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Synthesis and properties of a functional copolymer from *N*-ethylaniline and aniline by an emulsion polymerization

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Abstract

A series of functional copolymers was synthesized by an emulsion polymerization of *N*-ethylaniline (EA) and aniline (AN) in the presence of sodium dodecylbenzene sulfonate in HCl. Several important polymer parameters including the polymerization yield, molecular weight, solubility, film formability, solvatochromism, thermochromism, and alterable electrical conductivity were systematically studied by changing the comonomer ratio, emulsifier/monomer ratio, oxidant/monomer ratio, solvent, and temperature. The resulted copolymers were characterized in detail by infrared and UV–vis spectroscopies. It is found that these copolymers exhibit narrow molecular weight distribution, good solubility, excellent film flexibility, colorful solvatochromism in various solvents, reversible thermochromism in a wide temperature range, and widely controllable conductivity from 2.03×10^{-10} to 0.161 S/cm with changing the polymerization conditions and doping states.

Keywords: Aniline/*N*-ethylaniline copolymer; Electrically conducting polymer; Emulsion copolymerization

1. Introduction

Polyaniline (PAN) is one of the most extensively studied organic conducting materials because of its inherently excellent versatility including high stability, novel electronic and optical properties [1–3] and extremely high oxygen over nitrogen separation factor [4]. However, the conductive form of PAN is difficult to be processed through a traditional method because it is both unstable at melt-processing temperatures and insoluble in most organic solvents except for *N*-methylpyrrolidone (NMP), greatly limiting its further wide practical application. Several modifying ways have been developed to improve its solubility. Among them, alkyl, alkoxy, and amino ring-substituted [5–8] and *N*-substituted [9,10] PANs have caught great interest because of their much better solubility in many common solvents and, therefore, relatively good processibility. At the same time, a new question comes out, that is, lower molecular weight of the modified PANs than pure PAN.

Synthesis of PAN is commonly performed by a chemical oxidative polymerization or an electropolymerization [11, 12]. To improve the processability and also enhance the molecular weight of the PAN, an emulsion polymerization process in an emulsion of water and non-polar or weakly polar organic solvents was developed in 1993 and the PAN obtained thus was indeed found to exhibit good processability and high molecular weight [13,14]. Five years later, a new emulsion polymerization process for PAN was reported [15], in which dinonylnaphthalenesulfonic acid was employed as both the emulsifier and dopant. Recently, the emulsion polymerization processes for preparing PAN salts have been reported by several investigators with different emulsifiers, such as dodecylbenzenesulfonic acid [16,17], naphthalenesulfonic acid [18], sodium dodecylbenzenesulfonate (SDBS) [17,19], dodecylsulfate [17,20], and/or their derivatives. It is certain that the PAN obtained by the

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emulsion polymerization has good solubility, good solution processability, high molecular weight, and high electrical conductivity [16,20]. Consequently, it can be expected that the processability and molecular weight of the copolymers of aniline (AN) and its substituents can also be largely enhanced through the emulsion polymerization instead of traditional non-emulsion oxidative precipitation polymerization.

So far, the emulsion copolymerization of AN with its *N*-substituted derivatives has not been found. The synthesis of the copolymers of *N*-ethylaniline (EA) and AN by an emulsion oxidative polymerization is reported for the first time in this study. The emulsifier is used in the emulsion polymerization for two reasons: (1) to affect the locus of polymerization, and thus to enhance the molecular weight of the resulting polymers, and (2) to improve and stabilize the properties of the polymers with respect to solubility, processability, and electrical conductivity. The emulsion EA/AN copolymerization is carried out with the SDBS as emulsifier and ammonium persulfate [$(NH_4)_2S_2O_8$] as oxidant in the HCl aqueous solution. The reasons for selecting SDBS as emulsifier for synthesizing EA/AN copolymer are that the PAN obtained in a SDBS micellar solution exhibits high processability and conductivity (65.9 S/cm) [19]. The important effect of the EA/AN comonomer ratio, emulsifier content, oxidant/monomer ratio, and polymerization temperature on the polymerization yield, molecular weight, solubility, solvatochromism, thermochromism, film formability, and conductivity of the copolymers is discussed in detail. The molecular structure of the EA/AN copolymers is characterized by FT-IR and UV–vis spectroscopies, and gel permeation chromatography.

2. Experimental

2.1. Polymerization

EA (Merck-Schuchardt), AN, $(NH_4)_2S_2O_8$, SDBS and all solvents (Shanghai Reagent Factory of China) are analytical reagent grades and used as received. A series of copolymers with seven EA/AN molar ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0 was prepared by the emulsion polymerization in the presence of SDBS as emulsifier and dopant, and ammonium persulfate as an oxidant. The typical polymerization of an EA/AN (50/50) copolymer is described as follows. A solution containing 3.48 g of SDBS was prepared by dissolving the SDBS in 120 ml 1.0 M HCl accompanying with a constant agitation till the SDBS was completely soluble at 5 °C in an ice–water bath, then AN (5 mmol) and EA (5 mmol) were simultaneously added to the solution. A milky white emulsion was obtained after a mechanical agitation for about an hour. A precooled solution of ammonium persulfate (2.28 g) in 30 ml 1.0 M HCl was then added drop wise to the emulsion solution under a constant stirring for half an hour. During the progress in the polymerization reaction, the color of the emulsion changes from milky white to blue, and to dark-green at last. The reactant solution was magneto-stirred for 24 h in the ice–water bath at 5 °C. After the reaction was terminated by pouring the emulsion into 600 ml acetone, the dark-green powder was obtained by filtration and washing with an excess of distilled water, until the filtrate is colorless, and dried under infrared lamp for several days. The resultant copolymer salt, i.e., virgin doped sample, can be converted into their bases, i.e., dedoped samples, by dispersing the copolymer salts in 200 ml, 0.2 M NH_4OH with stirring for 24 h. The polymerization yield was determined using the dedoped products.

2.2. Characterization

The solubility of the copolymers was qualitatively evaluated using the following method: 10 mg of fine copolymer powder was added into the solvent of 1 ml in a small glass container and stirred vigorously for 2 h at room temperature Then the solubility and the solution color, i.e., solvatochromism, can be determined. The molecular weight and its dispersity were measured by a gel permeation chromatography (GPC) on a HP1100 with THF as elution solvent. The free-standing films of EA/AN copolymers were prepared by a solution casting method with NMP as solvent at the concentration (35 g/l) on glass, then heating at 60–70 °C until the film dried. After cooling to room temperature, the films were removed from the glass by soaking in water and then dried at 90–100 °C for 3 h. The bulk electrical conductivity of the dedoped and re-doped copolymers as pressed pellet was measured by a two-disk method using a UT 70A multimeter at 18 °C. The IR spectra were recorded with a Nicolet Fourier transform infrared (FT-IR) instrument on KBr pellets. The UV–vis spectra were measured for the characterization of molecular structure, solvatochromism, and thermochromism of the copolymers on a Lambda 35 UV–vis spectrophotometer with a heating/cooling sample system from Perkin–Elmer Ltd in a wavelength range of 190–1100 nm.

