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Polymerization of Aniline in an Organic Peroxide System by the Inverted Emulsion Process

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ABSTRACT: An inverted emulsion process for the synthesis of the emeraldine salt of polyaniline using a novel oxidizing agent, namely benzoyl peroxide, is described. The polymerization is carried out in a nonpolar solvent in the presence of a functionalized protonic acid (sulfosalicylic acid) as the dopant and an emulsifier (sodium lauryl sulfate). The influence of synthesis conditions such as the duration of the reaction, temperature, concentration of the reactants, etc., on the properties of polyaniline was investigated to determine the optimum conditions for the synthesis of polyaniline salt in high yield and conductivity. Using different substituted anilines and dopants, the synthesis of polyaniline derivatives was also carried out. The polymer salt and its base were characterized by a number of techniques such as UV−vis, FT-IR, FT-Raman, NMR and EPR spectroscopies, conductivity, particle size, SEM, X-ray powder diffraction, and TGA−DTA. The polyaniline−sulfosalicylic acid salt synthesized shows a conductivity of 2.53 S cm^{-1}, which is a marked increase over the ones synthesized employing ammonium persulfate as the oxidant and sulfosalicylic acid as the dopant (2×10^{-2} S cm^{-1}).

Introduction

Electrically conducting polymers have raised a great deal of interest after the successful synthesis of conducting polyacetylenes by Shirakawa et al.[1] Among these polymers, polyaniline (PANI) in particular is being increasingly studied in recent years. A unique feature of this phenylene-based polymer with chemically flexible N−H groups, flanked on either side by phenylene ring, is that its electrical properties can reversibly be controlled by both electrochemical (charge-transfer doping) and chemical (protonation) methods.[2] A wide range of technological applications have been associated with polyaniline, for example, electrostatic dissipation, anticorrosion coatings, and in various optoelectronic devices[3] and as an antistatic material.[4]

The facile chemistry of polyaniline allows for several routes of synthesis. These may broadly be classified as electrochemical and chemical oxidative polymerization methods.[5] The latter process is of importance to produce polyaniline on a large scale. The oxidizing agent traditionally employed in the polymerization of aniline has been ammonium persulfate, which yields an insoluble and infusible polymer. Moreover, ammonium persulfate being a strong oxidizing agent and aniline polymerization being exothermic, controlling the reaction temperature is rather difficult, and consequently polymers with a wide distribution of molecular weights result. The removal of inorganic byproduct (ammonium sulfate) from the polymer formed is also difficult. Several other oxidizing agents, for example $K_2Cr_2O_7$, $FeCl_3$, $KMnO_4$, $KBrO_3$, $KClO_3$, etc., have been used.[6] A new oxidizing agent, namely tetrabutylammonium persulfate (TBAP), has also been utilized for the polymerization of aniline.[7] Another oxidant that has been used for the synthesis

of polyaniline is hydrogen peroxide.[8−11] The influence of the synthesis conditions employed for chemical polymerization on the properties of polyaniline has also been studied.

In recent years emulsion polymerization of aniline has come to the forefront.[12,13] Ruckenstein and co-workers[14,15] have employed inverted emulsion polymerization for the synthesis of polyaniline composites using an isooctane−toluene mixture and water to form the emulsion employing ammonium persulfate as the oxidant. Emulsion polymerization is essentially a compartmentalized polymerization reaction taking place in a large number of loci dispersed in a continuous external phase. Electrically conducting polyaniline has also been synthesized by using the microemulsion method with sodium dodecylbenzenesulfonate acting as both a surfactant and a dopant.[16] A microemulsion is an organized microheterogeneous system which provides a large interfacial area and is generally less viscous.

In this paper we report the synthesis of conducting polyaniline by the inverted emulsion method. Inverse emulsion polymerization consists of an aqueous solution of the monomer which is emulsified in a nonpolar organic solvent, for example chloroform in the present study, and the polymerization is initiated with an oil-soluble initiator. This reaction carried out in a heterogeneous system has several distinct advantages as in the emulsion polymerization. The physical state of the emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than in bulk polymerization. The product of an emulsion polymerization can in many instances be used directly without further separations. High molecular weights and high reaction rates can simultaneously be attained. The oxidizing agent used is a novel organic compound, namely benzoyl peroxide, which is widely used as an initiator in many polymerization reactions. The present study is focused on the synthesis of polyaniline using this new oxidizing agent that is perhaps

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more soluble and of high purity. The inverted emulsion polymerization was carried out at different temperatures in the presence of sodium lauryl sulfate as an emulsifier (surfactant). During the course of the reaction, polyaniline remains as a soluble component in the organic phase. The dopants and the reaction conditions were varied, and the polymer obtained in each case was characterized. The study has been extended to methyl- and chloro-substituted anilines. The preparation of the polyaniline base as well as the reprotonation of the dedoped samples with various acids is also described.

Experimental Section

Materials. Aniline, *o*- and *m*-toluidines (all Merck), and *o*-chloroaniline (Ranbaxy) were distilled twice. All other chemicals were analytical grade reagents and were used as procured.

Preparation of Polyaniline Salt and Its Base. In a typical polymerization reaction, a solution of benzoyl peroxide (0.2 M) in chloroform was taken, and sodium lauryl sulfate in 50 mL of water (0.1 M) was added to it under constant stirring to obtain a milky white emulsion. Aniline (0.1 M) was added to it, followed by dropwise addition of the dopant (in 100 mL of water) over a period of $^{1}/_{2}$ h. During the progress of the reaction, the colorless emulsion turns green. The reaction was allowed to proceed for 24 h. The organic phase was separated and washed repeatedly with water. The dark green polyaniline solution in chloroform was then treated with anhydrous sodium sulfate to remove the excess of water. The viscous organic solution was then added to 1.5 L of acetone in order to break the emulsion and precipitate the polyaniline salt. It was filtered and washed with acetone, and the dark green powder obtained was dried under vacuum for 36 h.

Part of the polyaniline salt synthesized was converted into the emeraldine base by treatment with 0.5 M NH$_4$OH solution overnight. The base obtained was filtered, washed with 250 mL of 0.5 M NH$_4$OH, and dried in a vacuum for 36 h.

