

Chemical Synthesis and Characterization of Poly(aniline-co-ethyl 3-aminobenzoate) Copolymers

MARIJA R. GIZDAVIC-NIKOLAIDIS, ZORAN D. ZUJOVIC, SUDIP RAY, ALLAN J. EASTEAL, GRAHAM A. BOWMAKER

Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland Mail Centre, Auckland 1142, New Zealand

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ABSTRACT: Copolymers of aniline and ethyl 3-aminobenzoate (3EAB) were synthesized by chemical polymerization in several mole ratios of aniline to functionalized aniline, and their physicochemical properties were compared to those of poly(aniline-co-3-aminobenzoic acid) (3ABAPANI) copolymers. The copolymers were characterized with UV-vis, FTIR, Raman, SEM, EPR, and solid-state NMR spectroscopy, elemental analysis, and conductivity measurements. The influence of the carboxylic acid and ester group ring substituents on the copolymers was investigated. The spectroscopic studies confirmed incorporation of 3ABA or 3EAB units in the copolymers and hence the

presence of C=O group in the copolymer chains. The conductivity and EPR signals both decreased with increasing 3EAB content of the copolymers emeraldine salt (ES) form. The conductivity of the ES form of 3ABAPANI was found to be high ($1.4 \times 10^{-1} \text{ S cm}^{-1}$) compared with the conductivity (10^{-2} – $10^{-3} \text{ S cm}^{-1}$) of 3EABPANI (ES) copolymers. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 1339–1347, 2010

KEYWORDS: conducting polymers; copolymerization; ESR/EPR; FTIR; NMR

INTRODUCTION Conducting polymers such as polyaniline (PANI) and polypyrrole are interesting materials for incorporation in thermoplastics because of their useful electronic, optical, and redox properties. PANI has been extensively studied for its environmental stability in conducting form, ease and low cost of synthesis, unique redox properties, and high conductivity.¹ However, like most conjugated polymers, PANI is insoluble in common solvents and difficult to process.^{2,3} A number of attempts have been made to overcome the poor processability of PANI, including doping with functionalized protonic acids such as dodecylbenzenesulfonic (DBSA) and camphorsulfonic acids (CSA), preparation of PANI composites with thermoplastic polymers, and synthesis of copolymers of aniline and aniline with, for example, alkyl, carboxylic acid, and sulfonic acid substituents.^{3–8} Self-doping results from the polymerization of a mixture of aniline and an acid group-substituted aniline.⁹

Copolymerization of aniline with aminobenzoic acids (ABAs) gives copolymers that are soluble in aqueous basic media and in polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO).³ The solubility of the copolymer increases with the proportion of ABA in the copolymer chains. Copolymers of aniline and ABA have been synthesized by chemical and electrochemical routes and characterized by spectral, electrical, and thermal studies.^{3,9–13}

The molecular structure of PANI has been investigated by applying various ^{13}C solid-state nuclear magnetic resonance

(NMR) techniques.^{14–27} These techniques can sensitively reflect mutual interactions of the spins and their interactions with the external magnetic field, which makes them useful in structural investigations of the conducting polymers.²⁷ Several articles have reported the structure of aniline copolymers investigated by solution-state (^1H and ^{13}C) NMR.^{3,28–31} However, to the best of our knowledge, there are no previous reports on solid-state ^{13}C NMR studies of aniline copolymers.

In a previously reported study, the copolymerization of ABA, ethyl 3-amino benzoate, and butyl 3-aminobenzoate (obtained from 3ABA by direct esterification) with aniline was carried out by sonochemical polymerization in aqueous hydrochloric acid using ammonium persulfate.³² The prepared polymers were characterized by solution ^1H NMR spectroscopy, X-ray diffraction (XRD), FTIR, and differential scanning calorimetry. The results showed that the crystalline nature and the thermal stability of PANI were not noticeably affected by copolymerization, and that the solubility in organic solvents increased but the conductivity decreased with increasing incorporation of 3ABA and 3EAB in the polymer.³²

In this article, we report the chemical synthesis of poly(aniline-co-ethyl 3-aminobenzoate) (3EABPANI) copolymers using potassium iodate (KIO_3) as an oxidizing agent. The physicochemical properties of the 3EABPANI were compared with those of processable 3ABAPANI copolymers. A solid-

Correspondence to: M. R. Gizdavic-Nikolaidis (E-mail: m.gizdavic@auckland.ac.nz)

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state ^{13}C CP MAS and NQS NMR study was performed to investigate the differences in the molecular structure of 3EABPANI and 3ABAPANI copolymers, by comparison with chemically synthesized PANI.

EXPERIMENTAL

Materials

Aniline, ethyl 3-aminobenzoate (3EAB), and 3-aminobenzoic acid (3ABA) were purchased from Sigma-Aldrich. Aniline was distilled under reduced pressure and stored in the dark under nitrogen. KIO_3 was obtained from Ajax Finechem.

Chemical Synthesis of Poly(aniline-co-ethyl 3-aminobenzoate) and Poly(aniline-co-3-aminobenzoic acid) Copolymers

Polymerization of comonomer mixtures with 1:1 mole ratios of aniline to functionalized aniline (3ABA or 3EAB) was carried out with aniline (0.04 mol), 3ABA (5.85 g, 0.04 mol) or 3EAB (6.6 g, 0.04 mol), KIO_3 (8.64 g), and hydrochloric acid, HCl (240 mL, 1.25 mol L^{-1}). The synthesis of aniline with 3EAB with 1:2 and 2:1 aniline/3EAB mole ratios was carried out by using the same procedure. The homopolymer of 3EAB was also prepared (P3EAB).

