

# Shielding and Dielectric Properties of Sulfonic Acid-Doped $\pi$ -Conjugated Polymer in 8.2–12.4 GHz Frequency Range

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**ABSTRACT:** This article deals with dielectric and electromagnetic interference shielding properties of the polyaniline doped with dodecyl benzene sulfonic acid (DBSA) synthesized by microemulsion polymerization of aniline in aqueous solution of DBSA. Dielectric constant and shielding effectiveness due to absorption ( $SE_A$ ) were calculated using  $S$ -parameter obtained from the vector network analyzer in 8.2–12.4 GHz frequency range. Maximum  $SE_A$  of 26 dB (>99%) was achieved for polymer sample. The real part  $\epsilon'$  of complex permittivity shows small variation, whereas the imaginary part  $\epsilon''$  is found to decrease with

the increase in frequency. Different formulations have been performed to see the effect of monomer to dopant ratio on intrinsic properties of polyaniline. Further characterization of polymer was carried out by UV–visible and thermal gravimetric analysis, whereas the conductivity measurements were carried out by the four-probe method. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 498–503, 2010

**Key words:** conjugated polymers; emulsion polymerization; dielectric properties; surfactants; thermogravimetric analysis

## INTRODUCTION

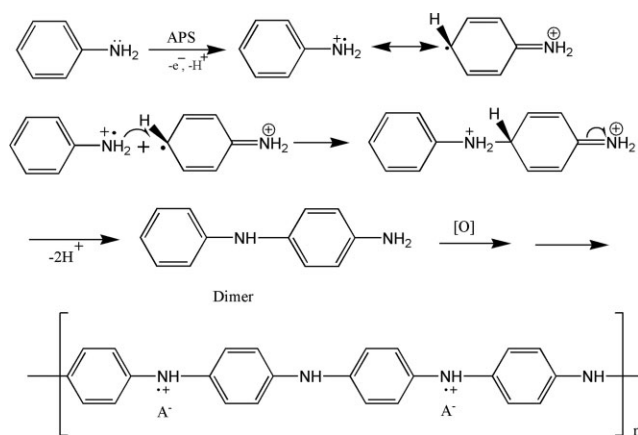
Organic polymers having extended conjugated system show the unique conduction mechanism when doped with organic and inorganic dopant. The conductivity increases with increase of doping level that can be tailored for a given application like EMI shielding and electrostatic charge dissipation,<sup>1–5</sup> sensors,<sup>6–8</sup> organic light-emitting diodes,<sup>9–11</sup> and polymer solar cells.<sup>11–13</sup> Electromagnetic interference (EMI), a specific kind of environmental pollution, is drawing more attention recently, because of the explosive growth in the utilization of electrical and electronic devices in industrial, commercial, and military applications. To avoid the EMI, an enclosure is required that can shield the electronic equipment. Generally, metals or ferrite are used, but nowadays intrinsic conducting polymers (ICPs) are attracting attention for being used as an EMI shielding material in the form of paints or coatings. ICPs as microwave absorber materials have many advantages in respect to light weight, low cost, design flexibility, and microwave properties over intrinsic ferrites. Among the conducting polymers, polyaniline possesses the unique structural, excellent environmental

stability, low redox potential, good thermal stability, and controllable physical and electrochemical properties. The molecular structure of polyaniline is composed of alternated reduced ( $-\text{B}-\text{NH}-\text{B}-\text{NH}-$ ) and oxidized ( $-\text{B}-\text{N}=\text{Q}=\text{N}-$ ) repeated units, where B and Q denote  $\text{C}_6\text{H}_4$  rings in the benzenoid and quinoid states, respectively. Polyaniline exists in different forms namely leucoemeraldine, pernigraniline, emeraldine and conductive emeraldine salt, these different forms refer to different oxidation state of polyaniline ( $[(\text{B}-\text{NH}-\text{B}-\text{NH}-)_y(\text{B}-\text{N}=\text{Q}=\text{N}-)_{1-y}]_x$ ), where  $y = 1, 0.5,$  and  $0,$  respectively. This shows that oxidant play a vital role in controlling the structure and properties of the polyaniline. To improve the conductivity, many research group have reported the indirect protonation of the polyaniline with organic and inorganic dopant, this not only improve the conductivity but also improve the processibility to some extent. Microwave absorption properties of ICPs are greatly associated to their conductivity, higher the conductivity higher will be the microwave absorption.

