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Chemical and Electrochemical Copolymerization of Aniline with Alkyl Ring-Substituted Anilines

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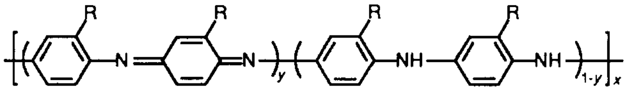
ABSTRACT: Poly(aniline-*co*-*o*-toluidine) and poly(aniline-*co*-*m*-toluidine) have been synthesized by both chemical and electrochemical copolymerizations of aniline with *o*-toluidine and with *m*-toluidine, respectively. The compositions of the copolymers were determined by ^{1}H NMR spectroscopy and could be altered by variation of the comonomer feed ratios. Thus, conductivity of copolymers can be controlled in a broad range, (e.g. when doped with 1 M HCl), from ca. 10 S/cm for homopolymer of aniline to ca. 0.1 S/cm for those of toluidines. The relationship between copolymer composition and comonomer feed ratio shows that the toluidines are more reactive than aniline in the copolymerization. The results are consistent with the proposed mechanism for the polymerization of aniline and its derivatives.

Introduction

Recent advances in the field of electrically conducting polymers have led to a variety of materials with great potentials for commercial applications. Among them, polyaniline is one of most interesting materials because of its moderately high conductivity (ca. 10 S/cm) upon doping with nonoxidizing Brønsted acids,[1,2] its well-behaved electrochemistry,[3-5] its possible processability,[6] and its good environmental stability.[2,7] Recently there have been several reports on the syntheses and properties of alkyl[8,9] or alkoxyl[10] ring-substituted polyanilines. These polyaniline derivatives have improved solubilities and different electronic and electrochemical properties in comparison with polyaniline. For example, poly(*o*-ethoxyaniline) was reported to be water soluble;[10] and both poly(*o*-toluidine) and poly(*m*-toluidine) showed interesting electrochemical properties which could be attributed to a reduction in π-conjugation of the polymers caused by steric effects of the substituent groups.[9] It is generally believed that polyaniline and related derivatives could be schematically represented by the following formula



where R is H for polyaniline, CH_3 for both poly(*o*-toluidine) and poly(*m*-toluidine), or CH_3O for polyanisidine, etc.; the value of y represents the oxidation state of the polymers.[11]

We have been interested in the kinetics and mechanism of the polymerization of aniline[12-14] in an effort to develop a new method to prepare the polymer with well-defined structure and improved electronic properties. Both chemical and electrochemical polymerization of aniline have been proposed to involve an incorporation of neutral aniline monomer into the growing polymer chain end via an electrophilic substitution reaction. The rate-determining step in the polymerization is the formation of dimeric species i.e., *p*-aminodiphenylamine, benzidine, and *N*,*N*-diphenylhydrazine. Kinetic studies of the electrochemical polymerization indicate that the rate of growth of the polymer chain is approximately 10^4 times higher than that of initiation.[13] This has been further confirmed by observation of a significant increase in the rate of polymerization when a small amount of the dimeric species was added as initiators.[14] It is well-known that studies of copolymerization could lead to the knowledge of the reactivities of monomers and their relationship with the chemical structure of the monomers and, therefore, to a better understanding of the mechanism of polymerization. Copolymerization also greatly increases the ability of the polymer scientists to tailor-make a material with specifically desired properties. As a typical example of application of copolymerizations in the field of conductive polymers, small quantities of *N*-(3-bromophenyl)pyrrole have been demonstrated to have a dramatic effect on the conductivity of the poly[pyrrole-*co*-*N*-(3-bromophenyl)pyrrole] with 10% incorporation resulting in a change in conductivity by 6 orders of magnitude.[15]

In the present paper, we report both chemical and electrochemical copolymerization of aniline with *o*-toluidine and with *m*-toluidine, respectively. The copolymers were characterized by IR and ^{1}H NMR spectroscopy, cyclic voltammetry (CV), and gel-permeation chromatography (GPC). The copolymer compositions were determined

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by ^{1}H NMR spectroscopy, and the electrical conductivities of the copolymers with various compositions were measured. Results are discussed on the basis of electronic and steric effects of the methyl substituent and in relation to the mechanism of polymerization.

Experimental Section

Materials and Instrumentation. Aniline, *o*-toluidine, and *m*-toluidine (Aldrich) were doubly distilled. Ammonium persulfate, $(NH_4)_2S_2O_8$ (99%, EM Science), was used as the oxidant in chemical polymerizations without further purification. All aqueous solutions were prepared by using freshly distilled water. Proton NMR spectra were recorded on an IBM Bruker WM250 spectrometer operating at 250 MHz. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent and tetramethylsilane (TMS) as an internal standard. Dilute solutions of the polymers (0.1–1% w/v) were prepared and used in NMR measurements to ensure a maximum dissolution of the polymers. A variable relaxation delay was used to ensure the reliability of the signal integrations. Electrochemical syntheses and cyclic voltammetry were performed on an EG&G PAR Model 273 potentiostat/galvanostat. A three-electrode cell was employed with a saturated calomel electrode (SCE) as reference. Platinum foils were used as both the working and counter electrodes. Conductivities were measured by using the four-probe technique on polymer–powder pressed pellets with an EG&G PAR Model 173 potentiostat/galvanostat as a source of constant current. Infrared spectra of polymer–KBr pellets were recorded on a Perkin-Elmer Model 467 grating IR spectrometer. Gel-permeation chromatography was performed on a Waters GPC Model IIA equipped with a Model 590 programmable solvent delivery module, a refractometer as detector, and an Ultrastyragel linear column at 35 °C using *N*-methyl-2-pyrrolidinone (NMP, Aldrich, HPLC grade) as the solvent. All the syntheses and measurements were performed in air.