Measurements. For recording the UV−vis absorption spectra a Hitachi UV-3400 spectrophotometer was used. The solution of the sample in dimethyl sulfoxide (DMSO) was used for recording the spectrum. The spectra were measured at three different concentrations and checked for consistency. The FT-IR spectra were recorded on a Bruker Equinox 55 instrument by the KBr pellet technique. The FT-Raman spectra were obtained using a Bruker RFS100/S spectrometer using Nd^{3+}: YAG laser with 30 mW power at the sample. The EPR spectra were recorded using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated before recording the spectrum to remove the moisture. To obtain the *g* value and spin concentration, the EPR spectra of the samples and charred dextrose as a standard were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), field set (3280 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s), and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of the polyaniline sample with that of charred dextrose. The calculated areas are likely to be within 5% of the true value.[11] The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AMX 400 MHz spectrometer in DMSO-d_6 using TMS as an internal reference. Solid-state ^{13}C NMR was recorded on a Bruker DSX 300 MHz spectrometer. The electrical conductivity (dc) of the samples was measured at ambient temperature using the four-probe method (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Kiethley model 195A digital voltammeter is less than 2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample. The SEM measurements were carried out using the JEOL JSM 480A scanning electron microscope. The X-ray diffraction

Table 1. Effects of Duration of the Reaction and Temperature on Polymerization of Aniline

reaction conditions	conductivity (S cm^{-1})	yield (%)	UV−vis spectra (λ, nm)			
duration (h)						
12	6.7×10^{-3}	19.9	330		620	
16	2×10^{-1}	23.8	310	436	565	
24	5.9×10^{-1}	30.8	330	440	635	830
36	1.1×10^{-2}	32.7	330	453	630	
temp (°C)						
0	2.53	28.2	315	440	640	865
27	5.9×10^{-1}	30.8	330	440	635	830
60 (reflux)	1.52×10^{-1}	33.9	320	440	630	880

Table 2. Effects of Oxidant/Dopant Concentration on the Polymerization of Aniline

concn (M)	conductivity (S cm^{-1})	yield (%)	UV−vis spectra (λ, nm)			
oxidant						
0.05	6.2×10^{-2}	28.2	310		630	
0.1	6×10^{-1}	26.0	310	440	600	830
0.2	5.9×10^{-1}	30.8	330	440	635	830
AIBN		0.9	305	440	615	
dopant						
0.05	5.9×10^{-2}	52.4	310		630	
0.1	5.9×10^{-1}	30.8	330	440	635	830
0.2	4.0×10^{-7}	17.8	325		635	

patterns were recorded using a Siemens D5005 X-ray diffractometer. The TGA and DTA were recorded up to 900 °C using a SDTA 851E thermal analysis system at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere.

Results and Discussion

Polyaniline synthesized by the emulsion polymerization is more soluble in organic solvents such as NMP, DMSO, and DMF. Also, the polymer obtained with benzoyl peroxide as the oxidant is of high purity. The excess benzoyl peroxide is readily removed with acetone, which is used to break the emulsion. The conductivity of polyaniline (2.53 S cm^{-1}) synthesized at 0 °C by this method is high compared to that prepared at the same temperature by solution polymerization using ammonium persulfate as the oxidant (2×10^{-1} S cm^{-1}).[4] There is also an increase in the crystallinity of the polyaniline obtained as seen from the powder X-ray diffraction patterns which is discussed later. The yield (in percent) of the polymer is given in Tables 1−4, taking into account the amount of dopant also.

Synthesis Conditions. a. Duration of Polymerization. The effect of duration over which the polymerization reaction was carried out on the properties of the polyaniline−SSA salt is shown in Table 1. The yield as well as the conductivity of the polyaniline−SSA salt was found to increase with increase in the duration of polymerization up to 24 h. However, the conductivity drops when the reaction time was 36 h or more. The decrease in conductivity may be attributed to the further oxidation of polyaniline from the conducting emeraldine form to the nonconducting pernigraniline form. The absorption spectra of the polymers synthesized showed two peaks around 635 and 330 nm in DMSO. The polymers obtained on keeping for longer duration of the reaction time (16 and 24 h) had an additional peak at 430 nm, which indicates that doping has occurred to a higher extent.

b. Reactant Concentrations. The conductivity and the yield of polyaniline−SSA synthesized were found to depend on the concentration of the oxidant (Table 2). The yield of the product increases when the oxidant

Table 3. Effects of Substituent on the Polymerization of Aniline

monomer	conductivity (S cm^{-1})	yield (%)	UV−vis spectra (λ, nm)			
aniline	5.9×10^{-1}	30.8	330	440	635	830
o-toluidine	1.17×10^{-2}	27.1	309		600	825
m-toluidine	1.21×10^{-3}	11.0	305		610	840
o-chloroaniline[a]		0.5	310		580	

[a] Yield was low; conductivity could not be measured.

Table 4. Effects of Dopants on Polymerization of Aniline

dopants[a]	conductivity (S cm^{-1})	yield (%)	UV−vis spectra (λ, nm)			
SSA	5.9×10^{-1}	30.8	330	440	635	830
TSA	b	1.2	330		630	
CSA	1.71	47.2	330	435	630	840
DBSA	b	poor				
HNO$_3$	5.94×10^{-1}	1.6	330	440	630	870
HCl	1.26	13.4	326	433	630	
HF	6.28×10^{-1}	24.5	270		560	
H$_2$SO$_4$	9.08×10^{-1}	6.8	330	435		840

[a] TSA = toluenesulfonic acid; CSA = camphorsulfonic acid, and DBSA = dodecylbenzenesulfonic acid. [b] Yield was very low; conductivity could not be measured.

concentration is increased from 0.1 to 0.2 M. However, a slight drop in the yield was noticed when the oxidant concentration was raised from 0.05 to 0.1 M. The conductivity of polyaniline increases with the concentration of the oxidant up to 0.1 M and then decreases at 0.2 M of the oxidant which could be attributed to the overoxidation of polyaniline to its nonconducting form. The polymerization of aniline was also carried out using another oxidizing agent, namely 2,2′-azobis(isobutyronitrile) (AIBN). However, the yield obtained was very poor.