A lot of research work has been performed on polyaniline, but no one has studied how the concentrations of dopant affect the dielectric and microwave absorption properties of the polyaniline. Hence, the main objective of this work is to study the microwave absorption behavior of polyaniline and to know how the dopant concentration affects the dielectric and shielding properties. This work deals with the microemulsion polymerization of

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**Scheme 1** Polymerization mechanism of aniline using ammonium peroxydisulfate as oxidant.

aniline in aqueous solution of dodecyl benzene sulfonic acid (DBSA) and reports the microwave absorption properties of the conductive polyaniline. The microwave absorption properties of polyaniline doped with DBSA were studied in 8.2–12.4 GHz. The shielding characteristics of materials are based on the reflection and absorption coefficients calculated from scattering parameters (*S*-parameters). Different samples of polyaniline have been prepared by taking different ratio of monomer to dopant to see the effect on intrinsic properties of polyaniline.

## EXPERIMENTAL

### Synthesis of polyaniline–DBSA

The conducting polyaniline doped with DBSA (PD) was obtained by microemulsion polymerization method. Solutions were prepared by emulsifying (DBSA) and aniline of different concentrations in aqueous medium at room temperature. These solutions were then polymerized at  $-3^{\circ}\text{C}$  using ammonium peroxydisulfate (APS) as oxidant with continuous stirring. After stirring for 6 h, a green precipitate of polyaniline was obtained. The resulting solution was treated with isopropyl alcohol to demulsify the green solution and filtered. The filtered precipitate so obtained was washed again with isopropanol and dried at  $60\text{--}70^{\circ}\text{C}$ . Different formulations of polyaniline doped with DBSA were synthesized by varying molar ratio of aniline to DBSA as 3 : 1 abbreviated as PD31, 2 : 1 (PD21), 1 : 1 (PD11), 1:2 (PD12), 1 : 3 (PD13), 1 : 4 (PD14), and 1 : 5 (PD15).

### Characterization

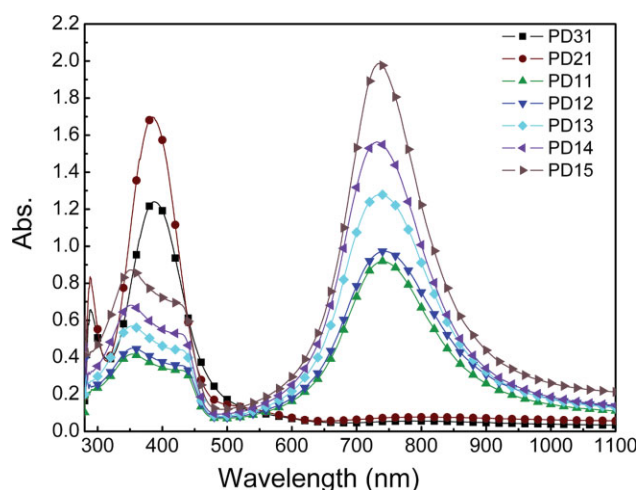
The conductivity of polyaniline doped with DBSA was measured by four-probe method using Keithley programmable current source and nanovoltmeter by compressing the powder sample in the form of

a rectangular pellet. Thermogravimetric analysis (TGA) of the polymer was carried out on a Mettler Toledo TGA 851e, and UV–visible absorption studies were carried on Shimadzu 1601 spectrophotometer. Electromagnetic shielding and dielectric measurements were performed on an Agilent E8362B vector network analyzer in a microwave range of 8.2–12.4 GHz (X-band). Powdered samples were compressed in the form of rectangular pellets (2-mm thick) and inserted in  $22.86 \times 10.14 \times 6 \text{ mm}^3$  copper sample holder connected between the wave-guide flanges of network analyzer. Full two-port calibration was performed along with the sample holder to neglect any loss and power redistribution due to sample holder.

