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THE CHEMICAL SYNTHESIS OF CONDUCTIVE POLYANILINE BY USING BENZOYL PEROXIDE

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ABSTRACT

The chemical polymerization of aniline was carried out in acetonitrile/water media by the use of benzoyl peroxide as an initiator. Among the acids chosen as dopant the highest yield was obtained in HCl with 24.8% and the highest conductance was observed in H_2SO_4 with $0.082\,S\,cm^{-1}$. The effect of HCl, benzoyl peroxide and aniline concentrations upon polyaniline yield and conductivity was also investigated. The polyaniline was characterized by conductivity measurements, UV-Vis and FTIR.

Key Words: Benzoyl Peroxide; Chemical Polymerization; Polyaniline

INTRODUCTION

Polyaniline (PAn) is a conductive polymer which electrical properties can be reversibly controlled by charge transfer doping or by protonation.[1] PAn also has a superior chemical and environmental stability in both doped and undoped states compared to other conductive polymers. These features of PAn combined with its electrochemical and optical properties make it potentially attractive for application as an electronic material. It has been

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used as a positive electrode in secondary batteries due to the redox properties of PAn.[2,3]

PAn can be prepared by either an electrochemical[4–7] or a chemical method. The polymerization of aniline and its derivatives, by the use of Ce(IV) sulfate as an oxidizing agent, is an example of the chemical method.[8] It was reported that aniline derivatives did not form polymer with ammonium peroxysulphate.[8]

The PAn yield increased up to an oxidizing agent/aniline ratio of 2.5 in the chemical polymerization of aniline with ammonium persulphate agent and showed a decrease after this value.[9]

The electrical conductivity and the yield of PAn synthesized at different aniline/oxidant ratios using four different kinds of oxidizing agents were compared by Pron et al.[10] They concluded that the redox potential of the oxidizing agents was not a dominant parameter in the chemical polymerization of aniline.

It was reported that only the oligomers were obtained in the polymerization of aniline with the use of NaClO.[11] Inoue[12] showed that aniline was chemically oxidized with $CuClO_4$ in organic media.

The polymerization rate of aniline has been accelerated using H_2O_2-Fe^{2+} redox system instead of H_2O_2.[13,14] The conductivity and the structure of PAn obtained by H_2O_2 or H_2O_2-Fe^{2+} are the same with that obtained by using the $(NH_4)_2S_2O_8$.[13]

In this study, the chemical polymerization of aniline in acetonitrile/water media using benzoyl peroxide was firstly reported. The effect of temperature, time, concentrations of benzoyl peroxide, HCl and aniline, acetonitrile/water ratio and type of acid employed upon the yield of PAn was also investigated.

EXPERIMENTAL

Materials

Aniline (An) was distilled under vacuum and benzoyl peroxide (Bz_2O_2) was crystallized from a methanol/chloroform mixture. Other chemicals were used as received.

Preparation of Polyaniline

Suitable amount of aniline and 10 mL solution of Bz_2O_2 prepared in acetonitrile (ACN) were added to a 40 mL aqueous solution of HCl (0.5 M). The mixture was kept in a thermostated water bath and, the temperature can be adjusted within $\pm 1°C$. At the end of polymerization, the dark green precipitate formed was separated by filtration and washed first with distilled water, then acetone and finally aqueous 0.5 M HCl. The polymer was dried at 50°C in vacuum. The percentage PAn yield was calculated gravimetrically.

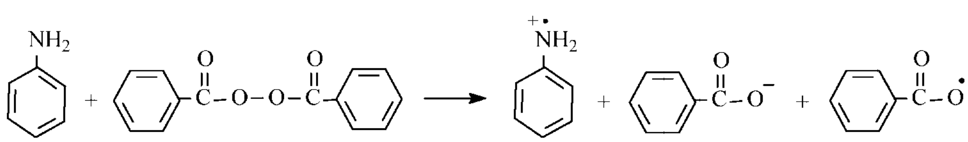
Measurements

The polyaniline samples used in conductivity measurements were prepared as pellets having a 1.3 cm diameter and 1 mm thick. The measurements were carried out with a standard four-probe technique. The UV-Vis spectra were taken with a Shimadzu Model 160 A spectrophotometer and FTIR spectra were recorded with a Matsoon 1000 Model FTIR spectrophotometer.