3. Results and discussion

3.1. Synthesis of the EA/AN copolymers

3.1.1. Effect of EA/AN comonomer ratio

The effect of the EA/AN ratio on the polymerization yield and molecular weight of EA/AN copolymers is shown in Fig. 1. It seems that EA and AN monomers are retardant of the other polymerization each other because both homopolymerizations exhibit higher polymerization yield. The polymerization yield of PAN exceeds 100%, suggesting the residue of the emulsifier that was testified by the following FT-IR spectra. It is seen from Fig. 1 that the

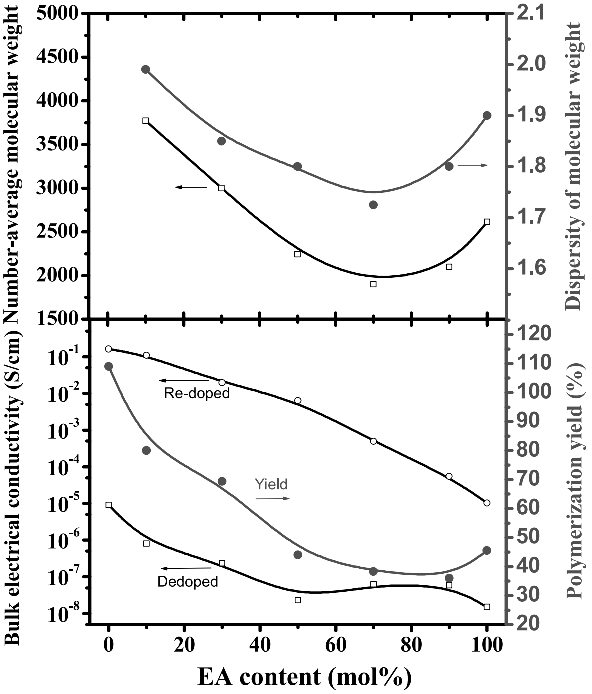

Fig. 1. The variation of polymerization yield, molecular weight, and bulk electrical conductivity of the EA/AN copolymers with EA content at 5 °C, O/M =1.0, E/M=1.0.

highest emulsifier residue of about 10% was observed for PAN because of its strongest doped ability by the emulsifier. The EA/AN (90/10) copolymer shows the minimal yield, indicating that there is a strongest retarding effect between the AN and EA monomers at this specific EA/AN ratio. A similar relationship between comonomer ratio and molecular weight or its dispersity (M_w/M_n) (Fig. 1) is observed. However, the EA/AN (70/30) copolymer shows the minimal molecular weight and its dispersity instead of the EA/AN (90/10) copolymer. The different effect of the comonomer ratio on the polymerization yield and the molecular weight may originate in the difference of the residue of the emulsifier on the AN and EA units with the steric hindrance of the ethyl group [21]. On the other hand, the electronic effect of the ethyl group on EA monomer plays an important role in the polymerization. Due to the electron-donating impact of the ethyl group, EA monomer could be easily oxidized to a cation radical, but the cation radical has higher stability than AN radical in the polymerization system. In summary, the addition of a small amount of AN will decrease the polymerization yield, molecular weight and its dispersity of the EA polymers, whereas the addition of EA comonomer will dramatically decrease the polymerization yield, molecular weight and its dispersity of the AN polymers because of higher stability or lower polymerizability of EA cation radical. This is similar to the dependency of the yield on the *m*-sulfonic AN content in an inverse emulsion *m*-sulfonic AN/AN copolymerization [21]. These phenomena imply a strong chemical copolymerization between EA and AN monomers, i.e., the polymer obtained thus is a real copolymer containing the both monomer units rather than a simple mixture of two homopolymers, because the yield or molecular weight of simple mixtures of homopolymers should be a simple linear addition between the two yields or molecular weights of individual EA and AN homopolymers with varying EA/AN ratio.

3.1.2. Effect of emulsifier/monomer ratio

The emulsifier concentration strongly affects the polymerization yield and molecular weight of the EA/AN (50/50 and 100/0) polymers as shown in Fig. 2. It is found that the EA/AN (50/50) copolymer exhibits the maximal yield, the maximal number-average molecular weight, and the maximal dispersity of molecular weight (M_w/M_n) with the variation of emulsifier/comonomer ratio. However, the emulsifier/comonomer ratio corresponding to the maximal yield is different from that corresponding to the maximal molecular weight. The maximal molecular weight appears at the emulsifier/monomer molar ratio of 0.25 and 1.0 for EA/AN (50/50 and 100/0) polymers, respectively, while the maximal yields of the both polymers are located at the emulsifier/monomer ratio of 0.50. It is seen from Fig. 2 that the top M_n could reach up to 2900–3900, indicating the highest M_n enhancement of 2–4 times by emulsion polymerization as compared with non-emulsion technique,

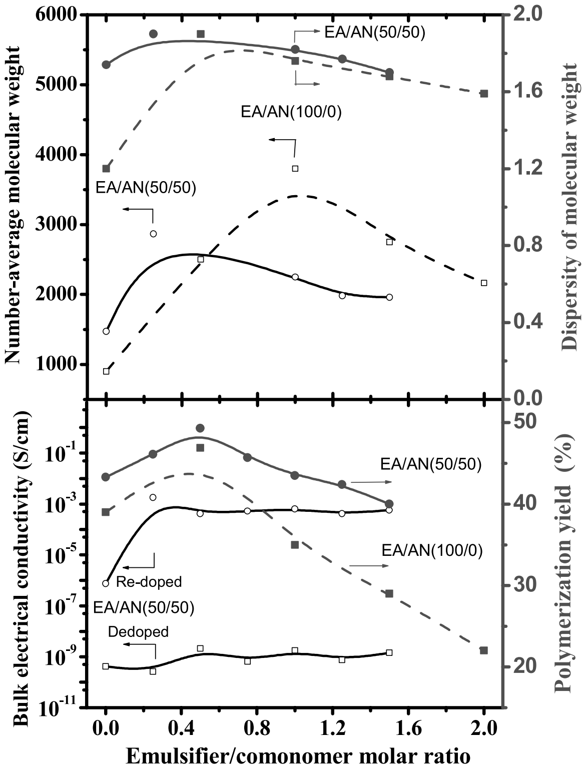

Fig. 2. The variation of polymerization yield and molecular weight of the EA/AN (50/50 and 100/0) copolymers with the emulsifier/monomer ratio at a fixed O/M of 1.0 at 5 °C.

basically achieving our aim. The emulsifier can influence the EA/AN polymerization in three ways:

(1) The number and size of the emulsifier micelles control the distribution of the reactants (monomers and oxidant) between the micella and aqueous phases, thus altering or even optimizing the locus and the course of polymerization;
(2) The SDBS emulsifier anions could act as counter ions for radical cations and then improve the stability of the monomer radical cations during the polymerization, redounding to the chain propagation reaction, and finally elevating the molecular weight of the polymers;
(3) The SDBS anionic emulsifier can also act as counter (or doping) ions for conducting polymer, leading to an increased polymerization yield and electrical conductivity, as discussed in the Section 3.3.4.