Chemical Copolymerization. Copolymers of aniline with *o*-toluidine and with *m*-toluidine were prepared by oxidation of aniline and the appropriate toluidine in various molar fractions (f_1) of the toluidine in the feed with ammonium persulfate as oxidant in an acidic (1.0 M HCl) aqueous medium.[9,16] The following is a typical procedure for preparation of the copolymers in low yields that are required for the determination of the reactivities of monomers. The low yield (<15%) was achieved by employing a low molar ratio (0.25:1) of the oxidant to the comonomers.

An *o*-toluidine/aniline comonomer solution (f_1 = 0.167) was prepared by dissolving 4.65 g (49.9 mmol) of aniline and 1.05 g (9.80 mmol) of *o*-toluidine in 200 mL of 1 M HCl and was cooled to below 5 °C in an ice-water bath. A precooled solution of 3.423 g (15.0 mmol) of ammonium persulfate in 200 mL of 1 M HCl was then added dropwise to the comonomer solution with stirring over a period of ca. 20 min. The solution was further stirred for ca. 2 h in the ice-water bath and was then filtered through a Buchner funnel. The resulting green precipitate was washed with 1 M HCl continuously until the filtrate was colorless, and the precipitate was then transferred into a beaker containing 200 mL of 1 M HCl. The resultant mixture was stirred at room temperature for ca. 1 h followed by filtration. The green precipitate was collected and dried under dynamic vacuum at room temperature for ca. 48 h. Using the above procedure, yields of the HCl-doped copolymers were 9–14%. The copolymers with high yields (74–85%) were also synthesized for comparison by using the same procedure but higher oxidant/comonomer molar ratio (1.25:1).

To convert the HCl-doped copolymers into their free bases, ca. 1 g of a fine powder of the HCl-doped copolymer was suspended in 200 mL of 0.1 M NH_4OH solution with stirring for ca. 4 h. The mixture was then filtered and the blue precipitate washed with 0.1 M NH_4OH followed by drying under dynamic vacuum for ca. 48 h to obtain the base form of the copolymer. The spectroscopic and GPC studies were performed on the base form of the copolymers.

Electrochemical Copolymerization and Cyclic Voltammetry. The copolymer films were deposited electrochemically on a platinum working electrode in a 1.0 M HCl aqueous solution of comonomers with various f_1 at room temperature using cyclic potential sweep techniques.[3] The potentials were swept continuously in the range of −0.2 to 0.7 V vs SCE at a scan rate of 25 mV/s. The cyclic voltammograms of the copolymerization were recorded continuously and coincidentally with the syntheses.[13] Cyclic voltammetry studies of the films after synthesis were performed in a monomer-free 1.0 M HCl aqueous solution. Chemically synthesized copolymers were also characterized by cyclic voltammetry. Thus, the copolymers were cast onto the Pt working electrode by evaporating a suspension of the copolymers in chloroform. Three to four casts were usually performed in order to deposited enough electroactive materials on the electrode. Upon drying in air, the Pt electrode coated with the copolymers was placed in 1.0 M HCl and preconditioned by cycling the potentials between −0.2 and 0.35 V vs SCE for ca. 10 min. The cyclic voltammograms of the chemically synthesized copolymers were then recorded.

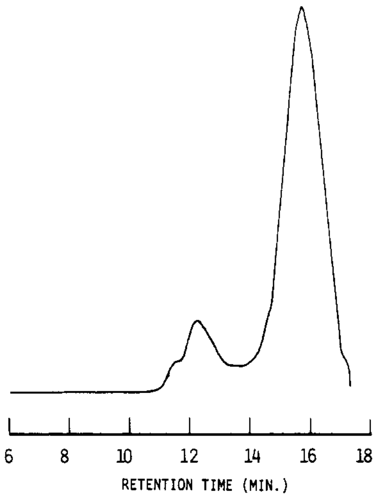


Figure 1. Gel permeation chromatogram of poly(aniline-*co*-*o*-toluidine) prepared with a molar fraction of *o*-toluidine in the feed of 0.333 (solvent, *N*-methyl-2-pyrrolidinone; flow rate, 0.6 mL/min).