After cooling the solution of KIO_3 and HCl to 7 °C, aniline and functionalized aniline monomers in the appropriate mole ratios were added, and the solution was stirred for 5 h at 7 °C. The reaction mixture was filtered, and the (finely divided black) solid product was washed thoroughly with distilled water, transferred to a flask, and stirred overnight with 150 mL of 6% ammonia solution to dedope the polymer and obtain the emeraldine base (EB) form. After filtering and washing repeatedly with distilled water, the product was stirred for 15 min with 75 mL of acetone, filtered again, and dried in a vacuum oven at 40 °C overnight.

The emeraldine salt (ES) forms of the copolymers were prepared by adding 0.1 g of synthesized copolymer in EB form to HCl solution (100 mL, 1 mol L^{-1}) and allowing the mixture to stand for 24 h. The sample was then filtered, washed repeatedly with distilled water, and dried in a vacuum oven at 40 °C overnight.

Characterization

Elemental analysis was performed by the Campbell Micro-analytical Laboratory at the University of Otago, Dunedin, New Zealand.

Fourier transform infrared (FTIR) spectra were recorded with a resolution of 2 cm^{-1} using a Nicolet 8700 FTIR spectrometer with KBr pellets. A total of 100 scans were averaged for each sample.

Raman spectra were recorded at 1 cm^{-1} resolution using a Renishaw Raman System-Model 1000 spectrometer with 785 nm (red) laser excitation.

UV-vis spectra of copolymers dissolved in a range of solvents with concentration 0.05 g L^{-1} were recorded with a Shimadzu UV-2102PC spectrophotometer over the wavelength range 250–800 nm at an ambient temperature.

SEM was carried out using a Philips XL30S Field Emission Gun with a SiLi (Lithium drifted) EDS detector with Super Ultra Thin Window. The samples were 10 mm in diameter, mounted on aluminum studs using adhesive graphite tape, and sputter coated using a Polaron SC7640 Sputter Coater at 5–10 mA and 1.1 kV for 5 min.

Electrical conductivity of compressed pellets of the EB and ES forms of the copolymers was measured using a Jandal Multi Height Four-Point Probe with DC current source at an ambient temperature.

EPR spectra of 20.0 mg samples of the EB and ES forms of 3EABPANI and poly(aniline-co-3-aminobenzoic acid) (3ABAPANI), in quartz EPR tubes, were recorded at an ambient temperature using a JEOL JES-FA 200 EPR spectrometer. The spin concentration was determined using hydrated copper sulfate (CuSO_4) as a standard. The EPR spectra of the samples and CuSO_4 were recorded under the same conditions.

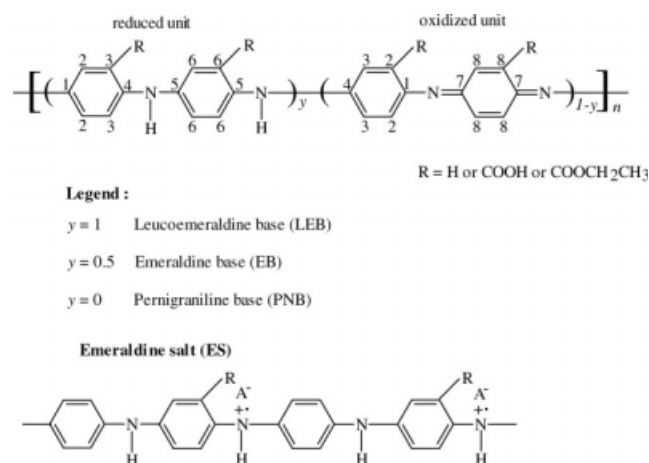
Solid-state NMR experiments were carried out on dry powder EB samples using a Bruker AVANCE 300 spectrometer operating at 300.13 MHz proton frequency. Basic spectra were obtained using the standard CP MAS technique. The experiments were carried out using a 7-mm Bruker spinning probe with zirconia rotors. The proton 90° pulse duration was 4.2 μs , and the RF field strength of the decoupling field was 62.5 kHz. The contact time was 1.5 ms, recycle delay was 2 s, and spectral width was 40 kHz. Nonquaternary suppression (NQS) experiments were carried out with 22,000 scans, whereas basic CP MAS experiments were carried out with 4800 scans at an ambient temperature using samples enclosed in the rotors. The ^{13}C chemical shift scale was referenced to TMS. Samples were rotated at 7000 ± 1 Hz, and the magic angle was adjusted by maximizing the sidebands of the ^{79}Br signal of a KBr sample.

RESULTS AND DISCUSSION

The general structure of the copolymers and homopolymers is shown in Scheme 1.

The EB forms of 3EABPANI were synthesized using KIO_3 as an oxidizing agent from comonomer mixtures with aniline/3EAB mole ratios 2:1, 1:1, and 1:2 (Table 1). 3ABAPANI was synthesized using a comonomer mixture with 1:1 mole ratio of aniline to 3ABA, which resulted in a good yield and a product with enhanced solubility as described in refs. 3, 10–14.

To obtain the copolymer composition, the ratio of aniline to ABA or EAB units was measured through elemental analysis, using C/N ratio. We assumed that aniline homopolymer has a C/N ratio equal to 6 and 3-aminobenzoic acid (P3ABA) or ethyl 3-aminobenzoate (P3EAB) homopolymer has a C/N ratio equal to 7 or 9, respectively. The calculated C/N ratio for all samples was in good agreement with the theoretically predicted values. The elemental analysis data also showed the presence of iodine in the copolymer powders. The results of the detailed investigation of polymerization of aniline by KIO_3 in aqueous acidic media reported by Armes and



SCHEME 1 General structure of 3EABPANI and 3ABAPANI copolymers.

