Macromolecules **2007,** *40,* 1489−1496

Synthesis, Film-Forming, and Electronic Properties of *o*-Phenylenediamine Copolymers Displaying An Uncommon Tricolor

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Received October 25, 2006; Revised Manuscript Received December 18, 2006

ABSTRACT: Novel electrochromic copolymers from *o*-phenylenediamine (*o*PD) with aniline (ANi) were facilely synthesized by a chemical oxidative polymerization. The synthesis, structure, and properties of the copolymers were systematically studied by changing *o*PD content and polymerization temperature. The dependence of the polymerization yield at 70 °C on the *o*PD content is quite different from that at 17 °C, indicating that the copolymerization between the *o*PD and ANi comonomers varies significantly with polymerization temperature, whereas the conductivity and solubility of the copolymers obtained at 17 and 70 °C demonstrate similar dependency of the *o*PD content. The reactivity ratios, r_{oPD} and r_{ANi}, of *o*PD and ANi were found to be 9.70 and 2.74, respectively, implying a stronger homopolymerization tendency than copolymerization between them. The copolymers exhibit stronger formability and uniformity of the film, much higher electroactivity, and better tricolor electrochromism than *o*PD and ANi homopolymers. The copolymer film, containing 50 mol % *o*PD unit is red at −0.5 to 0 V vs SCE, turns to green at 0 to +0.6 V vs SCE, and blue at +0.6 to +1.35 V vs SCE. Possible assignments of the macromolecular structures of the copolymers in different potential ranges are proposed. The difficulty of synthesizing electrochromic *o*PD/ANi copolymers could be overcome to some extent by the oxidative polymerization at 70 °C. Particularly, the copolymer has an uncommon combination of strong film formability, high electroactivity, and unique tricolor electrochromism, which could not be achieved by both homopolymers themselves.

Introduction

As one of the most important conducting polymers, polyaniline (PANi) has been extensively studied in the fields of chemistry, biochemistry, electronics, energy, and materials sciences[1] because of exigent demands for high-performance materials in advanced technologies including active electrodes,[2] microelectronic materials, electrochromic devices,[3] metal anticorrosive coatings,[4] rechargeable batteries,[5] energy storage and transfer, redox microtemplates,[6] sensors,[7] and actuators.[8] But the imperfect electrochromism and insolubility of PANi in common solvents except for H_2SO_4 and *N*-methylpyrrolidone (NMP)[9] confine its application fields to some extent. Recently, a great deal of attention has been paid to the copolymers of ANi and its derivatives.[10−11] As one of the influential derivatives of PANi, poly(*o*-phenylenediamine) (P*o*PD) has been widely synthesized by electropolymerization[12] and chemical oxidative polymerization.[13] The P*o*PD has demonstrated a great potentiality for use as electrochromic display materials,[14] humidity sensors,[15] electrode-modified materials,[16] pH response,[17] and protection against metal corrosion.[18] The *o*-phenylenediamine (*o*PD)/ANi copolymer has been also obtained by electropolymerization[19] and chemical oxidative polymerization.[13] However, large-area and uniform polymer films could not be easily prepared on a large scale by the electropolymerization due to the limit of electrode area and current-density nonuniformity. The optimal temperature for the oxidative polymerization has not been reported until now because low temperature (<20 °C) is suitable for ANi polymerization where high temperature (118 °C) is suitable for *o*PD polymerization. PANi generally displays yellow/green/blue tricolor between −0.5 and +1.35 V versus SCE potential, while P*o*PD displays red/green bicolor. Apparently, a better tricolor electrochromism of red/green/blue, allowing the creation of all colors of red/orange/yellow/green/cyan/blue/purple/white/black by various combination of the tricolor, has not been observed based on PANi or P*o*PD alone. On the other hand, the film formability, electronic properties, and especially, electrochromism of the *o*PD/ANi copolymers obtained by the chemical oxidative polymerization have not been reported systematically until now. In particular, *o*PD is chosen as a comonomer for efficiently enhancing the electroactivity and incorporating red electrochromism of the PANi film. Possible decreased conductivity caused by the introduction of *o*PD units should not influence the realization of a tricolor of red, green, and blue of the *o*PD/ANi copolymer films with high electroactivity.

The aim of this experiment was to synthesize real *o*PD/ANi copolymers with two types of molecular structure characteristics by the chemical oxidative polymerization. The variation in the polymerization yield, solubility, film formability, electrical conductivity, and electroactivity of the copolymers with the *o*PD/ANi comonomer ratio and polymerization temperature was carefully described. An appropriate temperature for *o*PD/ANi copolymerization was given. In particular, the unique electrochromism of the solution-casting copolymer films displaying the red/green/blue tricolor was elaborated. An important new insight into the real copolymerization between both comonomers and much better comprehensive performance of the copolymer films than both homopolymer films was provided based on several significant experimental facts.

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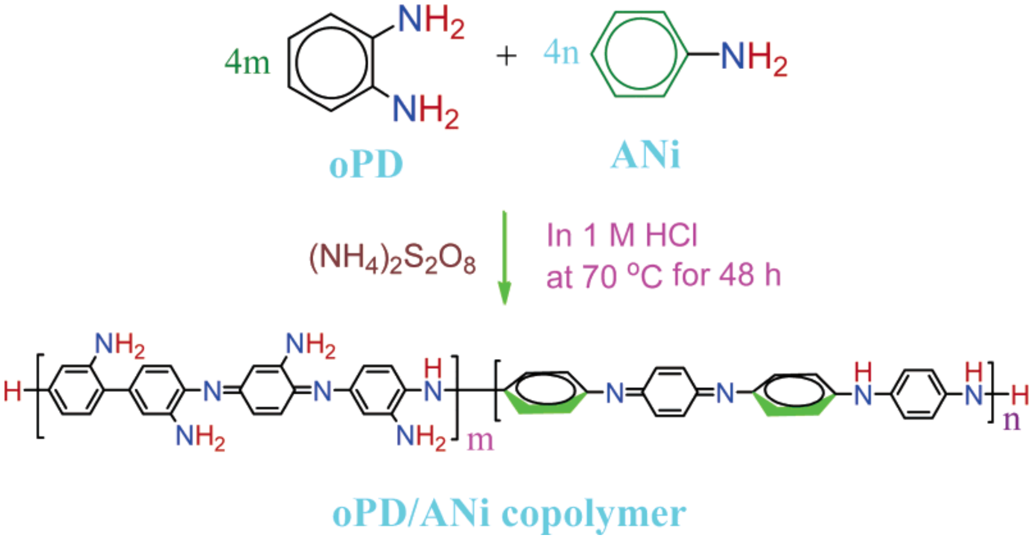
10.1021/ma062463g CCC: $37.00