Results and Discussion

Poly(aniline-*co*-*o*-toluidine) and poly(aniline-*co*-*m*-toluidine) were synthesized by both chemical and electrochemical copolymerization of aniline with *o*-toluidine and with *m*-toluidine at various molar fractions (f_1) of the toluidines in the feed. Molecular weights of the copolymers in the base form were studied by gel-permeation chromatography with *N*-methyl-2-pyrrolidinone (NMP) as solvent following reported procedures.[17] A typical chromatogram of poly(aniline-*co*-*o*-toluidine) (f_1 = 0.333) is shown in Figure 1 in which the molecular weights of the copolymer consists of two main fractions with areas of ca. 15% and 85% for the high and low molecular weight fractions, respectively. All of the copolymers gave similar bimodal types of molecular weight distributions. On the basis of the monodispersed polystyrene calibration, the GPC peak molecular weight was estimated to be approximately 9000 and 400 000 for the low and high molecular weight fractions, respectively. As one would expect, the chain conformations of the copolymers should be quite different from those of polystyrene, resulting in different hydrodynamic volumes of the polymer chains. Since the copolymer chains could be more rigid than those of polystyrene, the actual molecular weights of the copolymers should be lower than the values estimated from the polystyrene calibration. Further investigation is in progress in our laboratory in an effort to determine the molecular weights more accurately.

The representative infrared spectra of the copolymers (f_1 = 0.50) are shown in Figure 2 in comparison with those

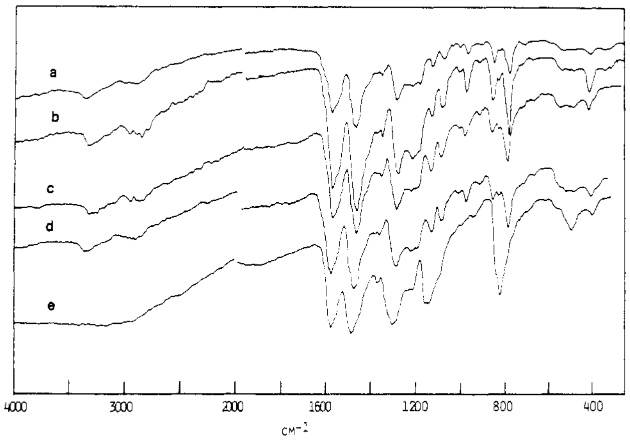


Figure 2. Infrared spectra of the base form of (a) poly(*o*-toluidine), (b) poly(*m*-toluidine), (c) poly(aniline-*co*-*m*-toluidine) (f_1 = 0.5), (d) poly(aniline-*co*-*o*-toluidine) (f_1 = 0.5), and (e) polyaniline in KBr pellets.

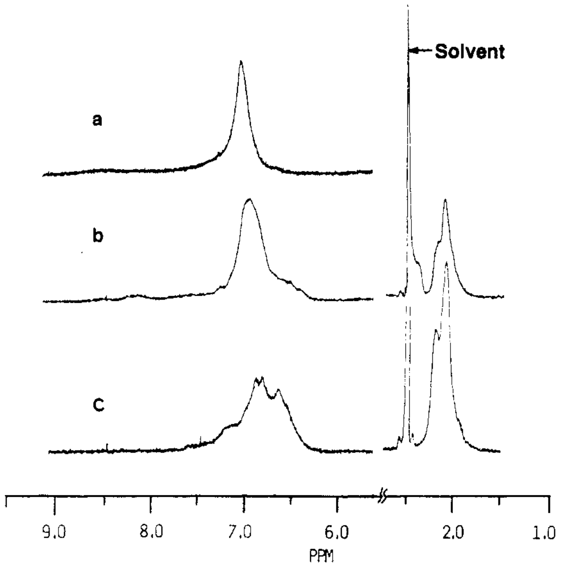


Figure 3. Proton NMR spectra of the base form of (a) polyaniline, (b) poly(aniline-*co*-*o*-toluidine) (f_1 = 0.167), and (c) poly(*o*-toluidine) in DMSO-d_6.

of the homopolymers, i.e. polyaniline, poly(*o*-toluidine), and poly(*m*-toluidine), which were prepared under the identical conditions as the copolymers. The IR spectra of poly(aniline-*co*-toluidines) (parts c and d of Figure 2) are very similar to those of polytoluidines (parts a and b of Figure 2) but different from that of polyaniline (Figure 2e) particularly in the region of ca. 800–900 and 1100–1200 cm^{-1} owing to the different substitution patterns of the aromatic rings.[18] This indicates a high content of the toluidine units in the composition of the copolymers. However, the compositions could not be accurately determined from the IR spectra owing to the lack of a reliable reference and to the overlap of the absorption bands where the spectra of polytoluidines differ from that of polyaniline.[18]

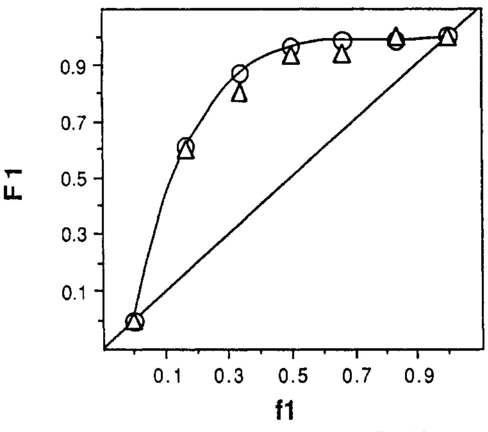


Figure 4. Dependence of the composition F_1 (the fraction of the toluidine units in the copolymers) of (○) poly(aniline-*co*-*o*-toluidine) and (△) poly(aniline-*co*-*m*-toluidine) on the comonomer feed composition f_1 (the fraction of the toluidines in the feed) for the copolymers with low yields (9–14%).