Consequently, a certain amount of emulsifier is of benefit to the formation of EA/AN polymers with high molecular weight, high yield, and high conductivity. However, too much emulsifier might result in the formation of too many micelles. As a result, there are no enough monomers or oxidants to participate in polymerization within each micelle. It can be concluded that emulsion polymerization indeed produces the EA/AN copolymers with higher molecular weight and high yield than non-emulsion polymerization without any emulsifier. However, too much emulsifier will induce a reduction of molecular weight, especially polymerization yield. The optimum emulsifier/monomer ratio could range from 0.25 to 0.50.

3.1.3. Effect of oxidant/monomer ratio

The influence of the oxidant/monomer ratio on the polymerization yield and molecular weight of EA/AN (50/50) copolymer is illustrated in Fig. 3. With the increase of the oxidant content, the copolymerization yield increases monotonically from 5.8 to 80.1%, but the copolymer has the minimal molecular weight at the oxidant/monomer molar ratio of 1.0. In general, more oxidant is beneficial to the formation of the AN cation radical with higher polymerizability, promoting chain propagation reaction and then increasing the length of polymer chain and polymerization yield. Less oxidant will result in formation of the less polymerizing active centers, favoring the chain propagation reaction but lowering polymerization yield.

3.1.4. Effect of polymerization temperature

As shown in Fig. 4, the polymerization temperature has a strong effect on the polymerization yield and molecular weight of the EA/AN (50/50) copolymer. The polymerization yield and molecular weight dispersity are found to diminish monotonically with elevating the temperature, because higher temperature will result in the formation of more micelles and, therefore, lower monomer concentration in the micelles. The polymerization reaction in the micelles completes faster at higher polymerization temperature. In addition, side reaction may occur at the elevated temperature, leading to the depression of the polymerization yield. The molecular weight has a maximum value at 20 °C, indicating a minimal chain-terminating rate of oxidative

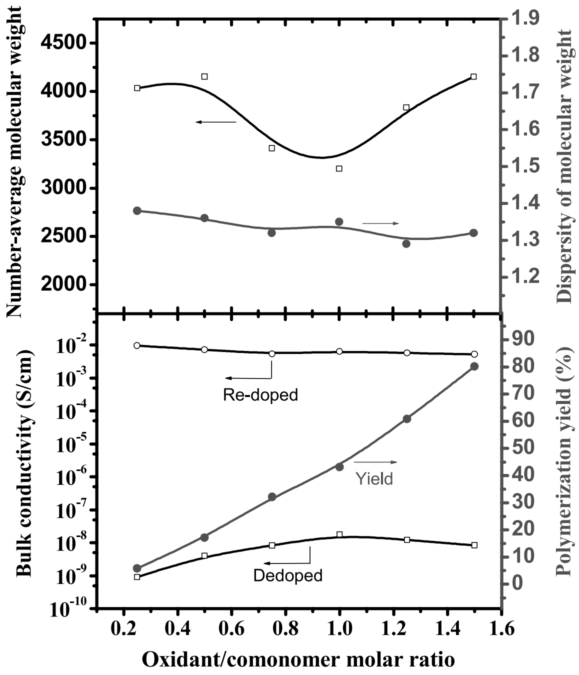

Fig. 3. The variation of polymerization yield and molecular weight of the EA/AN (50/50) copolymers with the oxidant/monomer ratio at a fixed E/M of 1.0 at 5 °C.

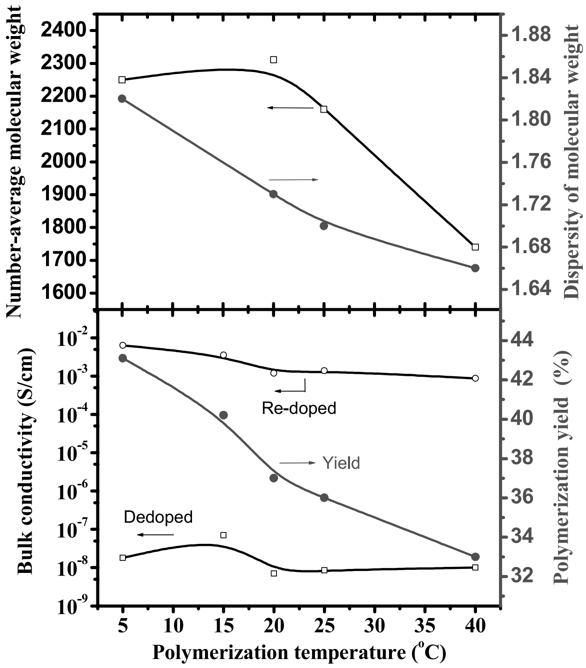

Fig. 4. The variation of polymerization yield and molecular weight of the EA/AN (50/50) copolymers with the polymerization temperature at fixed O/M of 1.0 and E/M of 1.0.

polymerization due to an optimal combination of micelle number and monomer/oxidant concentration in the micelles at this temperature. Note that the highest yield but slightly low molecular weight at low temperature (5 °C) could be attributed to slow diffusion rate of oxidant and monomers from aqueous phase into micelles, leading to occurrence of the traditional oxidative polymerization in aqueous phase.