Aldissi³³ suggested that the iodine species I_3^- and I^- were incorporated in the PANI product. In the series of 3EABPANI copolymers, the iodine content decreased somewhat with increased proportion of 3EAB in the feed, probably because of incorporation of $-COO^-$ as an alternative dopant in the copolymer chains.

The yield of EABPANI copolymer decreased markedly as the proportion of functionalized aniline, 3EAB, increased in the feed. This trend is consistent with the proposed mechanism for the copolymerization of aniline, which involves electrophilic substitution of the comonomer by the growing polymer chain.⁹ A similar trend was previously reported for 3ABAPANI copolymers.³ The electron-withdrawing carboxylic acid group deactivates the aromatic system and, coupled with steric factors, retards incorporation of ABA relative to aniline in the copolymer chains.

FTIR Spectroscopy

Figures 1 and 2 show FTIR spectra of 3EABPANI and 3ABAPANI copolymers in their EB and ES forms, respectively. The characteristic band due to C=O group was observed in the spectra of all copolymer samples (at 1690 cm^{-1} for carboxylic acid and shifted to 1712 cm^{-1} for ester), with higher intensity in the ES forms, confirming incorporation of ABA or EAB units in the copolymers. As expected, the intensity of this band decreased when the proportion of aniline in the feed increased. The bands at 1586 and 1500 cm^{-1} correspond to the C—C ring stretching vibrations of the quinoid and benzenoid structures, respectively. The band at 1235

cm^{-1} in the spectra corresponds to C—N stretching modes of the benzenoid ring. The C—O stretching vibration for ester overlaps with the aromatic amine stretching vibration ($1000\text{--}1030\text{ cm}^{-1}$). The peak at 800 cm^{-1} is ascribed to the out-of-plane C—H bending mode.

The NH^+ structure in ES forms of copolymers was confirmed with the band appearing at 1135 cm^{-1} . Shifts of the bands due to quinoid units from 1586 and 1162 cm^{-1} to 1574 and 1135 cm^{-1} , respectively, were observed in the protonated salt form of the 3ABAPANI and 3EABPANI copolymers.

The bands at 1220 , 1105 , 1010 , and 830 cm^{-1} arise from 1,4 substitution of the benzene ring. Bands due to functionalized aniline were also found in both ES and EB forms of the copolymers.

Raman Spectroscopy

Raman spectra of the synthesized copolymers showed similar bands to those for PANI.^{34,35} As an example, the Raman spectra of copolymers 3ABAPANI and 3EABPANI (1:1) in both EB and ES forms are presented in Figure 3.

Upon protonation of the copolymers, the intensities of the C=N stretching band of the quinoid diimine units at 1491 cm^{-1} and the C—N band of the benzenoid units decreased.³⁴ The appearance of the band at 1336 cm^{-1} in the ES form of the copolymers is assigned to C—N stretching of the cation radical species.^{34–36} This result confirms the doping of the PANI sample and the existence of a bipolaronic structure in the copolymers. The concentration of the cation radical is related to the charge localization of the N atoms. The copolymers show a strong ring deformation quinoid band at 770 cm^{-1} . An amine deformation band, N—H bending, at 1410 cm^{-1} was also observed in the ES forms of the 3ABAPANI and 3EABPANI (1:1) copolymers.

UV-Vis Spectroscopy

The 3EABPANI and 3ABAPANI copolymers are more soluble than PANI in common solvents, and the solubility of the copolymers increases with the amount of functionalized aniline in the feed.³ A comparative UV-vis study of 3ABAPANI and 3EABPANI (EB) copolymers synthesized from a reaction mixture with a 1:1 mole ratio of aniline to functionalized aniline was performed (Table 2). The 3EABPANI copolymer showed better solubility in common solvents than 3ABAPANI, probably because of the less polar ester group in the polymer chain. UV-vis spectra of the 3ABAPANI and 3EABPANI (EB) 1:1 copolymers in tetrahydrofuran (THF) and DMSO solvents are presented in Figures 4 and 5.

TABLE 1 Yield and Elemental Composition of the Synthesized Copolymers and Homopolymer

Sample	C (%)	H (%)	N (%)	I (%)	C/N	Yield (%)
3ABAPANI (1:1)	66.53	4.46	11.85	5.06	6.55	51
3EABPANI (2:1)	70.68	4.42	12.28	6.69	6.71	56
3EABPANI (1:1)	67.56	4.35	10.52	5.99	7.49	44
3EABPANI (1:2)	60.63	3.98	8.83	4.66	8.01	24
P3EAB	31.32	2.36	4.09	3.96	8.93	19

