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Aniline - aminobenzyl alcohol copolymers : preparation and characterization

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Aniline - Aminobenzyl Alcohol Copolymers: Preparation and Characterization

A Thesis
Presented to
The Faculty of the Department of Materials Engineering
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Binh Vu Cao
December, 1995

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Abstract

Aniline - Aminobenzyl Alcohol Copolymers: Preparation and Characterization

by Binh Vu Cao

Copolymers of aniline and 2-aminobenzyl alcohol were chemically polymerized in acidic conditions. The reaction times of the copolymers increase monotonically with the amount of 2-aminobenzyl alcohol. Recovered yields of insoluble polymer decrease as the amount of 2-aminobenzyl alcohol increases. Cyclic voltammetric analysis of the reaction solutions after the removal of polymers revealed the presence of electroactive materials but not high molecular weight polymer. Room temperature electrical conductivities of copolymers in the HCl protonated form vary monotonically between those for the two homopolymers. The thermal gravimetric (TG) analysis revealed that the thermal stability of HCl protonated copolymers in air is similar to the HCl protonated polyaniline. There is no significant effect of the structure on the thermal stability. The solubility of copolymers in the HCl protonated form is very poor. The quantitative determination of the solubility using ASTM #D-3232-84 (Re-approved 1990) was not feasible due to the strong coloration of the polymer solutions.

Acknowledgments

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And to my parents, I would like show the deepest gratitude for their sacrifices in instilling the values of education in my early years.

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Chapter I

Introduction

Conductive polymers have been the subject of intense research in the last twenty years, owing to their promise of new effects and applications. Conductive polymers combine easy processing, light weight, and good mechanical properties with many of the electrical properties found in conventional conductors such as silicon, carbon black, and copper. Conductive polymers are basically plastics with free electrons, capable of carrying charges. Conducting polymers are generally organized into two main classes: filled polymers and inherently conducting polymers. An extensive discussion of these two conducting polymer types had been presented by P. Kathirgamanathan [1]. Under the scope of this thesis work, only the inherently conducting polymers class will be discussed extensively. Some of the important polymers of the inherently conducting family are polyacetylene, polyaniline, polypyrrole, poly(p-phenylene), poly(p-phenylene sulfide), poly(metallophthalocyanines), poly(p-phenylene vinylene), and polythiophene [2].

While these conductive polymers are not going to replace metals at the present time, their semiconductor-like properties make them attractive for a multitude of electrical applications. The major applications for conductive polymers are in rechargeable batteries, microelectronics, power equipment, and microtools. A detailed discussion of the promising applications of conducting polymers can be found elsewhere [3]. The typical conductivities of the most common inherently conducting polymers in comparison to common metals, semiconductors, and insulators are shown in Table 1. Besides the great advantage of organic conducting polymers over the inorganic with respect to the architectural flexibility, inherently conducting polymers have been often pointed out to possess a combination of undesirable properties such as insolubility in common organic solvents, non-processability using conventional techniques, instability to air and moisture, and lack of mechanical strength [2].

Table 1. Conductivity Chart[1] (After P. Kathirgamanathan, 1990)

	Materials	**Conductivity ($S \cdot cm^{-1}$)**	**Inherently Conducting Polymers**
Metals:	Silver	10^6	
	Copper	10^4	Oriented doped (CH)x
			Polyphenylene(s) Polythiophene(s)
		10^2	
			Polyaniline(s)
Semiconductors:	Carbon black	1	
	Germanium	10^{-2}	
	Doped silicon		Undoped polypyrrole(s)
		10^{-4}	Trans undoped (CH)x
		10^{-6}	
			Undoped polyaniline(s)
		10^{-8}	
Insulators:	Glass	10^{-10}	Cis undoped (CH)x
	PVC		
		10^{-12}	
	Diamond	10^{-14}	
	Nylon		
	Polyethylene	10^{-16}	
	Polyimide		
	Polytetrafluoro-	10^{-18}	

Over the last two decades, a large research effort has been devoted to the resolution of the aforementioned problems in inherently conducting polymers. A review of publications on conductive polymers reveals that processability and high mechanical integrity can be attained for essentially any conducting polymer system with some compromises in electrical properties, e.g., electrical conductivity and electroactivity. A skillful materials scientist can apply the full range of polymer synthesis techniques such as copolymerization, processable precursors, substituent effects, blend formation, composite formation, latex formation, and electrochemical formation to develop useful electronically conducting polymers [3].

In the past, reasonable conductivity in polymers was only achieved by conductive fillers, e.g., carbon black and metallic conductors. At low levels of conductive fillers, the conductivity of the whole composite system is determined by the conductivity of the polymer matrix and is practically zero. With increasing filler content, the electrical conductivity increases very dramatically and a maximum is obtained with a conductivity equal to that of the pure filler. However, at the relatively high loading of fillers, i.e., 20-40 weight percentage, the reasonable conductivity is obtained at the price of good mechanical properties [4]. For that reason, the demand for intrinsically conductive polymers, which show good conductivities combined with the ease of processing and the outstanding properties of the traditional polymers is warranted.

Since the discovery of polyacetylene as an intrinsically conductive polymers in 1974 to the last few years, it was found that under normal processing conditions only a few polymers are stable enough to be incorporated in practical applications. Among the leading candidates are polyanilines, polypyrroles, and polythiophenes. In these important intrinsically conducting polymers, doped polyaniline, (i.e., protonation of base polyaniline through acid-base chemistry by exposure to protonic acids) has many advantages over other doped conducting polymers such as polypyrrole, polyacetylene, etc. It is thermally stable up to 250 °C. Polyanilines can be easily synthesized chemically and electrochemically via oxidative polymerization in aqueous acidic media. Li *et al.* [5], Wei *et al.* [6], Kathirgamanathan *et al.* [7], Conklin *et al.* [8], Diaz *et al.* [9], MacDiarmid *et al.* [10], Leclerc *et al.* [11], and Dao *et al.* [12] have published extensively their research efforts in making processable inherently conducting polyanilines, substituted polyanilines polymers, and copolymers of aniline and substituted aniline.

In the quest for soluble polyanilines, researchers have found that copolymers of aniline and alkyl, or alkoxy substituted aniline offer a compromised electrical conductivity, electroactivity, and solubility in common solvents [6-9], in comparison to homopolymers of substituted aniline. In other words, the low electrical conductivity and electroactivity level in the substituted homopolymer can be improved at the price of solubility. Although many copolymers of substituted anilines have been reported, copolymer with the aminobenzyl alcohol remain to be studied. The copolymers of aniline and methanol substituted aniline may render a reasonable solubility in common solvents such as methanol and ethanol while retaining reasonable electrical conductivity and electroactivity.

Hence, the main focus of this research is to verify the hypothesis that the incorporation of the methanol substituent into the main chain of the polyaniline will improve its solubility in common solvents and reduce the electrical conductivity. To verify the above hypothesis, three copolymers of aniline and methanol substituted aniline at 1:1, 2:1, and 1:1 monomer ratios and two homopolymers were prepared and their solubility in N-methyl pyrrolidinone solvent, electrical conductivity, electroactivity, and thermal stability properties were determined for comparative evaluation. These polymers were prepared by the oxidation polymerization of the appropriate monomers in 1 M HCl acid containing ammonium persulfate. The equation for the polymerization reaction is shown in Figure 1a, where F and F-1 are the mole ratios of aminobenzyl alcohol monomers and aniline monomers, respectively. The balanced chemical polymerization reaction for polyaniline is shown in Figure 1b. The progress of the chemical polymerization reactions was followed utilizing the open circuit potential (Voc) vs. time transient monitoring technique as discussed by Wei *et al.* [13]. The electrical conductivity of the newly synthesized polymers/copolymers was studied in detail using a standard four point probe. In addition, to evaluate the processability of the inherently conducting polymers, the solubility of the polymers in N-methyl pyrrolidinone was quantified in accordance to ASTM: D-3132-84 (Reapproved 1990). Furthermore, the thermal stability of the synthesized polymers was characterized using thermal gravimetric analysis (TGA) technique.

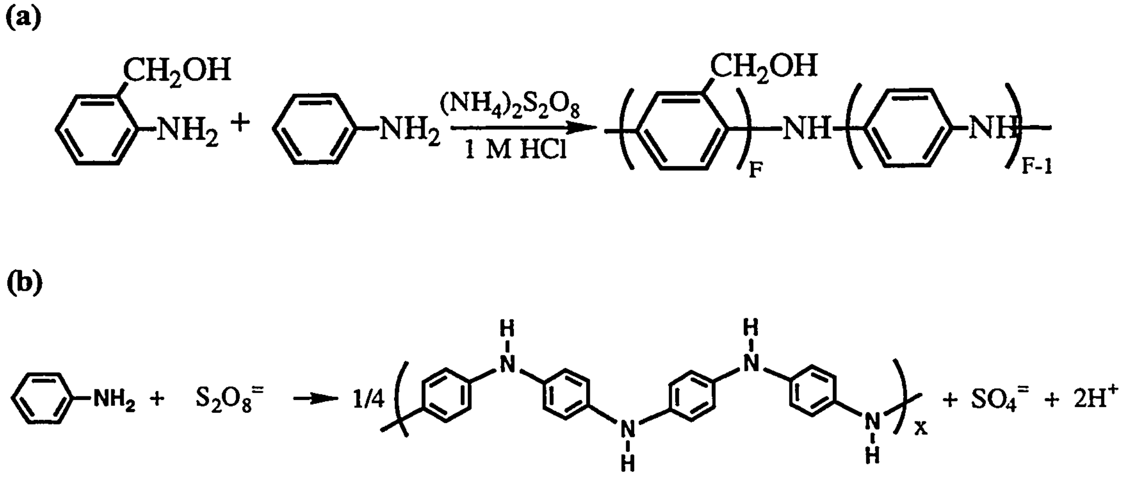


Figure 1. (a) The generalized chemical copolymerization reaction, and (b) the balanced chemical copolymerization reaction.

Chapter II

Soluble Polyaniline Research - A Review

Since the discovery of the "Shirikawa polyacetylene" in 1974, much effort has been devoted by chemists, materials scientists, and physicists to make intrinsically conductive polymers more processable, by improving their solubility in common organic solvents, and to increase their long term stability under normal conditions. The availability of soluble inherently conducting polymers is of great interest since they can facilitate post-synthesis processing. Surveying the great body of published literature in this area, it is evident that processability and reasonable mechanical integrity can be obtained for many of these materials[2]. Processable intrinsically conducting polymers and copolymers have been demonstrated using the wide range of materials development techniques such as: copolymerization, processable precursors, substituent effects, blend formation, composite formation, emulsion formation, and electrochemical film formation. However, over the last decade, it was found that under normal polymer processing conditions only a few polymers are stable enough to find practical applications. Some of the important polymers of the conducting family are polyacetylenes, polypyrroles, polythiophenes, and polyanilines.

Currently, the quest to synthesize new processable inherently conducting polymers is at an all time high. The research direction is leaning toward simple synthetic routes to prepare intrinsically conducting polymers with high stability, high solubility in common solvents, even water, to facilitate post-synthesis processing, while maintaining high electrical conductivity.

As an overview, polyaniline in the protonated form is insoluble in most organic and aqueous solvents; however, A. Andreatta *et al.* found that it has approximately20% w/w solubility in 97% sulfuric acid [14]. The different approaches to solubility include the polymerization in the media containing large proton acids or polymeric proton acids, the use of graft polymers, substituted aniline, and the copolymerization of aniline and substituted aniline. Unfortunately, the chemical modification of polyaniline produces a significant reduction of electrical conductivity, as shown in the work of Dao *et al.* and Leclerc *et al.* The solubility of these conducting polymers/copolymers is not well documented although this was the main driving force for the quest of new processable polymers. That is, the quantitative values of solubility are not provided in the literature.