3.2. Structure analysis of the EA/AN copolymers

3.2.1. IR spectra

Fig. 5 shows the FT-IR spectra of the EA/AN copolymer bases. All the seven IR spectra seem to be identical but exhibit systematically variable characteristics with EA/AN ratio after a close observation. The IR spectra are analogous to those of the traditional non-emulsion copolymers except for two strong bands at 1300 and 1125 cm^{-1} that verify the presence of SDBS emulsifier [22]. Both of the bands exhibit a steadily increased intensity with increasing AN content, implying that AN units in the polymers are more readily doped by DBSA emulsifier than EA units because the doping on the EA units would be more difficult due to the spatial hindrance from the ethyl group. A broad band centered at 3414–3378 cm^{-1} is assigned to the N–H stretching vibration of an aromatic amine [23]. Symmetric and asymmetric stretching vibrations of aliphatic C–H due to the ethyl group of the EA units in the EA/AN copolymers appear at 2870, 2929, 2969 and 3034 cm^{-1}. The absorption peak at 1606–1588 cm^{-1} is associated with the quinoid rings and shifts to higher wavenumber with the increase of the EA content. The band at 1504–1499 cm^{-1} due to the benzenoid rings of the copolymers becomes stronger with increasing EA content and finally seems to be the strongest for EA homopolymer. The fact that the peak around 1500 cm^{-1} always has higher intensity than that around 1600 cm^{-1} with increasing EA content suggests more benzenoid unit in all the EA/AN copolymers. A shoulder peak at 1257–1251 cm^{-1} is ascribed to the C–N stretching in the benzenoid–benzenoid–benzenoid triad sequence for EA/AN(0/100 and 10/90) polymers. However, its peak intensity steadily becomes stronger with increasing EA content, because each EA unit contains two C–N bonds whereas each AN unit contains only one C–N bond. A medium band at 829–818 cm^{-1} is attributable to the C–H out-of-plane bending vibration of the 1,4-phenylene ring on the EA and AN units. The presence of all these characteristic bonds and the regular variation of their intensity and wavenumber with EA/AN ratio may also suggest the formation of a series of real EA/AN copolymers.

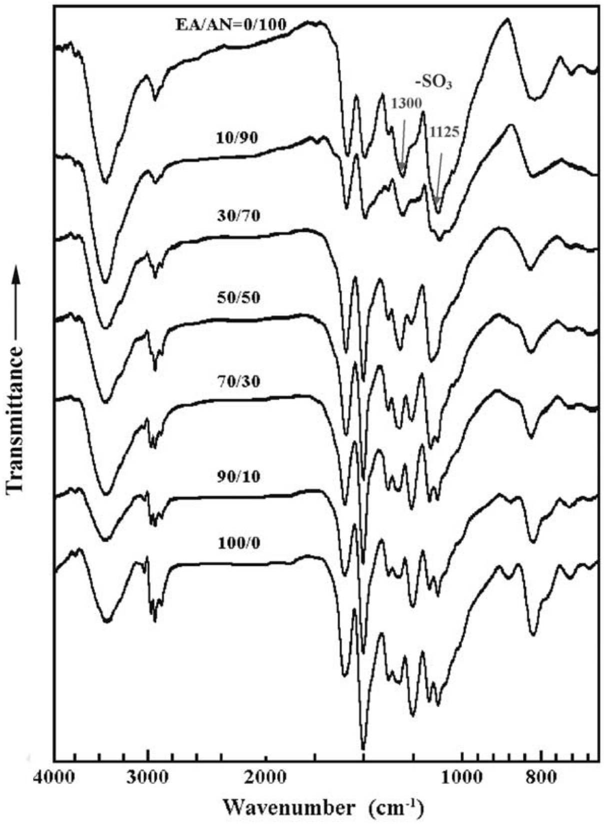

Fig. 5. FT-IR spectra of the copolymer bases with seven *N*-ethylaniline/aniline ratios of 0/100, 10/90, 30/70, 50/50, 70/30, 90/10 and 100/0 from KBr pellets.

3.2.2. UV–vis spectra

The UV–vis spectra of the EA/AN copolymer bases in DMF are shown in Fig. 6. There are two absorption peaks in the electronic spectra of the EA/AN copolymers, a strong peak (A_1) around 323–332 nm assigned to π–π* excitation (which corresponds to bandgap) and a broad peak (A_2) at 598–621 nm assigned to n–π* excitation band or interband charge transfer that is associated with the excitation of benzenoid to quinoid rings [24]. With increasing EA content, the absorbance around 600 nm becomes weaker and weaker. As a result, EA homopolymer displays the

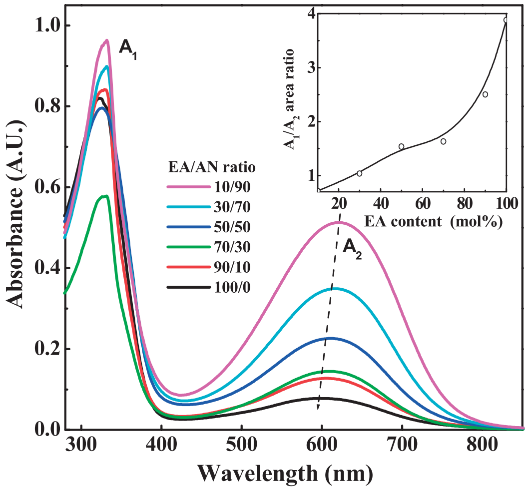

Fig. 6. UV–vis spectra of the copolymer bases with *N*-ethylaniline/aniline ratios of 10/90, 30/70, 50/50, 70/30, 90/10 and 100/0 in DMF at 10 mg/l at 25 °C.

weakest absorbance at 598 nm. Quantitatively, the area ratio of A_1/A_2 peaks shown in the inset of Fig. 6 increases steadily with raising EA content from 10 to 100 mol%, indicating a decreased concentration of the quinoid units in the copolymers [25], which is coincident with the result of FT-IR spectra. At the same time, the peak undergoes a large hypsochromic shift from 621 to 598 nm with enlarging the EA content from 10 to 100 mol%, because of the steric effect of ethyl side group that produces torsional twist and shortens the conjugation length in copolymer chain. Accordingly, the UV–vis spectra have been efficiently used to quantitatively characterize the solvatochromism and thermochromism of the copolymers below.

3.3. Properties of the EA/AN copolymers

3.3.1. Solubility

It can be seen from Table 1 that the solubility of EA/AN copolymer bases is influenced by the several polymerization conditions to some extent regardless of their complete solubility in H_2SO_4 [26] The EA/AN polymers exhibit a steadily improved solubility in most of solvents listed in Table 1 as compared with PAN. This results from the incorporation of EA units into PAN chains, because the ethyl side groups increase the distance between the macromolecular chains and then decrease the interaction between the adjacent chains. All the EA/AN(50/50) copolymers obtained at different emulsifier/monomer ratios are soluble in H_2SO_4, NMP, DMF, and HCOOH but sometimes mainly soluble in DMSO, THF, and $CHCl_3$. The EA/AN (50/50) polymers obtained at different oxidant/monomer ratios and various polymerization temperatures have almost the same solubility, i.e., soluble in H_2SO_4, NMP, HCOOH, DMF and DMSO, as well as mostly soluble in THF and $CHCl_3$. Good solubility of the EA/AN copolymers in most of the solvents lays the foundations of their solvatochromism, thermochromism, and film formability.