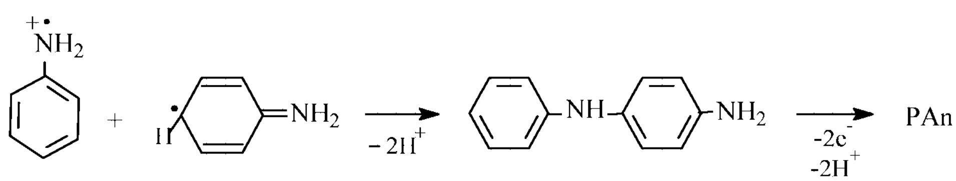
RESULTS AND DISCUSSION

The polymerization of aniline with H_2O_2-Fe^{2+} system has been investigated by Sun et al.[13] They reported that H_2O_2 was consumed during the polymerization and Fe^{2+} acted as an activator or a catalyst in polymerization. They also emphasized that the polymerization took place through the oxidation of aniline but did not give a detailed mechanism for the polymerization pathway.

The reactions between Bz_2O_2 and amines have been investigated by various workers,[15–17] and the following mechanism was proposed by Imoto et al. and Horner et al.[15,16]



We thought that the polymerization takes place through an oxidative mechanism as in H_2O_2[14] and the radical cation of aniline formed by the reaction given above might proceed as the reaction which follows:



The studies related to the reaction mechanism are currently continuing in our laboratory.

The first polymerization experiments were attempted in pure ACN chosen as a solvent, but the polymerization of aniline was not successful.

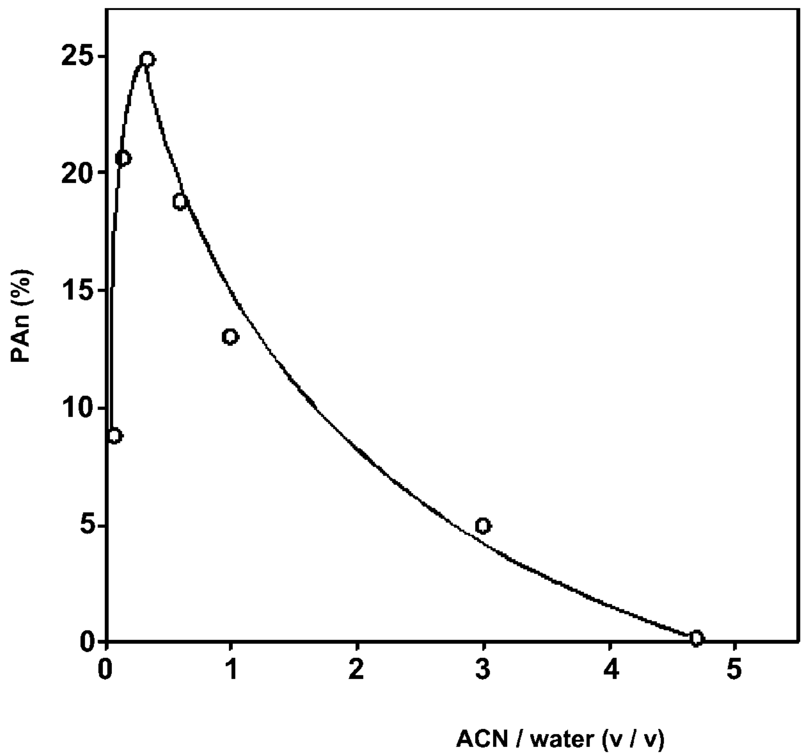


Figure 1. The change of PAn yield with the ratio of ACN/water (v/v). [An], 0.05 M; [HCl], 0.5 M; [Bz_2O_2], 8×10^{-3} M; temperature, 40°C; reaction time, 4 h.

Table 1. The Percentage Yield and Conductivity of PAn Synthesized Chemically in Media Containing Different Acids

Kind of Acid	PAn (%)	σ ($S\,cm^{-1}$)
HCl	24.8	0.180
HNO_3	15.2	0.126
$HClO_4$	9.4	0.710
H_2SO_4	1.8	0.820
H_3PO_4	0.3	0.008
HOOCCOOH	3.2	0.002
HCOOH	–	–
CH_3COOH	–	–

[An], 0.05 M; [acid], 0.5 M; [Bz_2O_2], 8×10^{-3} M; reaction temperature, 40°C; reaction time, 4 h.