Polyanilines with Counter-ion of Large Molecular Size & Graft Polyanilines:

Li *et al.* have been successful in chemically synthesizing soluble polyaniline using large size protonic acid dopants (such as toluene-*p*-sulfonic acid, sulfanilic acid or polymeric electrolyte-polystyrene sulfonic acid) to form a polymer salt. The salt favors dissolution and formation of a graft copolymer of aniline to the soft unsaturated polymer chain with the NH_2 site at a polymer pendant group [5]. The conductivities of these soluble polyanilines are comparable to that of the usual insoluble polyaniline.

Substituted Polyanilines:

The synthesis of processable polyanilines via prefunctionalized monomers has been aggressively carried out by Dao *et al.* [12], Leclerc *et al.* [17], and DeArmitt *et al.* [18]. Unfortunately, the incorporation of alkyl and alkoxy functional groups on polyaniline consistently reduces the polymer yields and electrical conductivities as shown in Table 2.

Table 2. Chemical polymerization yields and electrical conductivities of the alkyl ring-substituted polyanilines [11].

Polymers	**Yield (%)**	**Conductivity ($S \cdot cm^{-1}$)**
Polyaniline	82	5
Poly(2-methylaniline)	80	0.3
Poly(3-methylaniline)	29	0.3
Poly(2-ethylaniline)	16	1

Copolymers of Aniline and Substituted Aniline:

Copolymers from aniline and substituted aniline have been chemically and electrochemically synthesized by Wei *et al.*[6], Kathirgamanathan *et al.* [7], Conklin *et al.* [8], and Diaz *et al.* [22]. The resulting copolymers have been found to have a monotonic variation in their polymer yields and electrical conductivity with the monomer composition as shown in Table 3, Table 4, and Figure 2.

Table 3. Polymerization yields and electrical conductivities for the poly(aniline-co-anthranilic acid) [22].

Mole fraction of anthranilic acid in copolymer	**Yield (%)**	**Conductivity ($S \cdot cm^{-1}$)**
0.00	84	5.2
0.25	68	1.2×10^{-2}
0.50	57	4.5×10^{-5}
0.60	34	6.1×10^{-7}
0.75	28	1.0×10^{-8}
1.00	22	1.0×10^{-8}

Table 4. Polymerization yields and electrical conductivities for the poly(aniline-co-N-(4-sulfophenyl)aniline) [22].

Mole fraction of N-(4sulfophenyl)aniline in copolymer	Yield (%)	Conductivity $(S \cdot cm^{-1})$
0.00	84	5.2
0.25	71	0.11
0.50	58	0.075
0.60	37	0.023
0.75	26	0.013
1.00	19	0.0035

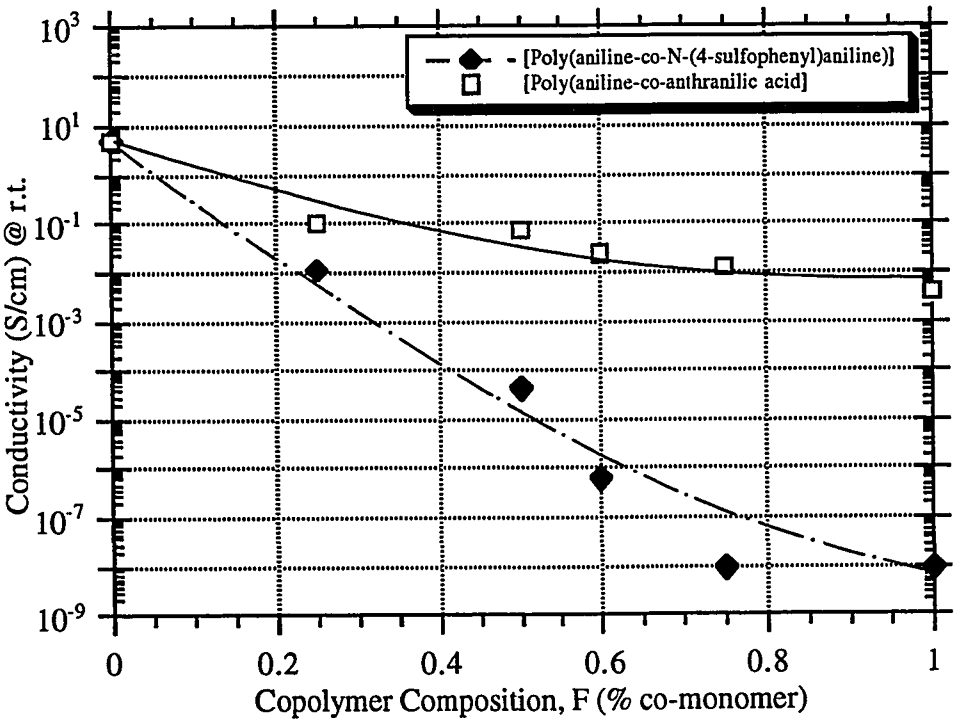


Figure 2. Room temperature conductivity vs. co-monomer mole fraction

In the cases studied, the introduction of a substitutuent always decreases the conductivity of polyaniline and the magnitude of the change depends on the substitutuent. Given the two copolymers considered in Figure 2, the effect appears to be related to the size of the substitutuent. The larger phenylsulfonic acid group has a larger effect than the ethyl and the -COOH group. This trend parallels the size differences of the group.

Chapter III

Methodology

A. Chemical Polymerizations and OCP Measurements

The aniline and the 2-aminobenzyl alcohol monomers purchased from Aldrich Chemicals were used as received without further purification. They were polymerized or copolymerized in 1M HCl acid media in the presence of $NH_4S_2O_8$ oxidant. Five different polymers were synthesized by varying the mole ratio of the two monomers. The mole ratios of aniline and 2-aminobenzyl alcohol monomers used are 1:0, 2:1, 1:1, 1:2, and 0:1, respectively. The solution of 0.1M aniline, 0.1M 2-aminobenzyl alcohol, and 0.1M ammonium persulfate each were prepared separately in 1M HCl. Table 5 shows the volumes of the monomer solutions used in the polymerization reactions. The generalized chemical polymerization reaction is structurally shown in Figure 1.

Table 5. Monomer solution volumes used in the polymerization reaction

Polymer Type:	**Monomer Mole Ratio, F**	**0.1M Aniline Monomer Solution (ml)**	**0.1M 2-aminobenzyl alcohol Monomer Solution (ml)**	**0.1M Ammonium Persulfate Solution (ml)**
Polyaniline	0	360	0	360
Copolymer [2:1]	0.33	240	120	360
Copolymer [1:1]	0.50	180	180	360
Copolymer [1:2]	0.66	120	240	360
2-aminol benzyl alcohol	1	0	360	360

The progress of the polymerization reaction was monitored utilizing the open circuit potential (OCP) - time transient technique discussed by Wei *et al.* [13]. The OCP/time transient technique had been demonstrated by many researchers to be an effective tool to quantitatively monitor chemical oxidative polymerizations. The open-circuit potential of the chemical polymerization was measured using a single compartment, two-electrode cell:

Pt // Analyte solution // Reference electrode (SCE)

A Corning platinum disc type electrode (cat. no. 476060) of 0.317 cm^2 area was used as the working electrode. The reference electrode was a saturated calomel electrode (SCE). The potential of each polymerization was recorded with an EG&G PAR 273 potentiostat/galvanostat. For each polymerization, the monomer solution was stirred in 1000 ml polypropylene beaker for 3 minutes to attain the initial OCP equilibrium at ambient room temperature. The ammonium persulfate solution was then added to the monomer solution in one portion. The reaction was allowed to proceed at ambient room temperature with continuous stirring and the OCP was monitored throughout the course of polymerization.

B. Polymer Isolation

The synthesized polymers or copolymers were isolated from the reaction media by vacuum suction filtering using #5 type (9 cm diameter) qualitative Whatman filter papers. The collected polymeric powders were dried in a dynamic vacuum oven at 40 °C for 48 hours.

C. Electrical Conductivity Measurements

The dried polymers were ground to fine powders using a mortar and a pestle and then pressed into pellets (approximately 0.5 gram) with a 12.7 mm diameter stainless steel extrusion die at 20,000 psi. Table 6 shows the resulting pellet thickness in millimeters. The electrical conductivity of each polymer pellet was measured using a collinear four-point probe conductivity meter equipped with a bipolar 240 volt, DC power supply.

Table 6. Polymer pellet dimensions

Polymer Type:	**Monomer Mole Ratio, F**	**Thickness (mm)**
Polyaniline	0	5.2
Copolymer [2:1]	0.33	4.3
Copolymer [1:1]	0.50	3.8
Copolymer [1:2]	0.66	3.4
Poly(2aminobenzyl alcohol)	1	2.8

D. Thermal Stability Analysis of Polymers -TGA

The thermal stability of the polymers were determined using a Seiko TG-220 thermal gravimetric analyzer. Approximately13 mg of each polymer was heated in air from 25 °C to 600 °C at 10 °C/min.

E. Solubility of Polymer in NMP

The solubility of polymer in N-methyl pyrrolidinone (NMP) was determined using the standard test method for solubility range of resins and polymers: ASTM #D 3132-84 (Reapproved 1990). Specifically, a known amount of polymer was dissolved in a known volume of solvent (27 - 66 mg/ml) and treated in a sonicator for an extended period of time, ca. 1 hour. The solutions were then let stand for 1 hour prior to solubility determination. The gross solubilities such as soluble, borderline soluble (solution), and insoluble were determined in accordance to ASTM: D-3132-84 (Reapproved 1990).

N-methyl pyrrolidinone was chosen as the solvent of choice because it has high polarity index (6.7) and a relatively low toxicity level. It is also slightly basic and should assist in the dissolution of polyaniline materials.

F. Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) was used to probe both the kinetic and thermodynamic aspects of the soluble species in the reaction media. Cyclic voltammetry is a popular member of a family of dynamic electrochemical methods in which the potential applied to the working electrode is scanned linearly between two preselected voltage limits. The output of cyclic voltammetry is a plot of the current flowing in the electrochemical cell during the cyclic potential scan versus the applied voltage. This analysis provides oxidation - reduction potentials plus information about the kinetics at the electrode surface. A typical three-electrode cell including a reference electrode, a counter electrode, and a working electrode was used in these studies. A platinum disc electrode (0.317 $cm^{2)}$ was used as the working electrode and a coiled platinum wire with a 0.02 cm radius and a 8.5 cm length was used as the counter electrode. A saturated calomel electrode was used as the reference electrode. The cyclic voltammograms were recorded using an EG&G PAR potentiostat/galvanostat (Model 173) connected to an EG&G x-y plotter (Model # RE-089). The voltage limits selected were -0.2 volt and +0.8 volt. Five different scan rates: 5, 10, 20, 50, and 100 mV/sec were used in every analysis and the measurements were performed on quiet solutions, i.e., no stirring.

Chapter IV

Results & Discussion

A. Chemical Polymerizations and OCP Measurements

The chemical polymerization initiates when the ammonium persulfate solution is added to the solution containing the monomer or the two co-monomers and there is a noticible change in the OCP of the solution. This is shown in Figure 3 for the chemical polymerization reaction of aniline with $(NH_4)_2S_2O_8$ as oxidant in aqueous 1M HCl. This response confirms the result for the chemical polymerization reaction of aniline with $(NH_4)_2S_2O_8$ as oxidant in aqueous 1M HCl reported by Wei et al [13]. The change in OCP of the solution was recorded during the course of reaction. Initially, the OCP changed rapidly through the induction period (labeled $\mathbf{t_1}$ in Figure 3). As the polymerization reaction proceeded, the potential reached a steady value (labeled $\mathbf{t_2}$). Finally, as the ammonium persulfate is consumed, the OCP rapidly decayed approaching the initial OCP value (labeled $\mathbf{t_3}$). These generalized features of the OCP-time transient are also seen in the plots for polymerization reactions of the four other monomers studied. The total time of $\mathbf{t_1+t_2}$ (minute) from the OCP-time transient plots and are listed in Table 7. The $(\mathbf{t_1} + \mathbf{t_2})$ period reflects the rate of ammonium persulfate consumption and therefore the overall polymerization rate. It can also be seen that the OCP depends on the monomer composition. The $(\mathbf{t_1+t_2})$ values for the chemical polymerizations is shown in Figure 4. The $(\mathbf{t_1} + \mathbf{t_2})$ period varies with monomer type and content in the mixture. The chemical polymerization of aniline is much faster than the chemical polymerization of 2-aminobenzyl alcohol. The $(\mathbf{t_1+ t_2})$ period for polyaniline is approximately7 minutes (as previously reported [13]); however, the $(\mathbf{t_1+t_2})$ period for poly(2-aminobenzyl alcohol) is approximately 715 minutes. The $(\mathbf{t_1+t_2})$ periods increase monotonically with the amount of 2-aminobenzyl alcohol as can be seen in Figure 4.