3.3.2. Solvatochromism

The optical absorption of polymer solution is valuable for an investigation on the change of the chain conformation induced by the interaction between the chain and the solvent as well as by thermal treatment. The solution color of the copolymer bases significantly changes in the various solvents, i.e., the copolymers exhibit an interesting solvatochromism that is similar to that of non-emulsion copolymers [27]. The copolymer solutions are violet in

Table 1
Effect of the EA/AN, emulsifier(E) and oxidant(O)/monomer(M) molar ratios and polymerization temperature on the solubility and solution color of the EA/AN copolymer bases in the presence of SDBS in 1.0 M HCl aqueous solution

	Solubility in solvent and the solution color in the parentheses						
	H_2SO_4	NMP	DMF	HCOOH	DMSO	THF	$CHCl_3$
EA/AN molar ratio at 5 °C, O/M = 1.0, E/M = 1.0							
0/100	S (v)	MS(b)	PS(b)	MS(g)	PS(b)	PS(b)	IS
10/90	S (v)	S (b)	MS(b)	S (g)	PS(b)	MS(b)	PS(y)
30/70	S (v)	S (b)	MS(b)	S (g)	MS(b)	MS(b)	PS(g)
50/50	S (v)	S (b)	S(b)	S (g)	MS(b)	MS(b)	MS(g)
70/30	S (v)	S (b)	S(b)	S (g)	MS(b)	S(b)	S(g)
90/10	S (v)	S (b)	S(b)	S (g)	MS(b)	S(b)	S(g)
100/0	S (v)	S (b)	S(b)	S (g)	MS(b)	S(b)	S(g)
E/M molar ratio at a fixed EA/AN = 50/50, 5 °C, O/M = 1.0							
0	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(y)
0.25	S (v)	S (b)	S (b)	S (g)	MS(b)	MS(b)	S (b)
0.5	S (v)	S (b)	S (b)	S (g)	MS(b)	MS(b)	S (b)
0.75	S (v)	S (b)	S (b)	S (g)	MS(b)	MS(b)	MS(b)
1.0	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(g)
1.25	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
1.5	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
O/M molar ratio at a fixed EA/AN = 50/50, 5 °C, E/M = 1.0							
0.25	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	S (b)
0.5	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	S (b)
0.75	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
1.0	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(g)
1.25	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
1.5	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
Polymerization temperature (°C) at a fixed EA/AN = 50/50, O/M = 1.0, E/M = 1.0							
5	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(g)
15	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(g)
20	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(g)
25	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)
40	S (v)	S (b)	S (b)	S (g)	S (b)	MS(b)	MS(b)

IS = insoluble, MS = mostly soluble, PS = partially soluble, S = soluble; b = blue, g = green, v = violet, y = yellow.

H_2SO_4, blue in NMP, DMF, DMSO and THF, and become green in HCOOH, as listed in Table 1. However, the copolymer solution color in $CHCl_3$ depends distinctly on its polymerization condition. The EA/AN(10/90) copolymer solution in $CHCl_3$ is yellow while the copolymers with other EA/AN ratios are green in $CHCl_3$, because the former copolymer has higher AN unit content and molecular weight (Fig. 1), leading to longer conjugated length and then longer visible light wavelength. The solutions of EA/AN (50/50) copolymers synthesized at 5–20 °C are green in $CHCl_3$ but blue at 25–40 °C because of higher molecular weight at lower temperature (Fig. 4). However, with changing E/M or O/M ratios, the $CHCl_3$ solution color of the copolymers with relatively low molecular weight (Figs. 2–3) is yellow or green with longer wavelength, indicating that other factors besides the molecular weight could also influence the solvatochromism.

The inviting solvatochromism of the copolymers with three EA/AN ratios in six solvents with different characteristics is further confirmed quantitatively by UV–vis spectra in Figs. 7–9. It is found that the UV–vis spectra of the copolymers in NMP, DMSO, and DMF show two absorption peaks around 320 and 610 nm. With changing the solvent from NMP, DMSO to DMF, the absorptions exhibit a hypsochromic shift. However, the copolymers in $CHCl_3$, THF, HCOOH, and H_2SO_4 exhibit more than two absorption peaks with stronger bands at much longer wavelength of 835–1086 nm. In THF, the spectrum seems to show three absorption peaks around 315, 420, and 890 nm. In $CHCl_3$, the spectrum shows four absorption peaks around 315, 420, 590, and 830 nm. In HCOOH, three EA/AN copolymers exhibit five bands around 310, 360, 590, 800, and 1070 nm. The EA/AN (50/50) copolymer/H_2SO_4 solution displays four absorbance peaks at 307, 475, 800, and 1070 nm. With lowering AN content from 50 to 0 mol%, the band around 890 or 840 nm in THF and HCOOH dramatically becomes weak, probably demonstrating that the band is ascribed to a decrease in polaron delocalization from the segments consisting of AN units in the polymers. In addition, the bands around 840 nm in formic acid and around 590 nm in $CHCl_3$ exhibit a hypsochromic shift with diminishing AN content from 50 to 0 mol%, implying that the conjugated length of the copolymers is shortened. It is easily observed that the band wavelength and intensity of the UV–vis spectra of the EA/AN copolymers in 520–1100 nm show an increased trend in the following solvents:

$$\mathrm{DMF} < \mathrm{DMSO} < \mathrm{NMP} < \mathrm{THF} \leq \mathrm{CHCl_3} < \mathrm{HCOOH} < \mathrm{H_2SO_4}$$

This order is similar to the variation of color wavelength of the copolymers solutions except for H_2SO_4 in Table 1.

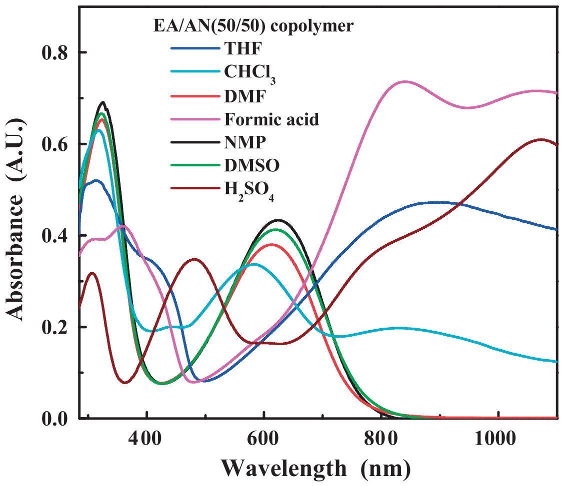

Fig. 7. UV–vis spectra of the EA/AN (50/50) copolymer base obtained at a fixed oxidant/monomer molar ratio of 0.5 and E/M molar ratio of 1.0 in seven solvents at 25 °C.