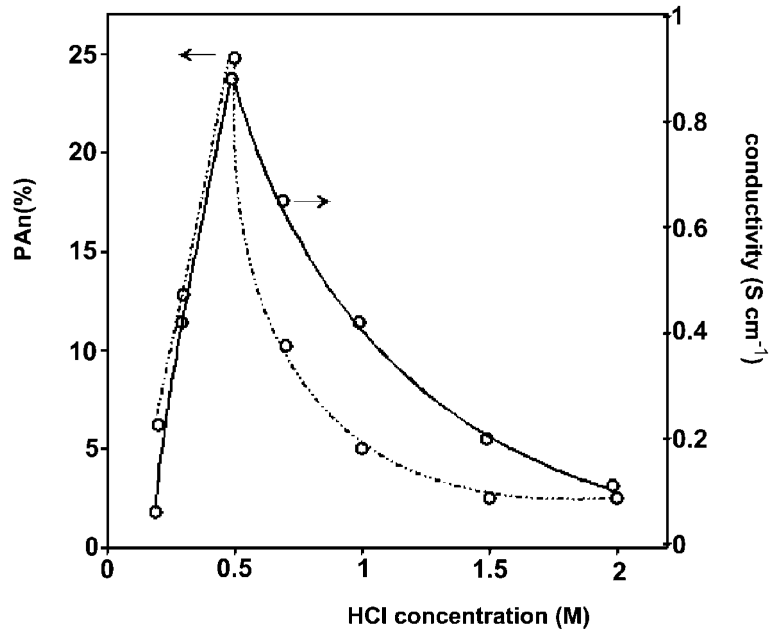


Figure 2. The effect of HCl concentration upon the yield and the conductivity of PAn. (- - -), yield (%); (—), conductivity (S cm^{-1}); [An], 0.05 M; [Bz_2O_2], 8×10^{-3} M, temperature, 40°C, reaction time, 4 h.

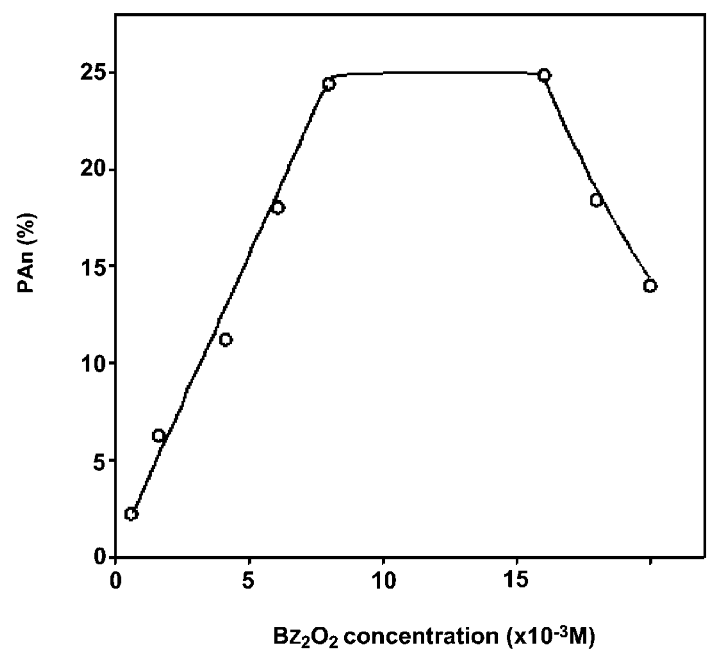


Figure 3. The effect of Bz_2O_2 concentration upon the yield of PAn. [An], 0.05 M; [HCl], 0.5 M; temperature, 40°C; reaction time, 4 h.

Bz_2O_2 has been used as an initiator in the polymerization carried out in a solvent-water mixture as done in most graft copolymerization systems.[18,19] We tried this kind of mixture and experiments showed that the aniline could be polymerized with Bz_2O_2 in ACN/water media. We also observed that the ratio of ACN/water affected the polymer yield. Therefore, the experiments were performed with different ACN/water ratios and the results are given in Fig. 1.

Figure 1 indicates that the highest PAn yield is obtained at a ACN/water ratio of 10/30 (v/v). The yield was observed to decrease at ratios higher or lower than that value. All the later experiments were carried out at a ACN/water ratio of 10/30 (v/v).