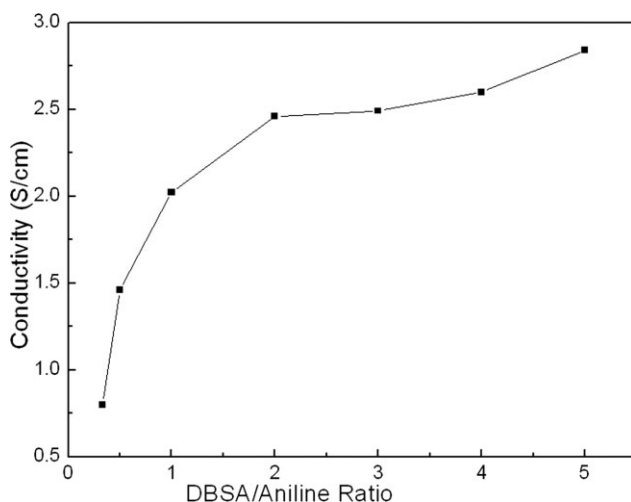
## RESULTS AND DISCUSSION

Polymerization methods generally play a vital role in polymer morphology, internal structure, defect and degree of doping. Microemulsion polymerization has precise control over the properties of the polymer as it has high degree of polymerization than the normal suspension and precipitation method. The addition of aniline to the micellar solution of DBSA leads to the formation of the aniline–DBSA complex. Here, DBSA works as both surfactant and dopant, addition of the APS leads to oxidative polymerization of aniline to conducting polyaniline. Aniline is oxidized to radical cations by losing an electron which form neutral dimer by consecutive reaction, which is further oxidized to trimers and finally to long chain of polymer. The polymerization mechanism is shown in Scheme 1.

The electronic absorption spectra of the polyaniline, synthesized with different concentration of DBSA, in chloroform medium is shown in Figure 1.



**Figure 1** UV/visible spectra of polyaniline doped with DBSA having different DBSA/An ratio. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** Variation of conductivity with different concentration of DBSA to aniline ratio at 300 K.

Three bands are observed, band at 350–355 nm was ascribed to the  $\pi$ - $\pi^*$  transition of the benzenoid ring, whereas bands at 428–435 nm and 725–735 nm were assigned to the polaronic transitions. Similar assignments have also been reported by Chan et al.<sup>14</sup> With the increase in concentration of DBSA, the intensity of the polaronic band transition increases, which reveals the higher doping in the polymer. In case of samples (PD31 and PD21) having small dopant concentrations, the intensity of the polaronic band transition ( $A_{735}$ ) is very low, which reveals the generation of less number of charge carriers in these systems. The generation of cation radicals and dication in the polyaniline system is governed by the extent of doping. Low doping of polyaniline with DBSA results in less number of formation of cation radicals, which leads to weak intensity signal at 735 nm.<sup>19,20</sup> Moreover, the bands at 350 and 430 nm have combined into a single peak with local maxima in between the two peaks at 385 nm. This shift in the absorption spectra of PD31 and PD21 may be due to the formation of less number of polarons resulting in merging of bands to a single band at 385 nm. Probably, at lower DBSA concentration, the quinoid segments are not fully protonated leading to shifting of bands from 430 to 385 nm. That is the reason of getting less conducting polyaniline when the polymerization is carried out at low DBSA concentrations.

The D.C. conductivity measurement has been performed using the compressed pellet of dimensions  $13 \times 7 \text{ mm}^2$  with thickness of 2 mm by four-probe method. The room temperature conductivity was found to vary from 0.8 to 2.8 S/cm. The variations in room temperature conductivity of the samples are shown in Figure 2, which shows that as the concentration of dopant increases the conductivity increases because of increases in doping level and remains

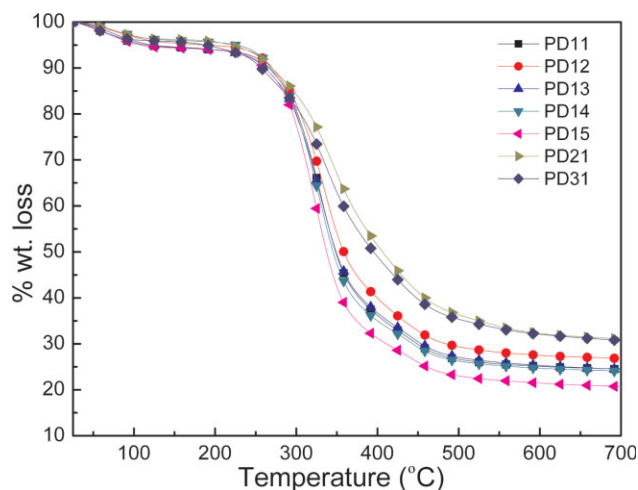
nearly constant after the monomer to dopant DBSA ratio of 1 : 2.

