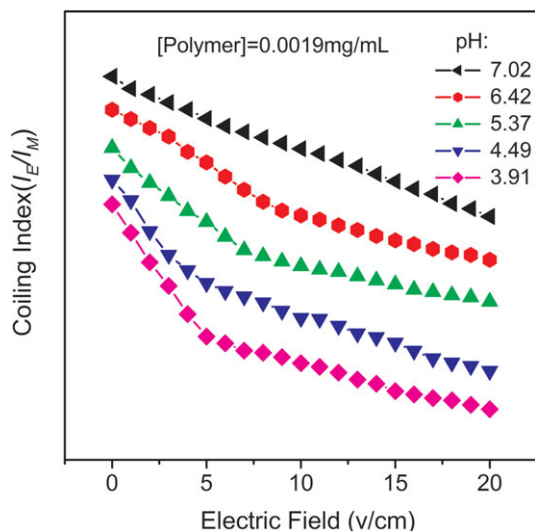


Figure 7. Plots of the I_E/I_M ratio as a function of electric field at different pH conditions for the Py-PHEMA-*b*-PDMAEMA diluted solution (0.0019 mg/mL) at 20°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mobility and the driving force relies entirely on the cationic block (PDMAEMA). Due to the conformational entropy of Py-PHEMA chains, the resistive drag of the Py-PHEMA block would pull back on the PDMAEMA block. The segregation of the PDMAEMA block and Py-PHEMA block can occur. In addition, the motion of random coil generates an additional friction force on Py-PHEMA-*b*-PDMAEMA chain due to the interaction of the diblock polyelectrolyte with solvent. The friction is opposite to electric force in direction. As a result of these conflicting forces, the Py-PHEMA-*b*-PDMAEMA macromolecular chain is stretched along the field direction, resulting in a stretching molecular chain conformation. With further increasing electric field strength, the molecule chain of diblock polyelectrolyte may be stretched with one or both block, leading to electric field-induced macromolecular chain stretch. The stretching macromolecular chain engenders a greater average distance between a ground-state and an excited pyrene monomer, reducing pyrene excimer formation. On the other hand, the amino groups of the PDMAEMA are an efficient quencher for the monomer and excimer fluorescence of pyrene.³⁰ The electric field-induced stretch also results in the reduced choices of the

contact between the amino groups of the PDMAEMA and pyrene, which further reduces efficiency of quenching. Hence, the observed experimental phenomena are that all of curves exhibit a general trend for the value of I_E/I_M ratio to decrease with increasing field strength (Figure 7). When the pH value is decreased (adjust by hydrochloric acid), the DMAEMA block is highly protonated and bear a strong positive charge. Consequently, the net positive charge of DMAEMA block is increased with decreasing pH value. In the conditions, the electric force is increased. As a result, the diblock weak polyelectrolyte macromolecular chain exhibits a further stretch along the field direction at the same condition, resulting in fewer pyrene excimers. Therefore, the reduced I_E/I_M ratio is a sharp decrease at lower pH value (see pH = 3.91 in Figure 7), and the degree of electric field-induced stretch is higher. Figure 8 shows the cartoon of electric field-induced stretch of the diblock weak polyelectrolyte macromolecular chain in dilute solution.

NaCl Concentration Dependence of Electric Field-Induced Stretch

When salt is added in solutions, the behavior of block polyelectrolyte is more complicated.⁶ The addition of salt can induce collapse or aggregation of chains, which causes phase separation. This is referred to as the “polyelectrolyte” effect. However, the addition of salt can also increase the weak polyelectrolytes solubility and chains expansion with increasing salt concentration, which is referred to as the “anti-polyelectrolyte” effect.^{31,32} When the electric field is applied across the solution, the behavior of polyelectrolyte chain conformation becomes even more complicated. Hence, the effect of NaCl Concentration on the electric field-induced stretch behavior of Py-PHEMA-*b*-PDMAEMA is expected. Figure 9 shows the effect of NaCl concentration on the I_E/I_M of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA solution under zero field strength at 20°C. The general tendency of the value of I_E/I_M ratio is reduced. The reduction of I_E/I_M ratio indicates the PDMAEMA chains to become slightly extended. The only possibilities are that addition of NaCl may affect the solvent quality and enhance the ionization of a weak polyelectrolyte.³² The screening of the electrostatic repulsive interactions is unimportant due to the low charge density on the DMAEMA block. However, the addition of NaCl still has sufficient capability to enhance the ionization; that is, addition of NaCl would be equivalent to a slight lowering of the pH. Hence, the PDMAEMA chains to become slightly