Table 1 shows the effect of the type of acid employed upon the polymer yield and the conductivity. Among the ten different acids used, there were no polymers with formic and acetic acid obtained. Although the highest conductivity was obtained with sulfuric acid, the experiments were carried out with HCl, which gave the highest polymer yield.

Figure 2 illustrates the effect of HCl concentration upon the PAn yield and conductivity. The polymer yield and conductivity rapidly increases up to a HCl concentration of 0.5 M and then shows a rapid decrease. This

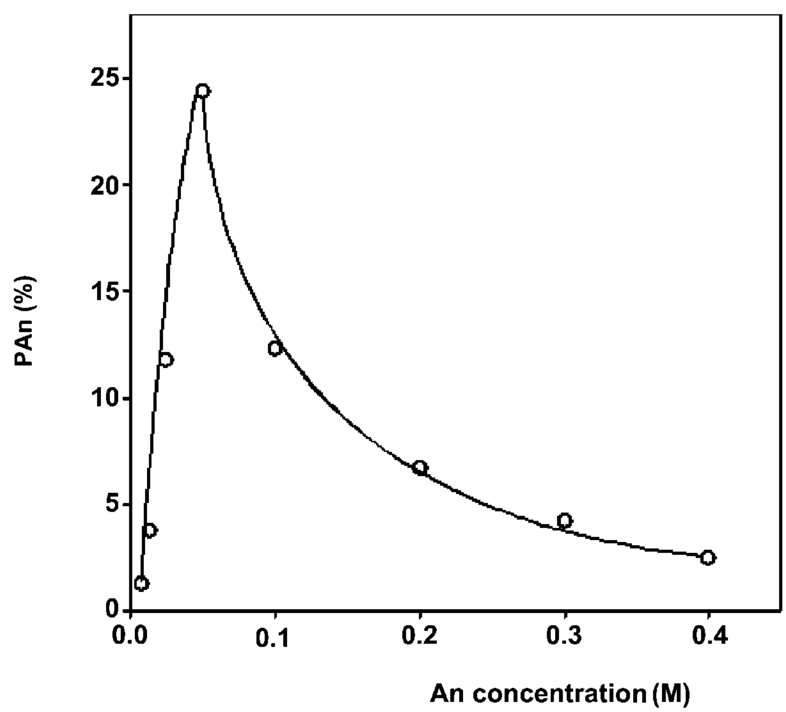


Figure 4. The effect of aniline concentration upon the yield of PAn. [HCl], 0.5 M; [Bz_2O_2], 8×10^{-3} M; temperature, 40°C; reaction time, 4 h.