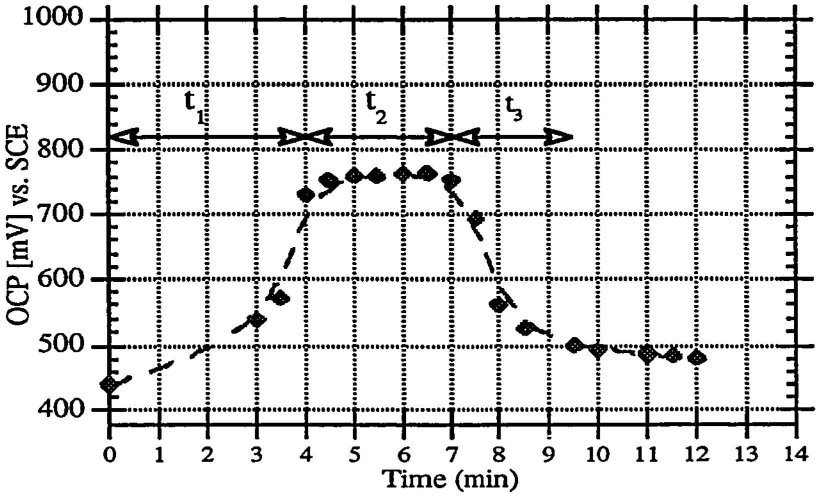


Figure 3. OCP - time transient for the chemical polymerization of aniline with $(NH_4)_2S_2O_8$ in aqueous 1M HCl.

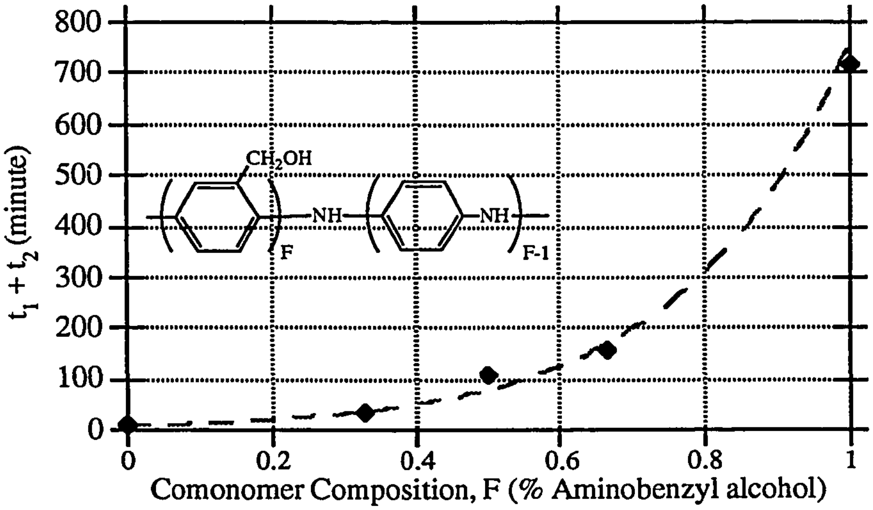


Figure 4. Dependence of (t_1+t_2) on the monomer composition, F.

From the knowledge of stereo-chemistry, it is quite reasonable to justify that the decreases in polymerization rate at the increased amounts of 2-aminobenzyl alcohol (ABA) monomer is primarily due the steric hindrance effect of the methanol substituent on the 2-amino benzyl alcohol monomer that prevented the ABA monomer to be oxidized readily. Wei *et al.* had discussed this steric hindrance effect of the alkyl ring substituent in copolymerization of aniline with alkyl ring-substituted anilines [6].

The mechanism of chemical polymerization of aniline monomers in the presence of oxidant ammonium persulfate in the hydrochloric acid media had been proposed and well documented by Wei *et al.* [13]. According to Wei *et al.*, when the ammonium persulfate solution was added to the aniline solution with stirring, an immediate change of OCP was noticed. After the short and unstable region (ca. 20 seconds), the OCP continuously increases to a plateau at approximately 0.77 V (volt) in approximately 4 minutes (**t_1**). In this stage, often called the induction period, persulfate ions dissociate into radical anions ($SO_4^{\bullet-}$) and anion (SO_4^{2-}), and the ($SO_4^{\bullet-}$) oxidizes the aniline mononomer (M_X, x = 1) and the oligomers (M_X, x>1), as they are formed. The redox reactions are:

$$M_X + S_2O_8^{2-} \longrightarrow M_X^{\bullet+} + SO_4^{2-} + SO_4^{\bullet-}$$

$$M_X + SO_4^{\bullet-} \longrightarrow M_X^{\bullet+} + SO_4^{2-}$$

$$M + M_X^{\bullet+} \longrightarrow M_{x+1}$$

The oxidized species ($M_X^{\bullet+}$) reacts with neutral aniline monomers via an electrophilic aromatic substitution reaction involving a chain growth step leading to M_{x+1}.

As the reaction proceeds through the plateau region (**t_2**), small green/blue particles started to appear in the solution and on the Pt electrode. These particles are indicative of the formation of high molecular weight polyaniline, which is not soluble in the reaction media. The polymerization continues until all of the persulfate is consummed, ca. the end of the plateau region. However, in the copolymerization and the 2-aminobenzyl alcohol polymerization, the resulting copolymers and homopolymer have a brownish color and the size of the precipitated particles are much smaller than those for polyaniline by visual inspection.

In the third stage (t_3), the OCP decays rapidly from 0.77 V to 0.5 V within 2 minutes, as shown in Figure 3. If the reaction is allowed to progress for an extended time, the OCP reaches the terminal potential of 0.44 V, a value that is close to the OCP of suspended polyaniline particles in 1 M HCl. During this period, aniline continues to polymerize with the polyaniline acting as oxidant instead of the persulfate.

In summary, for a given set of solution conditions at room temperature, we find that aniline reacts completely within 7 to 8 minutes (as previously reported) while the reaction time for 2-aminobenzyl alcohol is 715 minutes. The reaction time for anilines agrees with literature reports [13] and the slower reaction with the substituted aniline derivatives is not unexpected. The reaction duration times for mixtures of the two monomers are intermediate between these two times and scale with the monomer ratio in the reaction mixture.

Table 7. Open circuit potentials (Voc)* and (t_1+t_2) values for the aniline and 2-aminobenzyl alcohol polymerization reactions

Polymer Type:	**Monomer Mole Ratio,F**	**t_1+t_2 (minute)**	**V_o (V SCE)**	**V_{max} (V SCE)**	**V_f (V SCE)**
Polyaniline	0	**7**	0.43	0.77	0.44
Copolymer [2:1]	0.33	**34**	0.39	0.77	0.44
Copolymer [1:1]	0.50	**108**	0.41	0.71	0.44
Copolymer [1:2]	0.66	**158**	0.38	0.71	0.44
Poly(2-aminobenzyl alcohol)	1	**715**	0.37	0.66	0.43

(*) Voc values were measured in reference to SCE

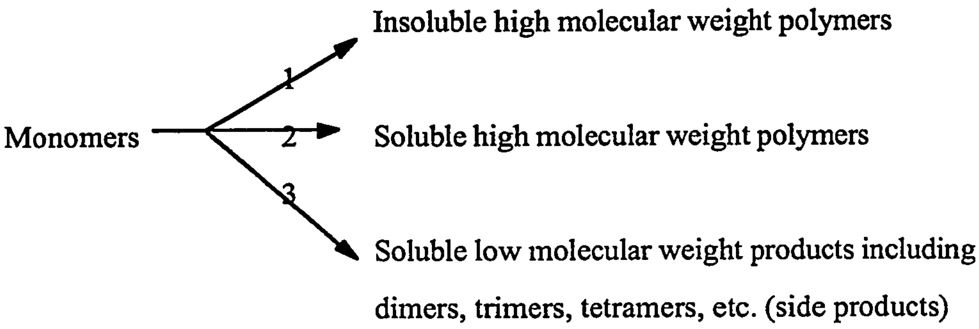
B. Polymer Isolation and Yield Quantification

The polymers were recovered by filtering the insoluble polymer which precipitated out of the reaction solution. The polymer percent yields were calculated from the dried weight of the recovered polymer and the total weight of the initial monomers. The polymerization yields of five polymers are listed in Table 8. The polymerization yield of polyaniline agrees with the literature reports. There is a linear dependence of chemical polymerization % yield of the poly(aniline-co-2-aminobenzyl alcohol) on comonomer composition, F, as shown in Figure 5. The polymerization yield decreases as the 2-aminobenzyl alcohol content increases. This effect is also seen in other copolymerization systems as shown in Tables 2 through 4.

Table 8. Recovered polymer yields

Polymer Type:	**Monomer Mole Ratio, F**	**% Yield**
Polyaniline	0	84
Copolymer [2:1]	0.33	64
Copolymer [1:1]	0.50	59
Copolymer [1:2]	0.66	48
Aminobenzyl Alcohol	1	41

This can be explained by the presence of bulky substituents which hinder the formation of head-to-tail couplings. In agreement with this assumption, recent theoretical calculations on unsubstituted polyaniline [24] have shown a strong steric interaction between the hydrogen atoms of neighbouring rings. Thus, substitution of hydrogen atoms by methanol groups increases the steric hinderance and further affects the polymerization processes. This decreases the polymer yield and correspondingly increases the low molecular weight oligomers yield. The low molecular weight polymers are soluble in the reaction media and are not collected in the filter membrane. The competitive formation of the high and low molecular weight products is shown schematically as follow:



While the interest is to favor reaction 2 over reaction 1 by the use of substituents, it appears that reaction 3 becomes the favor reaction.

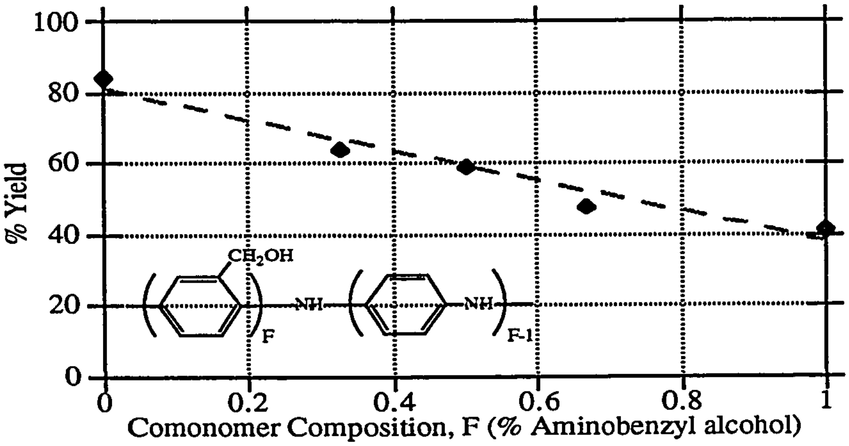


Figure 5. Dependence of recovered yield of poly(aniline-co-2-amino benzyl alcohol) on the monomer composition, F.