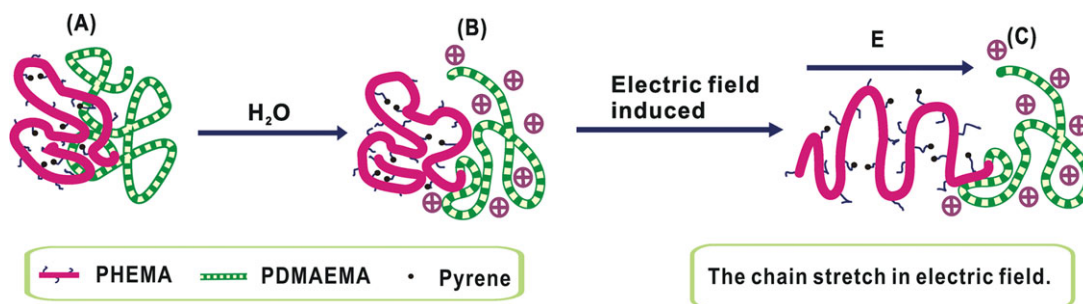


Figure 8. Schematic illustration of the chain conformation of Py-PHEMA-*b*-PDMAEMA diblock polyelectrolyte in electric field. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

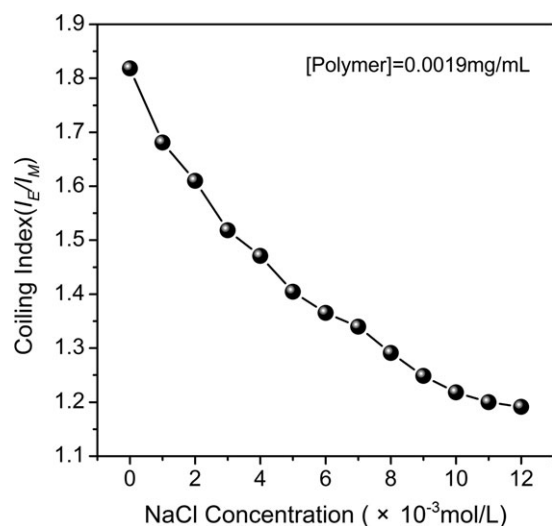


Figure 9. The effect of NaCl concentration on the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA solution under zero field strength at 20°C.

extended with an increasing NaCl concentration under zero field strength, resulting in greater average distance between a ground-state and an excited pyrene monomer, reducing pyrene excimer formation. Hence, the general tendency of the value of I_E/I_M ratio is reduced in Figure 9.