The molar concentration of the dopant, namely sulfosalicylic acid, also affects the yield and the conductivity of polyaniline obtained (Table 2). With increase in the dopant concentration from 0.05 to 0.1 M, there is an increase in the conductivity of the polymer salt. However, when the concentration is raised further to 0.2 M, a drastic decrease in the conductivity of polyaniline from 5.9×10^{-1} to 4×10^{-7} S cm^{-1} was noticed. This may be attributed to the degradation of polyaniline at higher acid concentrations. Table 2 shows that at 0.05 M sulfosalicylic acid the yield is marginally higher, although the conductivity is lower. The concentration of the emulsifier also influences both the yield and the conductivity of polyaniline. It was found that when the concentration of sodium lauryl sulfate was reduced from 0.1 to 0.05 M, the conductivity dropped sharply from 5.9×10^{-1} to about 10^{-7} S cm^{-1}.

c. Reaction Temperature. The polymerization of aniline in chloroform medium was carried out at three different temperatures, i.e., at 0, 27 (ambient temperature), and 60 °C (Table 1). The electrical conductivity of polyaniline−SSA salt prepared at 60 °C was found to be lower. The completion of the polymerization reaction occurs faster at higher temperatures. Thus, the rate of polymerization is higher at higher temperature (Table 1). The polymerization reaction was carried out only for 5 h at 60 °C under reflux conditions, in contrast to 24 h of duration at room temperature. However, side reactions may occur at elevated temperatures, leading to the loss in the regularity of the polymer chain and consequently lowering the conductivity.

d. Substituents. The above reaction was carried out for o- and m-toluidines and also for o-chloroaniline at room temperature. Table 3 gives the yield and conductivity of the polymers obtained. The presence of a methyl group in the meta position of the phenyl ring thus also the chlorine substituent in the ortho position leads to a decrease in the yield of the polymer relative to that obtained with aniline. However, 2-methylaniline (o-toluidine) gives a better yield of the polymer with higher conductivity than the 3-substituted aniline. Similar observations have been made by earlier investigators, wherein the conductivity of poly(o-toluidine) is reported to be higher than that of poly(m-toluidine).[17,18] Three peaks were observed for both poly(o-toluidine) and poly-(m-toluidine) in the absorption spectra recorded in

DMSO (Table 3) similar to that reported when toluidines were polymerized using ammonium persulfate as the oxidant.[19] The spectrum of poly(o-chloroaniline) exhibits only two bands, indicating that poly(o-chloroaniline) is possibly not doped effectively by sulfosalicylic acid (Table 3).

e. Dopants. The polymerization of aniline was carried out in the presence of different dopants. The absorption spectra of polyaniline doped with inorganic acids such as H$_2$SO$_4$ exhibit three bands around 840, 440, and 330 nm, indicating the presence of doped form of polyaniline as given in Table 4.[10] Thus, the inorganic acids are apparently more efficient dopants for polyaniline than organic sulfonic acids. The absorption spectrum of the polyaniline salt doped with HCl shows bands at 326, 433, and 630 nm, and the conductivity is also higher. The polyaniline salt doped with sulfonic acids has higher solubility. With organic sulfonic acids, namely sulfosalicylic and camphorsulfonic acids, better yields of the polyaniline salts were obtained.

f. Conductivity. The conductivity of the polyaniline salts measured using the four-probe technique (Tables 1−4) varies widely in the range 2.53 to 4.0×10^{-7} S cm^{-1}, depending on their synthesis, the dopant, and the concentration of the reactants used. The higher conductivity of polyaniline obtained by the present method could be attributed as due to a more homogeneous protonation of the imine nitrogen and better ordered chain conformation of the polymer.[20,21] The conductivity of the polyaniline−sulfosalicylic acid salt decreases with increase in the temperature at which it is synthesized; the highest conductivity was noted for the salt synthesized at 0 °C (Table 1). Previously reported conductivity of the polyaniline−sulfosalicylic acid salt synthesized by the solution method employing ammonium persulfate as the oxidizing agent at 0 °C was nearly 0.2 S cm^{-1}. In the present method, for the reaction carried out at 0 °C, the conductivity obtained for polyaniline−sulfosalicylic acid salt (2.53 S cm^{-1}) is almost 10 times higher than that obtained by the solution method.[4] The mineral acids such as HCl as the dopant yield polyaniline salt generally of higher conductivity when compared to polyaniline doped with organic sulfonic acids (Table 4). The conductivity of the dedoped polyaniline salt is less than 10^{-8} S cm^{-1}. On treating the base with HCl and sulfosalicylic acid, it was found that the conductivity increases respectively to 0.9×10^{-1} and 4.4×10^{-1} S cm^{-1}, demonstrating the doping of the base by the acids, which finds support from the electronic absorption and infrared spectral measurements.

Spectral Studies. a. Absorption Spectroscopy. The electronic absorption spectrum helps to detect the
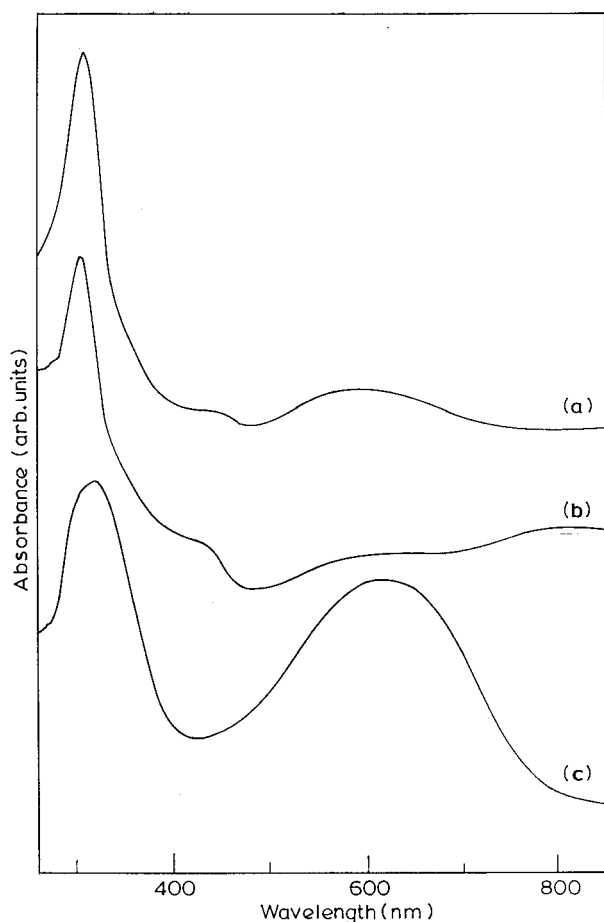
Figure 1. Electronic absorption spectra of (a) polyaniline–sulfosalicylic acid base redoped with sulfosalicylic acid, (b) polyaniline–sulfosalicylic acid salt, and (c) its base.