C. Electrical Conductivity Measurements

The room temperature electrical conductivities of HCl protonated polymers or copolymers in the pelletized form are presented in Table 9 and are plotted in Figure 6. The electrical conductivity decreases as the amount of 2-amino benzyl alcohol increases. Polyaniline in the HCl protonated form has a conductivity of approximately 4 S/cm and is approximately10^5 time more conductive than poly(2-amino benzyl alcohol). The three copolymers in the HCl protonated (conducting) form have conductivities that vary monotonically between those of the two homopolymers as shown in Figure 6. In other words, these results agree with the literature reports which show a monotonic variation in the conductivity with the composition of polymers [19, 22].

From the theoretical work of M. Leclerc *et al.* [17] on defining the structure-properties relationship in polyaniline derivatives, it is quite reasonable to rationalize that the incorporation of bulkier substituents (e.g. methanol group) induce additional deformation along the copolymer backbone, owing to an increase of the steric hindrance. This results in a decrease in the conjugation level and hence, a dramatic decrease of the electrical conductivity.

Table 9. Electical conductivity of polymers in pellet form

Polymer Type:	**Monomer Mole Ratio, F**	σ (S/cm) @ RT
Polyaniline	0	4
Copolymer [2:1]	0.33	4×10^{-3}
Copolymer [1:1]	0.50	2×10^{-4}
Copolymer [1:2]	0.66	5×10^{-4}
Poly(2-Aminobenzyl Alcohol)	1	6×10^{-5}

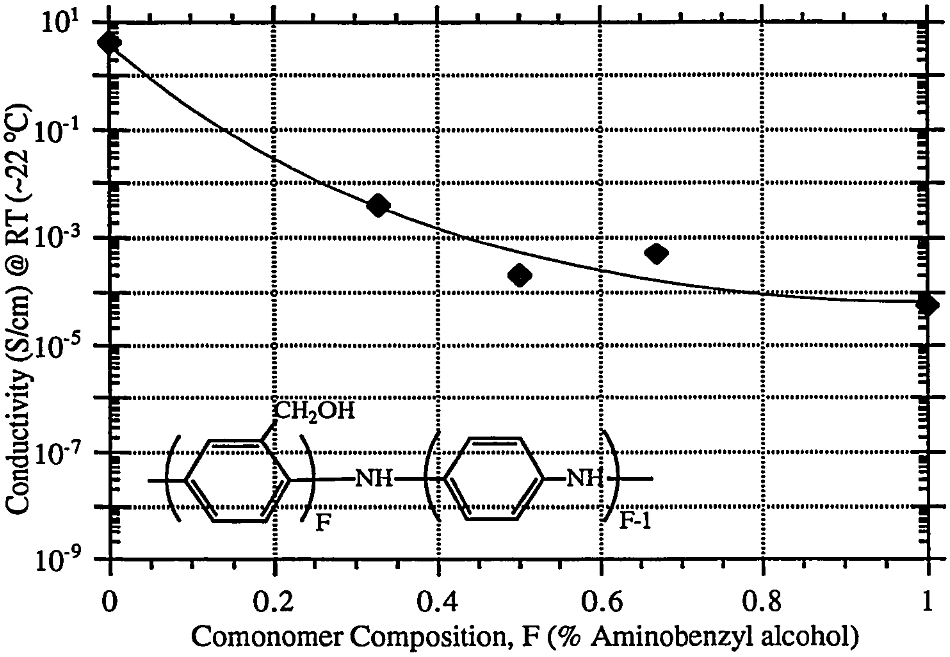


Figure 6. Dependence of log conductivity (S/cm) of poly(aniline-co-2-amino benzyl alcohol) copolymers on the monomer composition, F.

D. Thermal Stability Analysis of Polymers -TGA

The thermal stability of the HCl protonated copolymers and the HCl protonated homopolymer of aminobenzyl alcohol is summarized in Table 10 and is found to be very similar to the HCl protonated polyaniline. There is no noticeable effect of structure on the thermal stabilities. The thermogravimetric analysis (TGA) of the HCl protonated polymers demonstrates two major stages of weight losses at around 340 °C and 500 °C in ambient as shown in Figures 1 through 5 of Appendix A, respectively. The weight loss beyond 500 °C is probably due to the complete decomposition of the polymers. Table 10 lists the % weight loss of polymers at 100, 200, and 300 °C. At 100 °C, the weight loss is approximately 2-6% for all polymers. At 200 °C, the weight loss is 10-13%. At 300 °C, the weight loss is approximately 17-21%. Between 340 to 500 °C, the rate of weight loss is very fast and somewhat irregular. Polyaniline shows a slightly higher weight loss at 100 °C and which may be due to a high moisture content in the polymer.

From the early TGA study carried out under nitrogen atmosphere by LaCroix and Diaz [25] and Wei *et al.* [26], the weight loss at around 100 °C is assigned mainly to the loss of the water molecules. They analyzed the volatiles released from the samples at 100 °C with mass spectroscopy. In addition, from a detailed thermal aging study, the researchers had confirmed that the liberation of HCl is responsible for the major weight loss of the HCl protonated polyaniline at approximately 200 °C in the TG curves. The liberation of HCl at high temperatures is accompanied by a loss of polymer conductivity since the latter depends on protonation [26]. Furthermore, these reseachers also reported that the base form of polyaniline (non-conducting) shows no weight loss up to 500 C by TGA study. In the same fashion, it is reasonable to expect that these poly(aminobenzyl alcohol-co-aniline) copolymers to be more thermally stable in a nitrogen atmosphere.

Table 10. Percent weight loss of polymers at different temperatures

Polymer Type:	**Monomer Mole Ratio, F**	**% Wt. Loss @ 100 °C**	**% Wt. Loss @ 200 °C**	**% Wt. Loss @ 300 °C**
Polyaniline	0	6	11	17
Copolymer [2:1]	0.33	2	10	21
Copolymer [1:1]	0.50	3	13	20
Copolymer [1:2]	0.66	4	11	19
Poly(2aminobenzyl alcohol)	1	4	12	21

E. Solubility of Polymer in NMP

The quantitative solubility of these conducting polymers in NMP is indeterminable per ASTM #D-3132-84 (Reapproved 1990) as is shown in Table 11. The solubility observations were made after 24 hours and 7 days. There is no change in solubility over this period of time. After one week, the solutions of all five polymers have two distinctive phases: a brownish liquid phase and a dark blue solid polymer phase. Sonication did not appear to affect the solubility.

The coloration of the solution obscures the solubility determination which invalidates the desire to determine the solubility quantitatively. However, there must be some minute quantities of very low molecular weight polymers that are soluble in NMP solvent which produces the brownish coloration.

A separate experiment was attempted to determine the quantitative solubility by gravimetric method. Unfortunately, the complete separation of the liquid phase and the dark solid polymer phase was not possible even after the solution was centrifuged at 5000 RPM for 5 minutes. The failure to completely separate the two phases would lead to a large error in determining the solubility quantitatively.

Table 11. Solubility of polymers in NMP solvent

Polymer Type:	**Solubility**
Polyaniline [1:0]	Indeterminable
Copolymer [2:1]	Indeterminable
Copolymer [1:1]	Indeterminable
Copolymer [1:2]	Indeterminable
Poly(2-aminobenzyl Alcohol) [0:1]	Indeterminable

F. Cyclic Voltammetry Measurements

The polymerization reaction solutions were analyzed electrochemically to determine the amount of soluble polymer remaining in the solution. The cyclic voltammograms revealed the presence of electroactive materials; however, the voltammograms did not resemble those of polyaniline polymers nor those of the monomeric aniline derivative. The normal cyclic voltammogram of polyaniline polymer in a 1 M HCl at five different scan rates has been reproduced in our laboratory and is shown in Figure 7. The voltammogram shows two major oxidation peaks at approximately 0.2 V and 0.45 V and two major reduction peaks at around 0.4 V and 0.1 V (in the 100 mV/sec scan rate). In contrast, the cyclic voltammogram of the reaction media after the removal of polyaniline (Figure 8) shows only one major oxidation peak at approximately 0.6 V and one major reduction peak at approximately 0.25 V. Therefore, the solutions contain only low molecular weight polymers and/or oligomers. Figure 9 to 12 show the cyclic voltammograms of the poly(aniline-co-aminobenzyl alcohol) copolymers and the homopolymer of poly(2-aminobenzyl alcohol), respectively. Here again, there is no evidence of high molecular weight polymer in the remaining solution.

The oxidation or anodic peak currents at various scan rates for the reaction solutions are tabulated in Table 12. Since the curves show considerable broadening, the relationship between curve size and concentration is best measured with the faster sweep rates, e.g., 100 mV/sec. A semi-quantitative comparison of the areas with 100 mV/sec sweep rate indicates an increasing area, therefore increased concentration, as the 2-aminobenzyl aniline content increases. This indicates that the low molecular weight product content increases. This results agree with the decreasing trend in the polymer yield as illustrated in Figure 6. The current (i) vs. voltage (E) plot can be converted to a current vs. time plot by the use of the voltage sweep rate ($\partial E/\partial t$). Therefore, the area under the curve provide the charge (q), since $i = dq/dt$ and $q = (\partial q/\partial t) \times t$. The charge (q) is related to moles.

Therefore, it is the peak area and not the height that relates to the concentration of material in the solution.

Figures 13 and 14 show the dependence of the anodic peak current (μA) on the potential sweep rate for all five polymers The anodic peak currents plot linearly with both the square root of the potential sweep rate and the potential sweep rate. However, regression analysis indicates that the anodic peak currents have a better linear fit with the potential sweep rate which indicates that the electrochemical reactions involve some adsorption of the aniline material on the electrode.

Table 12. Anodic peak currents from the cyclic voltammetry analysis of the reaction solutions

Polymer Type:	**Monomer mole ratio, F**	**Anodic peak current (μA)**				
		5 (mV/sec)	**10** (mV/sec)	**20** (mV/sec)	**50** (mV/sec)	**100** (mV/sec)
Polyaniline	0	90	120	155	250	360
Copolymer [2:1]	0.33	105	145	210	365	600
Copolymer [1:1]	0.50	80	130	200	325	490
Copolymer [1:2]	0.66	55	85	140	235	340
Poly(2-aminobenzyl alcohol)	1	25	40	70	125	210