The copolymers in the base form with the low yields were studied by ^{1}H NMR spectroscopy. Figure 3 gives the ^{1}H NMR spectra of (a) polyaniline, (b) poly(aniline-*co*-*o*-toluidine) prepared at f_1 = 0.167, and (c) poly(*o*-toluidine). Proton NMR spectra of poly(aniline-*co*-*m*-toluidines) have essentially the same characteristics as those of poly(aniline-*co*-*o*-toluidines). The signals in the region of 7.8–6.35 ppm are assigned to the aromatic protons and those in the region of 1.8–2.1 ppm to the methyl protons. No signal in the latter region was observed in the spectrum of polyaniline (Figure 3a). More detailed assignments of the ^{1}H NMR spectra were made on the basis of a series of model compounds and will be reported elsewhere.[19] Therefore, the composition of copolymers can be determined from the ratio of the peak area of the aromatic to the methyl protons. The composition of the copolymers (F_1, defined as the molar fraction of the toluidine units in the copolymers) thus obtained from the ^{1}H NMR spectra was plotted against the molar fraction of the toluidine in the feed (f_1) as shown in Figure 4. The diagonal line represents the case that both monomers have identical reactivity. All of the values of F_1 for the copolymers are above the diagonal line, indicating that the copolymers consist of higher fractions of the toluidine units than that of aniline units. The plots of F_1 vs f_1 for both toluidines are very close to each other, suggesting similar reactivities in their copolymerizations with aniline. As demonstrated in Figure 4, even a small fraction (e.g. f_1 = 0.167) of the toluidine comonomer in the feed leads to a high content (F_1 = 0.6) of the toluidine unit in the copolymer. Therefore, the relative monomer reactivities of both toluidines should be higher than that of aniline in the copolymerization.

In order to establish that the materials are genuine copolymers of aniline with the toluidines rather than a mixture of homopolymers of aniline and the toluidines, the copolymers were further characterized by cyclic voltammetry (CV). It was reported[9] that the cyclic voltammogram of polyaniline differs from those of the polytoluidines in the redox potentials represented by values of $E_{1/2}$. The electrochemical copolymerization of aniline with *o*-toluidine and with *m*-toluidine were carried out by using the cyclic potential sweep method[3,9] in a 1.0 M HCl aqueous solution with the electrode potentials swept continuously between −0.2 and 0.7 V vs SCE at a scan rate of 25 mV/s. The electrode coated with the copolymer was washed with 1.0 M HCl and transferred to a comonomer-free 1.0 M HCl to record the cyclic voltammogram. The CV's of the copolymers demonstrate similar features as the homopolymers of aniline and the toluidines,[9] which mainly consist of two redox processes at the $E_{1/2}$ of 0.21 and 0.59 V vs SCE, respectively. Only a single pair of peaks was observed for each redox process rather than two pairs that would be expected for a mixture of the two homopolymers. Since the electrochemical reactions for the first redox process at the lower potential (ca. 0.21 V vs SCE) is well-established[5,9] as the oxi-

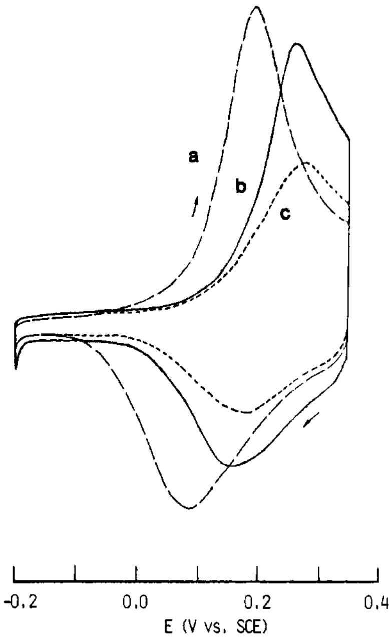


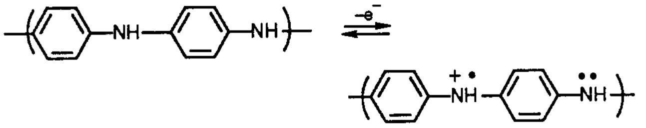
Figure 5. Cyclic voltammograms of electrochemically prepared (a) polyaniline, (b) poly(aniline-*co*-*o*-toluidine) (f_1 = 0.5) and (c) poly(*o*-toluidine) in 1.0 M HCl with the potential sweep between −0.2 and 0.35 V vs SCE at a scan rate of 25 mV/s.