When an electric field (E) is applied to the Py-PHEMA-*b*-PDMAEMA solution, the electric field-induced stretch behavior of diblock weak polyelectrolyte Py-PHEMA-*b*-PDMAEMA chain can be affected by different NaCl concentrations. Figure 10 shows plots of the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA dilute solution as a function of electric field with different salt concentrations at 20°C. The experimentally determined dependence of all I_E/I_M curves on field strength shows a monotonic decrease and a subsequent level-off (Figure 10). Compared with the effect of NaCl concentration on the I_E/I_M ratio, the reduced I_E/I_M ratio is a sharp decrease with an increased NaCl concentration. As for the observed phenomena, the reasonable explanation of this behavior is following. The electric field acts directly on the charged PDMAEMA block and pulls the Py-PHEMA-*b*-PDMAEMA in one direction. It also acts on the counterions surrounding the PDMAEMA block, which generate an electroosmotic flow that exerts additional friction on both the PDMAEMA block and the neutral Py-PHEMA block. The friction of the Py-PHEMA-*b*-PDMAEMA (f_{D-H}) is the sum of the frictions of the two blocks $f_{D-H} = (f_H + f_D)$, where f_H is the Py-PHEMA block friction and f_D is the PDMAEMA block friction. In electric fields experiment, the PDMAEMA coil tends to move along the field direction, however the neutral Py-PHEMA slows down this motion and these friction forces pull the coil in the opposite direction. As a result of these conflicting forces, the Py-PHEMA-*b*-PDMAEMA macromolecular chain is stretched along the field direction, leading to a stretching molecular chain conformation and an increased distance between adjacent pyrene groups. With the increase of field strength, the Py-PHEMA-*b*-PDMAEMA macromolecular chain is further stretched. It can be seen from the observed experimental phenomena that all of curves of I_E/I_M ratio exhibit a

monotonic decrease with increasing field strength (Figure 10). When the NaCl concentration is increased, the additional NaCl may be further enhance the ionization due to the “anti-polyelectrolyte” effect of salt.³² The addition of NaCl would be equivalent to a slight lowering of the pH, resulting in a more net positive charge of PDMAEMA block. Under the conditions, the electric force acting directly on the charged PDMAEMA block is increased. As a result, the Py-PHEMA-*b*-PDMAEMA macromolecular chain exhibits a further stretch along the field direction. The observed experimental phenomenon is that the reduced I_E/I_M ratio is a sharp decrease with an increasing NaCl concentration (Figure 10). Hence, the degree of electric field-induced stretch is increased with an increasing NaCl concentration. Incidentally, a subsequent level-off in I_E/I_M is due to the possibility of the spontaneous saturation of stretch.

Solvent Viscosity Dependence of Electric Field-Induced Stretch

It is well known that the intramolecular long range polymer chain dynamics were affected by changes in solvent viscosity.^{33–36} Here the dependence of I_E/I_M ratio on the solvent viscosity was studied in mixtures of solvents. Intrinsic viscosities of Py-PHEMA-*b*-PDMAEMA in the solvents are given in Table II. Under zero field strength, Figure 11 shows the effect of solvent viscosity on the I_E/I_M of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA solution at 20°C. The I_E/I_M trend of the Py-PHEMA-*b*-PDMAEMA shown in Figure 11 is decreased. The following reasons can be used for interpretation of experimental results. Based on the model of Cerf,³⁷ Class I conformational changes involved larger numbers of repeating units and Class II conformational changes demanded surmounting of potential barriers are controlled by the fast process. According to Wang and Lowry,³³ the I_E/I_M depends on k_1 , which is the rate constant for the diffusion-controlled association of an excited pyrenyl group and a ground-state pyrenyl group to form a pyrenyl

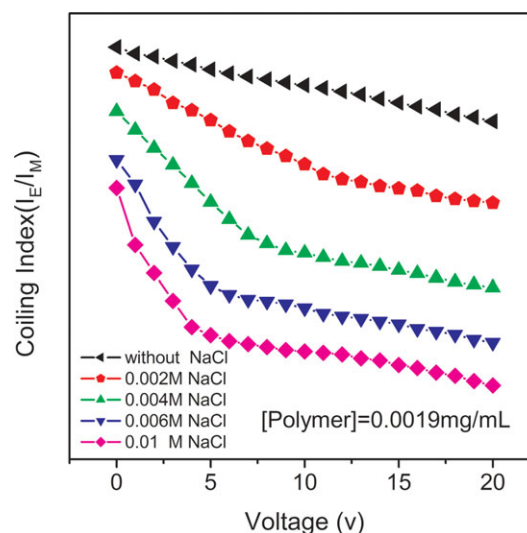


Figure 10. Plots of the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA solution as a function of electric field at different salt concentration (at 20°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. The Different Intrinsic Viscosities of the Py-PHEMA-*b*-PDMAEMA Sample in the Different Solvent Mixture Used in This Study