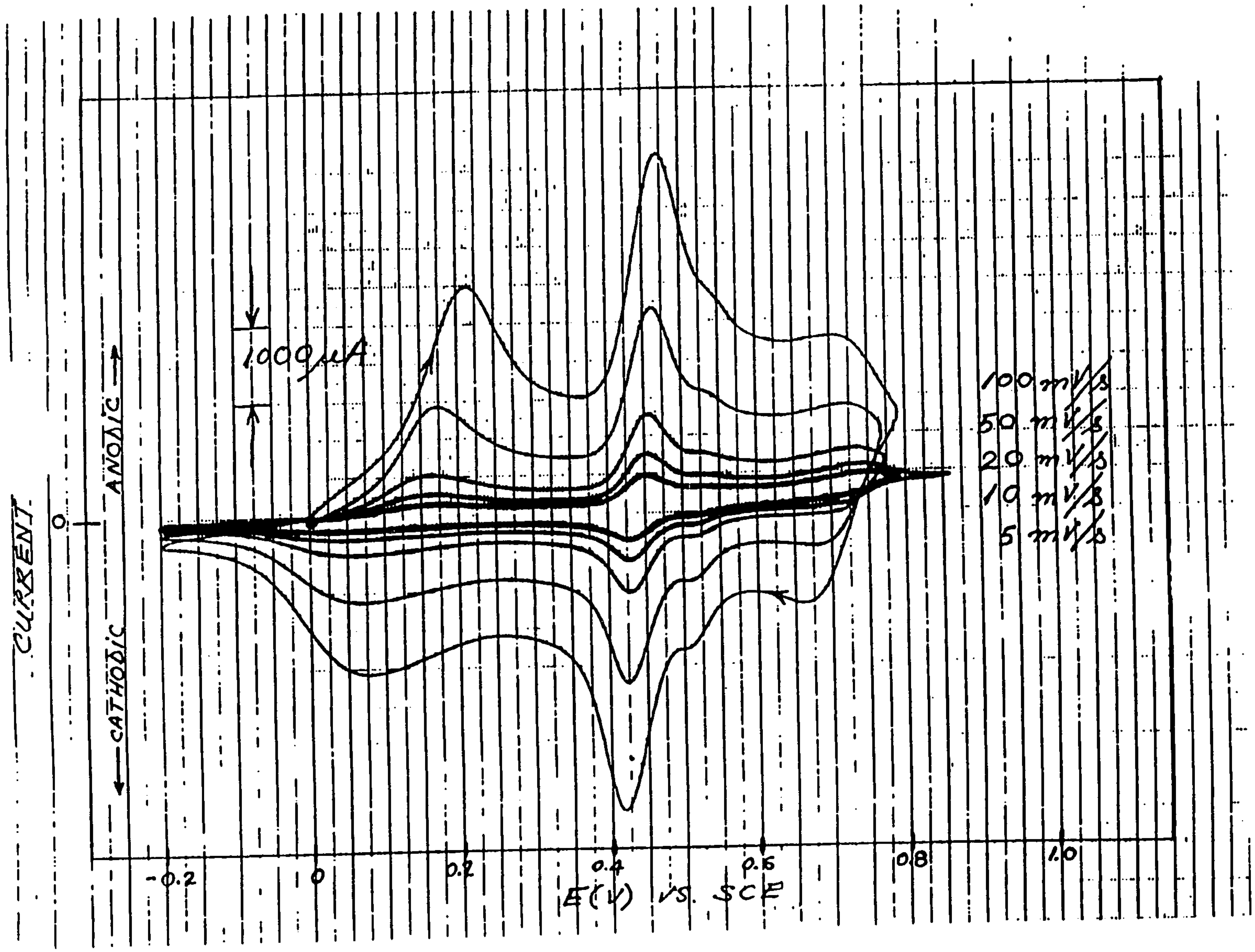


Figure 7. Cyclic voltammograms of chemically prepared polyaniline in 1 M HCl

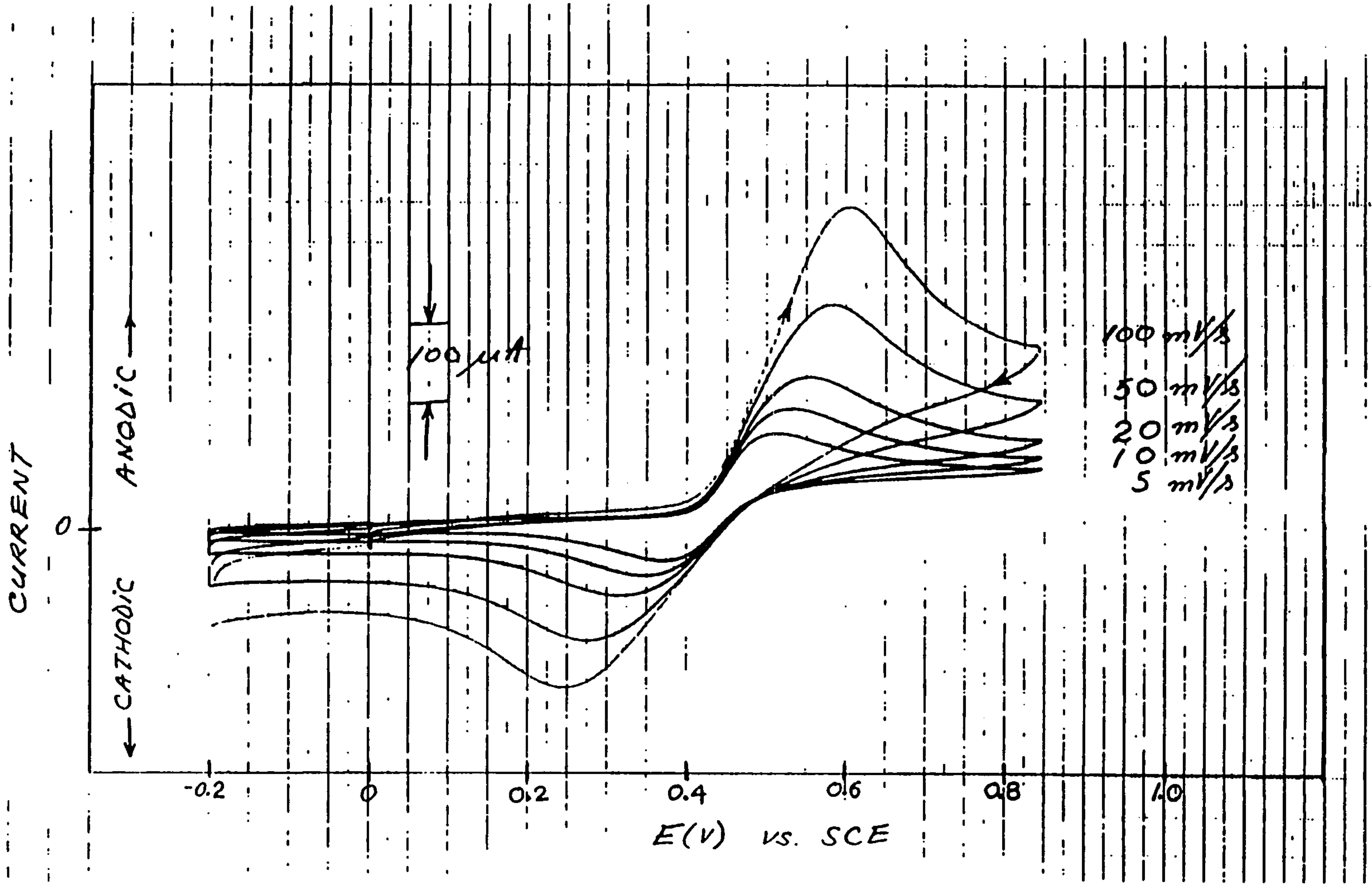


Figure 8. Cyclic voltammograms of reaction solution after removal of polyaniline, F=0

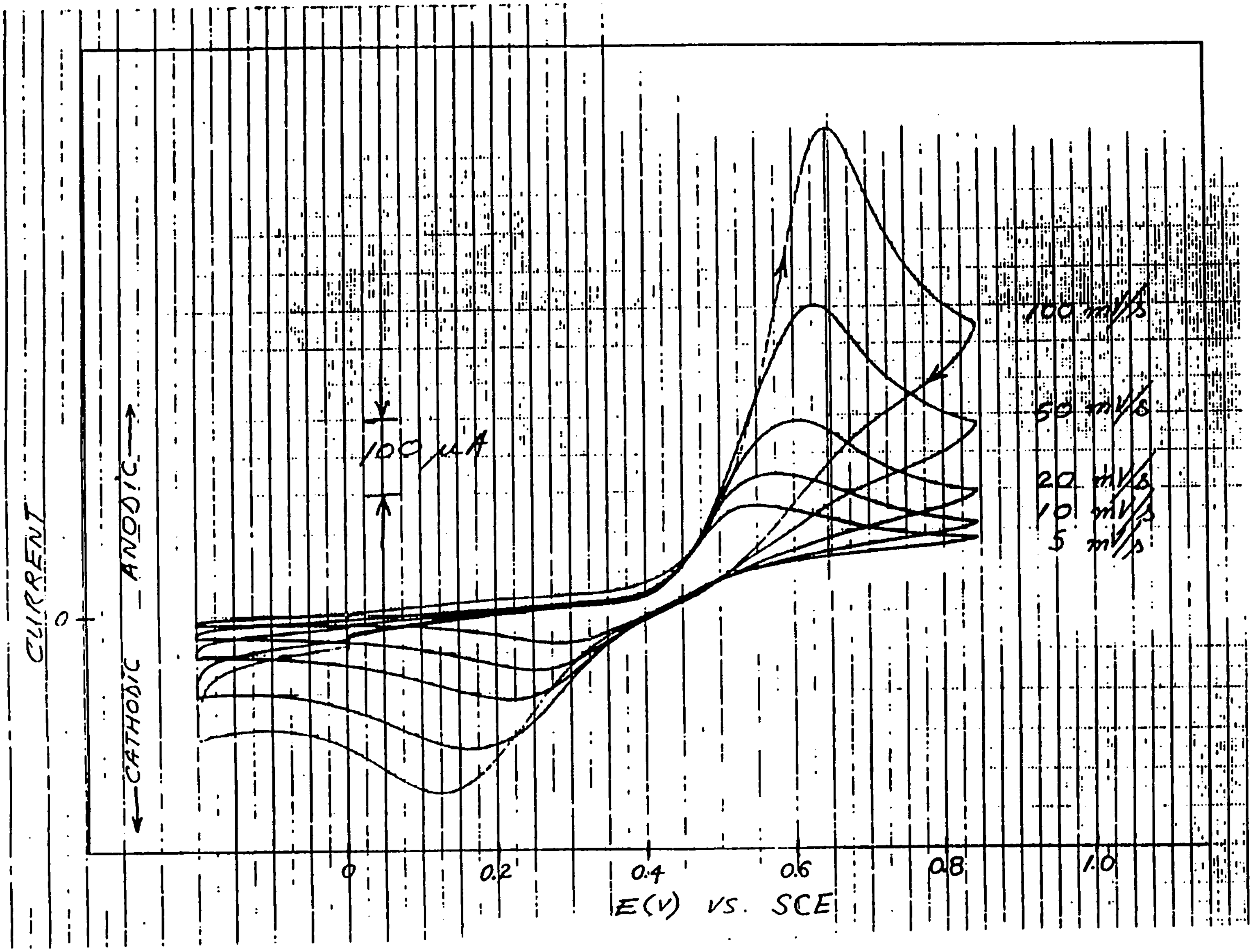


Figure 9. Cyclic voltammograms of reaction solution after removal of poly(aniline-co-aminobenzyl alcohol), F=0.33