Scheme 1. Copolymerization between *o*PD and ANi and Nominal Copolymer Structures



Experimental Section

Polymerization. *o*PD, ANi, oxidant, acids, and solvents were commercially obtained as chemical pure reagents and used as received. The *o*PD/ANi copolymers were prepared by the chemical oxidative polymerization. A representative procedure for the preparation of the *o*PD/ANi(50:50) copolymer was described as follows: 50 mL of 1 M HCl solution was added with 1.08 g (10 mmol) of *o*PD and 0.91 mL (10 mmol) of ANi in a 250 mL glass flask in water bath at a constant temperature of 17 or 70 °C and magnetostirred vigorously for half an hour. Ammonium persulfate [$(NH_4)_2S_2O_8$], 2.28 g (10 mmol), was dissolved separately in 50 mL of 1M HCl to prepare an oxidant solution. The monomer solution was then treated by dropwise adding the oxidant solution at a rate of one drop for every 3 s in 30 min (the total monomer/oxidant molar ratio is 2:1). Immediately, after the first few drops, the reaction solution turned dark red. The reaction mixture was continuously stirred at 17 or 70 °C for 48 h. The copolymer was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and water-soluble oligomers. The obtained copolymer was red and black solid powders at 17 and 70 °C, respectively, and was left to dry at 60 °C. The copolymerization formulation of *o*PD and ANi was shown in Scheme 1.

Measurements. The solubility of the *o*PD/ANi copolymers was evaluated with the following method: a copolymer powder sample of 10 mg was added into the solvent of 0.5 mL and dispersed thoroughly. After the mixture was swayed continuously for 2 h at room temperature, the solubility was characterized semiquantitatively. The bulk electrical conductivity of the copolymers was measured by a two-disk method using a UT70A professional digital multimeter (UNI-T). UV−vis spectra were measured on an 8453 exoteric spectrophotometer (Agilent Ltd.) in a wavelength range of 260−1000 nm with a homogeneous solution of the copolymers in NMP. FTIR spectra of the polymers in KBr pellets were recorded on a Nicolet Magna 550 FTIR spectrometer made in the U.S.A., at 2 cm^{-1} resolution. The copolymer film with the thickness and area of 4−5 μm and 8 × 20 mm^2, respectively, was obtained by casting an NMP solution at the copolymer concentrations of 0.5 and 1 wt % onto an ITO glass electrode. The electroactivity and electrochromism of copolymer films on the ITO were measured by the method of cyclic voltammogrammetry, which was conducted in a standard three-electrode cell using a ZF-3 laboratory potentiostat. The electrochemical experiments were performed on a CH830 electrochemical workstation (Chenhua Instruments, Shanghai, China) using the ITO as working electrodes for its conductivity and transparency, a saturated calomel electrode (SCE) as reference electrode, and a platinum electrode as counter electrode. All potential values are reported versus SCE. The copolymer films in 1 M HCl supporting electrolyte were scanned for two cycles between −0.5 and +1.35 V vs SCE at a potential scanning rate of 10, 20, 50, and 100 mV vs SCE/s. The spectroelectrochemical properties of the copolymer films were characterized by using the ITO as working electrode, a platinum wires as counter electrode, and a SCE as reference electrode in 1 M HCl as supporting electrolyte in a colorimetric utensil as electrolytic cell. The spectroelectrochemical experiments were conducted by scanning UV−vis spectra in a wavelength range of 350−700 nm when the current of electrolytic cell has been constant for 30 s at a stable potential between working electrode and reference electrode.

Table 1. Influence of *o*PD/ANi Molar Ratio on the Color of *o*PD/ANi Copolymers and Their Dense Thin Films with Comonomer Concentration of 20 mM and Monomer/Oxidant Molar Ratio of 2:1 for Polymerization Time of 48 h at Two Polymerization Temperatures of 70 and 17 °C in 1M HCl

	70 °C		17 °C	
*o*PD/ANi molar ratio	powder	thin film	powder	thin film
100:0	dark red	red	red	red
80:20	dark red	red	red	red
70:30	black needle crystal	red	red	red
50:50	dark red	red	dark red	red
30:70	black	green	dark red	red
20:80	black	green	black	red
0:100	black	green	dark green	green

Results and Discussion

Synthesis of the *o*PD/ANi Copolymers. The copolymerization of both *o*PD and ANi monomers with ammonium persulfate as an oxidant in HCl at two different temperatures for 48 h affords a fine precipitate as the product. The variation of the appearance, yield, and bulk electrical conductivity of the copolymer with *o*PD fraction is shown in Table 1 and Figure 1. It is found that the copolymerization is significantly dependent on the *o*PD fraction and reaction temperature. With increasing *o*PD content from 0 to 100%, the color of the polymer powders obtained at both temperatures gradually lightens. Particularly, the polymer powders obtained at 17 °C rapidly change their color from dark green to black to red with increasing *o*PD content from 0 to 20 to 30 mol %. It can be observed from Figure 1 that, in the case of 70 °C, the yield declines at first and then rises as the *o*PD content increases, illustrating a minimum when the *o*PD fraction is 50 mol %. These phenomena can be explained based on a viewpoint of Malinauskas:[19] (1) in the case of low *o*PD fraction, the inhibition of *o*PD to ANi