The thermal analysis of polyaniline–DBSA was performed to know the effect of the concentration of DBSA to the stability of the polymer. The typical thermograms of different samples are shown in Figure 3. The thermograms indicate three major stages of weight loss, which are attributed to different causes, first weight loss at lower temperature near 100–110°C results from moisture evaporation, second weight loss at higher temperature between 220 and 380°C arises because of the loss of degradation of dopant DBSA from the polymeric chain, and third one is attributed to the structural decomposition of the polymer backbone. From the thermogram, it was observed that total weight loss increases from 69 to 79% as the concentration of the dopant DBSA increases with slight irregularity of trends in PD15 that has total weight loss of 79% than PD14 having total weight loss of 75%. This irregularity in trend arises because of the higher degree of doping level of PD15 than PD14. The thermogram suggests that the polyaniline doped with DBSA is thermally stable up to 230°C, which is much more stable than the inorganic acid-doped polyaniline like HCl, which is stable up to 180°C.

### Electromagnetic theory and electromagnetic shielding behavior

The EMI shielding effectiveness (SE) of a material is defined as the ratio of transmitted power to incident power and given by

$$SE \text{ (dB)} = -10 \log \frac{P_t}{P_o}, \quad (1)$$



**Figure 3** Thermogravimetric analysis of polyaniline doped with different concentration of DBSA. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

where  $P_t$  and  $P_o$  are the transmitted and incident electromagnetic power, respectively. The amount of attenuation offered by the shield depends on three mechanisms. The first is usually a reflection of a wave from the shields, second is an absorption into the shields as it passes through the shield, and the third is rereflection, that is, multiple reflection at various surface. For a shielding material, total SE is the sum of  $SE = SE_R + SE_A + SE_M$ , where  $SE_R$  is due to reflection,  $SE_A$  is due to absorption, and  $SE_M$  is due to multiple reflections.<sup>15</sup>

In two-port network, S-parameter  $S_{11}$  ( $S_{22}$ ),  $S_{21}$  ( $S_{12}$ ) represents the reflection and the transmission coefficients

$$T = \left| \frac{E_T}{E_I} \right|^2 = |S_{21}|^2 = |S_{12}|^2 \quad (2)$$

$$R = \left| \frac{E_R}{E_I} \right|^2 = |S_{11}|^2 = |S_{22}|^2 \quad (3)$$

$$A = 1 - R - T. \quad (4)$$

Here, it is noted that  $A$  is given with respect to the power of the incident EM wave. If the effect of multiple reflection between both interfaces of the material is negligible, then the relative intensity of the effectively incident EM wave inside the materials after reflection is based on the quantity as  $1 - R$ . Therefore, the effective absorbance ( $A_{eff}$ ) can be described as

$$A_{eff} = \frac{1 - R - T}{1 - R} \quad (5)$$

with respect to the power of the effectively incident EM wave inside the shielding material. It is convenient that reflectance and effective absorbance are expressed as the form of  $-10\log(1 - R)$  and  $-10\log(1 - A_{eff})$  in decibel (dB), respectively, which provide the  $SE_A$  as follows:

$$SE_R = -10\log(1 - R) \quad (6)$$

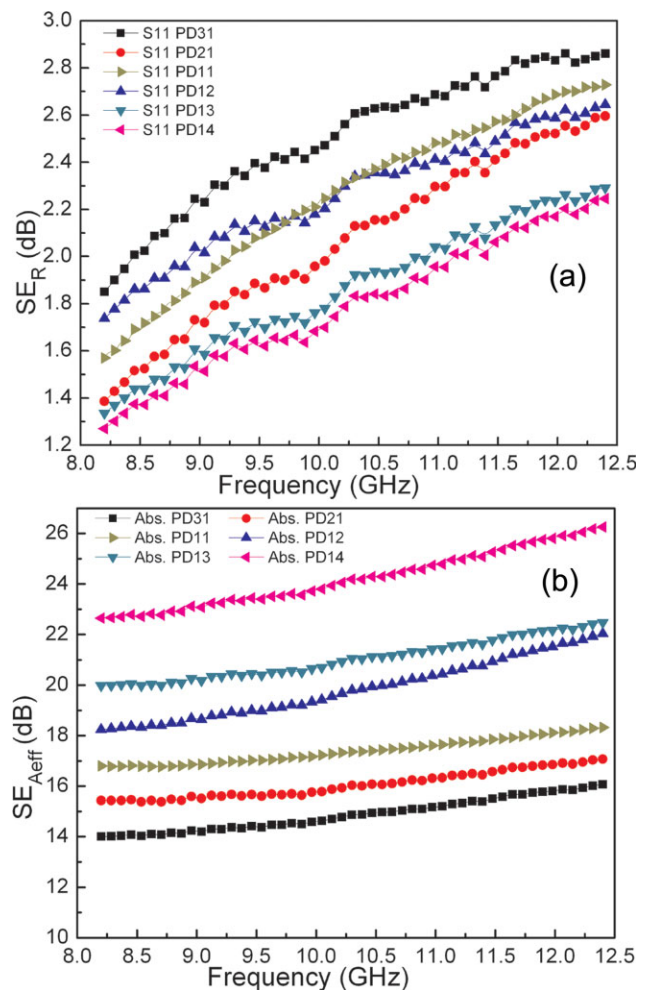
$$SE_A = -10\log(1 - A_{eff}) = -10\log\frac{T}{1 - R} \quad (7)$$