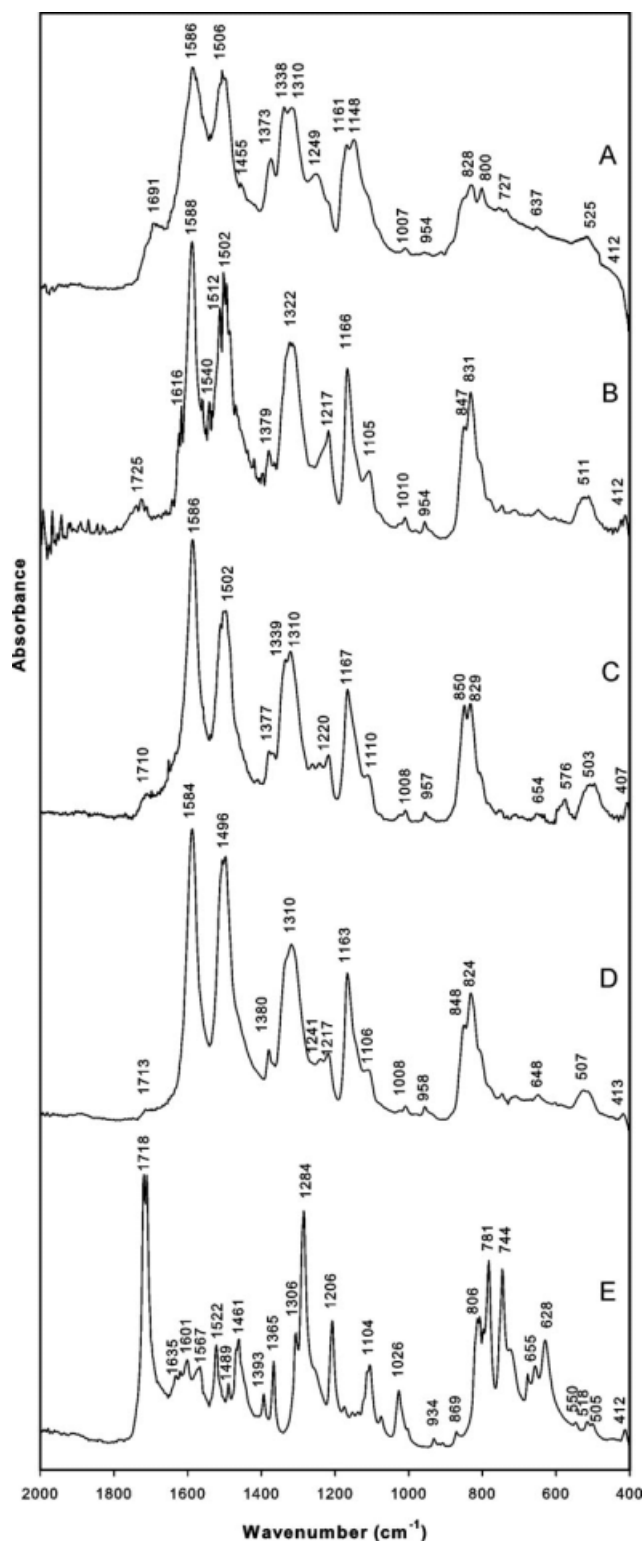


FIGURE 1 FTIR spectra of the copolymers in EB forms. (A) 3ABAPANI 1:1, (B) 3EABPANI 1:1, (C) 3EABPANI 1:2, (D) 3EABPANI 2:1, and (E) homopolymer P3EAB.

The UV-vis spectra showed two main absorptions at 313–338 nm and 550–629 nm. The shoulder of the first peak observed at 273 nm for 3ABAPANI and at 290 nm for 3EAB-

PANI in THF solvent (Fig. 4) is attributed to the $n \rightarrow \pi^*$ transition because of the presence of nonbonding electrons on the COO^- groups.¹³ The first peak is attributed to the $\pi \rightarrow \pi^*$ transition in the benzenoid ring (called the B peak).³⁷ This peak appears at a shorter wavelength than in PANI, because copolymers are less conjugated. The B peak undergoes a blue shift when the solvent is changed from DMSO to THF. The second peak (called the Q peak) is assigned to the transition of an electron from the highest occupied molecular orbital (HOMO, π_b) of the benzenoid part of EB to the lowest unoccupied molecular orbital (LUMO, π_q) of the quinoid ring.^{38–40}

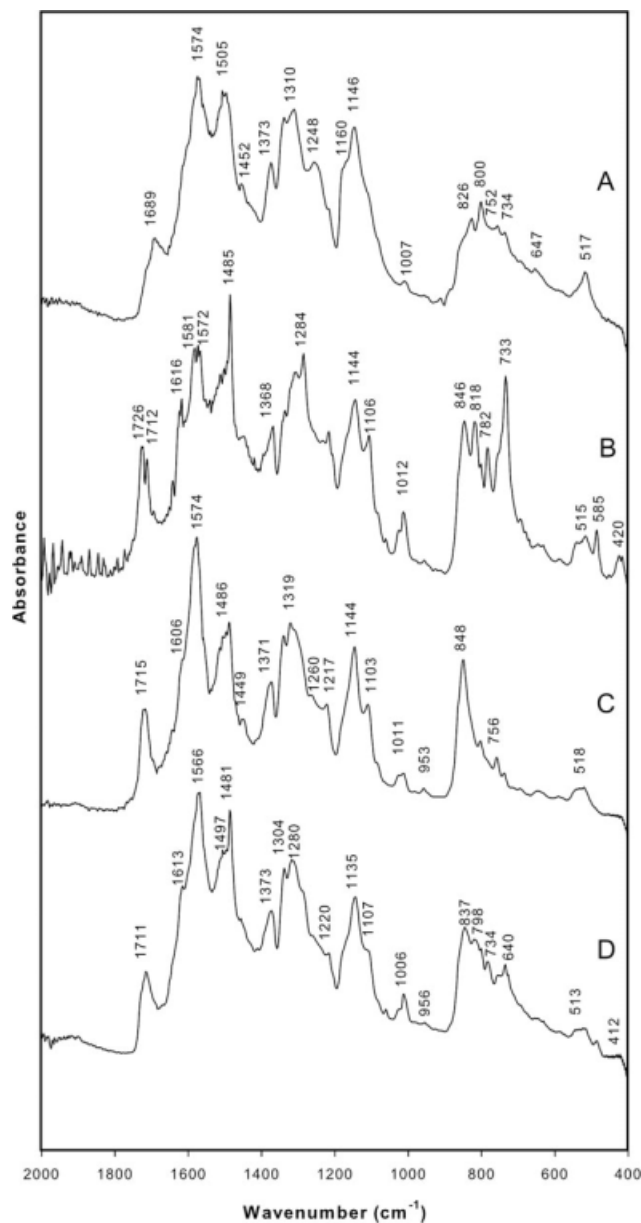


FIGURE 2 FTIR spectra of the copolymers in ES forms. (A) 3ABAPANI 1:1, (B) 3EABPANI 1:1, (C) 3EABPANI 1:2, and (D) 3EABPANI 2:1.