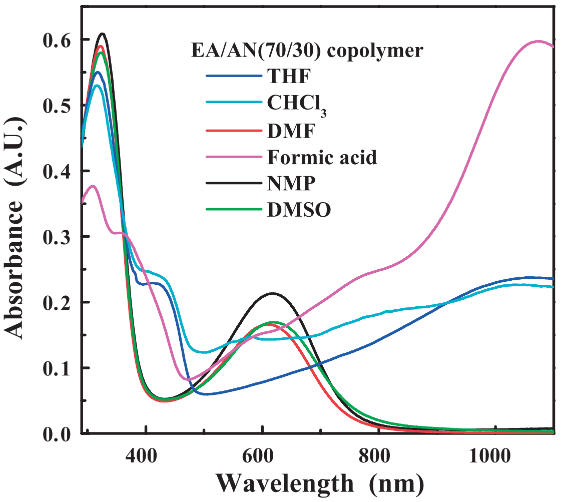

Fig. 8. UV–vis spectra of the EA/AN (70/30) copolymer base at a fixed oxidant/monomer molar ratio of 1.0 and E/M molar ratio of 1.0 in six solvents at 25 °C.

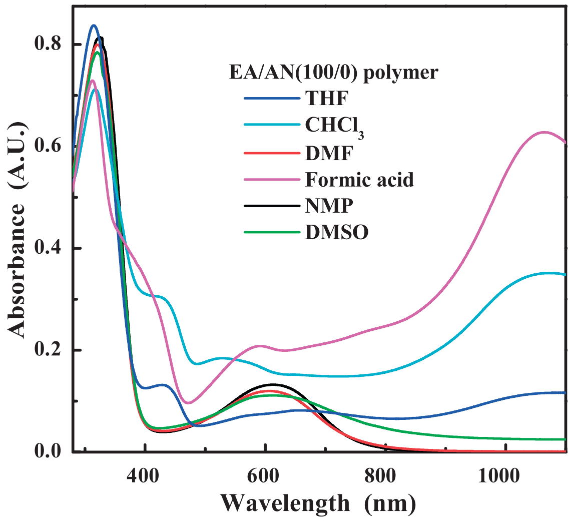

Fig. 9. UV–vis spectra of the EA/AN (100/0) copolymer base at a fixed O/M of 1.0 and E/M of 1.0 in six solvents at 25 °C.

That is to say, the copolymers have a more expanded chain conformation and longer conjugation length in the solvents such as THF, $CHCl_3$, HCOOH and H_2SO_4 than in DMF, NMP and DMSO. A significant bathochromic shift observed in THF and $CHCl_3$ suggests a strong interaction between the *N*-ethyl groups in the copolymers and THF or $CHCl_3$ molecules, i.e., a deaggregated effect of the copolymer chains in both solvents [28]. The strongest red shift in HCOOH and H_2SO_4 is because of their strong doping effect on the EA/AN copolymers. In summary, the interesting strong solvatochromism should be attributed to the variations of doping level, conjugating extent, polymer nature, and polymer–solvent interaction with solvent nature. The solvatochromism might originate from the electron transfer between the solvent molecules and the imine groups of the solvated polymer [29,30]. This electron transfer will enhance the electron density of the imine nitrogen and the dipole moment directed toward the nitrogen atom and consequently lower the energy of the ground state. This fact points out that the dipole moment of EA/AN copolymers at excited state is greater than the corresponding dipole moment in ground state.

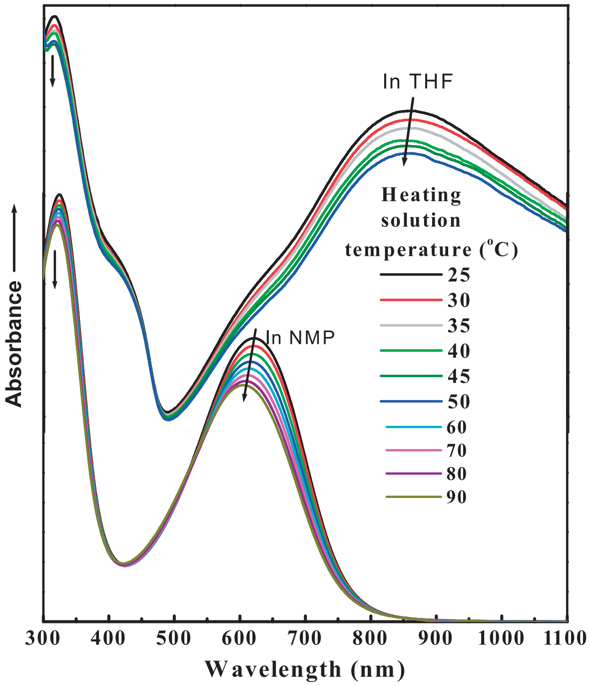

Fig. 10. In-situ UV–vis spectra of the EA/AN (50/50) copolymer base obtained at a fixed O/M of 0.5 and E/M molar ratio of 1.0 at various solution temperatures during heating solution from 25 to 90 °C in THF and NMP.

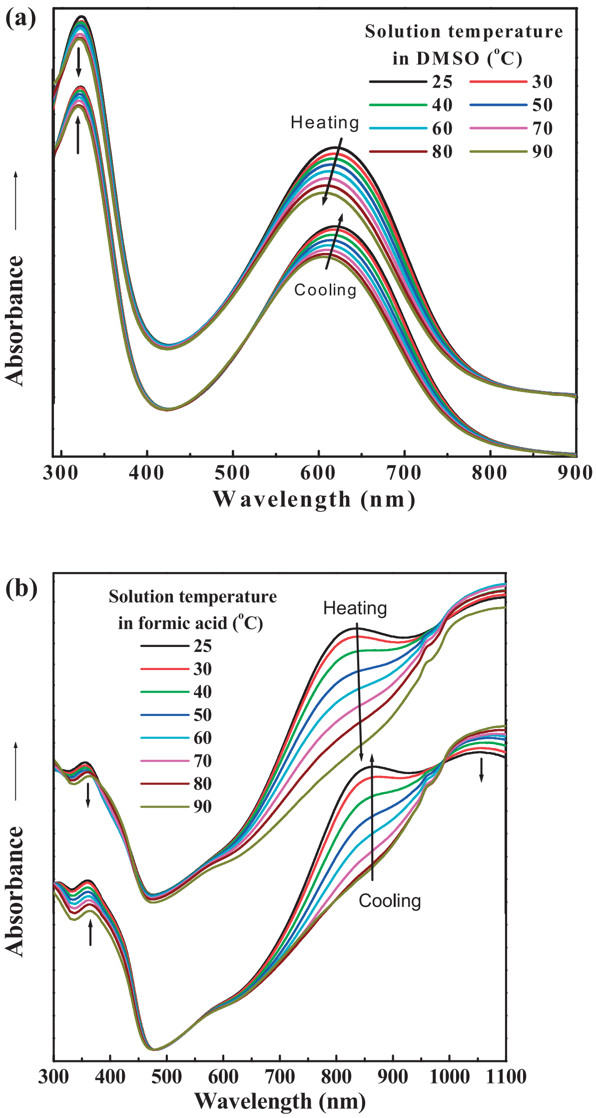

Fig. 11. (a) In-situ UV–vis spectra of the EA/AN (50/50) copolymer base obtained at a fixed O/M molar ratio of 0.5 and E/M molar ratio of 1.0 during heating from 25 to 90 °C and then cooling from 90 to 25 °C in DMSO. (b) In-situ UV–vis spectra of the EA/AN (50/50) copolymer obtained at a fixed O/M molar ratio of 0.5 and E/M ratio of 1.0 during heating from 25 to 90 °C and then cooling from 90 to 25 °C in formic acid.