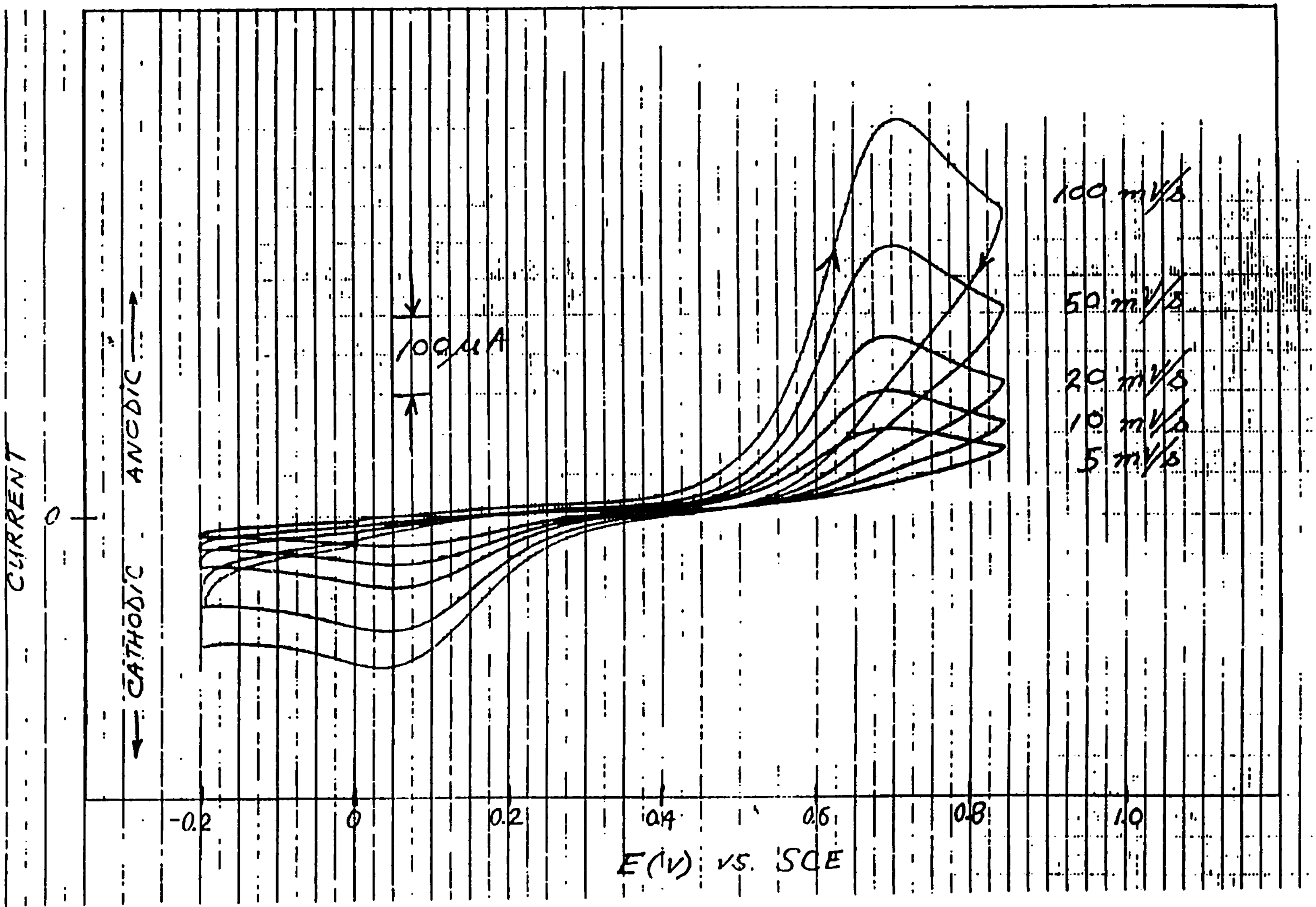


Figure 10. Cyclic voltammograms of reaction solution after removal of poly(aniline-co-aminobenzyl alcohol), F=0.5

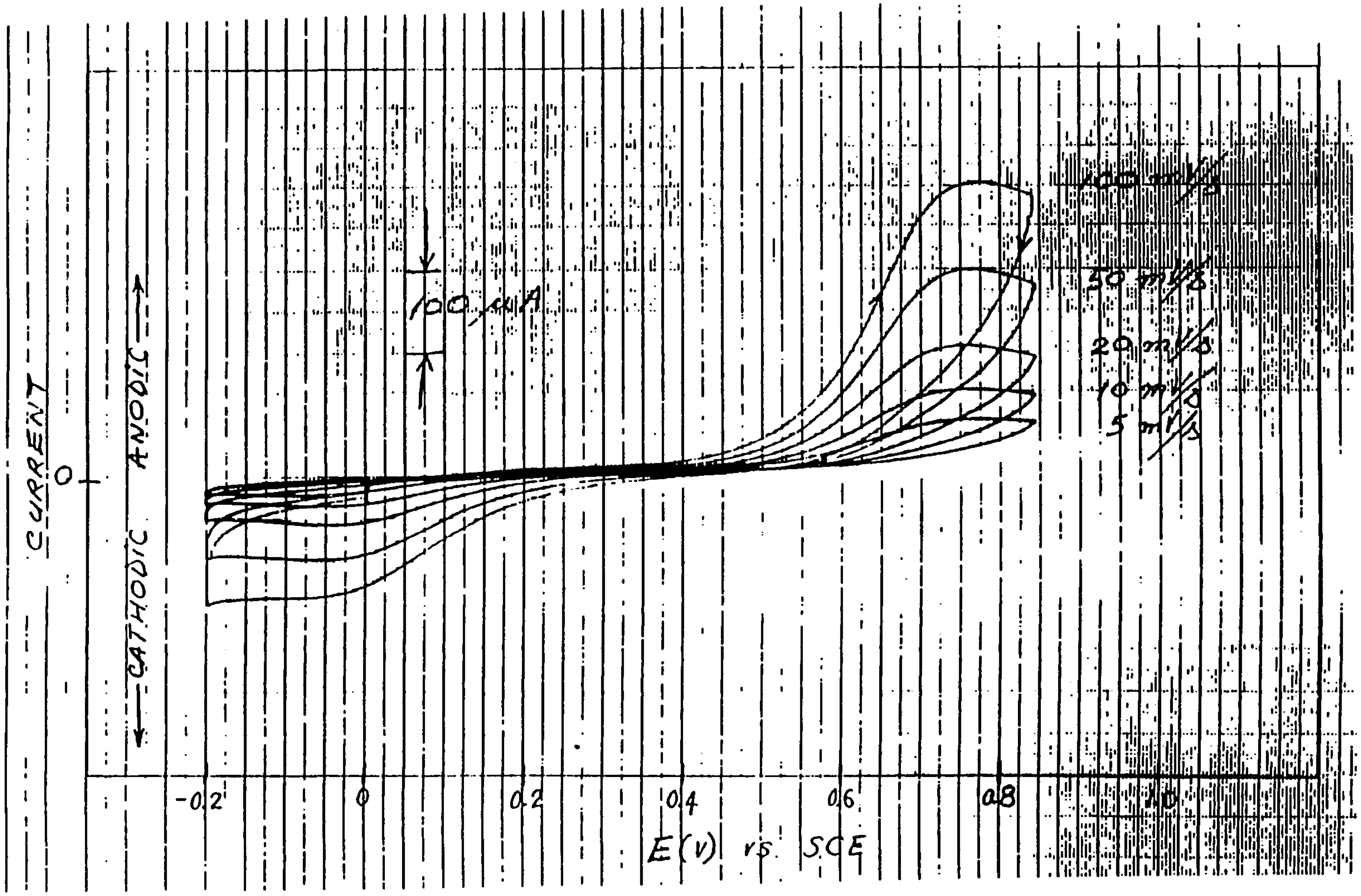


Figure 11. Cyclic voltammograms of reaction solution after removal of poly(aniline-co-aminobenzyl alcohol), F=0.66

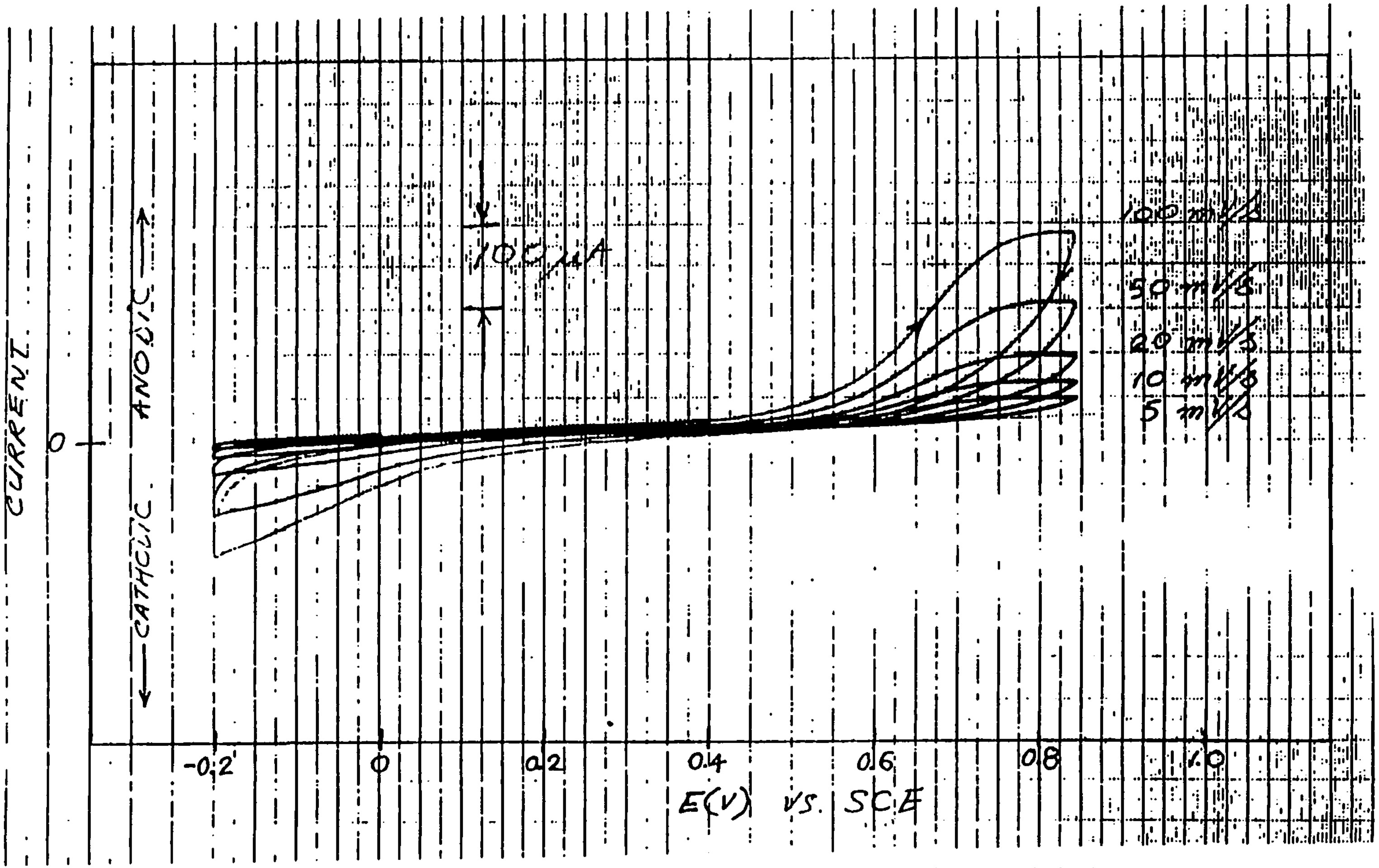


Figure 12. Cyclic voltammograms of reaction solution after removal of poly(aminobenzyl alcohol), F= 1

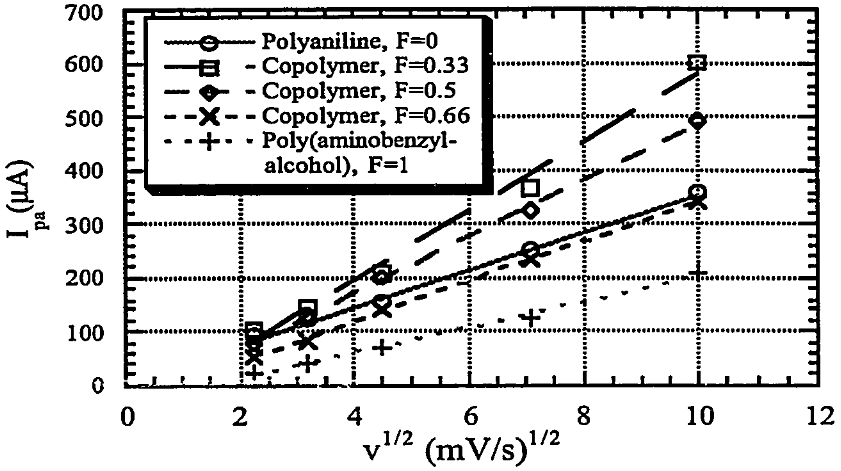


Figure 13. Dependence of anodic peak current on the square root of the potential sweep rate, v

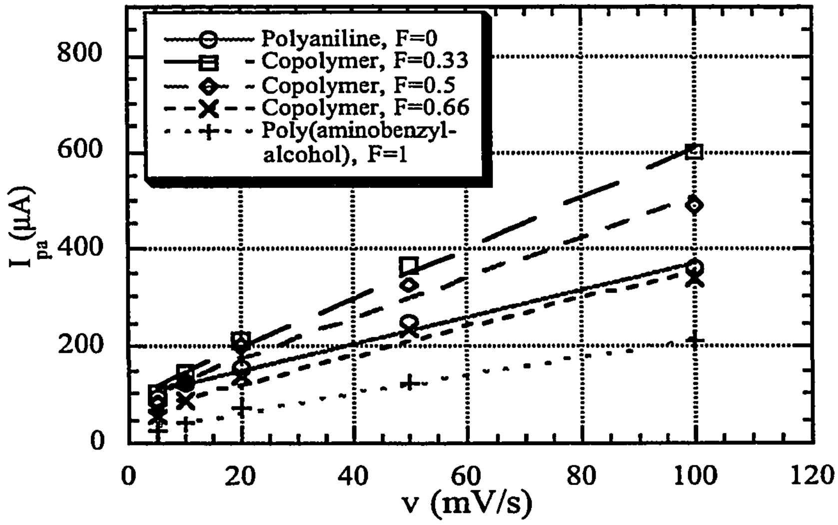


Figure 14. Dependence of anodic peak current on the potential sweep rate, v

Chapter V
Conclusions

The preparation and characterization of poly(aniline-co-aminobenzyl alcohol) copolymers were performed in accordance with the thesis proposal. The following summarize the findings of this study:

- The reaction time for complete polymerization is strongly dependent on the ratio of the two monomers. The time required for polymerization completion increases exponentially with the 2-aminobenzyl alcohol content. The reaction times for polyaniline and poly(2-aminobenzyl alcohol) are approximately 7 minutes and 715 minutes, respectively. The reaction times of the copolymers are intermediate between these values and increase monotonically with the 2-aminobenzyl alcohol content.

