Aromatic Polyimides: Synthesis, Characterization, and Evaluation of Electric Strength

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SYNOPSIS

Aromatic polyimides have been synthesized via the formation of polyamic acids in solution. This solution was cast into films that were thermally imidized. The imidization process was monitored using FTIR. The degree of imidization was also determined with thermogravimetric analysis. The electric breakdown field strength was tested under ac and dc conditions. Ac electric breakdown field strength measured in transformer oil was shown to follow a power-law dependence on film thickness. This dependence was not affected by the molecular mass of the polymer but changed with the degree of imidization and the electron-accepting properties of the diamine. High ac breakdown field values of polyimides were obtained in dibutyl phthalate medium due to the suppression of partial discharges that occurs under these conditions. Measurements on films with thicknesses up to 60 μm showed no thickness dependence. No significant influence of the chemical structure on the breakdown field strength was observed under these conditions. Breakdown field measurements under dc conditions showed high values, which were in good agreement with the peak values of the ac measurements in dibutyl phthalate. This indicates similarities in the intrinsic ac and dc breakdown processes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyimides have over the years developed into a very important high-performance class of materials. For a long time, aromatic polyimides have been the materials of choice in electrical insulation applications where high performance electrically as well as thermally during a long period of time has been desired.

However, the behavior of polymers under high electric stress is not particularly well understood on a molecular level. A substantial amount of work concerning the electric breakdown of solids has been performed and is extensively reviewed.[1-4] A comparatively small part of this work considers the influence of the chemical structure of the material on its electric properties[5-9] and on the processes that are taking place in the material during the different stages of electric breakdown.[10-13]

The objective of the present investigation was to elucidate the influence of the chemical structure, the degree of imidization, and the polymer molecular mass on the electric breakdown properties of polyimides, under ac as well as dc conditions.

The influence of the chemical structure and the degree of imidization on the electric breakdown properties was tested on five structurally different polyimides[14-16] prepared in the lab (Scheme 1). To investigate the influence of the polymer molecular mass on the electric breakdown properties. A series of polyimides with different molecular mass were synthesized and tested.

Measurements of electric breakdown field strength were carried out under both ac and dc conditions. By using two different media, transformer oil and dibutyl phthalate, for the ac measurements, it was possible to determine the ac electric breakdown field strength under conditions both with partial discharges (PD) occurring at the electrodes and with PD strongly suppressed.[17]

The measurements of dc electric breakdown field strength of the polymer films show that this property is not sensitive to the variations in the chemical

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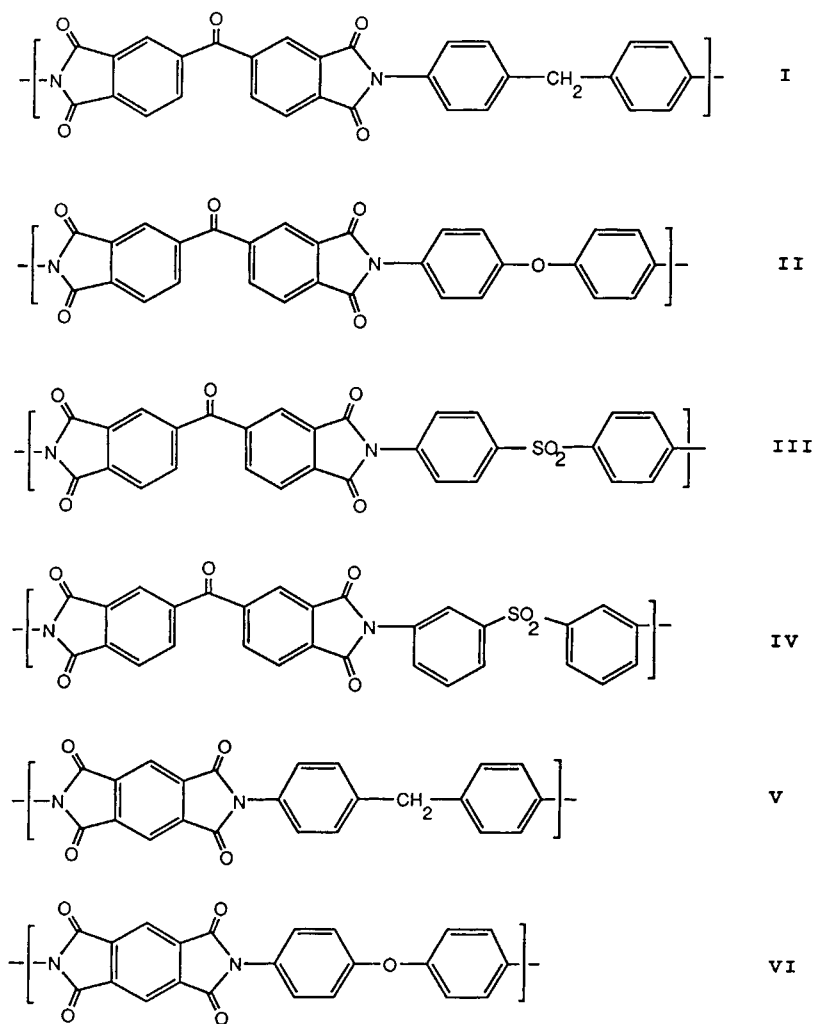
Scheme 1