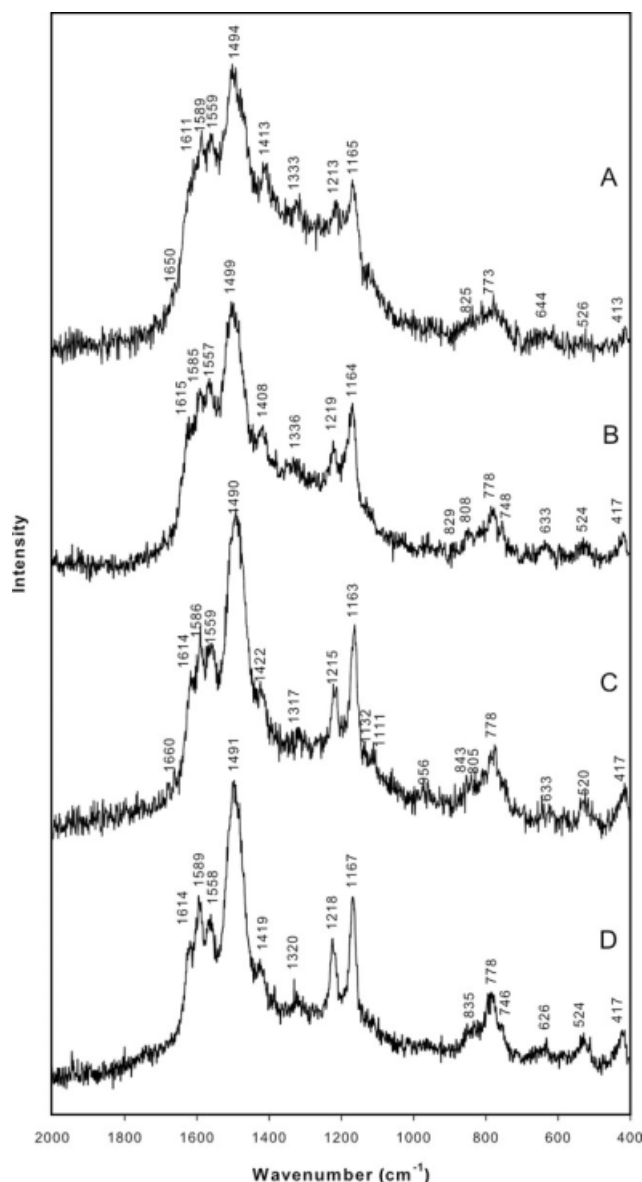


FIGURE 3 Raman spectra of the copolymers. (A) 3ABAPANI 1:1 ES, (B) 3EABPANI 1:1 ES, (C) 3ABAPANI 1:1 EB, and (D) 3EABPANI 1:1 EB.

When Kosower's Z -value,⁴¹ which is often taken as a measure of the polarity of a solvent, increases from the less polar THF to highly polar DMSO, the lower energy absorption peak shifts from 550 and 580 nm for 3ABAPANI and 3EABPANI, respectively, to 629 nm, that is, a hypsochromic shift.⁴¹ This can be explained by the ability of the solvent to interact with the amine group as a hydrogen bond acceptor thus replacing the interchain hydrogen bonding between the amine groups acting as H-bond donors and the imine groups of adjacent chains (acting as H-bond acceptors). Thus, the copolymers are soluble in solvents such as NMP and insoluble in *N*-methylpyrrolidine solvent because of the possibility of hydrogen bonding of NMP to the polymer.

TABLE 2 Absorption Maxima for 0.05 g L⁻¹ Solutions of 3EABPANI and 3ABAPANI 1:1 (EB) in Various Solvents

Solvent	λ_{max} , A	λ_{max} , B	λ_{max} , C
<i>N</i> -Methyl-2-pyrrolidone	629	327	–
Pyridine	614	338	–
2,6-Dimethyl pyridine	621	329	–
2,4,6-Trimethyl pyridine	626	326	–
Dimethyl sulfoxide (DMSO)	629	328	–
<i>N,N</i> -Dimethyl acetamide	629 ^a /621 ^b	324	–
Tetrahydrofuran (THF)	580 ^a /550 ^b	313	273 ^a /290 ^b
Dimethylformamide (DMF)	615	320	–
Dichloromethane ^c	543	319	275
Chloroform ^c	561	321	343

^a For 3EABPANI (1:1) copolymer.

^b For 3ABAPANI (1:1) copolymer.

^c The solubility of 3ABAPANI in these solvents was <0.05 g L⁻¹.

SEM

SEM micrographs for the copolymer 3EABPANI 1:1 and homopolymer P3EAB are presented in Figure 6. The copolymer 3EABPANI 1:1 shows two features, one amorphous and the other a crystalline domain. PANI is known to have amorphous morphology, so this may be associated with the different reactivities of the monomers. It is also possible that small amounts of the homopolymer (P3EAB) could be present in the copolymer 3EABPANI 1:1. P3EAB displays crystalline morphology with particles with well-defined edges and lamellar structure, which confirmed previously observed crystalline structure of P3EAB by XRD in ref. 32. As similarly observed for poly(3-amino benzoic acid) (P3ABA),³ the crystalline morphology may result from intramolecularly hydrogen-bonded 3EAB units.