- The recovered copolymer yields decrease monotonically as the amount of 2-aminobenzyl alcohol monomer in the reaction solution increases.

- The room temperature conductivities of copolymers in the HCl protonated form decrease as the amount of 2-aminobenzyl alcohol increases, and the variation is monotonic between the two homopolymers.

- The thermal stability of HCl protonated copolymers and the homopolymer of 2-aminobenzyl alcohol (in air) are similar to the HCl protonated polyaniline. Hence, there is no significant effect of the structure on the thermal stability.

- Solubility of the HCl protonated homopolymer of 2-aminobenzyl alcohol and HCl protonated copolymers in NMP solvent are very poor. The quantitative determination of the solubility of these polymers using the ASTM # D-3132-84 (Reapproved 1990) was not feasible due to the strong coloration of the polymers which interfered with the measurement.

- Cyclic voltammetry analysis of the solution after removal of polymers revealed the presence of electroactive materials but no high molecular weight polymers. Therefore, the inference is made that they are low molecular weight oligomers which are solublized in the aqueous HCl.

Chapter VI

Suggestions for Further Research

The characterization techniques that were used to form a structure-properties relationship of conducting copolymers in this study are by no mean an exhaustive list. However, they are the most feasible in terms of the scope of this project and equipment availability. Other characterization techniques could be utilized to provide structure formation and molecular weight distribution of the conducting form and non-conducting form. Here are some of the characterizations that can be performed, if the equipment were available:

- The elemental analysis of the copolymer would provide the structural information.

- Determination of the molecular weight (MW) distributions of the conducting and non-conducting forms of copolymers using gel permeation chrommatography (GPC) would render the average molecular weight of the copolymers. In addition, the MW distributions of the solution of NMP and polymer would allow us to elucidate the limited quantitative solubility of conducting copolymer in NMP.

- It would be useful to determine the solubility of other polymers that are considered "soluble".

- Copolymerization reactions could be carried out in a more dilute solution to produce lower MW material which may be soluble in NMP.

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Appendix A

TGA thermograms of HCl protonated homopolymers/copolymers in air with a heating rate of 10 °C/min.

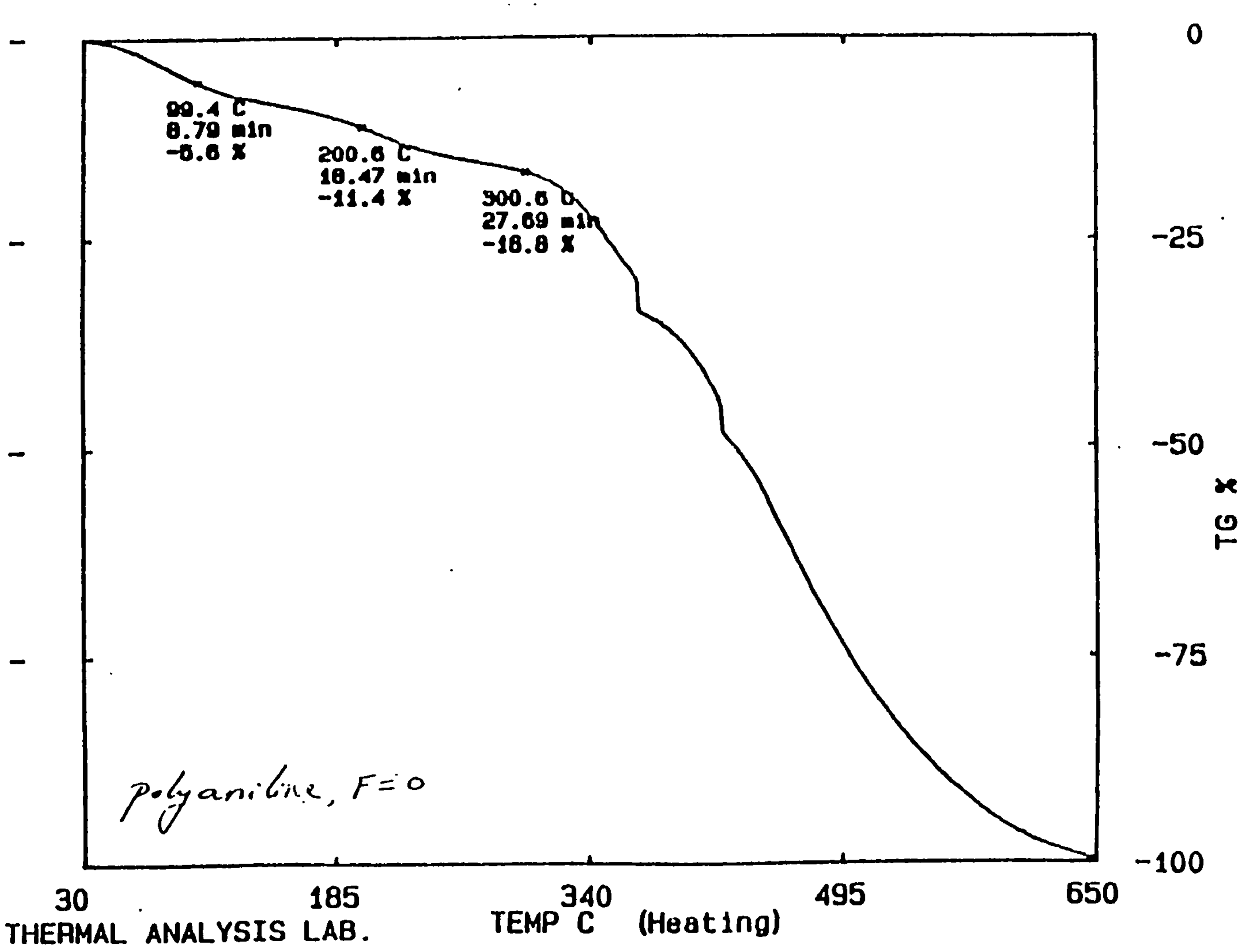

Figure 1: TGA thermogram of HCl protonated Polyaniline in air with a ramping rate of 10 C/min

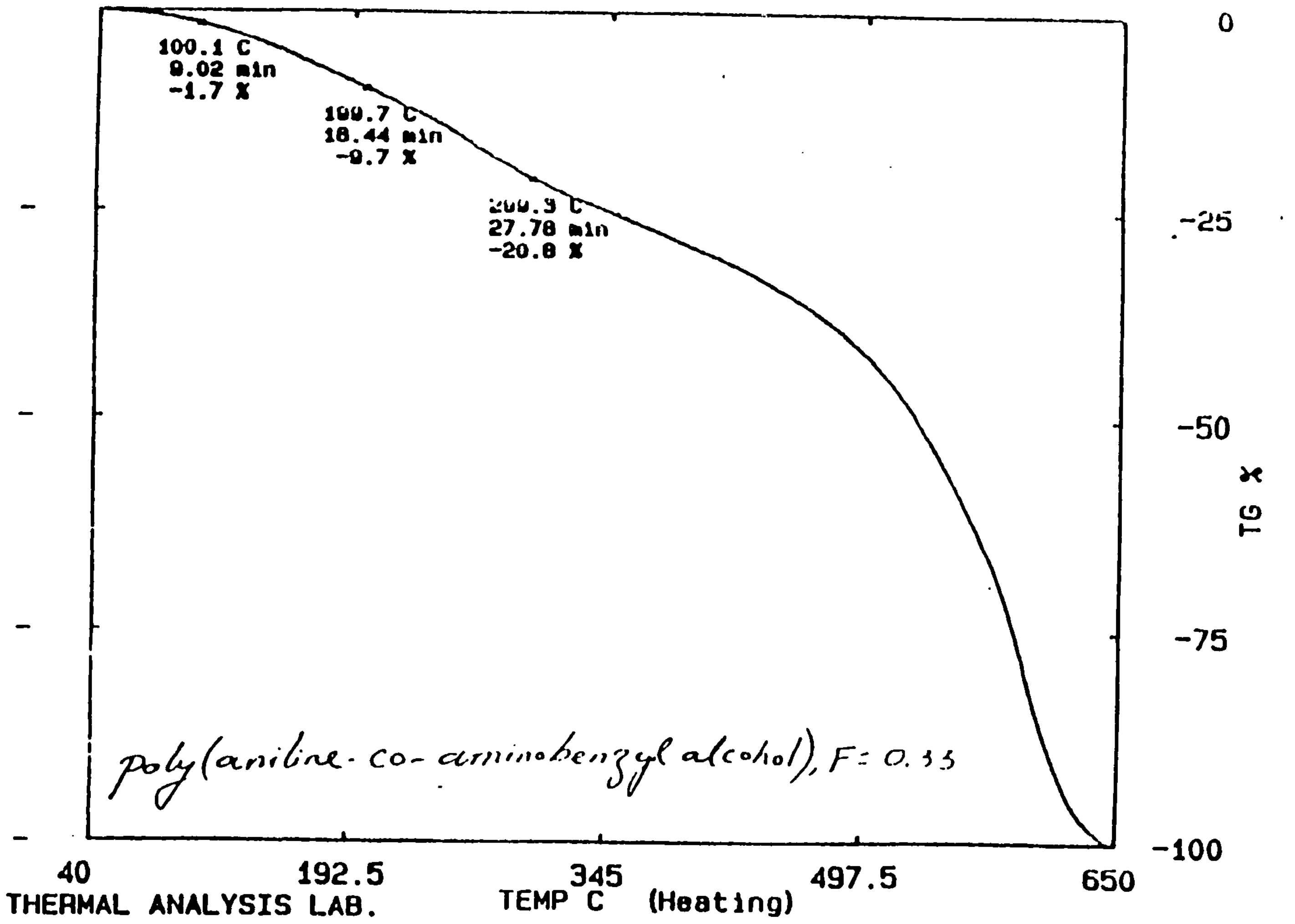

Figure 2: TGA thermogram of HCl protonated Poly[(aniline)0.66-co-(aminobenzyl alcohol)0.33] in air with a ramping rate of 10 C/min