structure present in this series of polyimides. The breakdown field strength of the polyimides, measured under ac conditions in transformer oil, followed the previously described[8] power-law dependence on sample thickness.

The measurements of ac electric breakdown field strength under PD suppressing conditions revealed an absence of film thickness dependence for thin films. A certain influence of the chemical structure on the ac electric breakdown field strength was observed.

It has been shown that commercially available polyimide films contain substantial amounts of unimidized amic acid groups.[18] By comparing breakdown field data from polyimides imidized at different temperatures, and, consequently, with different degrees of imidization, different behavior was observed, depending on the type of tetracarboxylic acid residue present in the polymer. The molecular mass of the

polymers was shown not to influence the breakdown field strength measured under ac conditions in transformer oil.

EXPERIMENTAL

Materials

The chemicals used were all of commercial-grade quality and purified before use as described in the following: Pyromellitic dianhydride (PMDA) and benzophenon tetracarboxylic dianhydride (BTDA) were both recrystallized from acetic anhydride and dried in a vacuum oven at 60°C until no acetic anhydride was present. 4,4'-Diaminodiphenylether, 4,4'-diaminodiphenylmethane (MDA), 4,4'-diaminodiphenylsulfone, and 3,3'-diaminodiphenylsulfone were all recrystallized from water and dried in a vacuum oven until constant weight. N,N-Dimethy-

lacetic amide (DMAc) was passed through activated alumina (Woelm Aktiv Neutral Super 1) prior to use.

Polymer Synthesis

A typical polymer synthesis proceeded as follows: 40 mmol of diamine was placed in an oven-dried conical flask equipped with a magnetic stirring bar and 45 mL of freshly purified DMAc was added. To this solution, 40 mmol of the appropriate dianhydride was added as a solid, followed by 45 mL of DMAc. Subsequently, the flask was flushed with dry nitrogen and sealed. The reaction mixture turned viscous and was stirred overnight. This polyamic acid solution was cast into films on glass plates and dried. The conversion of the polyamic acid films to polyimides was achieved by heat treatment. The rate for the temperature rise was 2°C/min from 30 to 300°C. The temperature was held constant for 1 h at 100, 200, and 300°C during the temperature increase. The films were allowed to cool down slowly. The glass plates with imidized film were immersed in water to release the films.

Endcapped polyimides with controlled molecular masses were prepared from BTDA and MDA. The degree of polymerization was controlled by upsetting the stoichiometry of BTDA and MDA and adding phthalic anhydride as the endcapping agent. In the preparation of a polyimide of about 50,000 g/mol in theoretical molecular mass, the reagents were used in the following amounts: BTDA 30 mmol (9.66 g), diaminodiphenyl methane 30.32 mmol (6.003 g), and phthalic anhydride 0.64 mmol (0.094 g).

Characterization

IR spectra were obtained on a Perkin-Elmer 1750 FTIR instrument. In the evaluation of the IR data, the increase in the height of the symmetric carbonyl stretch at 1780 cm^{-1} normalized with the aromatic vibration band at 1020 cm^{-1} was used to monitor the imidization process.[19]

Thermogravimetric (TGA) measurements were performed on a Perkin-Elmer DSC 7 system. The measurements were performed in a nitrogen atmosphere and the samples were initially heated to 150°C for 80 min, which resulted in constant weight at this temperature. The isothermal period was followed by a 5°C/min temperature increase until 450°C.