Table I
$E_{1/2}$ of the First Redox Process for the Homopolymers and the Copolymers

polymer or copolymer	f_1[a]	$E_{1/2}$,[b] V vs SCE
polyaniline	0	0.14
poly(aniline-*co*-*o*-toluidine)	0.17	0.16
	0.50	0.21
poly(aniline-*co*-*m*-toluidine)	0.40	0.18
	0.50	0.21
poly(*o*-toluidine)	1	0.22
poly(*m*-toluidine)	1	0.22

[a] The molar fraction of the toluidine in the comonomer feed. [b] Determined by cyclic voltammetry (CV) of electrochemically prepared polymer films (thickness ca. 1 μm) in a 1.0 M HCl aqueous solution.

dation and reduction of the polymers corresponding to the conversions between the amine units and the radical cations (semiquinone)



the cyclic voltammograms and the $E_{1/2}$ values of the copolymers for the first redox process are compared with those of homopolymers in Figure 5 and Table I, respectively. All of the $E_{1/2}$ values for the copolymers are between those for polyaniline and for the polytoluidines. Furthermore, the cyclic voltammetry of the chemically prepared copolymers was also investigated by the same method, and the results are essentially identical with those of the electrochemically prepared copolymers. Therefore, this strongly suggests that both electrochemical and chemical oxidations of the aniline/*o*-toluidine or aniline/*m*-toluidine comonomer pair generate true copolymers rather than the mixture of the corresponding homopolymers.

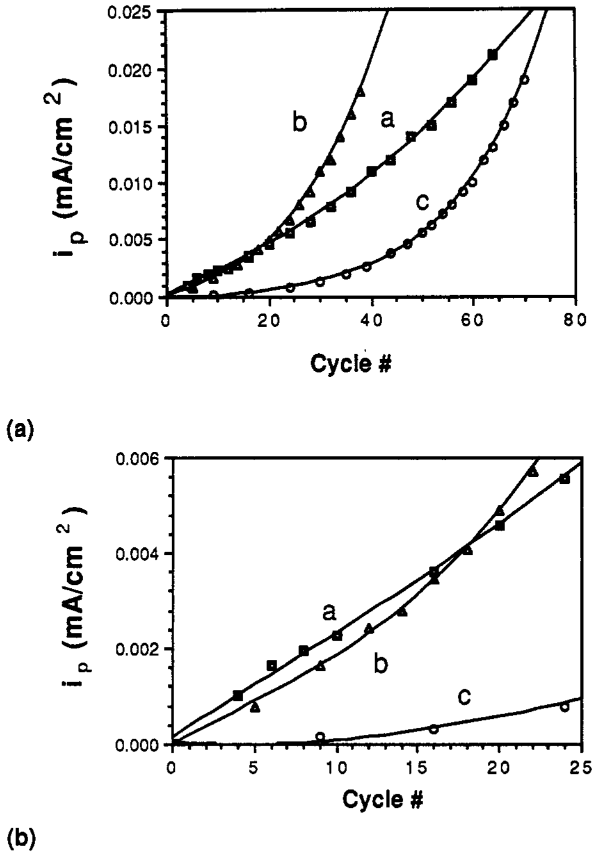


Figure 6. Plots of the anodic peak current (i_p) of the first redox process against the number of cycles in the electrochemical polymerization of (□) aniline, (△) *o*-toluidine, and (○) *m*-toluidine. Polymerization conditions: cyclic potential sweep between −0.2 and 0.7 V vs SCE at a scan rate of 25 mV/s; concentration of monomer, 0.20 M; electrolyte, 1.0 M HCl aqueous solution. Plot ranges: (a) 0–80 cycles and (b) 0–25 cycles.

In order to gain further insights into the reactivities of the toluidines and aniline in the electrochemical copolymerizations, the course of the electrochemical oxidation of aniline, *m*-toluidine, and *o*-toluidine by cyclic potential sweep techniques was monitored by cyclic voltammetry continuously and coincidentally with the synthesis.[13] The amount of the electroactive polymer deposited on the Pt working electrode has been found to be proportional to the anodic peak current i_p in the first redox pair.[13] Figure 6 shows the plots of the anodic peak current (i.e., amount of the polymer formed, [P]) against the number of cycles (i.e. the reaction time t) for electrochemical polymerization of aniline, *o*-toluidine, and *m*-toluidine under identical reaction conditions. The slope (i.e. $d[P]/dt$ or di_p/dt) at any point of the curves in Figure 6 gives the rate of the polymer formation. The initial stage of polymerization up to 25 cycles is enlarged as shown in Figure 6b. It is very interesting to note in Figure 6b that the initial rate of polymerization within ca. 17 cycles is in the order:

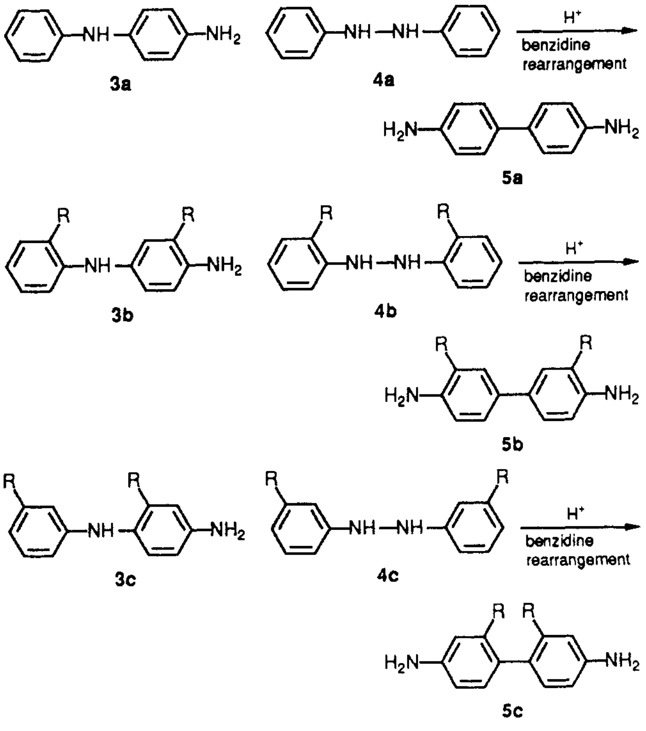
polyaniline > poly(*o*-toluidine) > poly(*m*-toluidine)

After the initial stage (Figure 6a), the rate of polymer formation has the following order:

poly(*o*-toluidine) ≈ poly(*m*-toluidine) > polyaniline

The rates of copolymerizations of aniline with *o*-toluidine and with *m*-toluidine were found to be between those of homopolymerizations, respectively. These results are in excellent agreement with those in the chemical copolymerizations as discussed previously. Since the yields in chemical polymerization (9–14%) are much higher than those of electrochemical polymerization (<0.1%), the chemically synthesized copolymers consist of many more toluidine units than aniline units.

The above results strongly support the mechanism proposed for the polymerization of aniline and its derivatives[12] in which the initial formation of the aniline dimers is slow in comparison with the succeeding growth of the polymer chains via an electrophilic substitution reaction as demonstrated in Figure 7 with aniline as a typical example. Since *N,N*-diphenylhydrazine undergoes the benzidine rearrangement reaction in acidic media,[20] two dimers, *p*-aminodiphenylamine and benzidine, will contribute to the growth of the polymer chains. Soon after formation, the two dimers will be oxidized to their diimine forms[12] which could be deprotonated to afford nitrenium ions.[21] An electrophilic attack of aniline monomer by the diimines or the nitrenium ions would accomplish a growth step and lead eventually to the final polymer. Since methyl groups are electron donating as indicated by their Hammett constant ($\sigma_I = 0.04$),[22] the toluidines should be more reactive than aniline in electrophilic substitution reactions. This is consistent with the results in both the chemical copolymerizations and electrochemical copolymerizations after the initial stage of reactions. On the other hand, the differences in the initial rate of polymerization among aniline, *o*-toluidine, and *m*-toluidine monomers could be explained by examining the steric effect of the methyl substituent during the formation of the dimeric species (R = CH_3):



Apparently, the formation of 2,2′-ditolylhydrazine (**4b**) from *o*-toluidine monomers is less favorable than that of diphenylhydrazine (**4a**) from aniline monomers because of the steric hindrance of the methyl substituent groups. This would result in fewer 3,3′-dimethylbenzidine (**5b**) molecules generated from the benzidine rearrangement. Since the polymer chain could grow on both the *p*-aminodiphenylamine type and the benzidine type of dimers (Figure 7), a lower rate of formation of the benzidine-type dimers should lead to a lower initial rate of polymerization. Therefore, the initial rate of polymerization of *o*-toluidine is lower than that of aniline. The steric hindrance in 2,2′-dimethylbenzidine (**5c**) formed from *m*-toluidine monomers could be expected to be the highest among all of the dimeric species. Thus, the initial rate of polymerization of *m*-toluidine should be the lowest compared to aniline and *o*-toluidine. It should be noted that there are two possible growing centers in the benzidine type of dimers but only one in the *p*-aminodiphenylamine type of dimers. Thus, the rate of formation of the benzidine type of dimers could have a greater effect on the initial rate of polymerization than that of the *p*-aminodiphenylamine type of dimers.