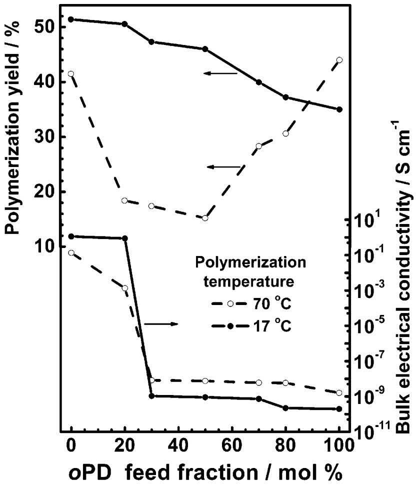


Figure 1. Influence of *o*PD fraction on polymerization yield and bulk electrical conductivity of *o*PD/ANi copolymers with monomer concentration of 20 mM and monomer/oxidant molar ratio of 2:1 for polymerization time of 48 h in 1M HCl at two polymerization temperatures of 70 and 17 °C.

polymerization would become stronger as the *o*PD fraction increases, leading to a reduced yield because the *o*PD mainly as an inhibitor might induce the formation of some low-molecular-weight water-soluble oligomers that would be washed out during the posttreatment of the as-obtained copolymers; (2) *o*PD would polymerize more rapidly than ANi when *o*PD fraction is higher than ANi fraction, resulting in a P*o*PD-like copolymer and thereby gradually enhanced yield as the *o*PD fraction further increases. At 17 °C, it is observed that the yield monotonically decreases as the *o*PD fraction increases. This may be caused by a special combination of the inhibition of *o*PD unit with the polymerization advantage of ANi at a relatively low temperature. Comparing two yield curves at 70 and 17 °C in Figure 1, it is revealed that the yield at 17 °C is higher than that at 70 °C at the *o*PD fraction of less than 90 mol %. This may be ascribed to very low polymerizing activity of *o*PD monomer but high polymerizing activity of ANi monomer at low temperature. Therefore the inhibition effect of *o*PD to ANi polymerization is weak at low temperature. However, this inhibition effect will get stronger with elevating temperature, and accordingly, the yield decreases. On the contrary, when the *o*PD fraction predominates over the composition of the comonomer and hence copolymer chain, the polymerizability of *o*PD monomer would increase as the temperature rises. This could be used to explain the higher yield of *o*PD homopolymerization at 70 °C than at 17 °C. Contrastingly, the yield of PANi increases steadily from 41.5 to 51.4 to 83.0% with lowering polymerization temperature from 70 to 17 to 1 °C.[9] It is reported that *o*PD monomer could homopolymerize successfully at 118 °C to form a black polymer.[20] In summary, the copolymerization effect between *o*PD and ANi comonomers is much stronger at 70 °C than 17 °C. A P*o*PD-like polymer containing a small amount of PANi units could successfully be synthesized at 70 °C. This is one of the purposes of this study. Most of polymers used in the following investigation were prepared at a constant polymerization temperature of 70 °C.

UV−Vis Spectra of the *o*PD/ANi Copolymers. Figure 2 shows the UV−vis absorption spectra of seven copolymers with *o*PD content from 0 to 100% in NMP. It is seen that the polymers with *o*PD content of 30−100 mol % have almost the same UV−vis spectral characteristics as P*o*PD, but the polymer with *o*PD content of 20 mol % has a combination of the UV−vis characteristics of P*o*PD and PANi. The band at 315 nm due to $\pi-\pi^*$ transition between conjugated adjacent benzenoid rings and the band at 623 nm due to electronic transition of quinoid imine structures might be assigned to PANi segments.[1,7,8,21,22] The band at 623 nm remarkably becomes weaker with decreasing ANi fraction. In the spectra of P*o*PD, there exist two bands at 291 and 421 nm. Shorter wavelength may be responsible to the influence of the amino side group on the polymer chains. The intensity of the band at 421 nm first decreases, then increases, and finally decreases again as the *o*PD fraction

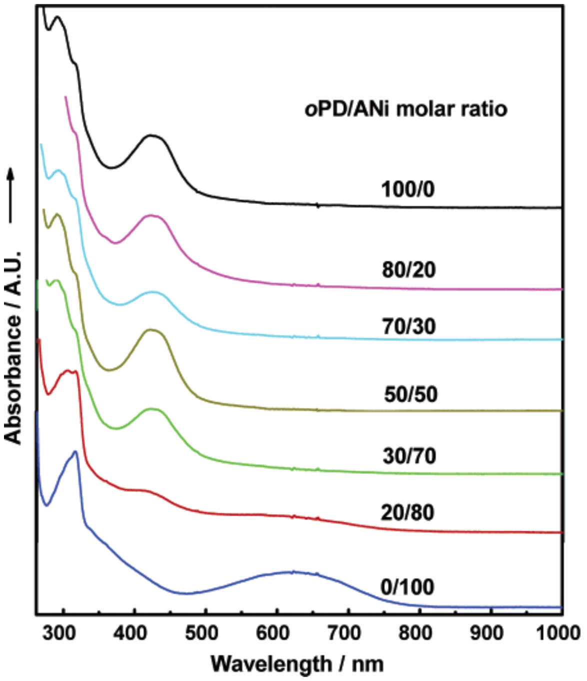


Figure 2. UV−vis absorption spectra of the copolymers prepared at 70 °C with *o*PD/ANi molar ratios of 100:0, 80:20, 70:30, 50:50, 30:70, 20:80, and 0:100 in NMP.