3.3.3. Thermochromism

It is discovered that EA/AN copolymer bases show not only the colorful solvatochromism in solvents, but also interesting reversible thermochromism Figs. 10–12 quantitatively illustrate the temperature dependence of UV–vis absorption spectra of the EA/AN (50/50) copolymer in THF, NMP, DMSO, formic acid, and H_2SO_4. In Fig. 10, the absorption peaks around 867 nm in THF and 621 nm in NMP reflecting the conjugated length of the copolymers show a hypsochromic shift to 844 and 605 nm, respectively and a reduced intensity with raising the temperature from 25 to 50 and 90 °C, and an isosbestic point at around 460 nm in THF and around 520 nm in NMP is observed, but the color of the copolymer solution does not seem to change with naked eye. As shown in Figs. 11, EA/AN (50/50) copolymer exhibits quite different thermochromisms in DMSO, formic acid, and H_2SO_4 upon heating from 25 to 90 °C and subsequently cooling from 90 to 25 °C. At 25 °C, two peaks about 323 and 618 nm of the copolymer/DMSO are observed, and the solution color is blue. With elevating the temperature from 25 to 90 °C, the intensity and

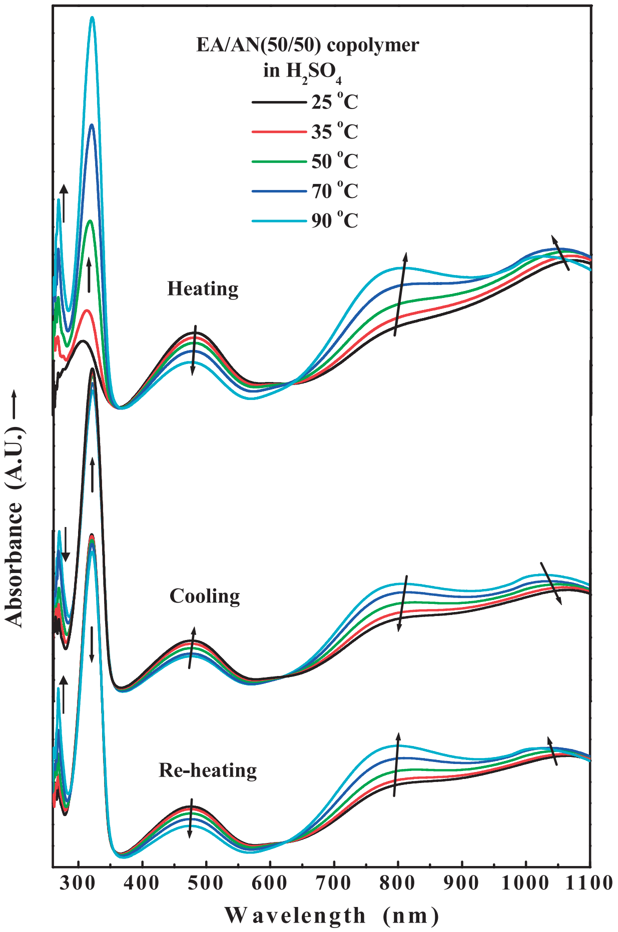

Fig. 12. In-situ UV–vis spectra of the EA/AN (50/50) copolymer obtained at a fixed O/M of 0.5 and E/M ratio of 1.0 at five temperatures by heating, cooling, and re-heating in a temperature range from 25 to 90 °C in concentrated H_2SO_4.

wavelength of the two peaks continuously decline, together with an apparent blue shift from 618 to 605 nm. It is of interest that the transition process is basically reversible with lowering the temperature from 90 to 25 °C. However, the strong peak at 837 nm of the copolymer/formic acid solution significantly becomes weak, while the peak at 1070 nm exhibits an increased tendency with elevating temperature from 25 to 90 °C. With cooling from 90 to 25 °C, the process is also reversible, and two isosbestic points are observed. The EA/AN (50/50) copolymer/H_2SO_4 solution exhibits a steadily decreased absorbance around 475 nm but a steadily increased absorbance around 268, 310, 790, and 1070 nm with raising solution temperature from 25 to 90 °C in Fig. 12. In particular, the bands at 268, 307, and 790 nm bathochromically shift to 269, 321, and 810 nm, respectively, and their absorbances grow very rapidly with elevating temperature, while the band at 1073 nm undergoes a blue shift to 1050 nm and two isosbestic points were observed in the spectra. When cooling from 90 to 25 °C, the bands at 321 and 475 nm strengthen slightly, but the bands at 269, 810 and 1050 nm weaken. When raising the temperature from 25 to 90 °C again, a substantially reverse spectral change was observed. A similar thermochromism has been revealed for aniline derivative copolymers [28], the substituted polythiophenes and *N*-alkylated PANs [29] in the solid state. The thermochromism should be attributed to a change of polymer conformation involving torsions of the main chains caused by thermal effects, and these torsions result in a reduction of the π-conjugation extent of the main chains. For the EA/AN (50/50) copolymer, the introduction of the ethyl side group increases the torsional angle between adjacent aromatic rings because of the steric hindrance. As the temperature rises, the thermal motion of the ethyl side group increases the torsional angle of the main chains, leading to the occurrence of the blue shift in solution. Different thermochromic behaviors of the copolymers in different solvents should be ascribed to the diverse interactions between the copolymer chains and solvent molecules. Relatively weak interaction between the copolymer chains and NMP or DMSO molecules leads to a simple thermochromism, while a strong interaction between the copolymer chains and formic or sulfuric acids or THF leads to complicated thermochromism. Especially, the doped form of copolymers in H_2SO_4 and formic acid exhibits strong polaron absorption at 650–900 at 90 °C and 700–950 nm at 25 °C, respectively; that can be assigned to conformational change due to strong doping effect of the acids on polymer chains. Note that the polaron band around 810 nm at 90 °C in H_2SO_4 with high boiling point is becoming stronger after the thermal treatment cycle from heating, cooling to re-heating, indicating that the increase in polaron delocalization with temperature from 25 up to 90 °C due to the thermal activation [28]. On the contrary, the polaron band around 850 nm is more intense at 25 °C in formic acid with relatively low boiling point, but drops gradually with elevating temperature and finally disappears at 90 °C. The decrease of polaron delocalization with temperature from 25 to 90 °C is due to the overcompensation of the thermal activation effect by the loss of some polarons and also reversible thermal dedoping effect induced by gradually enhanced thermal movement of formic acid molecules [28,29]. The reversible colorful solvatochromism and thermochromism would provide a new application potential of the AN polymer materials.