The inherent viscosity of the amic acid solutions was measured on a 0.5 g/dL solution using an Ub-

belohde viscosimeter. The film thickness was determined using a Mitutoyo Digimatic Indicator with resolution 1 μm.

Electric Measurements

Electric Strength dc

The electric breakdown voltage of the films under dc conditions was measured at ABB Corporate Research, Västerås, Sweden. The film sample was placed on a copperfoil on the bottom of a jar filled with transformer oil. A 5 mm-diameter brass cylinder with rounded edges was placed on top of the film. Between the electrodes, the copper foil and the brass cylinder, a dc voltage was applied with a continuous voltage increase at the rate of 500 V/s. The breakdown voltage was determined by recording the voltage on a chart recorder. Each experiment consisted of 20–30 individual measurements.

Electric Strength ac

The electric breakdown field of the films under ac conditions was measured with a slightly modified Hipotronics OC 60 A electric oil tester. Instead of the original electrode setup, one with opposing cylinders measuring 5 mm in diameter and with rounded edges was mounted. One of the cylinders was spring-loaded to allow good contact with the tested film. The entire electrode setup was immersed in a vessel containing transformer oil or dibutyl phthalate. All measurements were performed using a continuous increase in the voltage with the rate of 500 V/s. All ac voltage values are rms values. In some cases, and in particular when thick samples were tested, partial discharge occurred at high voltages. Each film thickness was subjected to more than 20 breakdown experiments and the sites of the breakthrough were distributed all over the electrode area. The test conditions used are in good agreement with ASTM standard D149-87.
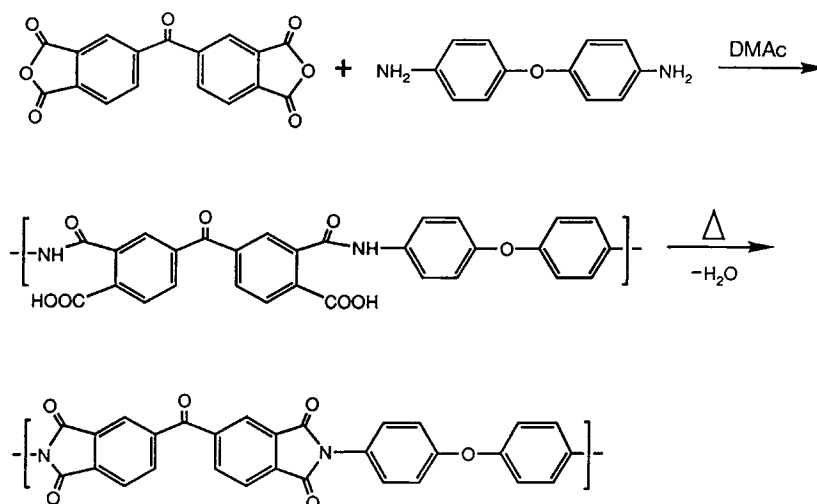
Evaluation of Breakdown Field Data

All breakdown field data were evaluated using Weibull statistics.

RESULTS AND DISCUSSION

Synthesis

The polyimides were synthesized in solution from dianhydrides and diamines via the formation of polyamic acids and a final heat treatment to yield the polyimides (Scheme 2). Since the polyimides

Scheme 2

are insoluble in all solvents, any characterization in solution has to be made on the polyamic acid prepolymer. Table I shows representative viscosity data obtained for polyamic acids about 24 h after the polymerization was started.

By adjusting the stoichiometry and introducing monofunctional endcapping groups, a series of polymers with different molecular mass was synthesized. Data on the inherent viscosity and the calculated molecular masses of these polymers are shown in Table II. It has been shown[20] on a similar polymer system (PMDA and diaminodiphenyl ether) that the calculated and the experimental molecular masses agree very well for polyimides synthesized using the method of stoichiometric imbalance.