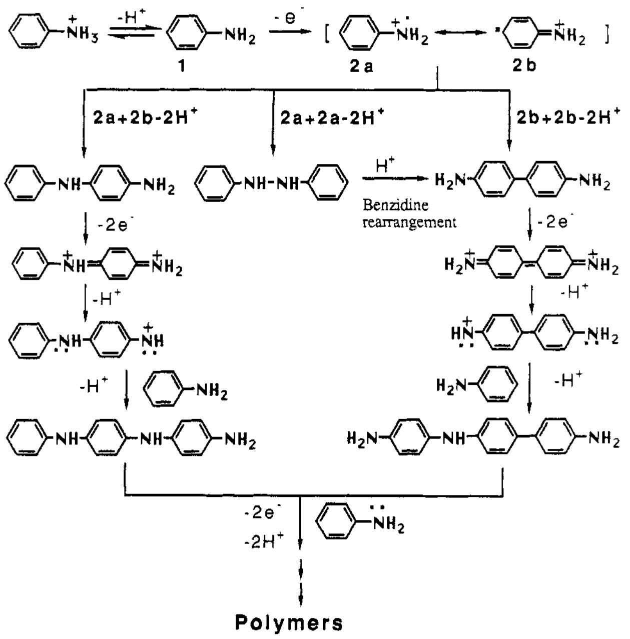


Figure 7. Proposed mechanism for polymerization of aniline and its derivatives.

The electrical conductivities of the chemically prepared copolymers at various molar fraction of the toluidines in the feed (f_1) were measured by using the four-probe technique on the copolymer powder pressed pellets. As shown in Figure 8a, the conductivities of the copolymers doped with 1 M HCl decrease with increase in f_1. The conductivities of the copolymers were in the range between ca. 10 S/cm for the homopolymer of aniline and ca. 0.1 S/cm for those of the toluidines. The lower conductivity of the polytoluidines in comparison with polyaniline was suggested[9] to arise from the steric effect of the methyl group that could result in an increase the torsional angle between adjacent phenyl rings and, therefore, in a decrease in the π-conjugation along the polymer backbone. This is supported by the conductivity data of the copolymers (Figure 8). Thus, the more toluidine units in the copolymer the more decrease in the π-conjugation resulting in lower conductivities. The conductivities of the copolymers should be, therefore, between those of polyaniline and of the polytoluidines depending on the compositions of the copolymers (Figure 8b). The copolymers prepared with high yields demonstrate a similar dependence of conductivity on the compositions of comonomer feed (Figure 9a) and the copolymers (Figure 9b).

In conclusion, both *o*-toluidine and *m*-toluidine can be copolymerized with aniline by either chemical or electrochemical method to generate true copolymers rather than a mixture of the corresponding homopolymers. The compositions of the chemically synthesized copolymers can be determined by ^1H NMR spectroscopy. After the initial stage of copolymerization, the reactivities of both toluidines are very similar but both are higher than that of

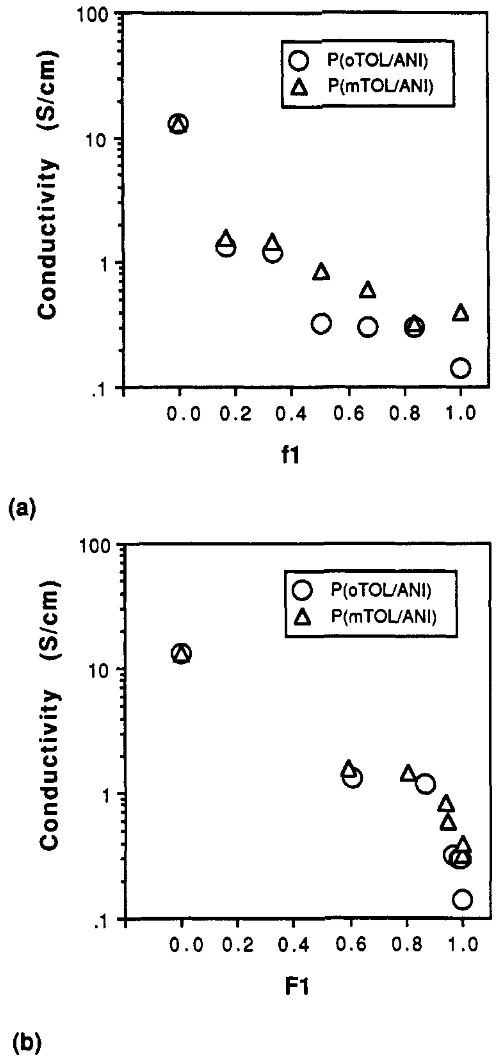


Figure 8. Dependence of log conductivity of chemically synthesized (○) poly(aniline-*co*-*o*-toluidine) and (△) poly(aniline-*co*-*m*-toluidine) on (a) comonomer composition composition f_1 and (b) the copolymer composition F_1, respectively. The yields of the copolymers: 9–14%.

aniline, which are attributed to the electronic effects of the methyl substituent groups. The initial rate of polymerization of aniline is higher than that of *o*-toluidine and that of *m*-toluidine is the slowest. This order in the initial rates are interpreted in terms of the steric hindrance provided by the methyl groups in the formation of the dimeric species. All of the results are consistent with the mechanism proposed for the polymerization of aniline and its derivatives.[12] By varying the fraction of comonomers in the feed, therefore the copolymer compositions, the electrical conductivities of the copolymers upon doping with 1 M HCl can be controlled in a broad range of ca. 0.1–10 S/cm. For further exploration in fundamental understanding and in better control of the physical properties of polyaniline and its derivatives, copolymers of aniline with a variety of substituted anilines (e.g. alkoxyanilines) are under active investigation in our laboratory.