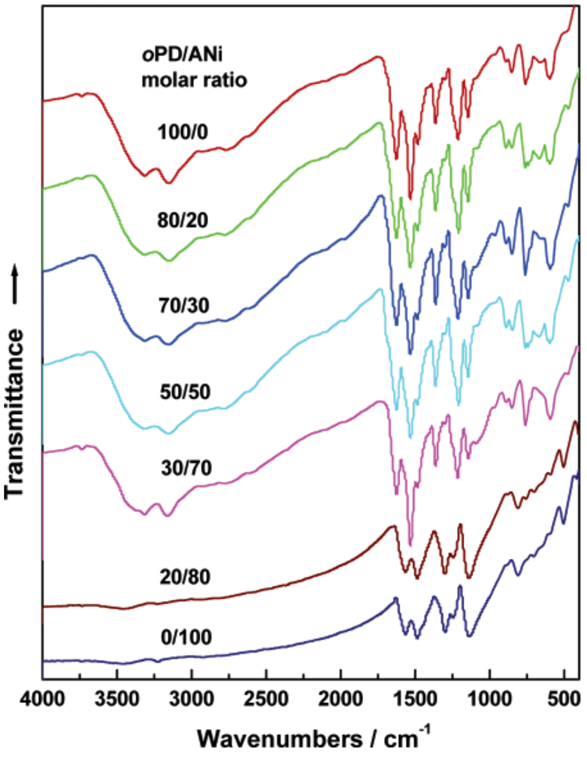
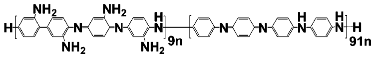
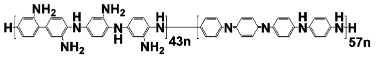
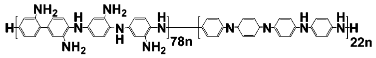
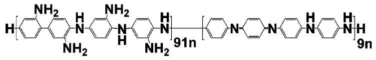
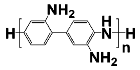


Figure 3. FTIR absorption spectra of the copolymers prepared at 70 °C with *o*PD/ANi molar ratios of 100:0, 80:20, 70:30, 50:50, 30:70, 20:80, and 0:100.

Table 2. Elemental Analysis and Possible Macromolecular Structure of *o*PD/ANi Polymer Microparticles

*o*PD/ANi feed ratio (mol%)	C/H/N/Total (wt%)	Experimental formula	Calculated formula	Proposed nominal macromolecular structure
20/80	58.67/4.11/12.16/74.94	$C_{12}H_{8.35}N_{2.13}(HCl)_{1.74}$	$C_{12}H_{8.62}N_{2.13}$	
30/70	57.71/4.28/14.91/76.90	$C_{12}H_{9.05}N_{2.66}(HCl)_{1.62}$	$C_{12}H_{9.38}N_{2.66}$	
50/50	48.98/5.03/15.26/69.27	$C_{12}H_{11}N_{3.2}(HCl)_{2.6}(H_2O)_{0.6}$	$C_{12}H_{11}N_{3.2}$	
80/20	48.49/5.10/15.42/69.01	$C_{12}H_{11.12}N_{3.27}(HCl)_{2.59}(H_2O)_{0.7}$	$C_{12}H_{11.12}N_{3.27}$	
100/0	49.92/4.65/14.84/69.41	$C_{12}H_{10.93}N_{3.05}(HCl)_{2.49}$	$C_{12}H_{11}N_3$	

reduces. Maximal band intensity appears at the *o*PD fraction of 50 mol %. This nonmonotonic variation of the intensity of UV−vis bands may result from a copolymerization effect of *o*PD with ANi monomers. In other words, the polymer formed by the chemical oxidative polymerization of *o*PD with ANi monomers is a real copolymer of two monomer units rather than a mixture of two homopolymers.

FTIR Spectra of the *o*PD/ANi Copolymers. FTIR spectra of the copolymers with various comonomer ratios are shown in Figure 3. With increasing *o*PD content from 20 to 30 mol %, the bands centered at 3317 and 3153 cm^{-1}, due to the characteristic N−H stretching vibration in −NH− and $-NH_2$ groups on *o*PD units, respectively, suddenly become strong. In fact, the polymers with *o*PD content of 30−80 mol % have almost the same IR characteristics as P*o*PD, whereas two polymers with *o*PD contents of 0 and 20 mol % possess nearly identical IR characteristics. The IR spectra of the two polymers with *o*PD contents of 0−20 mol % do not display obvious peaks between 3000 and 4000 cm^{-1}, suggesting the presence of few $-NH-/-NH_2$ groups in the polymers. The peaks at 1564−1625 cm^{-1} and 1485−1534 cm^{-1} are assigned to quinoid and benzenoid rings, respectively.[1,22] The fact that the peak intensity at 1485−1534 cm^{-1} is stronger than that of 1615−1625 cm^{-1} might signify more benzenoid units in the whole polymers. The peaks at 1300−1365 cm^{-1} are attributed to the C═N stretching vibration in the quinoid imine units. The peaks at 1140−1214 cm^{-1} are assigned to the C−N stretching vibration in benzenoid units. The appearance of these IR bands should verify the formation of the *o*PD/ANi copolymers.

Copolymer Composition and the Reactivity Ratios between *o*PD and ANi Comonomers. Table 2 shows the C/H/N ratio and their macromolecular structure in the *o*PD/ANi copolymers determined by elemental analysis. The total contents of the C/H/N elements are less than 100%, suggesting the presence of other elements besides C/H/N elements in the copolymers. For example, Cl and O elements might exist in the resulting copolymers because of HCl doping during the copolymerization and also water adsorption. The P*o*PD structure derived from the element ratio suggests that a denitrogenation happens during the polymerization. The denitrogenation of P*o*PD-like units reduces the π-conjugation that has been confirmed by much lower conductivity in Figure 1 and UV−vis spectra in Figure 2. Figure 4 shows the variation of the observed *o*PD content in the copolymers with the feed *o*PD content. It can be observed that the actual *o*PD content in the copolymers is higher than the feed *o*PD content at an *o*PD concentration of more than 24 mol % but lower than the feed *o*PD content at an *o*PD content of less than 24 mol %. The 24 mol % *o*PD concentration is an identical point for the *o*PD/ANi copolymerization. As a result, the reactivity ratios of *o*PD and ANi can be calculated: $r_{oPD} = 9.70$ and $r_{ANi} = 2.74$, which means a stronger homopolymerization tendency than their copolymerization. The copolymers are likely to be block copolymers, as shown in Table 2.