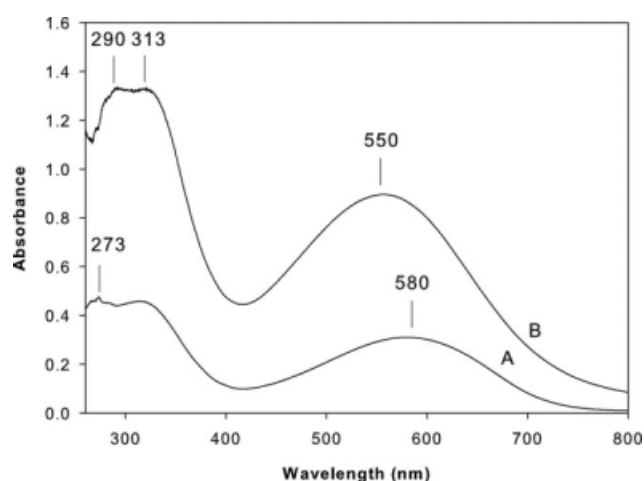


FIGURE 4 UV-Vis spectra of (A) 3ABAPANI and (B) 3EABPANI 1:1 copolymers in EB form, in THF solvent.

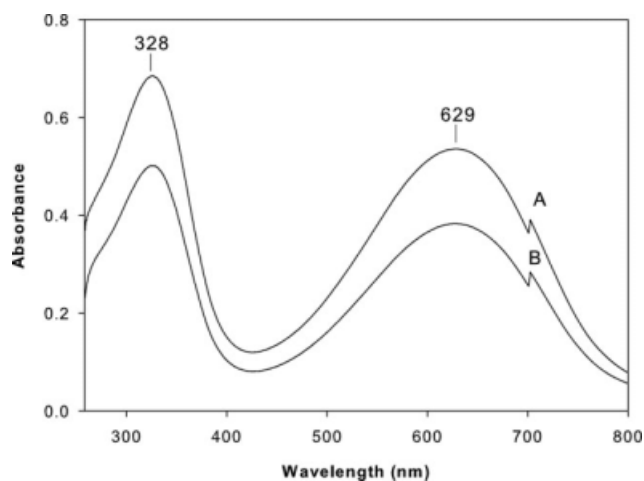


FIGURE 5 UV-vis spectra of (A) 3ABAPANI and (B) 3EABPANI 1:1 copolymers in EB form, in DMSO solvent (the discontinuity at 700 nm is due to an instrumental artifact).

Conductivity Measurements

The EB forms of the copolymers have low conductivity in the range 10^{-5} – 10^{-6} S cm^{-1} , similar to PANI (Table 3). The conductivity of PANI increased with doping level and reached a maximum value of 0.5 S cm^{-1} for PANI doped with 1 mol L^{-1} HCl. No significant change in the conductivity was observed at higher doping levels, in agreement with previously reported results.⁴² Hence, the ES forms of 3EABPANI and 3ABAPANI copolymers were prepared by doping the EB forms with 1 mol L^{-1} HCl; the conductivity data are presented in Table 3. The protonation of 3ABAPANI and 3EABPANI was confirmed by the FTIR and Raman spectra (Figs. 2 and 3).

The relatively high conductivity (1.4×10^{-1} S cm^{-1}) obtained for 3ABAPANI 1:1 copolymer compared with PANI was similar to previously published results.^{3,13} Lower conductivities in the range 10^{-2} – 10^{-3} S cm^{-1} were found for 3EABPANI copolymers. The conductivity decreased with decreasing proportion of aniline in the comonomer reaction mixture, and hence with decrease of the proportion of aniline units in the 3EABPANI copolymer backbones. The conductivity of the copolymers decreased ~ 10 orders of magni-

tude for 3EABPANI 1:2 compared to 3EABPANI 2:1. This result is consistent with the FTIR results and can be explained by nonregularity of the copolymer structure caused by the incorporation of 3EAB that breaks the conjugation in the polymer chains. In addition, the anionic “self-doping” effect may further limit the mobility of the charge carriers.³

EPR Spectroscopy

EPR spectra of 3ABAPANI and 3EABPANI (ES) forms are presented in Figure 7. Spin concentrations (Table 3) of the recorded samples were determined using CuSO_4 as a standard. The following equation (eq 1) was used in the calculation of the spin concentrations:

$$N_{\text{sample}} = \frac{I_{\text{sample}}}{I_{\text{CuSO}_4}} \times \left(\frac{n_{\text{CuSO}_4} \times N_A}{m_{\text{sample}}} \right), \quad (1)$$

where N_{sample} is the spin concentration of the sample, m_{sample} is mass of sample (50×10^{-3} g), n_{CuSO_4} is the amount of copper sulfate (2.04×10^{-3} mol), N_A is the Avogadro constant 6.02×10^{23} mol^{-1} , I_{sample} and I_{CuSO_4} (3.37×10^7) are the EPR signal intensities of the sample and copper sulfate, respectively.

The presence of the $-\text{COOH}$ group in the 3ABAPANI polymer chain increased the spin concentration toward or the same feed ratio of aniline to functionalized aniline in the comonomer reaction mixture for 3EABPANI samples.

The spin concentration increased with the proportion of 3EAB in the feed for 3EABPANI samples. The spin concentration in 3EABPANI forms was ~ 2.0 – 2.5 times higher than in the EB forms.