Characterization

The ring closure of the polyamic acid to form the polyimide was accomplished via a thermal treatment of the polyamic acid cast into films. Figure 1 shows the temperature profile used when the imidization reaction was carried out up to 300°C. The degree of

imidization of polymer I as determined with IR measurements and normalized with the maximum value at 300°C set to 1.0 is also included in Figure 1. The IR analysis reveals that the imidization process closely follows the temperature increase profile and, when a dwell time is introduced in the temperature program, the degree of imidization levels out rapidly. Figure 2 shows the degree of imidization at different temperatures when the imidization of the films is performed without dwell times. According to these measurements, the imidization reaction starts around 150°C and proceeds rapidly as the temperature increases. At about 250°C, the increase in the degree of imidization starts to level out as is expected when most of the amic acid groups have been converted to imides and the chain mobility in the polymer has decreased due to the high content of imidized groups.

Table I   Inherent Viscosity Data for Polyamic Acid Precursor Polymers

Polymer	η_{inh} (dL/g)
I	0.85
II	0.86
III	0.54
IV	0.47
V	1.75
VI	1.90

Table II   Inherent Viscosity Data for Polyamic Acid Polymers Corresponding to I of Different Molecular Masses

Molecular Mass[a] 10^{-3} (g/mol)	ν_{inh} (dL/g)
5	0.31
10	0.41
20	0.55
30	0.60
40	0.65
50	0.69
60	0.71

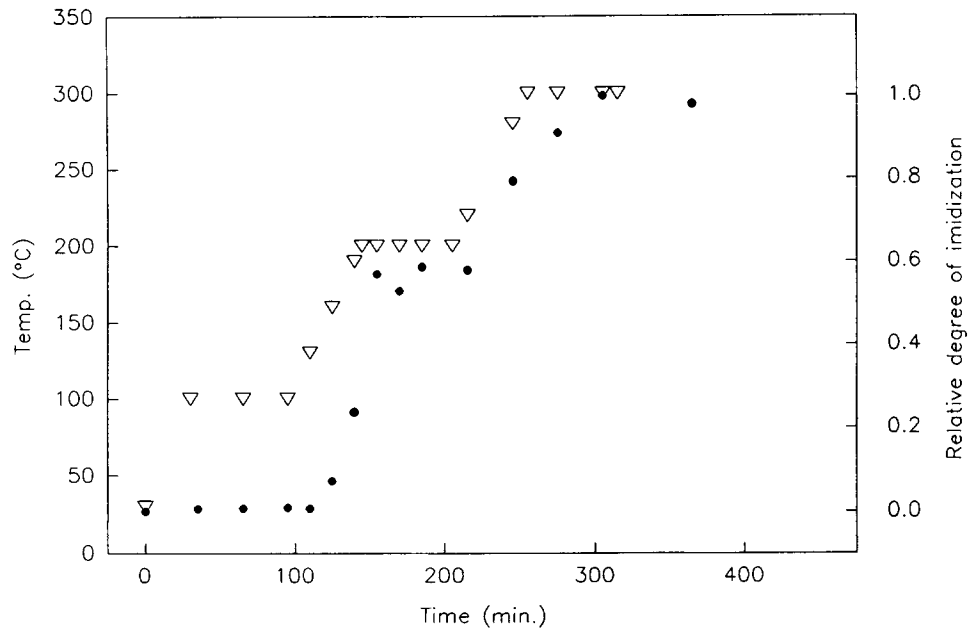[a] Theoretical values based on stoichometry.

Figure 1 Temperature profile (∇) for the imidization of films up to 300°C and ($\bullet$) the relative degree of imidization of polymer I along this profile.

The degree of imidization has also been determined using thermogravimetric analysis (TGA) (Tables III and IV). To avoid the interference of water, not originating from the imidization reaction, the samples were conditioned at 150°C for 80 min to reach constant weight, before the actual TGA scan was started. The main weight loss occurred in the interval 180–310°C at a temperature increase rate of 5°C/min from 150°C. The polymer systems im-