Bulk Electrical Conductivity of the *o*PD/ANi Copolymers. The variation of the bulk electrical conductivity of the copolymers with *o*PD fraction and polymerization temperature is shown in Figure 1. It can be observed that the difference between the conductivities of the copolymers obtained at 70 and 17 °C is not big. It is of interest that the polymers with *o*PD content of 0−20 mol % exhibit higher conductivity at 17 °C than 70 °C. Contrarily, the polymers with *o*PD fraction of 30−100 mol % exhibit higher conductivity at 70 °C than 17 °C. That is to say, 17 °C is advantageous for the polymerization of ANi monomer, while 70 °C is advantageous for the polymerization of *o*PD monomer. The conductivity of the copolymers sharply decreases as the *o*PD fraction increases from 20 to 30 mol %. As a matter of fact, the polymers with *o*PD content of 0−20 mol % have similar conductivity to PANi, whereas the polymers with *o*PD content of 30−100 mol % have similar conductivity to P*o*PD. These results are coincident with IR spectra in Figure 3. The fact that the conductivity of the copolymers decreases with the increase of *o*PD content should be attributed to:[10,23] (1) bulky $-NH_2$ substituents would cause main-chain twisting, which reduces its coplanarity and results in a barrier to the intrachain transfer and interchain jumping of the electrons, thereby shortening the conjugation length, (2) bulky $-NH_2$ substituents will prevent acid doping of the polymers due to static repulsion and steric hindrance, and (3) the decline of the molecular weight of the polymer that is confirmed by the lightening of the polymer color in Table 1. Medium conductivity should be one of the important performances to successfully actualize good electroactivity and electrochromism.[22]

Solubility and Film Formability of the *o*PD/ANi Copolymers. Good solubility is the foundation of film formation by a solution casting method. The copolymer could be uniformly cast and spread on an electrode to form a dense thin film when it has dissolved in proper solvents. Table 3 and Table S1 (Supporting Information) list the solubility of copolymers in various kinds of solvents. Apparently, the solubility of the two series of copolymers depends strongly on the solvents used, the *o*PD/ANi ratio, and also polymerization temperature. Although all of the polymers are completely soluble in H_2SO_4 with the highest dielectric constant of 101, the polymers with *o*PD

Table 3. Solubility[a] and Solution Color[b] of *o*PD/ANi Copolymers Prepared at 70 °C with Monomer/oxidant Molar Ratio of 2:1 for Polymerization Time of 48 h in 1 M HCl

solvent				*o*PD/ANi comonomer molar ratio						
name	dielectric constant	solubility parameter $J^{1/2}$ $cm^{3/2}$	hydrogen-bonding strength	100:0 [23.3][c]	80:20 [24.2][c]	70:30 [24.6][c]	50:50 [25.5][c]	30:70 [26.4][c]	20:80 [26.9][c]	0:100 [27.8][c]
benzene, toluene, or xylene	2	18.5	poor	PS(C)	PS(C)	IS	IS	IS	IS	IS
$CHCl_3$	5	18.9	poor	MS(BR)	PS(BR)	IS	SS(Y)	IS	PS(R)	PS(R)
THF	7	19.5	moderate	PS(BR)	MS(Y)	PS(Y)	PS(R)	PS(Y)	SS(BR)	SS(BR)
CH_2Cl_2	9	19.9	poor	PS(BR)	PS(C)	IS	PS(Y)	IS	IS	IS
CH_2ClCH_2Cl	11	20.0	poor	SS	SS	IS	SS	IS	IS	IS
m-cresol	12	22.7	strong	S(R)	MS(R)	S(R)	S(B)	S(B)	MS(B)	PS(B)
NMP	32	22.9	moderate	S(BR)	S(Y)	S(Y)	S(R)	S(R)	MS(B)	PS(B)
DMF	38	24.9	moderate	S(BR)	S(R)	S(R)	S(BR)	S(R)	MS(B)	SS(Y)
DMSO	47	26.5	moderate	S(BR)	S(R)	S(R)	S(BR)	S(R)	MS(B)	PS(BR)
H_2SO_4	101	26.4	strong	S(B)	S(B)	S(B)	S(B)	S(B)	S(B)	S(B)

[a] IS, insoluble; MS, mainly soluble; PS, partially soluble; S, soluble; SS, slightly soluble. [b] The letters in parentheses indicate the color of polymer solutions. C, colorless; B, black; Bl, blue; BR, brown; G, gray; O, orange; R, red; Y, yellow. [c] The data in the square brackets are the solubility parameters of the polymers calculated by the method in Table S2 (Supporting Information).[24]

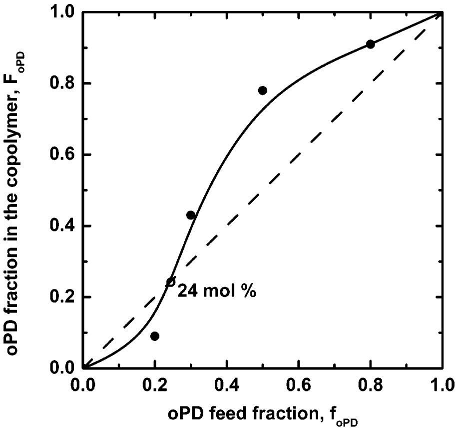


Figure 4. Variation of the observed *o*PD content of *o*PD/ANi copolymers with the feed *o*PD content for polymerization time of 48 h at 70 °C in 1M HCl with monomer/oxidant molar ratio of 2:1.

content of 30−100 mol % are well soluble in DMSO, DMF, NMP, and *m*-cresol with medium dielectric constant of 12−47. This phenomenon should be attributed to their P*o*PD-like structure, as mentioned in UV−vis and IR sections. Note that almost all polymers are only partially soluble or even insoluble in benzene, toluene, xylene, $CHCl_3$, tetrahydrofuran(THF), CH_2Cl_2, and CH_2ClCH_2Cl with low dielectric constant of 2−11. The polymers with *o*PD/ANi molar ratios from 100:0 to 30:70 are totally soluble in five protic solvents with the solubility parameters of 22.7−26.5 $J^{1/2}$ $cm^{3/2}$ because the difference between the solubility parameters of the polymers and solvents is small. The difference between the solubilities of two series of polymers synthesized at 70 and 17 °C is not much, possibly due to their similar structure.