presence or otherwise of the polyaniline salt and its base. As a representative system, the spectra of the polyaniline–SSA salt, its base, and the base redoped with SSA are given in Figure 1. The spectrum of polyaniline base measured in DMSO exhibits two bands near 325 and 625 nm, whereas the polyaniline salt in DMSO shows four peaks at 330, 440, 630, and 825 nm. The sensitivity and position of the 630 nm band in a convenient region of the spectrum free from the solvent peaks make it suitable for probing the polyaniline systems. The extent of doping can roughly be known from the absorption spectra of the polyaniline salt and its base.[14]
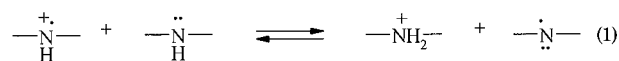
Although there is general agreement regarding the assignment of the 325 nm absorption of the base as arising from the $\pi-\pi^*$ transition of the benzene rings, there has been no unambiguous identification of the origin of the 620 nm band. Duke et al.[22] on the basis of CNDO/S3 calculations have assigned it to the creation of a localized molecular exciton with the electron on a quinoid moiety and a hole on the two neighboring benzenoid moieties. The molecular exciton is associated with a locally distorted segment of the polyaniline backbone. On the other hand, Kim et al.[23] have proposed that the optical absorption at 620 nm in the emeraldine base is due to exciton transition (n–π^*) between the HOMO orbital of the benzenoid ring (nonbonding nitrogen lone pair) and the LUMO (π^*) of the quinoid ring. Recently, Wan et al.[24] have attributed the absorption bands at 325 and 620 nm as due to the excitation of the amine and imine segment, respectively, of the polyem-

eraldine chain. The bands around 430 and 830 nm have been assigned as due to the polaron transitions.[25]

The spectrum of polyaniline salt shows up to four bands while that of the base exhibits only two bands as noted above. The polyaniline base on redoping with sulfosalicylic acid shows three bands at 310, 440, and 600 nm, revealing redoping of the base to the salt form by the dopant. However, the extent of redoping is not high as can be gauged from the conductivity data (0.9×10^{-1} and 4.4×10^{-1} S cm^{-1} for the base redoped with SSA and HCl, respectively) and the absence of the band around 830 nm (Figure 1).

While the spectrum of polyaniline–sulfosalicylic acid salt in DMSO shows four bands, the substituted polyanilines, namely poly(*o*-toluidine), shows three bands at 305, 600, and 825 nm, while poly(*m*-toluidine) exhibits only two bands at 305 and 605 nm and also poly(*o*-chloroaniline) around 310 and 580 nm (Table 3). It reveals that the degree of doping by sulfosalicylic acid may be higher for poly(*o*-toluidine) than for the other two polyaniline derivatives.

A correlation between the conductivity of the polyaniline salt and the intensity of the 830 nm band was noticed. The 830 nm band is due to the $-NH_2^+-$ species which is generated on doping of the polymer (eq 1). Its intensity is a measure of the $-NH_2^+-$ group present. Continued oxidation of the polymer would lead to the conversion of the $-NH_2^+-$ to $-NH^+-$ group, consequently resulting in a decrease in the intensity of the 830 nm band and also a decrease in the conductivity of polyaniline.

$$-\overset{+\cdot}{\underset{H}{N}}- \;+\; -\overset{\cdot\cdot}{\underset{H}{N}}- \;\rightleftharpoons\; -\overset{+}{N}H_2^{\cdot\cdot}- \;+\; -\overset{\cdot}{\underset{\cdot\cdot}{N}}- \quad (1)$$

b. FT-IR and FT-Raman Spectra. As representative systems, the IR spectra of polyaniline–sulfosalicylic acid salt, its base, and the base redoped with HCl are given in Figure 2. The IR and Raman spectra of polyaniline can be interpreted on the basis of the assignment of the vibrational spectra of *p*-diaminobenzene and benzoquinone by the ab initio calculations.[26,27] Changes in the infrared spectrum of the emeraldine base on protonation to the salt form may be expected due to changes in the dihedral angle between adjacent rings and changes in the electronic structure. The characteristic bands in the IR spectrum of the polyaniline–sulfosalicylic acid base occur at 1574, 1489, 1371, 1296, 1234, 1135, and 797 cm^{-1}. The bands of the emeraldine sulfosalicylic acid salt are found at 1590, 1573, 1466, 1293, 1218, 1122, 1073, 1029, 991, 971, 946, 789, and 696 cm^{-1}. The band at 1573 cm^{-1} in the salt spectrum is assigned to the C=C ring stretching vibration. The bands at 1122 and 789 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending modes, respectively. The strong band around 1135 cm^{-1} in the spectrum of the base becomes broader, more intense, and rather unsymmetric and is found in the salt spectrum at 1122 cm^{-1}. The 1489 cm^{-1} peak observed in the polyaniline base spectrum is shifted to a lower frequency (1466 cm^{-1}) in the salt spectrum. The band at 1466 cm^{-1} is assigned to C–N stretching of the quinoid ring that arises on the protonation of polyaniline by the dopant. Low-frequency shifts observed in the salt for most of the bands of the base reveal some changes in the benzenoid structure due to the polaron lattice.
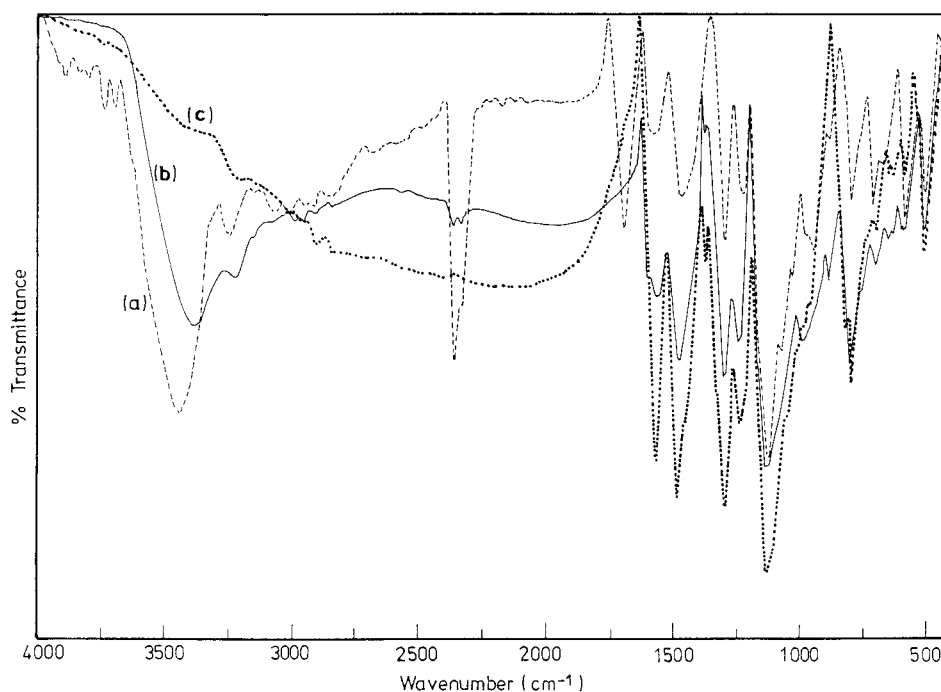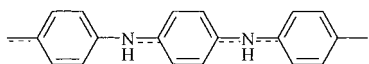
Figure 2. FTIR spectra of (a) polyaniline−sulfosalicylic acid salt (synthesized at 27 °C), (b) its base redoped with HCl, and (c) base.