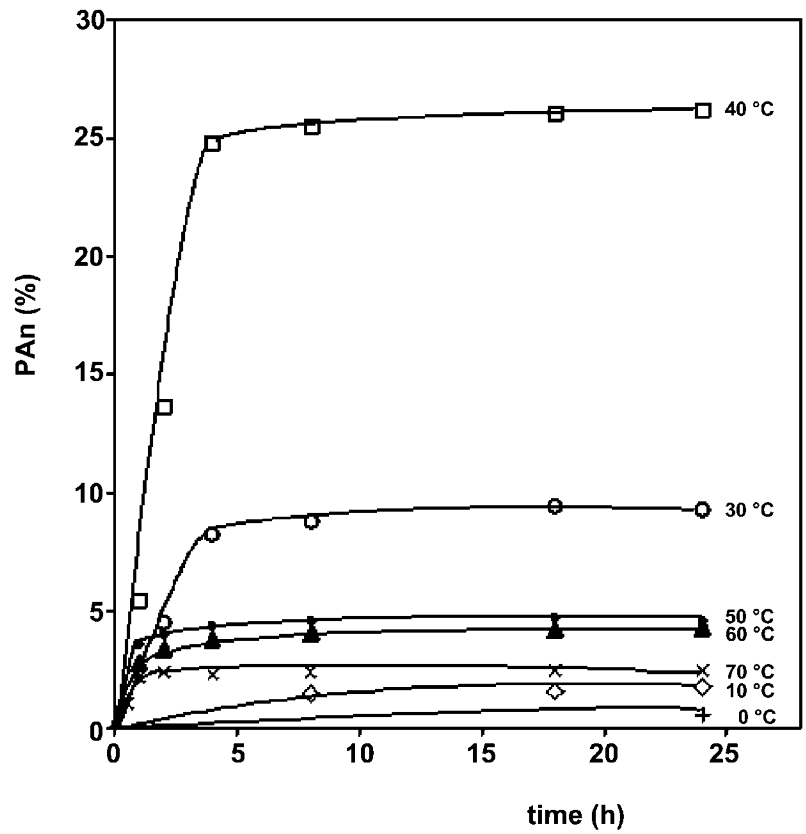


Figure 5. The change of the PAn yield with temperature and time. [An], 0.05 M; [HCl], 0.5 M; [Bz_2O_2], 8×10^{-3} M.

behavior is typical with respect to the effect of the acid concentration upon the PAn yield. It was proposed that aniline molecules made head-to-tail coupling in acidic media.[20,21] After coupling, H^+ must be eliminated from the structure for the growth of PAn. There forms significant amounts of aniline salt in the medium at acid concentrations higher than 0.5 M thus, aniline cannot act as H^+ acceptor. When H^+ is not eliminated from the cation radical oligomer, not only does the oligomer not grow, but also decomposes by hydrolysis.[1]

The effect of Bz_2O_2 concentration upon PAn yield is illustrated in Fig. 3. It was observed that there was a marked increase in the polymer yield up to 8×10^{-3} M Bz_2O_2, remained constant between 8×10^{-3}–16×10^{-3} M, and decreased thereafter. The reason for the decrease in PAn yield with the increase in Bz_2O_2 concentration is the formation of excessive aniline radical cation and soluble oligomers due to rapid polymerization.[22]

Figure 4 shows the effect of aniline concentration upon the PAn yield. The optimum aniline concentration was found to be 0.05 M from this figure.

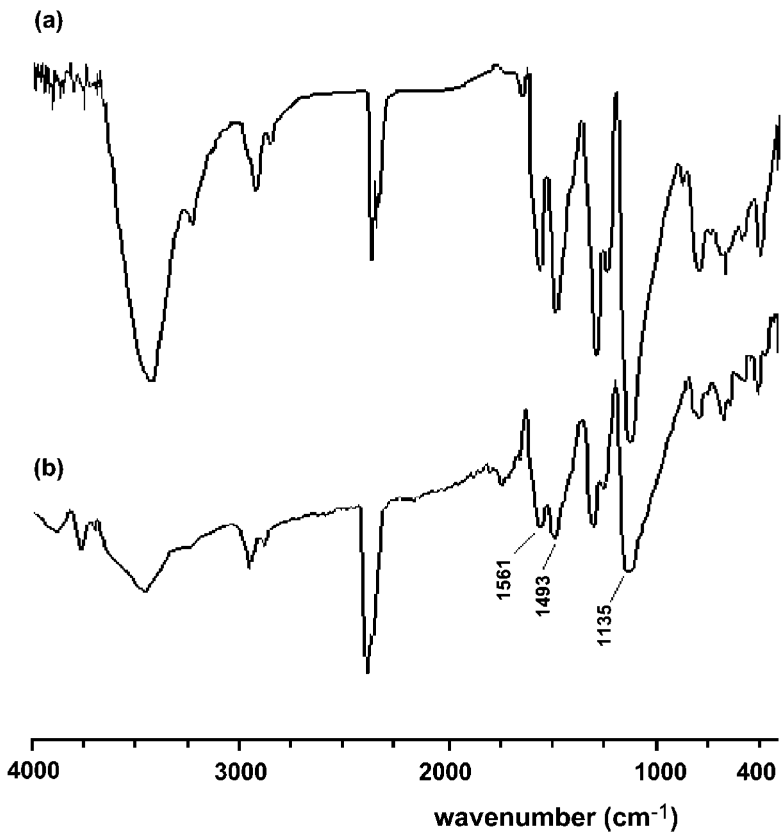


Figure 6. The FTIR spectra of HCl doped PAn samples synthesized by the chemical method with (a) Bz_2O_2 and (b) $K_2Cr_2O_7$.