On the basis of the study of polymer solubility, it seems that NMP is an appropriate solvent for the formation of the polymer films because NMP possesses relatively low toxicity, low corrosive ability, and appropriate volatility that makes the volatilization rate easily controlled during film formation. H_2SO_4 was not chosen as film-forming solvent because of its high toxicity, strong corrosive ability, and low volatility. The film formability of the copolymers in NMP and resulting film features (Table 1) depend significantly on the polymer concentration and *o*PD fraction. The polymer solution at the concentration of 0.5 wt % displays better film formability than that of 1 wt % due to relatively low solubility of the polymer in the latter solution. Particularly, the polymers with *o*PD fraction of 0−30 mol % have excellent formability, toughness, and uniformity of the films.

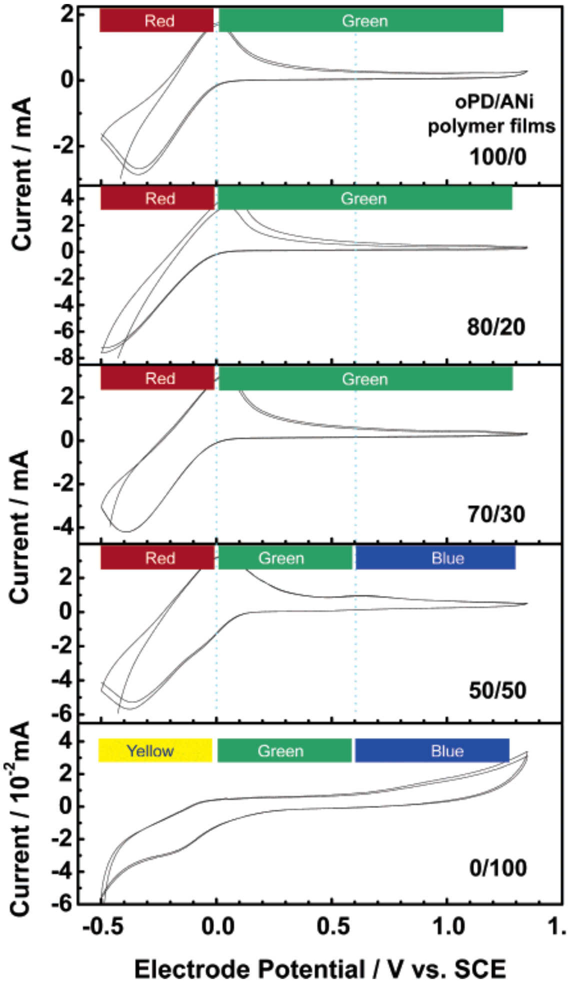


Figure 5. Cyclic voltammogram curves of the polymer films with *o*PD/ANi molar ratios of 100:0, 80:20, 70:30, 50:50, and 0:100 on ITO electrode between −0.5 and +1.35 V vs SCE potential in 1M HCl at a scanning rate of 50 mV vs SCE/s. The polymers were prepared at 70 °C.

The Electroactivity of the *o*PD/ANi Copolymer Films. Figure 5 shows the cyclic voltammogram curves of copolymer films with different comonomer ratios. Figure 6 illustrates the cyclic voltammograms of *o*PD/ANi(50:50) copolymer film at four potential scanning rates. All of the copolymers for the

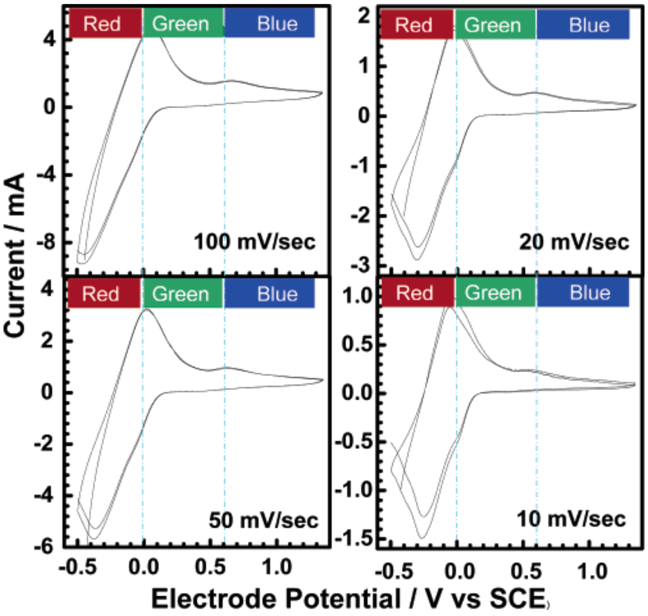


Figure 6. Cyclic voltammoram curves of *o*PD/ANi(50:50) copolymer films on ITO electrode between −0.5 and +1.35 V vs SCE potential in a solution of 1M HCl at the potential scanning rates of 10, 20, 50, and 100 mV vs SCE/s. The copolymers were prepared at 70 °C.