The doping of polyaniline base leads to the formation of −Q=N$^+$H− groups. The positive charge on the polymer chain may lead to an increase in the dipole moment of the molecule and consequently resulting in an increase in the intensity of the IR bands.[28] In the IR spectrum of the salt a fairly intense band appears at 946 cm^{-1}, which is absent in the spectrum of the base. It may be assigned to the ring-breathing mode of the quinoid group, which becomes active on protonation. In addition, the spectrum of the polyaniline salt exhibits new bands near 3450, 3230, and 700 cm^{-1}. The intense broad band near 3450 cm^{-1} and a medium intensity band at 3230 cm^{-1} may be assigned to the asymmetric and symmetric −NH$_2$$^+$ stretching modes, respectively. These bands are absent in the dedoped sample. The −NH$^+$ stretching may overlap with the asymmetric NH$_2$ stretching mode, which accounts for the broadness of the 3450 cm^{-1} band. The −NH$_2$$^+$ group may also be involved in hydrogen bonding. On redoping the base with 1 M HCl, the bands are observed at 3370, 3225, and 700 cm^{-1}, demonstrating that the salt is once again regenerated (Figure 2). The band at 1693 cm^{-1} is characteristic of the presence of the carboxylic acid group of the dopant sulfosalicylic acid. The presence of the SO$_3$$^-$ group is confirmed by the appearance of a band around 590 cm^{-1} in the spectrum of polyaniline−sulfosalicylic acid salt attributed to degenerate bending mode of the SO$_3$$^-$ group.

The FT-Raman spectra were recorded for the polyaniline emeraldine base and the salts obtained by doping the base with hydrochloric, sulfuric, *o*-phosphoric, hydrofluoric, and sulfosalicylic acids. As a representative system, the Raman spectra of the polyaniline base and the salt doped with HCl are given in Figure 3. The characteristic Raman frequencies of the polyaniline base and the salts are presented in Table 5. The polyaniline undergoes protonation of the amine nitrogen

on doping, leading to the formation of Q=N$^+$H species, thereby causing an increased conjugation. The higher frequency bands could be assigned to the quinoid ring while the lower ones could be attributed to the benzenoid rings of the polyaniline emeraldine salt. The intensity of these bands appears to be related to the degree of doping. The 1328 cm^{-1} band may be assigned to C−C stretching mode of the quinoid ring. Because of some difference in the conformation of the polymer and the extent of doping in the salt, the frequency of the C−C stretching vibration varies. The C−C bond is strengthened in the protonation-induced polaron lattice. In particular, the Raman band at 1173 cm^{-1} assignable to out-of-plane −CH bending, which is of weak to medium intensity, appears upon doping with dramatically enhanced intensity as the strongest band in the spectrum. The intensity of this band at 1173 cm^{-1} appears to increase with the degree of protonation. It can be assigned to the Q=N$^+$H structure which is formed on protonation.