^{13}C CP MAS NMR Spectroscopy

To get the information about the structural characteristics of copolymers in EB forms, solid-state ^{13}C CP MAS experiments were carried out (Fig. 8). All peaks previously assigned to chemically synthesized PANI^{26,27} at 123.3, 137.4, 141.1, 147.2, and 158.3 ppm were observed. The peak at 123.3 ppm is broad and consists of several resonances, which indicate differences in the chemical environments of protonated carbons C-2 and C-3 (Scheme 1). The peaks at 137.4 and

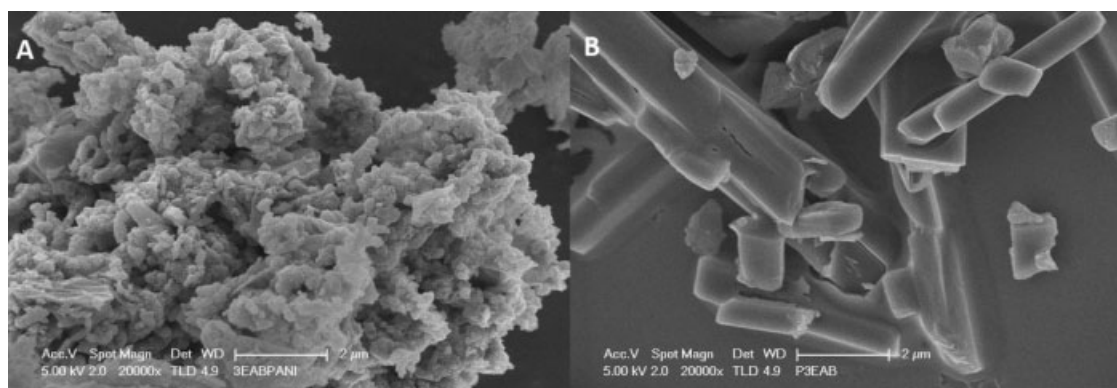


FIGURE 6 The SEM micrograph of (A) 3EABPANI 1:1 and (B) P3EAB.

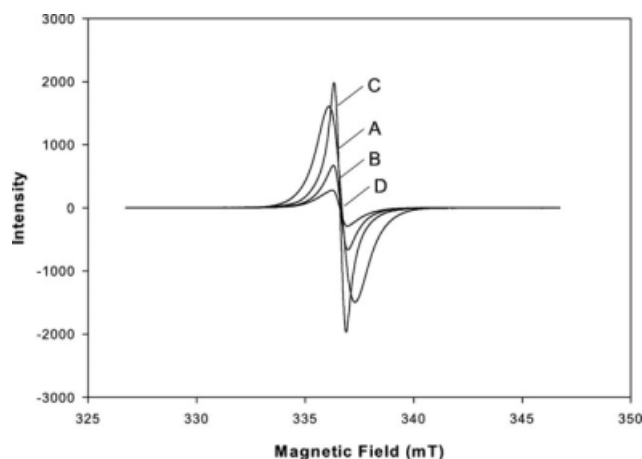
TABLE 3 Conductivity and Spin Concentration N_{sample} for the Synthesized Copolymers

Sample	Conductivity (S cm^{-1})	Spin Concentration N_{sample} (spin g^{-1}) $\times 10^{18}$
3ABAPANI ES (1:1)	1.4×10^{-1}	4.892
3EABPANI ES (2:1)	3.2×10^{-2}	1.958
3EABPANI ES (1:1)	7.1×10^{-3}	3.598
3EABPANI ES (1:2)	2.4×10^{-3}	6.932
3ABAPANI EB (1:1)	9.6×10^{-5}	2.038
3EABPANI EB (2:1)	1.9×10^{-5}	0.792
3EABPANI EB (1:1)	3.7×10^{-6}	1.457
3EABPANI EB (1:2)	1.2×10^{-6}	2.772

158.3 ppm originate from protonated C-8 and the nonprotonated C-7 carbons, respectively, in the quinoid part of the copolymer structure. The peaks at 141.1 and 147.2 ppm are associated with the C-4, 5 and C-1 nonprotonated carbons, respectively.

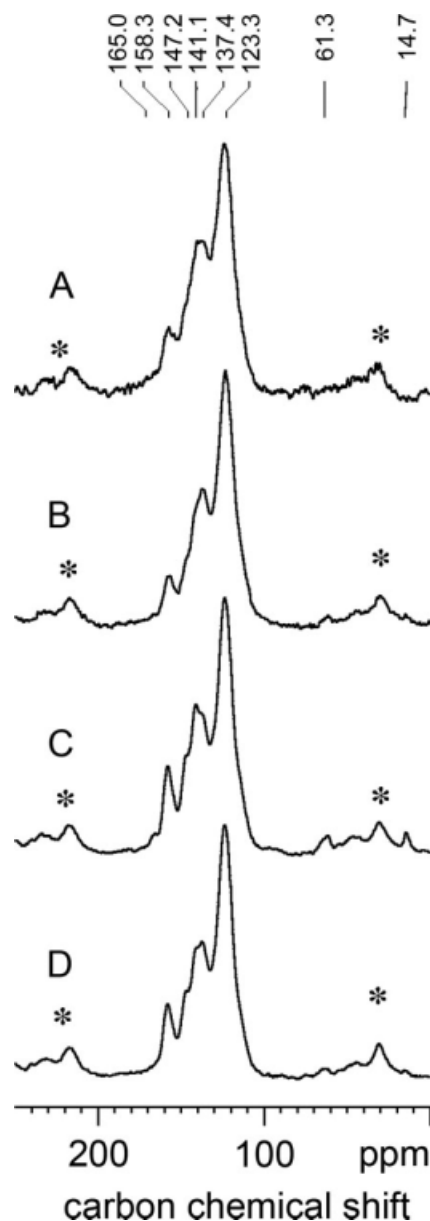
The characteristic peak due to carbonyl group $\text{C}=\text{O}$ ⁴³ was observed at 165.0 ppm in the spectra of copolymer samples for which the incorporation of ABA or EAB units in the copolymer chain was confirmed by the FTIR spectra. In addition, confirmation of incorporation of EAB units is provided by the peaks at 14.7 and 61.3 ppm originating from the CH_3 and CH_2 units, respectively, of the ethyl ester group [Fig. 8(B–D)]. However, the peak at 61.3 ppm is partially overlapped with spinning sideband from the peak at 123.3 ppm, and therefore, the peak at 14.7 ppm peak could indicate the presence and the amount of ethyl ester groups more precisely.