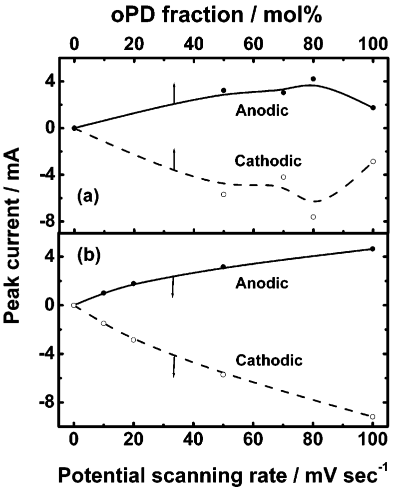


Figure 7. Dependence of the electroactivity(the maximal peak current) of (a) the *o*PD/ANi polymer films on the *o*PD fraction at a fixed potential scanning rate of 50 mV vs SCE/s and (b) the *o*PD/ANi(50:50) copolymer films on the potential scanning rate. The polymers were prepared at 70 °C.

measurement of electroactivity and electrochromism were prepared at 70 °C. It is found from Figure 7 that the polymer films exhibit basically reversible electroactivity that is significantly affected by comonomer ratio and potential scanning rate. Apparently, all of the *o*PD/ANi copolymers demonstrate much higher electroactivity than both *o*PD and ANi homopolymers in the same potential range. Among the five polymers, the electroactivity of *o*PD/ANi(80:20) copolymer is the highest, but that of PANi is the lowest,[25] signifying that the *o*PD/ANi copolymerization does largely improve the electroactivity. The potential of anodic peaks shifts toward the negative direction as the *o*PD fraction decreases, which may be caused by the redox processes of some low-molecular-weight products.[19] In addition, the only *o*PD/ANi(50:50) copolymer displays an additional small anodic peak at around 0.6 V versus SCE in its cyclic voltammogram (Figure 5). Obviously, the additional peak at around 0.6 V versus SCE should be ascribed to the PANi units and the strong peak at around 0 V versus SCE to the P*o*PD units.[19] These nonmonotonic variations of the electroactivity of the polymers with *o*PD fraction again confirm that the *o*PD/ANi polymers formed are true copolymers of *o*PD with ANi rather than a simple mixture of both homopolymers. On the basis of a close comparison of Figure 1 with Figure 5, it can be concluded that the copolymer films with high electroactivity do not have high conductivity, implying that the conductivity is not simply and directly proportional to the electroactivity.

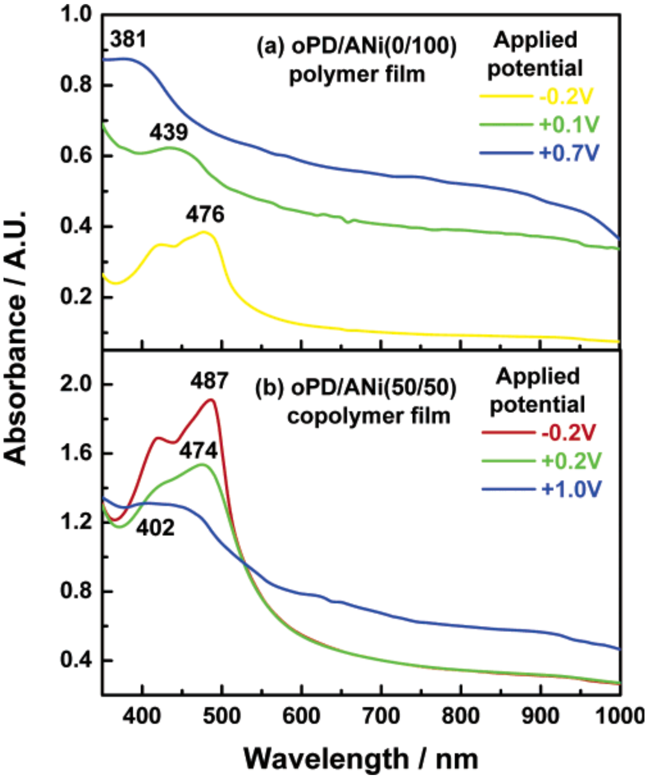
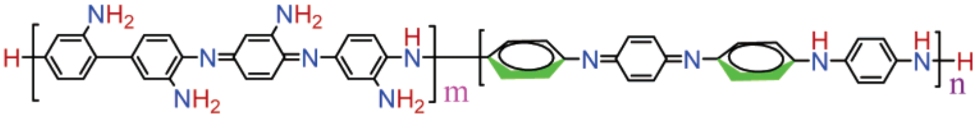
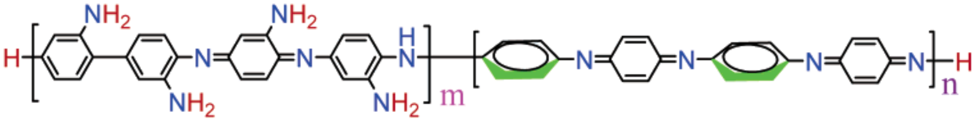


Figure 8. Spectroelectrochemical behavior of the polymer films with *o*PD/ANi molar ratios of (a) 0:100 and (b) 50:50 on ITO electrode in 1M HCl electrolyte at different applied potentials. The polymers were prepared at 70 °C.

It can be seen from Figure 6 that the anodic peak current becomes consistently stronger as the scanning rate raises, which means that the electroactivity of copolymer films increases. It can also be discerned that the potential of anodic peaks shifts toward the positive direction as the scanning rate rises, indicating that the reversibility of the redox reaction between different redox states of the copolymers is different.[26] An almost linear enhancement in the peak current with elevating the scanning rate shown in Figure 7 suggests a good adhesion of the copolymer films onto the ITO electrodes. In fact, the copolymer films cannot be peeled from the ITO by a traditional method. Just by considering the electroactivity of copolymer films, it is advantageous to increase the scanning rate to improve the electrochromism, but this will shorten the life of copolymer films. Therefore, an appropriate scanning rate should be carefully chosen for a concurrent optimization of the electroactivity and electrochromism.