On redoping the polyaniline base with HCl, the bands of the base are split as in the case of the polyaniline HCl salt (Table 5). The intensity of the bands in the spectrum of the base redoped with HCl is lower than that of the polyaniline−HCl salt, revealing once again that the redoping is not very effective, in agreement with the conductivity studies. The spectrum of the polyaniline salt exhibits intense and well-resolved bands in contrast to the less intense and less resolved bands of the polyaniline base. The spectrum of polyaniline base exhibits fairly strong bands at 1598, 1508, 1376, and 1173 cm^{-1} and less intense bands at 1328, 1268, 1232, 524, and 417 cm^{-1}. A band near 1500 cm^{-1} is assigned mainly to the benzenoid C−C ring stretching vibration and a band near 1600 cm^{-1} to the quinoid C=C stretching mode of the polymer chain.[29] Both these Raman bands register increased intensity and a small low-frequency shift in the spectrum of the salt. New bands are observed at higher frequencies, at 1617 and 1535 cm^{-1}, in the spectrum of the salt due to stretching
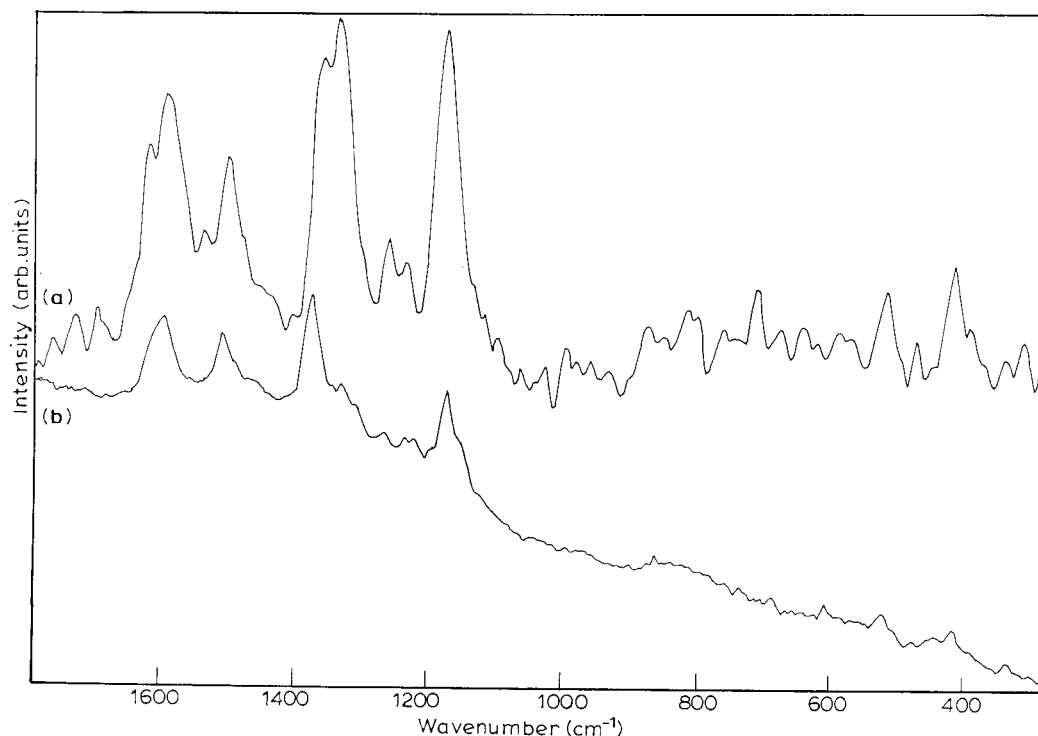
Figure 3. FT-Raman spectra of (a) polyaniline−HCl acid salt (synthesized at 27 °C) and (b) its base.

Table 5. Selected Raman Bands (cm⁻¹) of Polyaniline Base and Its Salts

sample														
Pani[a] base		1598		1508			1376	1268	1232	1173	524		417	
Pani HCl salt	1617	1589	1535	1499	1358		1335	1256	1230	1171	513	467	410	380
Pani H₂SO₄ salt	1616	1579		1500	1346		1332	1254		1170	518	474	414	372
Pani H₃PO₄ salt		1592		1503	1369, 1352, 1332			1269	1236	1174	523	468	417	380
Pani HF salt		1593		1506	1372		1335	1266	1232	1174	514	483	417	386
Pani SSA[b] salt	1617	1592	1533	1504	1352		1332	1269	1244	1171	514	477	415	380
		1575										460		
Rd-HCl[c]		1598	1508	1463	1371		1332	1261	1237	1174	513	475	414	383
				1426										

[a] Pani = polyaniline. [b] SSA = sulfosalicylic acid. [c] Rd-HCl = polyaniline base redoped with HCl.

vibration of the quinoid and benzenoid rings, respectively. It suggests a greater contribution of the quinoid structure to the bonding in the polymer salt. The former band has weak to medium intensity.

The bands, which occur in the base at 1598, 1508, 1376, and 1268 cm⁻¹, are intensified, and new bands appear on the high/low-frequency side for each of these bands in the spectra of the polyaniline salts. Several less intense new bands also appear in the Raman spectra of the salts. The Raman spectrum thus appears to be better suited when compared to the IR spectra to probe to the changes occurring in the polyaniline base and its salt.

c. NMR Spectra. Figure 4 shows the ¹H NMR spectra of polyaniline−sulfosalicylic acid salt synthesized at room temperature and its base. The proton NMR spectrum of polyaniline−sulfosalicylic acid salt synthesized at room temperature as well as at 60 °C exhibits peaks near δ 7.30 ppm due to the aromatic protons of the quinoid ring (doped state) and the peaks at δ 6.95 ppm due to the benzenoid protons. The resonance at δ 3.81 ppm in the spectra of the polyaniline salt prepared at 27 and 60 °C is assigned to the N−H groups. The peaks at δ 8.06, 7.93, 7.91, 7.72, and 7.69 ppm in the spectrum of the salt arise from the dopant sulfosalicylic acid. They are absent in the spectrum of the base. The peaks at δ = 7.3 and 3.81 ppm are shifted
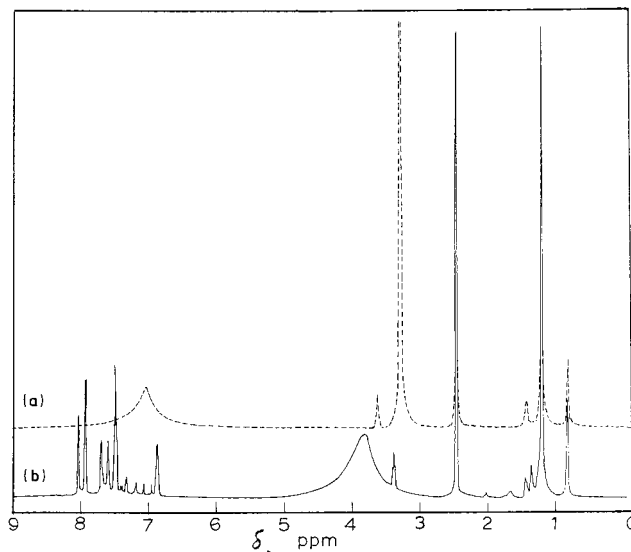

Figure 4. ¹H NMR spectra of (a) polyaniline base and (b) polyaniline−sulfosalicylic acid salt (synthesized at 27 °C).

to δ = 7.04 and 3.29 ppm, respectively, in the spectrum of the base. The downfield shift of the signals corresponding to the aromatic and N−H protons is attributed to the conversion of some of the −NH groups to −NH₂⁺−