The effect of the temperature and polymerization time upon the PAn yield after the optimization of ACN/water ratio and HCl, aniline, and Bz_2O_2 concentrations was investigated, and the results were plotted in Fig. 5. The highest PAn yield was obtained at 40°C and the temperature increase above 40°C caused a remarkable decrease in the yield. We found that polymerization times longer than four hours do not affect the yield of PAn. This observation may be explained by the fact that Bz_2O_2 reacts easily with amines at low temperatures such as 30–35°C.[16]

FTIR

PAn can be easily polymerized by conventional oxidants such as $K_2Cr_2O_7$[4,23] and $(NH_4)_2S_2O_8$.[24] The comparative FTIR spectra of PAn synthesized in Bz_2O_2-HCl and $K_2Cr_2O_7$-HCl are given in Fig. 6. The FTIR spectrum of polymer prepared by Bz_2O_2 is quite similar to that prepared by

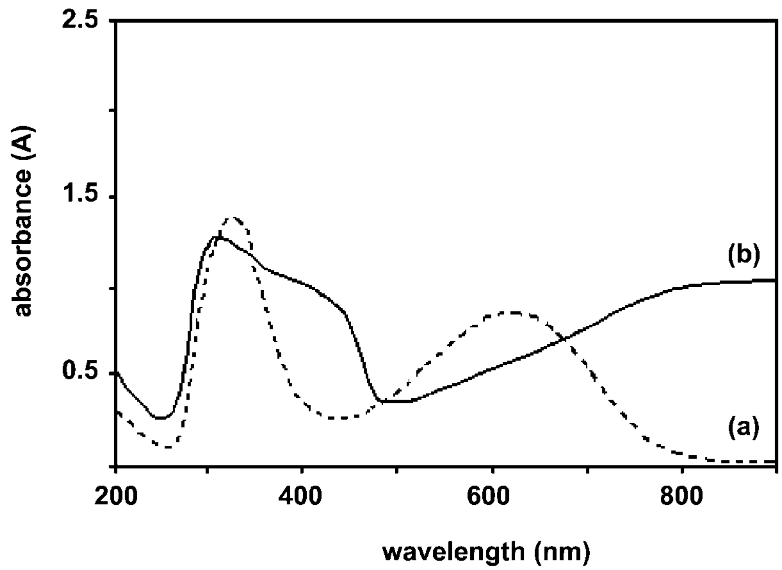


Figure 7. UV-Visible spectra of PAn solution in N-methyl pyrolidone at (a) pH 7 and; (b) pH 3.

$K_2Cr_2O_7$. The bands observed at 1493 and 1561 cm^{-1} are due to C-N bonds of benzenoid units and C=N bonds of quinoid units,[8] respectively. The characteristic conduction band of conductive PAn is the broad and intensive peak located at 1135 nm[25] which was attributed to charge delocalization on the polymer backbone.[26]

However, the fact that the conduction band in PAn obtained with $K_2Cr_2O_7$-HCl is broader than the band of PAn obtained with Bz_2O_2-HCl in Fig. 6 shows that the conductivity of the former is higher.

UV-Vis

Figures 7a and 7b are the UV-Vis spectra of doped PAn in N-methyl pyrolidon at pH 7 and pH 3, respectively. The bands observed at 325 nm in Fig. 7a and 310 nm in Fig. 7b correspond to $\pi-\pi^*$ transitions of aniline and/or anilinium radical.[27] The adsorption band observed at 630 nm at pH 7 belonging to a $\pi-\pi^*$ transition of quinone-imine groups[27] (Fig. 7b) disappears at pH 3 (Fig. 7b) and forms new bands at 430 nm and about 800 nm. The second absorption band resulting in Fig. 7b (430 nm) is found only for $pH < 7$ and represents the protonation stage of PAn.[28] The absorption around 800 nm is related to the presence of polaron formed after doping procedure[28] or delocalized free electron states.[29]

CONCLUSION

Our results showed that the aniline could be polymerized by the use of Bz_2O_2 in a ACN/water mixture. The highest polymer yield was obtained at a ACN/water ratio of 10/30. Among the acids employed as dopants, the highest yield was obtained with HCl (24.8%) The optimum conditions for polymerization in HCl were 0.5 M HCl, 0.05 M aniline and 8×10^{-3} M Bz_2O_2. The FTIR data revealed that PAn synthesized in the medium of Bz_2O_2-HCl has the similar chemical structure synthesized in $K_2Cr_2O_7$-HCl.

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