Solvent mixture	Volume ratio (V: V)	Viscosity (mPa·s)
Methanol/water	1 : 1	2.43
Ethylene glycol/water	1.5 : 1	4.05
Ethylene glycol/water	2.1 : 1	5.49
Ethylene glycol/water	6.2 : 1	7.56
Ethylene glycol/water	13.7 : 1	9.52

excimer. The rate constant (k_1) depends on the polymer-segment mobility. The higher solvent viscosities hinder the mobility of the chain, and the change in Class I and Class II conformations are decreased with increasing solvent viscosity. Subsequently, the rate constant (k_1) of excimer formation inside the polymer coil containing one ground-state and one excited pyrene is decreased, resulting in a larger fraction of isolated pyrene monomers. Hence, under zero field strength, the I_E/I_M calculated from the steady-state fluorescence spectra is decreased with increasing solvent viscosity and tended to a flat in high solvent viscosity (Figure 11). The observation is similar to these reported publications.^{31,32}

Due to the effect of solvent viscosity on the mobility of the chain, the stretch of the Py-PHEMA-*b*-PDMAEMA chain can be obviously affected by the solvent viscosity under electric fields. Figure 12 shows plots of the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA dilute solution as a function of electric field at different solvent viscosities at 20°C. At first, the experimentally determined dependence of I_E/I_M curve on field strength shows a monotonic decrease at low solvent viscosity (for example $\eta = 2.43$ mPa·s). With increasing solvent viscosity, the I_E/I_M curve presents a plateau in the middle of decreasing process (for example $\eta = 4.05$ and 5.09 mPa·s). At higher solvent viscosity, the I_E/I_M curve is almost a plateau (for example

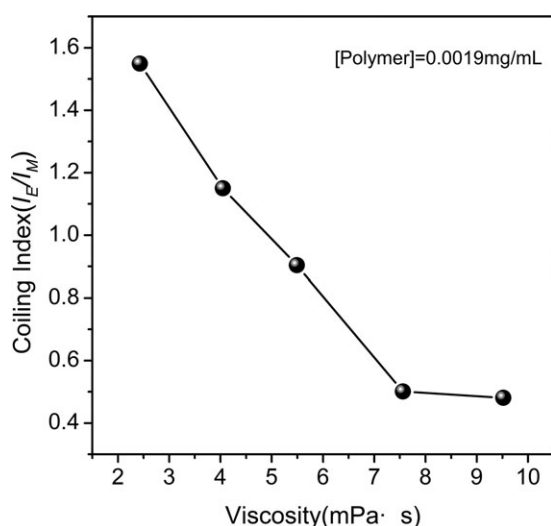


Figure 11. The effect of mixed-solvent viscosity on the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA solution under zero field strength at 20°C.