**Table 6. EPR Spectral Parameters for the Polyaniline Base and Its Salts**

sample	spins g^{-1}	g value	ΔH (G)	A/B ratio
polyaniline−SSA salt (27 °C)	2.2287×10^{20}	2.0037	1.40	0.97
polyaniline−SSA salt (0 °C)	5.8042×10^{20}	2.0057	4.00	0.99
polyaniline−SSA salt (60 °C)	1.1265×10^{20}	2.0025	1.75	0.98
polyaniline base	2.9245×10^{18}	2.0025	8.5	1.03
polyaniline base redoped with HCl	1.1948×10^{20}	2.0037	2.15	0.99
polyaniline base redoped with SSA	7.3876×10^{19}	2.0028	2.25	1.01

on doping (protonation) of polyaniline by sulfosalicylic acid. The proton NMR studies carried out on polyaniline synthesized employing benzoyl peroxide as the oxidant are consistent with those reported earlier for both polyaniline salt and its base prepared using ammonium persulfate as the oxidant.[30]

The carbon-13 NMR spectrum of the polyaniline−sulfosalicylic acid salt shows signals at δ 167.3, 136.9, 129.8, and 128.2 ppm arising from polyaniline. The low intensity signal at $\delta = 167.3$ ppm is assigned to the C=N carbon of the quinoid rings. The moderately intense medium field peak at δ 136.9 ppm corresponds to the −CH carbon atoms of the quinoid rings.[31] The remaining high-intensity peaks at δ 129.8 and 128.2 ppm are attributed to the −CH carbons of the benzenoid rings.[32] The spectrum of the polyaniline−sulfosalicylic acid base has a peak at δ 128.7 ppm, arising from the −CH carbons of the benzenoid rings. In addition to the above bands, the polyaniline salt shows peaks at δ 171.5, 161.1, 139.4, 132.9, 127.6, 116.4, and 111.7 ppm attributable to the dopant sulfosalicylic acid, which are absent in the spectrum of the base.

The solid-state ^{13}C NMR spectrum of the base obtained by dedoping the salt synthesized at room temperature exhibits strong peaks at $\delta = 125.1$ and 32.08 ppm and less intense peaks at about δ 210 and 300 ppm. The peak at 125.1 ppm is unsymmetrically broad and is spread over 40 ppm with shoulders near δ 130 and 140 ppm. This region has contributions from all the aromatic carbons of polyaniline.[33] The intense peaks at $\delta = 125.1$ and 32.08 ppm in the spectrum of the base shift to δ 132.8 and 32.7 ppm, respectively, in the spectrum of polyaniline−sulfosalicylic acid salt. The signal at $\delta = 132.8$ ppm due to the aromatic carbons of polyaniline and the dopant sulfosalicylic acid is also broad (spread over 30 ppm) and unsymmetrical in the spectrum of the salt as in the base. The spectrum of polyaniline−sulfosalicylic acid salt has less intense peaks at δ 165, 175, 225, and 330 ppm. The former two peaks are due to the quinoid ring carbons,[34] which is also observed in the ^{13}C spectrum of the salt measured in DMSO-d_6. The intensities of these peaks are lower in the spectrum of the polyaniline base due to the absence of the dopant.

d. EPR Spectra. The ambient temperature EPR spectra of the polyaniline−sulfosalicylic acid salt synthesized at three different temperatures, the polyaniline base, and the base redoped with hydrochloric and sulfosalicylic acids display a single signal without hyperfine structure. The spectral data are collected in Table 6. As representative systems, the EPR spectra of polyaniline−sulfosalicylic acid salt, its base, and the base redoped with HCl are shown in Figure 5. The g value and the A/B ratio (that is, the ratio of the area of the positive to the negative peak) do not throw much
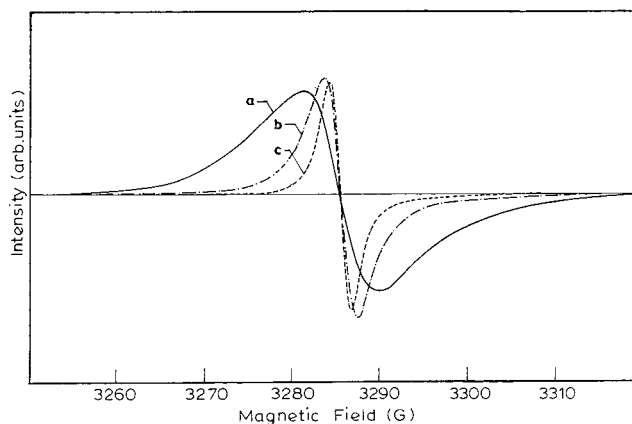
Figure 5. EPR spectra of (a) polyaniline−sulfosalicylic acid base, (b) polyaniline−sulfosalicylic acid salt (synthesized at 27 °C), and (c) its base redoped with hydrochloric acid.

light on the nature of the polymer (i.e., whether it is polyaniline salt or the base). The actual differentiation between the polyaniline salt and the base comes from the spin concentration and the line width (ΔH). In the case of polyaniline salt, the spin concentration is higher, around 10^{20} spins g^{-1}, and the ΔH value is lower, about 2.0−3.0 G. For the polyaniline base, the spin concentration is lower, about 10^{18} spins g^{-1}, while the ΔH value is greater, about 8.0−12.0 G.[35]

The g value of the polyaniline−sulfosalicylic acid salt and its base is nearer to that of the free electron (2.0023). The A/B peak ratio is also nearly unity, indicating that the spins are free electron type. The line width of the EPR signal of the polyaniline base is larger than that of the polyaniline−sulfosalicylic acid salt (Table 6). For example, the line width of the polyaniline base redoped with HCl decreases from 8.5 to 2.15 G and the spin concentration increases from 10^{18} to 10^{20}. A similar increase in spin concentration and a narrowing of the EPR line width take place when the polyaniline base was redoped with sulfosalicylic acid, demonstrating the conversion of the polyaniline base into the salt. This is consistent with the results of the conductivity and absorption spectral measurements.