idized at 200°C show a low to moderate degree of imidization except for the polymers III and IV. The weight losses for these two polymers exceed the weight of the theoretical amount of water that is formed in the imidization process. By IR spectroscopy, it was shown that the solvent, DMAc, used in the synthesis was still present in significant amounts in polymers III and IV after imidization at 200°C. For the rest of the polymers, only a trace amount of solvent was found after imidization at 200°C. However, no residual solvent was detected in any of the polymers after imidization at 300°C.
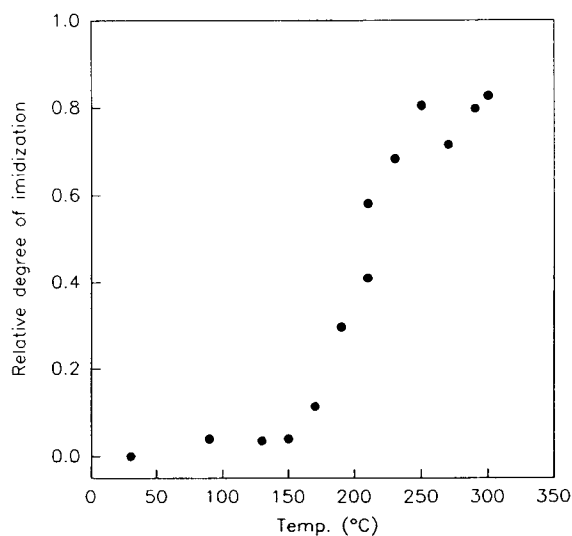

Figure 2 Relative degree of imidization of polymer I vs. temperature. Temperature increase 2°C/min.

Reactivity

Regarding the polymers that have been heat-treated up to 300°C, it appears that polymers III and IV, containing sulfone bridging groups in the diamine units, are imidized to a lower extent than the average. This can be due to lower reactivity of the amide nitrogen in the ring closure reaction when the diamine residue contains an electron-attracting sulfone bridging group compared to electron-donating ether or methylene groups.[21] Regarding the dianhydride units, it appears that, under the same imidization conditions, the polyamic acids containing pyromellitic units reach a higher degree of imidization than do those containing benzophenon tetracarboxylic units. The reason for this is probably found in the electron-withdrawing effect of the car-

Table III   Material Constants from eq. (2) for ac Measurements in Transformer Oil on Polyimides Imidized at 200°C

Polymer	Imidization[a] (%)	$I \mp s$[b]	$n \mp s$	Corr.[c]
I	21	940 $\mp$ 42	−0.40 $\mp$ 0.01	.97
II	33	1119 $\mp$ 55	−0.46 $\mp$ 0.03	.98
V	73	1683 $\mp$ 112	−0.56 $\mp$ 0.04	.96
VI	67	2070 $\mp$ 78	−0.59 $\mp$ 0.02	.99

[a] Degree of imidization as determined by TGA.
[b] Unit V/μm at film thickness 1 μm.
[c] Correlation coefficient.

bonyl substituents on the rings that makes the units electron-deficient, and, as pyromellitic units have the higher electron deficiency, they also have higher reactivity toward nucleophilic attack by amide nitrogen on the carboxylic acid group. These types of structure reactivity behavior of PMDA and BTDA have been observed both in studies of the formation of polyamic acids,[22] where the reaction rate for PMDA was found to be a factor 2 higher than for BTDA, and in the studies on the imidization reaction,[23] where BTDA was shown to have a lower imidization rate than PMDA at all temperatures. BTDA also needed a higher temperature to reach complete imidization even though its glass transition temperature is significantly lower than that of the PMDA system.

Electrical Properties

In the evaluation of the electrical properties of polymers I–VI, the electric breakdown field strengths under both ac and dc conditions have been determined. The measurements have been carried out using electrode configurations where the electrodes are pressed against the tested film. These types of electrode arrangements[24] allow rapid and convenient testing under conditions that are similar to those in

practical applications. Although vacuum-evaporated electrodes have not been used in this study, very good data have been obtained as is seen on the Weibull B parameter (Table V). The B parameter of the Weibull plot is a measure of the data fit and a value of $B \geq 1$ is satisfactory, while $B \geq 5$ is very good. Under ac conditions, measurements have been carried out with transformer oil or dibutyl phthalate as the surrounding medium, whereas only transformer oil has been used under dc conditions. In transformer oil, partial discharges (PD) occur to a large extent, whereas in dibutyl phthalate, this behavior is suppressed.[17] Figures 3–8 show plots of the breakdown field strength of polyimides imidized at 300°C vs. sample thickness measured under ac conditions in both transformer oil and dibutyl phthalate media.