From the theoretical results, EMI SE for the plane electromagnetic wave in far field region is ascribed as,<sup>16</sup>

$$SE(\text{dB}) = SE_R(\text{dB}) + SE_A(\text{dB}), \quad (8)$$

$$SE_R(\text{dB}) \approx 10\log\left(\frac{\sigma_{AC}}{16\omega\epsilon_o\mu_r}\right), \text{ and} \quad (9)$$

$$SE_A(\text{dB}) = 20 \cdot \frac{d}{\delta} \cdot \log e, \quad (10)$$



**Figure 4** Variation of shielding effectiveness due to reflection ( $SE_R$ ) and shielding due to absorption ( $SE_A$ ) in the frequency range of 8–12.4 GHz. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

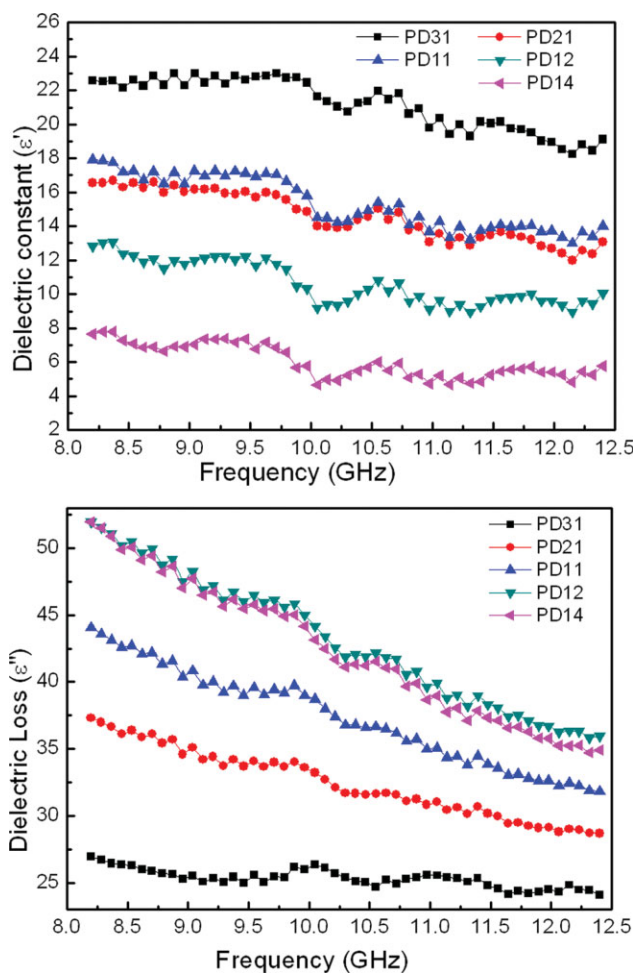
where  $\sigma_{AC}$  is the ac conductivity and depend on the dielectric properties<sup>17</sup> ( $\sigma_{AC} = \omega\epsilon_o\epsilon''$ ) of the material,  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ),  $\epsilon_o$  is the free space permittivity,  $\mu_r$  is the relative magnetic permeability,  $d$  is the thickness of the electromagnetic shield, and  $\delta$  is the skin depth of the sample. The skin depth is the distance up to which the intensity of the electromagnetic wave decreases to  $1/e$  of its original strength. The skin depth is related with the attenuation constant ( $\beta$ ) of the wave propagation vector  $\delta = 1/\beta = \sqrt{2/\omega\mu\sigma_{AC}}$  with the approximations that  $\sigma \gg \omega\epsilon$ . In eq. (8), the first term is related to the reflection of the EM wave and contributes as the SE due to reflection. The second term expresses the loss due to the absorption of the wave when it passes through the shielding material. In microwave range, the contribution of the second part becomes more when compared with the reflection term.