Morphology. a. Scanning Electron Microscopy. The scanning electron micrographs showed a granular morphology for polyaniline−sulfosalicylic acid salt similar to the one reported for polyaniline doped with sulfuric acid[36] but unlike the needle-shaped structure observed for the polyaniline−dinonylnaphthalenesulfonic acid salt[8] or the fibrillar nature reported for the polyaniline−DBSA salt.[12] The SEM pictures obtained for the polyaniline−sulfosalicylic acid salt are similar to those reported recently for polyaniline doped with methanesulfonic acid and p-methylbenzenesulfonic acid.[37] The micrographs of polyaniline−sulfosalicylic acid salt revealed a granular nature with sharp-edged particles and lamellar structure on one side and comparatively smoother pattern on the other side (Figure 6).

b. Particle Size Measurement. The particle size measurement was carried for the polyaniline−sulfosalicylic acid salt synthesized at room temperature. The mean diameter of the polymer particles was 54.34 μm and the density, 1.20 g mL^{-1}. The surface area of the sample was 0.1604 sq m g^{-1}.

c. X-ray Diffraction. The X-ray powder diffraction patterns for the polyaniline salt synthesized at three different temperatures and for its base are typical of

Table 7. Positions of Bragg's Peaks for Polyaniline Base and Its Salt (2θ {d (Å)})[a]

sample										
polyaniline−sulfosalicylic acid base				24.20 (3.66)	20.69 (4.29)	20.27 (4.38)	15.79 (5.61)		9.46 (9.34)	
polyaniline−sulfosalicylic acid salt (0 °C)	27.92 (3.20)	27.13 (3.28)		25.49 (3.49)	20.06 (4.42)		15.20 (5.82)		9.38 (9.42)	9.12 (9.69)
polyaniline−sulfosalicylic acid salt (27 °C)			26.93 (3.31)	25.34 (3.51)		19.91 (4.46)	15.81 (5.60)	14.87 (5.95)		8.86 (9.98)
polyaniline−sulfosalicylic acid salt (60 °C)				25.60 (3.48)	20.30 (4.37)			14.76 (6.00)		

[a] The value in parentheses is the Bragg's distance d in Å.
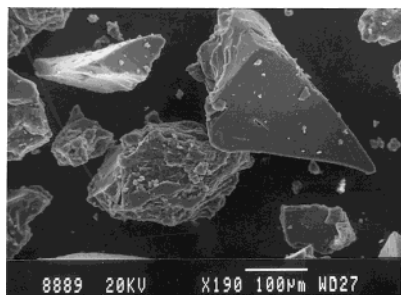
Figure 6. SEM micrograph of polyaniline−sulfosalicylic acid salt.

semicrystalline/amorphous polymers. The positions of the main Bragg's peaks and their corresponding d values are summarized in Table 7. The X-ray diffraction patterns are in good agreement with those reported by Pouget et al.[38] for the polyaniline−emeraldine salt prepared using ammonium persulfate as the oxidant and HCl as the dopant and its base. The polyaniline salt synthesized at 0 °C was found to be more crystalline than that synthesized at 27 and 60 °C. The conductivity results have revealed that higher the crystallinity, the higher is the electrical conductivity, in agreement with the observations of Luzny and Banka.[39]

Thermal Analysis. TGA−DTA. The TGA and DTA of the samples were recorded from 25 to 900 °C at a heating rate of 20 °C min^{-1} with nitrogen as the purge gas at a flow rate of 80 mL/min. The thermograms showed that the polyaniline−sulfosalicylic acid salt synthesized at ambient temperature is thermally more stable than that prepared at 60 °C. The TGA of the polyaniline salt synthesized at room temperature shows a three-step weight loss. The weight loss in the first step up to about 100 °C due to the loss of moisture is about 6%. In the second step (up to 260 °C), the weight loss is around 31%, which could be due the removal of the dopant sulfosalicylic acid. A slow and somewhat gradual weight loss profile was noticed for the polyaniline salt after about 480 °C, which is ascribed to the degradation of the salt. For the polyaniline salt synthesized at 60 °C, there is a smaller initial weight loss of about 4% up to 110 °C due to the loss of moisture expectedly due to the higher temperature of synthesis. The second step starts at about 250 °C, after which a slow and continuous weight loss of the dopant occurs. The loss of the dopant is followed by the degradation of the polymer at about 400 °C. Hence, the third step could not be identified unlike in the case of polyaniline salt synthesized at room temperature. The inverted emulsion method apparently yields polyaniline-sulfosalicylic acid salt of higher thermal stability (degradation begins around 400 °C) than that obtained using the solution and the microemulsion methods (HCl doped) with ammonium persulfate as the oxidant where the decomposition begins at 320 and 350 °C, respectively.[14]

The thermogram of the polyaniline base dedoped from sulfosalicylic acid salt shows a weight loss of about 7% at 130 °C due to the loss of water. There is a small second step at about 350 °C, which is attributed to the loss of oligomeric species present in the polyaniline base. Thereafter, from 480 °C a gradual weight loss is seen due to the degradation of the polymer base.

The DTA curve of the polyaniline base shows an exotherm around 560 °C, corresponding to its degradation. In the case of polyaniline−sulfosalicylic acid salt prepared at room temperature as well as at 60 °C, the DTA curve shows an endothermic and an exothermic peak. The exotherm is attributed to the degradation of the polyaniline salt and the endotherm to the loss of dopant. For the polyaniline−sulfosalicylic acid salt synthesized at room temperature, the peaks are found at 305 and 540 °C, respectively, whereas for the salt synthesized at 60 °C, the peaks are shifted to a lower temperature; the endotherm occurs at 260 °C and the exotherm at 520 °C. Thus, the polyaniline−sulfosalicylic acid salt prepared at room temperature is apparently more stable than the one synthesized at 60 °C as noted from the TGA curve. As noted from the DTA studies, the polyaniline base is thermally more stable than the salt.

Conclusions

A new inverted emulsion process has been employed for the synthesis of polyaniline salt using benzoyl peroxide as a novel oxidant. The polyaniline obtained is of high purity and is free from contaminants that are present when ammonium persulfate is used as the oxidant. The optimum conditions for the emulsion polymerization of aniline in weakly polar solvents, e.g. chloroform, are established. The polyaniline salt synthesized has granular morphology, enhanced conductivity, and crystallinity. The low-temperature synthesis leads to a more crystalline and an enhanced conducting form of the polyaniline salt. The polyaniline−sulfosalicylic acid salt prepared at room temperature apparently is more stable thermally than that synthesized at a higher temperature.

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