Local fluctuations in conformational and configurational geometries and a distribution in chain packing contrib-

**FIGURE 7** EPR spectra of the copolymers in ES form. (A) 3ABAPANI 1:1, (B) 3EABPANI 1:1, (C) 3EABPANI 1:2, and (D) 3EABPANI 2:1.

ute to line broadening and produce inhomogeneously broadened resonances, which consist of superposed overlapping narrow peaks.^{26,43} For that reason, we carried out NQS experiments at different dephasing times in which protonated carbon resonances were partially suppressed, so that the nonprotonated carbons dominate the spectra.

As an example, NQS spectra at 0.0057 ms for the copolymers in EB forms are presented in Figure 9. The peak at 165 ppm was clearly observed in all NQS spectra, again confirming incorporation of ABA and EAB units in the copolymer chains.

**FIGURE 8** ^{13}C CPMAS NMR spectra of the copolymers in EB forms. (A) 3ABAPANI 1:1, (B) 3EABPANI 1:1, (C) 3EABPANI 1:2, and (D) 3EABPANI 2:1.

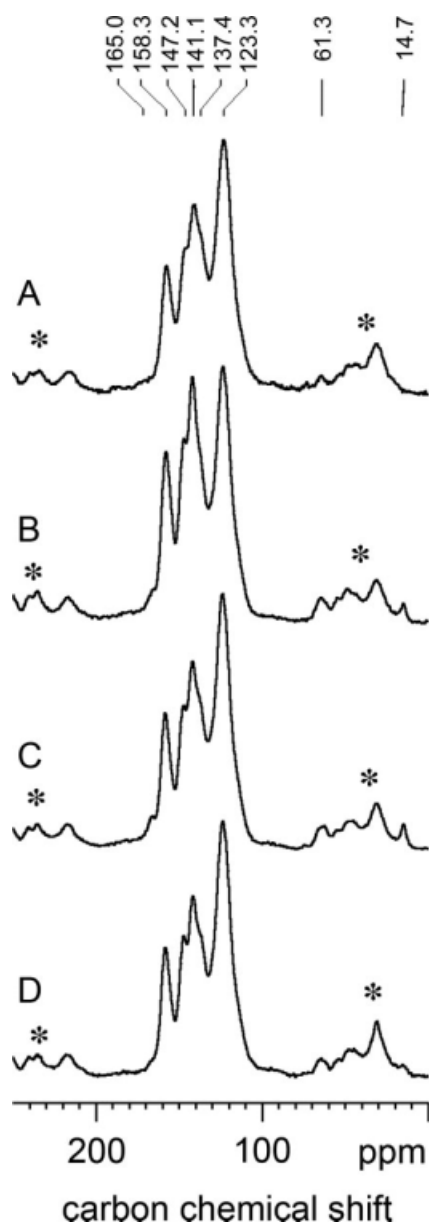


FIGURE 9 Series of spectral editing (^{13}C NQS) at 0.0057 ms for the copolymers in EB forms. (A) 3ABAPANI 1:1, (B) 3EABPANI 1:1, (C) 3EABPANI 1:2, and (D) 3EABPANI 2:1.

CONCLUSIONS

3EABPANI was chemically synthesized by oxidative polymerization of aniline and 3-ethylamino benzoate in 1.25 mol L^{-1} aqueous HCl using KIO_3 as an oxidizing agent. FTIR, Raman, UV-vis, elemental analysis, and solid-state NMR results confirmed incorporation of EAB units in the copolymer chains. The 3EABPANI copolymers showed higher solubility than 3ABAPANI in common solvents probably because of the less polar ester group (compared to $-\text{COOH}$) in the copolymer chains. Good conductivity ($1.4 \times 10^{-1} \text{ S cm}^{-1}$) was found for 3ABAPANI ES 1:1 copolymer, and lower conductivity in the range 10^{-2} – $10^{-3} \text{ S cm}^{-1}$ for 3EABPANI ES copolymers, for which the conductivity decreased further with increase

in the proportion of 3EAB units in the copolymer chains. SEM micrographs of the copolymers reveal regions of amorphous and crystalline domain. EPR spectra of 3ABAPANI (ES) and 3EABPANI (ES) show that with the presence of the $-\text{COOH}$ group in the copolymer chains the spin concentration is higher for the same feed ratio of aniline to functionalized aniline in the reaction mixture. The EPR spectra of the 3EABPANI copolymers indicate a decrease in spin concentration when the proportion of EAB in the copolymers is increased. CP MAS and NQS NMR results confirmed incorporation of ABA and EAB units in the copolymer chains with appearance of the resonances at 165.0 ppm due to $\text{C}=\text{O}$ and at 14.7 ppm (CH_3) and 61.3 ppm (CH_2) from the ethyl group. NMR data further suggest that the benzenoid/quinoid order is mainly retained in the copolymer structure and that copolymer structures consist of benzenoid and quinoid alternating units.

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