Figure 4 shows the SE of polyaniline doped with DBSA in the frequency range of 8.2–12.4 GHz. The

$SE_R$  and  $SE_A$  values were calculated by using eqs. (6) and (7). It was found that on increasing the DBSA concentration during the polymerization of aniline to polyaniline, the  $SE_R$  value decreases from 2.8 to 2.2 dB, whereas  $SE_A$  increases from 16.3 to 26.5 dB calculated at 12.4 GHz. From the  $SE_R$  and  $SE_A$  values, it was concluded that  $SE_A$  contribute more toward the SE than  $SE_R$ . Polyaniline synthesized with low DBSA concentration (PD31) has maximum  $SE_R$  of 2.8 dB but with minimum  $SE_A$  of 16.3 dB, whereas PD14, where aniline is synthesized with higher concentration, shows minimum  $SE_R$  of the order of 2.2 dB but with highest  $SE_A$  value of the order of 26.5 dB. This increase in the SE, because of absorption where polyaniline is synthesized in higher DBSA concentration, is due to the increase in the conductivity of the polyaniline sample, which leads to increase in the number of free charge carriers which results in higher polarizability and high ac conductivity. That is why, we are getting pronounced transitions in the UV-vis absorption spectra of polyaniline at 420–430 nm, when the ratio of aniline to DBSA in the reaction chamber is greater than 1 : 2, whereas this band is getting shifted to 385 nm when the ratio of aniline to DBSA is less than 1 : 0.5. These results suggest that the microwave absorption loss in polyaniline depends upon the concentration of DBSA.

### Dielectric measurements

The electromagnetic absorption behavior of material depends on the dielectric properties represented by complex permittivity ( $\epsilon'$  and  $\epsilon''$ ) and permeability ( $\mu$ ). As polyaniline is nonmagnetic, only complex permittivity ( $\epsilon'$  and  $\epsilon''$ ) contributes to the microwave absorption properties. The complex permittivity was obtained through scattering parameters  $S_{11}$  and  $S_{21}$  using Nicolson and Ross technique.<sup>18</sup> The real part of complex permittivity ( $\epsilon'$ ) and imaginary part of complex permittivity ( $\epsilon''$ ) vs. frequency are shown in Figure 5. The real part of complex permittivity ( $\epsilon'$ ) and imaginary part of complex permittivity ( $\epsilon''$ ) depend on the polarizability of the material, which in turn depends on the dipole density and their orientation. In the case of polyaniline, two types of charged species are present, one polaron/bipolaron system, which is mobile and free to move along the chain, and the others are bound charges (dipoles), which have only restricted mobility and account for strong polarization in the system. When the frequency of the applied field is increased, the dipoles present in the system cannot reorient themselves fast enough to respond to the applied electric field and as a result dielectric constant decreases. With the increase in the dopant concentration, the number of mobile charges increases, which results in higher



**Figure 5** Dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of PD31, PD21, PD11, PD12, and PD14. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

dielectric loss ( $\epsilon''$ ), whereas the values of real part decrease. The polyaniline sample synthesized in low DBSA concentration (PD31) has the highest dielectric constant ( $\epsilon' = 22.5$ – $19.1$ ), whereas the PD14 has the lowest dielectric constant ( $\epsilon' = 7.6$ – $5.8$ ), while the PD14 has highest imaginary permittivity ( $\epsilon'' = 51.9$ – $34.9$ ) and PD31 has lowest dielectric loss ( $\epsilon'' = 26.9$ – $24.1$ ).

### CONCLUSIONS

Polyaniline–DBSA synthesized by emulsion polymerization, doped with different concentration of DBSA, has shown the maximum dielectric constant ( $\epsilon'$ ) of 22 for the higher dopant concentration. The SE due to absorption ( $SE_A$ ) was found to be 26.5 dB with  $SE_R$  of 2.8 dB for higher dopant concentrated polyaniline, whereas minimum dopant containing polyaniline has lower value of  $SE_A$  of 16.3 dB with  $SE_R$  value of 2.8 dB. From these studies, it was

concluded that the microwave absorption properties of polyaniline doped with DBSA are the function of dopant concentration in the polyaniline matrix.

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