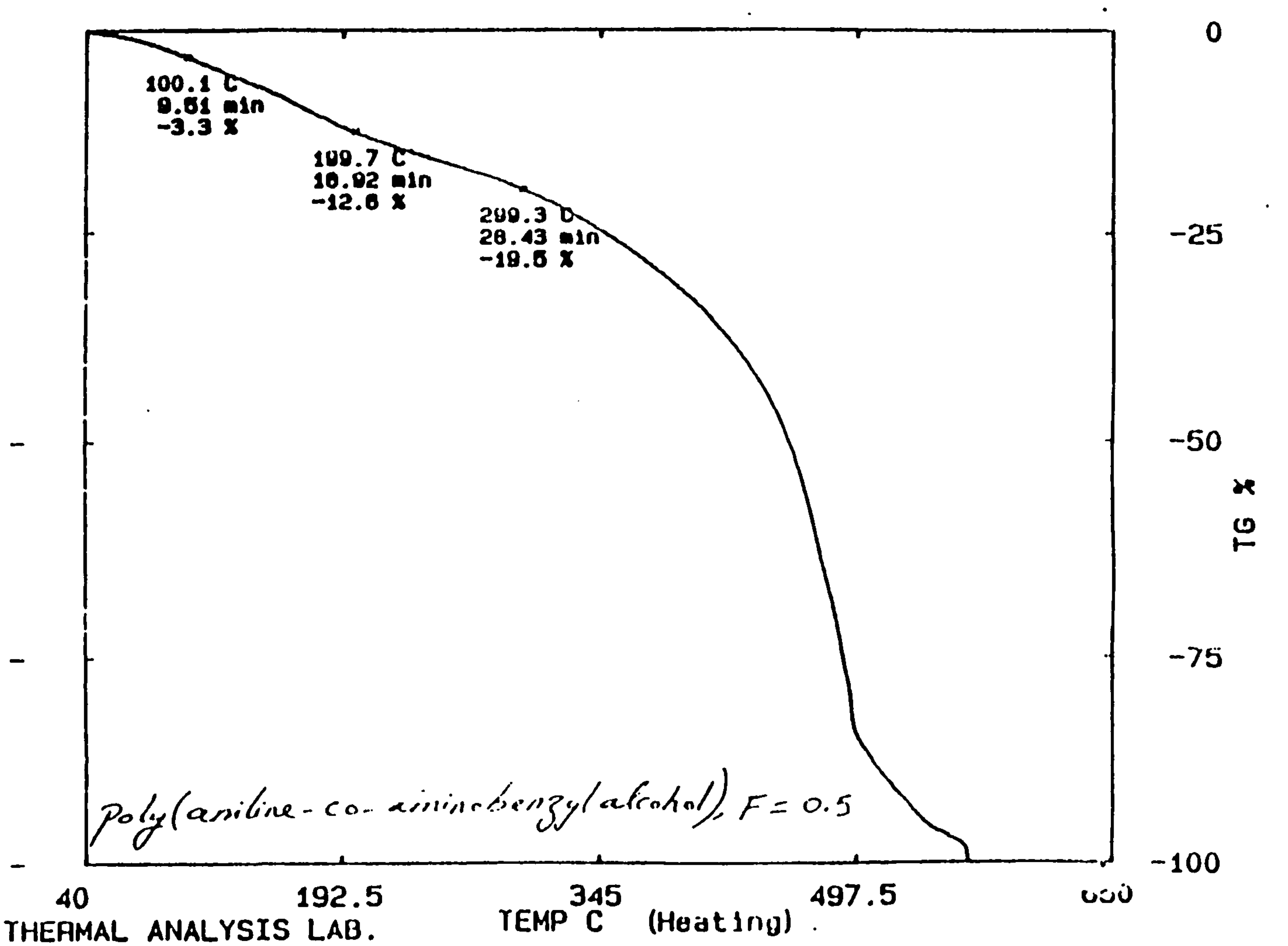

Figure 3: TGA thermogram of HCl protonated Poly[(aniline)0.50-co-(aminobenzyl alcohol)0.50] in air with a ramping rate of 10 C/min

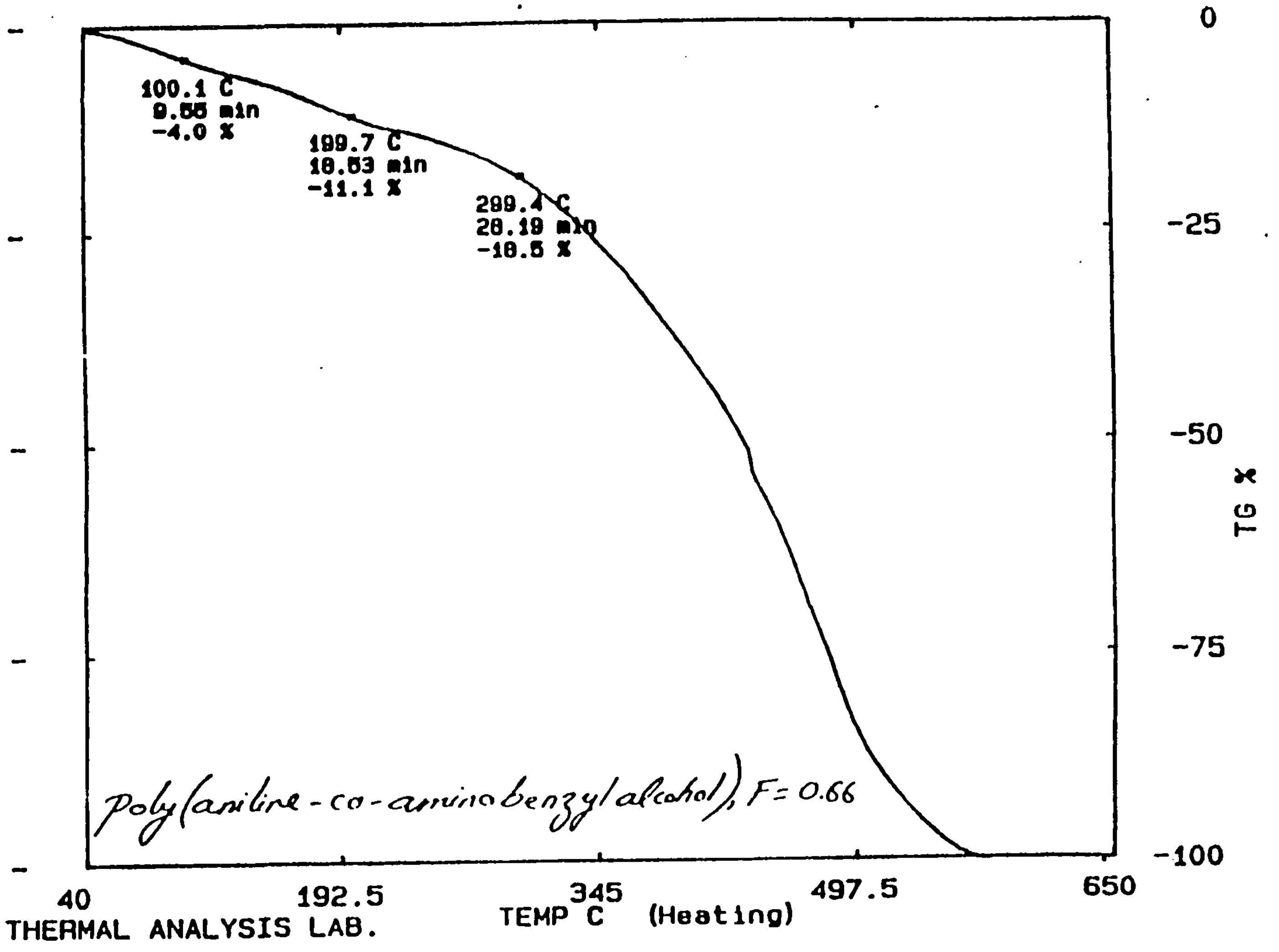

Figure 4: TGA thermogram of HCl protonated Poly[(aniline)0.33-co-(aminobenzyl alcohol)0.66] in air with a ramping rate of 10 C/min

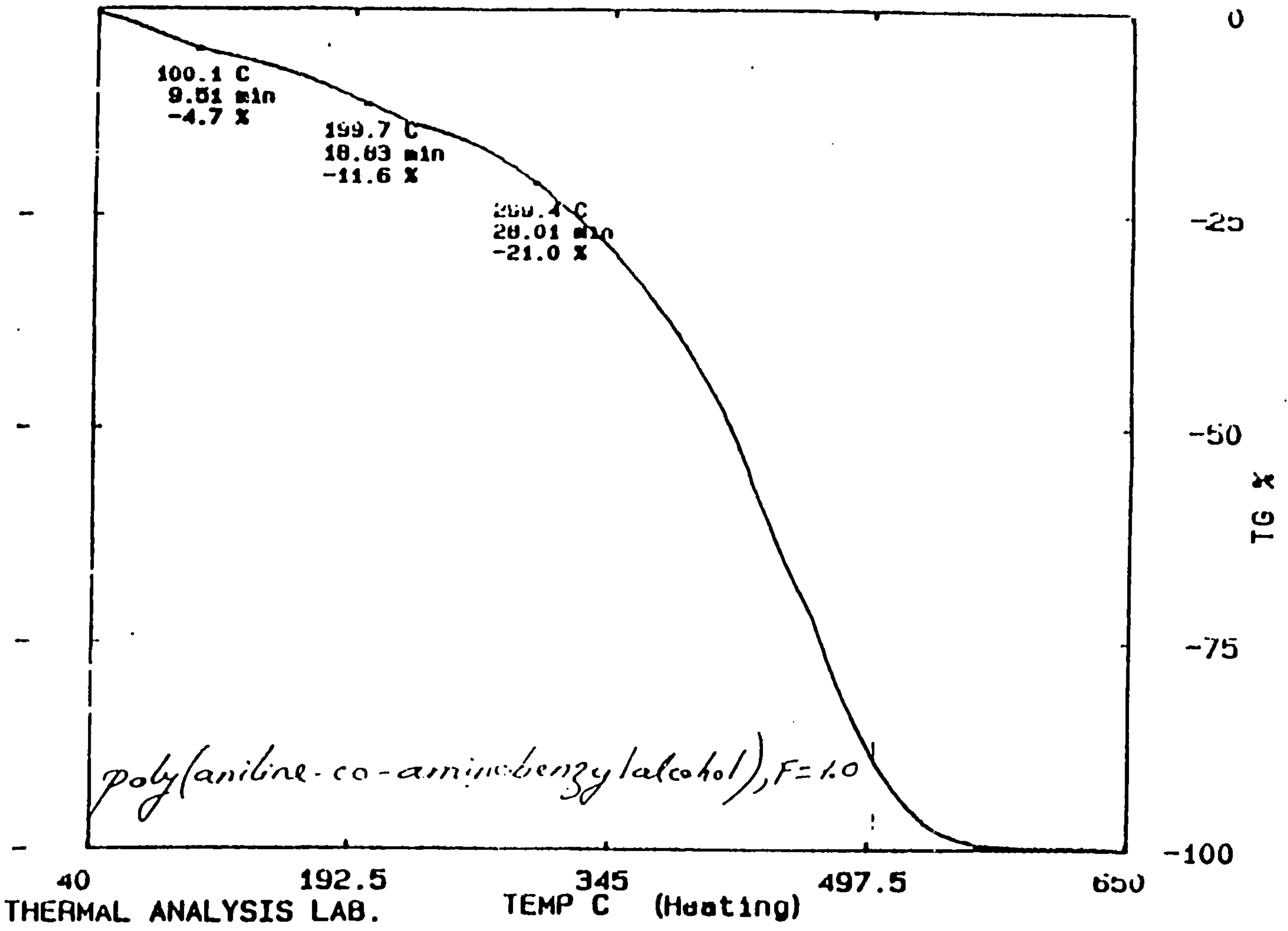

Figure 5: TGA thermogram of HCl protonated Poly(aminobenzyl alcohol) in air with a ramping rate of 10 C/min