Ac Behavior in Transformer Oil

It has been shown that the breakdown field strengths of aromatic polymers in transformer oil follow a power-law dependence on sample thickness [eq. (1)][8]:

$$F_B = F_0 (\tfrac{d}{d_0})^n \tag{1}$$

Table IV   Material Constants from eq. (2) for ac Measurements in Transformer Oil on Polyimides Imidized at 300°C

Polymer	Imidization[a] (%)	$I \mp s$[b]	$n \mp s$	Corr.[c]
I	89	1403 $\mp$ 40	−0.52 $\mp$ 0.02	.98
II	95	1374 $\mp$ 39	−0.51 $\mp$ 0.02	.98
III	82	937 $\mp$ 54	−0.39 $\mp$ 0.03	.95
IV	66	1096 $\mp$ 100	−0.46 $\mp$ 0.03	.95
V	97	1288 $\mp$ 12	−0.45 $\mp$ 0.01	.998
VI	95	1469 $\mp$ 32	−0.50 $\mp$ 0.02	.99

[a-c] See footnotes to Table III.

Table V Breakdown Field Strength of Polyimides under ac Conditions Measured in DBP

Polymer	Film Thickness Interval (μm)	F_B (V/μm)[a]	s (V/μm)	B[b]
I	26–60	370	45	8.16
II	27–63	368	41	8.90
III	19–60	344	46	7.44
IV	29–64	346	50	6.87
VI	25–63	315	37	8.44

[a] Weibull A parameter.
[b] Weibull B parameter.

In the logarithmic form,

$$\log F_B = \log I + n \log d \qquad (2)$$

where

$$I = F_0 d_0^{-n} \qquad (3)$$

where F_B is the breakdown field strength; d, the sample thickness; and F_0, the breakdown field strength at the sample thickness d_0. It is seen in Tables III and IV that the dependence of F_B on sample thickness for polyimides **I–VI** reasonably well satisfies eq. (2). It has also been shown that the n parameter for aromatic polymers[8] (PI, PEI, PET, PEEK, and PES) gives a good correlation with ease of reduction in terms of the reversible reduction potentials of suitable model compounds. Since poly-

Figure 4 Ac breakdown field strength vs. film thickness, for polymer **II** imidized at 300°C, measured in transformer oil (∇) and DBP ($\square$).

mers **I–VI** differ comparatively little in their chemical structures, the influence of these structural changes on the n values is expected to be smaller than what is seen for the different aromatic polymers.[8] Studies on the electron affinity, E_A, of polyimides and their model compounds[25] show that PMDA-based systems are stronger electron acceptors than are BTDA-based systems. The difference in E_A values of the two systems is approximately 0.2 eV. The influence of the diamine structure on E_A is rather small.[26] For the polymers imidized at 300°C

Figure 3 Ac breakdown field strength vs. film thickness, for polymer **I** imidized at 300°C, measured in transformer oil (∇) and DBP ($\square$).
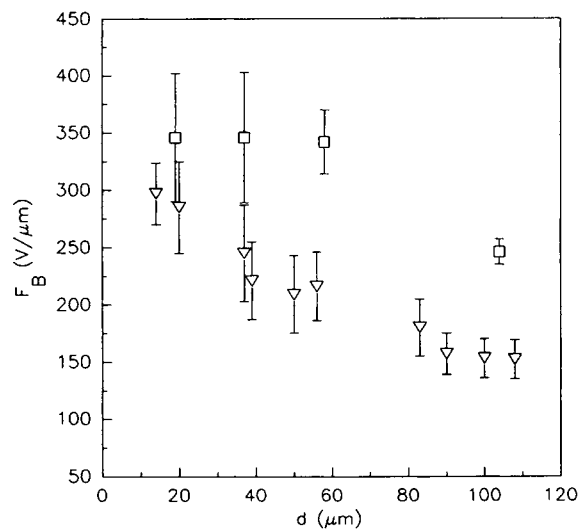
Figure 5 Ac breakdown field strength vs. film thickness, for polymer **III** imidized at 300°C, measured in transformer oil (∇) and DBP ($\square$).
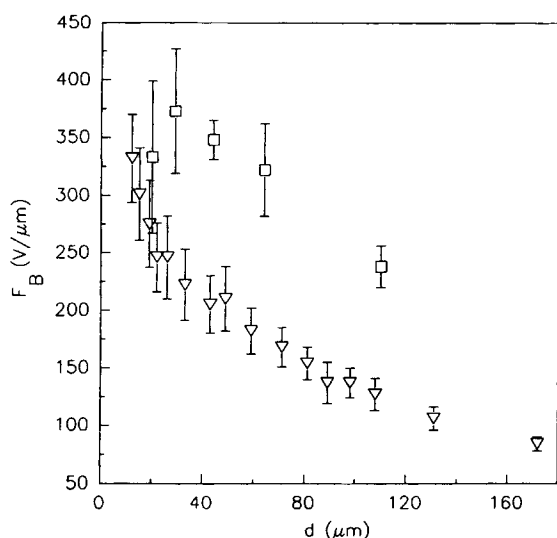
Figure 6 Ac breakdown field strength vs. film thickness, for polymer **IV** imidized at 300°C, measured in transformer oil (∇) and DBP (□).