The Electrochromism of the *o*PD/ANi Copolymer Films. It is easily noticed from Figure 5 that there are anodic peaks located at approximately 0 V vs SCE in the cyclic voltammogram of copolymer films. These anodic peaks shift toward the negative direction with reduction of the *o*PD fraction and eventually disappears at the *o*PD fraction of 0%. These peaks correspond apparently to the redox processes of P*o*PD units.[27]

Table 4. The Macromolecular Structure, Redox Form, and Color of *o*PD/ANi(50:50) Copolymer Films in Three Potential Ranges

Potential V vs SCE	Macromolecular structure	Film color
-0.5 – 0		Red
0 – +0.6		Green
+0.6 – +1.35		Blue

Note that the dark-red polymer film containing *o*PD units at around 0 V vs SCE turns to dark green at 0.3 V versus SCE (and blue at 1.0 V versus SCE for only *o*PD/ANi(50:50) copolymer film), suggesting that the *o*PD/ANi polymer films show a typical electrochromism. It seems that only the *o*PD/ANi(50:50) copolymer film displays an amazing tricolor of red, green, and blue.

The possible macromolecular structures of the *o*PD/ANi(50:50) copolymers at different potentials are listed in Table 4. It could be speculated on the basis of previous studies on P*o*PD[26,28] and PANi[29,30] that there were P*o*PD-like segments and PANi-like segments in copolymers. It is known that a reduced state of P*o*PD segments was colorless and unstable and tended to be oxidized to a semi-oxidized state rapidly. The semi-oxidized state of P*o*PD segments was red and the most stable state in a potential range between −0.6 and 0 V versus SCE, whereas the reduced state of PANi segments was colorless/yellow in this potential range. Therefore, the whole color of the *o*PD/ANi(50:50) copolymers should be red at −0.6 to 0 V versus SCE. With increasing the potential to 0 to +0.6 V versus SCE, the semi-oxidized P*o*PD could be oxidized to a total-oxidized state, accompanied by a color change from red to green. Similarly, the wholly reduced PANi segments could be oxidized to a semi-oxidized state, accompanied by a color change from yellow to green. Apparently, the *o*PD/ANi(50:50) copolymers should be green at 0 to +0.6 V versus SCE. When the potential was more positive than +0.6 V versus SCE, the color of PANi segments turned from green to blue, resulting in the appearance of blue color of the whole copolymer.

Spectroelectrochemistry of the *o*PD/ANi Polymer Films. In situ spectroelectrochemical experiments were used to further verify the electrochromism of *o*PD/ANi polymer films by characterizing their UV−vis absorbance in several typical potentials.[31] Transmittance UV−vis spectra recorded in an applied potential range from −0.2 to 1.0 V versus SCE are shown in Figure 8. It is seen that polymer films display various UV−vis absorbance characteristics, i.e., the wavelength, shape, and intensity of the UV−vis band, with changing potential and *o*PD/ANi ratio. In detail, the electrochromic tricolor transitions involve a red [for *o*PD/ANi(50:50) copolymer at 487 nm] or yellow [for *o*PD/ANi(0:100) polymer at 476 nm] leucoemeraldine reduced form at −0.2 V to a green emeraldine half-oxidized form at 474−439 nm at +0.1 to +0.2 V to a blue pernigraniline fully oxidized form at 402−381 nm at +0.7 to +1.0 V, as listed in Table 4. *o*PD/ANi(0:100) polymer exhibits a steadily increased UV−vis absorbance in a wavelength range between 350 and 1000 nm with elevation of the potential, whereas *o*PD/ANi(50:50) polymer demonstrates a gradually declined band intensity in a wavelength range from 403 to 528 nm. These regular variations of UV−vis spectral characteristics of the polymer films with the potential and *o*PD/ANi ratio would serve to explain the film color change from red(yellow) to green to blue when the potential rises from −0.2 to +0.2(+0.1) to +1.0(+0.7) V because the absorption of specific mixed lights is responsible for the film color. The unusual tricolor electrochromism should be attributed to a reversible transition between particular redox states of the copolymer chain structures that are different from both homopolymer structures. The spectroelectrochemistry semiquantitatively proves the appearance of the different colors of the polymer films at various potentials.

Conclusions

The *o*PD/ANi copolymerization and copolymer properties strongly depend on the polymerization temperature and *o*PD/ANi ratio. Quite unlike dependence of the copolymer yield on *o*PD fraction at 17 and 70 °C, this significantly suggests different copolymerization mechanisms between *o*PD and ANi comonomers. The difficulty of synthesizing an *o*PD/ANi copolymer could be overcome to some extent by the oxidative copolymerization at 70 °C. The *o*PD/ANi(20:80) copolymer exhibits the optimal electrical conductivity as well as formability, uniformity, and adherence of the film on the ITO electrode. The *o*PD/ANi(50:50) copolymer film displays uncommon electrochromism with a typical tricolor of red, green, and blue. The film color changes reversibly with the electrode potential, i.e., red at −0.5 to 0 V versus SCE, green at 0 to +0.6 V versus SCE, and blue at +0.6 to +1.35 V versus SCE. The *o*PD/ANi(80:20) copolymer has the highest electroactivity that is also remarkably influenced by the potential scanning rate. The copolymer has an uncommon combination of stronger film formability, higher electroactivity, and better tricolor electrochromism than both homopolymers because of the significant copolymerization effect between *o*PD and ANi monomers. The nonmonotonic variation of the film properties with the *o*PD/ANi ratio confirms the formation of an *o*PD/ANi copolymer. The chemical oxidative polymerization combined with the solution cast method would be potentially utilized to synthesize the novel functional large-area film of the *o*PD/ANi copolymers on a large scale, which is not easily realized by the electropolymerization.

Acknowledgment. The project was supported by the National Natural Science Foundation of China (20274030) and also the Foundation of the Key Laboratory of Molecular Engineering of Polymers, Fudan University, China. We are also grateful to Professor Dr. Yu-Liang Yang from Fudan University for his valuable help.

Supporting Information Available: Solubility and solution color of *o*PD/AN copolymers prepared at 17 °C; the estimation method of the solubility parameter (δ) of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA062463G