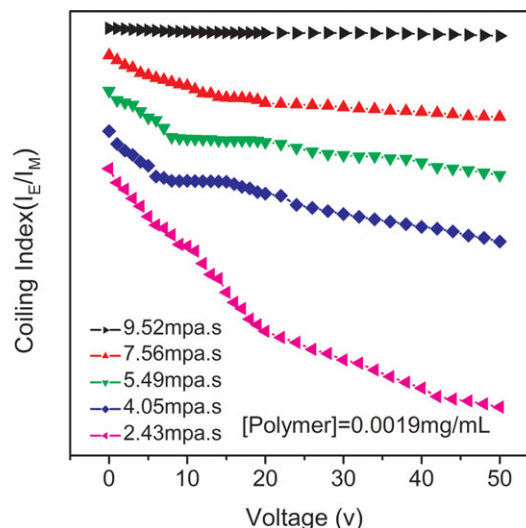


Figure 12. The plots of the I_E/I_M ratio of 0.0019 mg/mL Py-PHEMA-*b*-PDMAEMA dilute solution as a function of electric field at different mixed-solvent viscosities at 20°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$\eta = 9.52$ mPa·s). As for the observed phenomena, the reasonable explanation of this behavior is following. In electric fields, the electric force acts directly on the charged PDMAEMA block and pulls the Py-PHEMA-*b*-PDMAEMA chain coil along the electric field direction. The motion of Py-PHEMA-*b*-PDMAEMA chain coil generates a solvent flow that exerts additional friction force on both the PDMAEMA block (f_D) and the neutral Py-PHEMA block (f_H). The friction force of the Py-PHEMA-*b*-PDMAEMA (f_{D-H}) is the sum of the friction forces of two blocks $f_{D-H} = (f_H + f_D)$. The direction of friction forces is opposite to electric force. As a result of these conflicting forces, the Py-PHEMA-*b*-PDMAEMA macromolecular chain is stretched along the field direction, leading to a stretching molecular chain conformation and an increased distance between adjacent pyrene groups. The friction coefficient ζ_i for random coil i in a buffer of viscosity η is following:³⁸

$$\zeta_i = 6\pi\eta R_{Hi}$$

R_{Hi} is the hydrodynamic radius of the random coil. The friction force is proportional to friction coefficient ζ_i . At low solvent viscosity, although the increasing solvent viscosity slightly add the friction force between the random coil and solvent, the electric force can overcome these friction force and the entropic force maintaining the random coil conformation, leading to an stretching molecular chain conformation and an increased distance between adjacent pyrene groups. The experimentally determined dependence of I_E/I_M curve on field strength shows a monotonic decrease in Figure 12 (for example $\eta = 2.43$ mPa·s). However, with further increasing solvent viscosity, the electric force can not overcome these friction forces and the entropic force after a slightly electric field-induced chain stretch, resulting in a plateau in the decreasing I_E/I_M curve (for example $\eta = 4.05$ and 5.09 mPa·s in Figure 12). With further increasing electric force, the electric force can surmount these opposite forces

in direction, and stretch Py-PHEMA-*b*-PDMAEMA macromolecular chain again. The reduction of I_E/I_M ratio appears again (for example $\eta = 4.05$ and 5.09 mPa·s in Figure 12). However, at higher solvent viscosity, the electric force can not overcome these friction forces and the entropic force in total field strength range (0–50v/cm), so that the electric force can not stretch Py-PHEMA-*b*-PDMAEMA macromolecular chain. In this situation, the I_E/I_M curve is almost a plateau (for example $\eta = 9.52$ mPa·s in Figure 12). In other words, it is more difficult that the Py-PHEMA-*b*-PDMAEMA macromolecular chain is stretched with increasing solvent viscosity at the same electric field gradient. As a result, an increasing solvent viscosity is disadvantageous to the formation of the field-induced stretch.

CONCLUSIONS

In this article, a model pyrene-poly (2-hydroxyethyl methacrylate)-*b*-poly (2-(Dimethylamino) ethyl methacrylate) (Py-PHEMA-*b*-PDMAEMA) diblock weak polyelectrolyte was synthesized by ATRP. The diblock weak polyelectrolyte contained positively ionizable PDMAEMA block and pyrene-labeled neutral Py-PHEMA block. The steady-state fluorescence spectroscopy is conveniently used to investigate the electric field-induced stretch in dilute solution of the diblock weak polyelectrolyte. The change in the ratio (I_E/I_M) of excimer-to-monomer emission intensities can be interpreted on the basis of the stretched macromolecular chains with the increase of the external electric field strength. In addition, the effect of changes in diblock polyelectrolyte concentration, pH, NaCl salt concentration and solvent viscosity on electric field-induced stretch was investigated. An increasing polyelectrolyte concentration is advantageous to electric field-induced stretch. A decreasing pH value by adding acid is found to cause an increase in the degree of electric field-induced stretch. For the presence of NaCl, the degree of electric field-induced stretch is increased with an increased NaCl concentration. However, an increasing solvent viscosity is disadvantageous to the formation of the field-induced stretch.

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