(Table IV), one would expect the n values of **V** and **VI** to be lower than those of **I** and **II** because of the differences in electron-accepting capability. However, this is not found.

Apart from data on the thickness dependence of the ac breakdown field strength in transformer oil, Tables III and IV also show the degree of imidization of the different polyimides. It appears that the n values change differently with the degree of imidization depending on the nature of tetracarboxylic acid residue present in the polyimide. When each
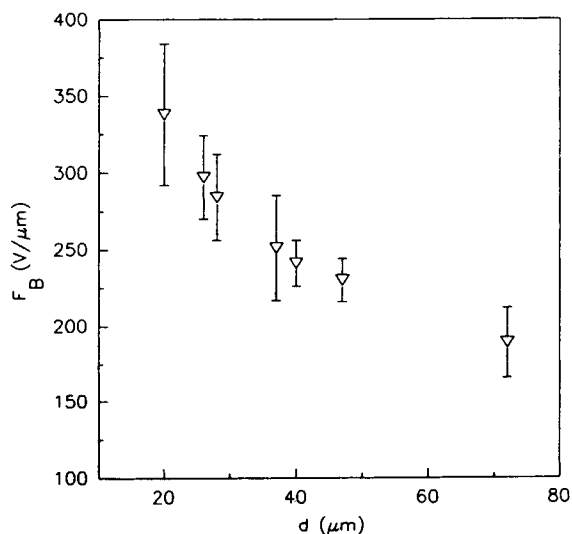

Figure 7 Ac breakdown field strength vs. film thickness, for polymer **V** imidized at 300°C, measured in transformer oil (∇).
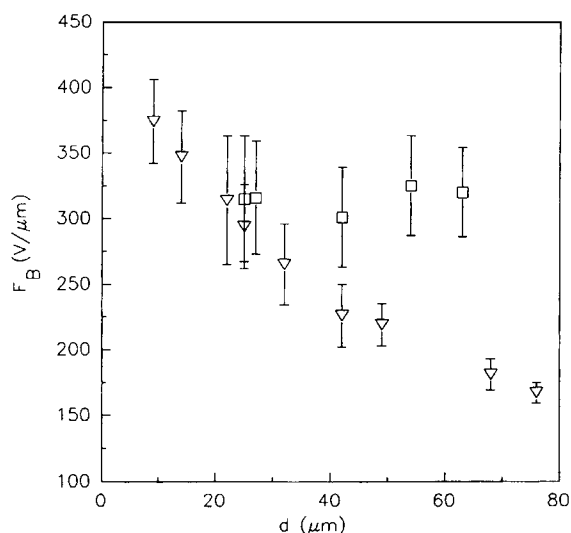

Figure 8 Ac breakdown field strength vs. film thickness, for polymer **VI** imidized at 300°C, measured in transformer oil (∇) and DBP (□).

polymer is looked at separately, it appears that for polymers containing BTDA the n values become more negative when the imidization temperature is increased from 200 to 300°C and the degree of imidization is increased. This means that the breakdown field strength decreases faster with increasing sample thickness when the degree of imidization is high. When the PMDA systems are looked at in the same way, the opposite behavior is observed. The polyimides with a high degree of imidization show a lower decrease in ac breakdown field strength with an increase in sample thickness than do the polymers with a low degree of imidization.

The influence of the molecular mass of the polymers on the ac electric breakdown field strength in transformer oil was investigated using polyimides formed by imidization of the polyamic acids for which molecular mass and inherent viscosity are shown in Table II. These polymers have been imidized at 200°C, which means that their degree of imidization is in the order of 20–30%. However, this should not have any effect on the desired comparisons within the group of polymers as they all are imidized to the same degree. Because of poor mechanical properties, the systems of molecular masses of 5000 and 10,000 g/mol had to be excluded from the electrical measurements. No dependence of n or F_0 on molecular mass was found in the evaluation of the breakdown field measurements.