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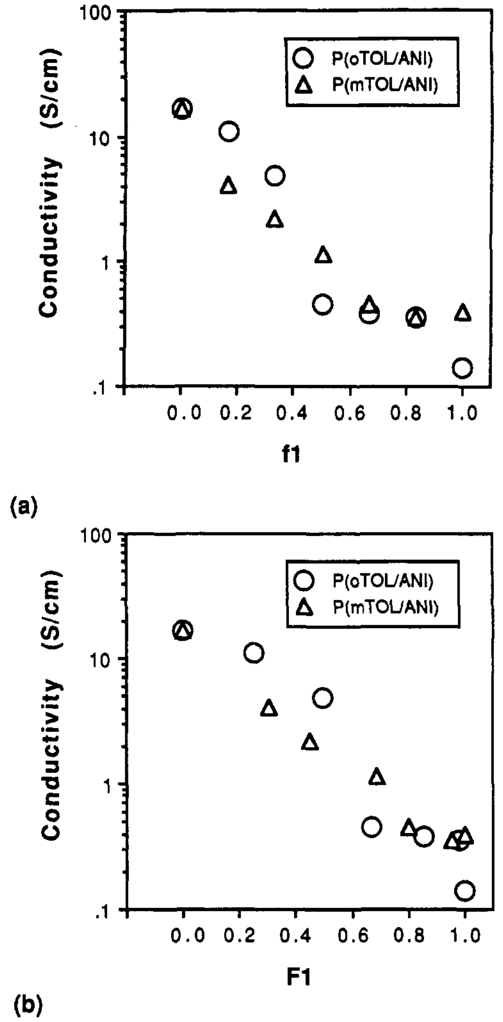

Figure 9. Dependence of log conductivity of chemically synthesized (○) poly(aniline-*co*-*o*-toluidine) and (△) poly(aniline-*co*-*m*-toluidine) on (a) comonomer composition composition f_1 and (b) the copolymer composition F_1, respectively. The yields of the copolymers: 74–85%.

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Registry No. (Aniline)(*o*-toluidine) (copolymer), 124287-76-9; (aniline)(*m*-toluidine) (copolymer), 124287-77-0; *m*-toluidine, 108-44-1; aniline, 62-53-3; *o*-toluidine, 95-53-4.

Effect of Solvent Polarity on Functionalized Polyethylene–Solution Interfaces

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ABSTRACT: Entrapment functionalized films containing dansyl fluorescent labels were prepared and changes in the polymer–solution interface were investigated as a function of solvent polarity. Changes in the emission maximum, the extent of fluorescence quenching, and the rate of fluorescence quenching showed that the polymer–solution interface depth varied depending on the polarity of the solvent used. Functional groups in the polymer–solution interface existed in one of three types of chemical environments—the bulk of the polymer where functional groups were unreactive to reagents in solution and in which they did not interact with solvent, an interfacial region where soluble reagents could react with the functionalized polymer to varying extents but in which the reactivity of external reagents was approximately the same regardless of the external solvent, and a highly solvated region where the functional groups acted as if they were in solution and where the polyethylene-bound dansyl were readily accessible to reagents in solution.

Polymer surfaces play an important role in many polymer applications including adhesion, composite formation, biocompatibility, mass transport, and biodegradation.[1-4] Surface modification of preformed polymers is a practical and useful method of altering the surface properties of a polymer without changing the polymer's bulk properties. Examples of this approach for the functionalization of hydrocarbon polymers include the use of chromic[5-11] or nitric acid etching[12] and corona discharge treatments.[13-16] We have previously described an alternative to these chemical procedures in which terminally functionalized ethylene oligomers are entrapped from solutions of such oligomers and additive-free polyethylene to form functionalized polyethylene powders or films.[17,18] This procedure, which we have called entrapment functionalization, has proven to be useful both in preparation of functionalized polyethylenes and as a technique to facilitate the use of homogeneous catalysts.[19-22] One advantage of entrapment functionalization is that we can prepare entrapment functionalized polyethylene films selectively and reproducibly by controlling conditions such as the method of precipitation, the crystallinity of the host polymer, the size of the functional group, the polarity of the functional group, and the extent of branching in the ethylene oligomer.[18] Therefore, consecutive samples may be prepared with similar distributions and concentrations of functional groups. Further, since we have a measure of control over the degree of surface functionalization, we can prepare functionalized polymers that are suitable for probing the solid–liquid interfaces involving polyethylene and organic solvents.

One poorly understood aspect of polymer surface chemistry is the question of exactly what constitutes a polymer surface. Complicating this question are subtle effects such as the degree to which such a surface changes with time, heating, or different chemical environments. The case of a non-cross-linked polymer like polyethylene suspended in various organic solvents is one example of a situation in which the term "surface" is ambiguous. In our prior work we have described this surface as the region

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