3.3.4. Film formability

It is seen from Table 2 that the film formability of the EA/AN copolymer bases in NMP exhibits a significant dependency on the EA/AN ratio. Generally, the EA/AN(10/90) copolymers display excellent formability and flexibility and very smooth surface of the film. Note that the EA/AN (70/30) copolymer demonstrates relatively poor film formability and flexibility, possibly because of its lowest molecular weight (Fig. 1). Indeed, the film formability and flexibility of the copolymers are directly proportional to the molecular weight. Therefore, the EA/AN

Table 2
A comparison of 20 μm-thick film formability of emulsion and non-emulsion EA/AN copolymer bases in NMP at a copolymer concentration of 35 g/l at 60–70 °C

EA/AN molar ratio	Emulsion copolymer films			Non-emulsion copolymer films [31]		
	Formability	Flexibility	Appearance	Formability	Flexibility	Appearance
0/100	Good	Excellent	Smooth, lustrous black	Good	Good	Smooth, lustrous black
10/90	Excellent	Excellent	Very smooth, lustrous black	Excellent	Excellent	Very smooth, lustrous black
30/70	Excellent	Good	Smooth, dull black	Good	Poor	Smooth, dull black
50/50	Good	Fair	Smooth, dull black	Good	Poor	Smooth, dull black
70/30	Fair	Poor	Smooth, dull black	Good	Poor	Smooth, dull black
90/10	Good	Fair	Smooth, dull black	Fair	Poor	Smooth, dull black
100/0	Good	Good	Smooth, dull black	Fair	Poor	Smooth, dull black

emulsion copolymer with higher molecular weight and narrower molecular weight distribution exhibits better film performance than corresponding non-emulsion copolymer (Table 2) [31].

3.3.5. Bulk electrical conductivity

The electrical conductivity of the EA/AN copolymers in HCl re-doped and dedoped forms is summarized in Figs. 1–4. It is noticed from Fig. 1 that the conductivity of the doped EA/AN copolymers falls monotonically from 0.161 to 1.03×10^{-5} S/cm with the increase of the EA content from 0 to 100%, because of an increase in the content of the ethyl group with steric effect that can produce a twist in the polymer backbone and hence reduce its coplanarity and the conjugation length [21,32]. As shown in Fig. 2, the conductivity of the doped EA/AN (50/50) emulsion copolymers is much higher than that of non-emulsion copolymers. Especially, the EA/AN copolymer exhibits the highest conductivity of 1.79×10^{-3} S/cm at the emulsifier/monomer molar ratio of 0.25 due to its highest molecular weight and also the highest doping level in the presence of the emulsifier. Note that the conductivity of the doped EA/AN (50/50) copolymers falls slightly with elevating the oxidant content or the polymerization temperature [21,32], respectively. It is interesting that the doped EA/AN (50/50) copolymers with the largest molecular weight dispersity exhibit the highest conductivity, as illustrated in Figs. 1–4, possibly due to the presence of a certain amount of high-molecular weight copolymers as a highly effective conductor. In addition, all dedoped copolymers exhibit much lower conductivity than corresponding doped copolymers, and different variation of the conductivity with the polymerization parameters mentioned above as compared with the doped copolymers. In conclusion, the bulk conductivity of the EA/AN copolymers could be adjusted in an extensive scope from 2.0×10^{-10} to 1.6×10^{-1} S/cm through controlling a series of polymerization parameters and doping degree. Note that the EA/AN polymer materials should exhibit a surface conductivity of higher than 1.6×10^{-1} S/cm because the surface conductivity value of the same sample is usually 100–1000 times higher than the bulk conductivity due to a large interparticle contact resistance [33].

4. Conclusions

A series of functional EA/AN copolymers has been successfully synthesized by an emulsion polymerization in the presence of SDBS in HCl aqueous medium. The polymerization yield, molecular weight and electrical conductivity of the copolymers depend significantly on the comonomer ratio, emulsifier/monomer ratio, oxidant/monomer ratios and polymerization temperature. The solubility, solvatochromism, and thermochromism of the copolymers are influenced by EA/AN ratio, emulsifier/monomer ratio, and solvent characteristics but not by oxidant/monomer ratio and polymerization temperature. The minimum polymerization yield and molecular weight/its distribution are observed at the EA/AN molar ratio of 70/30 and 90/10, respectively, implying lower reactivity of copolymerization between EA and AN than that of both homopolymerizations. The optimized emulsifier/monomer ratio, oxidant/monomer ratio, and temperature for the EA/AN (50/50) copolymerization system for the preparation of the copolymer with a high yield, a high molecular weight, and a high conductivity, are 0.25–0.50, 1.5, and 5 °C, respectively. The copolymers are completely soluble in H_2SO_4, NMP, formic acid, and DMF. In fact, their solubility in all chosen solvents is much higher than pure PAN. In particular, the copolymers exhibit colorful solvatochromism from yellow, green, blue to violet and reversible thermochromism with changing solvents and temperature in a range from 25 to 90 °C, respectively, narrow molecular weight distribution, as well as excellent film flexibility. The optimal EA/AN molar ratio for the copolymers with the excellent film formability is 10/90, suggesting a dominance of copolymer in comparison with homopolymers. The bulk electrical conductivity of the copolymers could be adjusted in a wide range from 2.0×10^{-10} to 1.6×10^{-1} S/cm with artificially controlling a series of polymerization parameters. The EA/AN emulsion copolymer exhibits higher polymerization yield, narrower molecular weight distribution, longer UV–vis wavelength than some AN copolymer like AN/1,4-dihydrobenzo[*d*][1,2]dithiin-5-ylamin copolymer [34] and higher conductivity, higher molecular weight, narrower molecular weight distribution, and better film performance than corresponding non-emulsion copolymer [31]. The successful preparation of the processible multifunctional AN copolymers suggests that the facile emulsion copolymerization method described in this article could be used to synthesize a series of new processible AN copolymers, which might offer new opportunities for both fundamental research and technological applications.

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