Ac Behavior in Dibutyl Phthalate (DBP)

As mentioned above, partial discharges have a substantial effect on ac measurements performed in

transformer oil. In a previous paper,[17] we showed that by using a medium with a higher dielectric constant a reduction in partial discharges occurs. This results in a completely different breakdown field vs. film thickness behavior. The results for polyimides **I–IV** and **VI** are shown in Figures 3–6 and 8. As seen in the figures, the power-law dependence of the ac breakdown field strength on film thickness found in the transformer oil medium changes to a constant value independent of film thickness, at least up to about 60 μm film thickness, when the measurements are performed in DBP. For films thicker than about 70 μm, a decrease in breakdown field strength is observed that is probably due to PD that occurs at the very high voltages needed for breakdown.

Table V and Figure 9 present results where data from a wide range of sample thicknesses have been analyzed in one Weibull plot for each polymer. These results do not show any effects that can be attributed to the differences in the chemical structure of the polymers. The same conclusion was reached in the previous work on aromatic polymers[17] with more pronounced differences in their chemical structures.

Dc Behavior

In Table VI, dc breakdown field data for the various polymers are presented. In the previous study[17] on aromatic polymers, a certain linear thickness dependence was observed for the polyimide under dc conditions. However, no sample thickness dependence has been determined in the present case. The films of polymers **V** and **VI** are thinner than the films of the rest of the polymers, which means that the breakdown field values for polyimides **V** and **VI** might be somewhat high in comparison with the other polymers. Analogous to the results from the ac measurements in DBP, it is obvious that there is no strong influence of the chemical structure of the

Table VI   Breakdown Field Strength for Polyimides under dc Conditions

Polymer	Film Thickness (μm)	F_B (V/μm)[a]	s (V/μm)	B[b]
I	55	534	30	17.68
II	53	540	28	19.49
III	60	557	42	13.33
IV	67	534	35	15.11
V	33	540	55	9.85
VI	37	551	41	13.59

[a] Weibull A parameter.
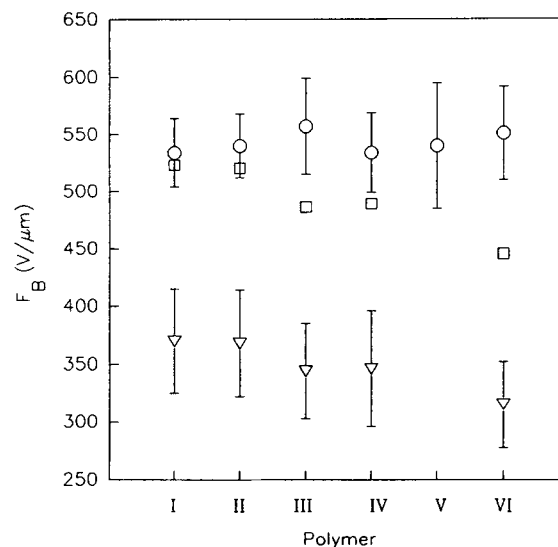[b] Weibull B parameter.

Figure 9   Comparison of the breakdown field strength of the polymers, imidized at 300°C, under dc conditions (O), under ac conditions in DBP rms values (∇) and peak values ($\square$).

polyimides on their dc electric breakdown field strength.

Comparison among ac/Oil, ac/DBP, and dc Results

In comparison of ac and dc data, one has to take into account that the voltages in the ac measurements are rms values, which means that in order to make the ac peak voltages comparable to the dc data the ac values have to be multiplied by the square root of 2 (Fig. 9).

When the ac breakdown behaviors of the polymers in oil and in DBP are compared, the changes in thickness dependence and the level of the breakdown field strength are striking. Studies on stiff PVC (free from plasticizer) have shown similar results.[27] A decrease in thickness dependence and an increase in breakdown field strength of PVC was observed when the permittivity of the immersion medium was changed from 5.5 to 9. The increase in breakdown field strength was of the same order as is described in the present paper. By changing the electrode surround from oil to epoxy resin,[28] a similar increase in breakdown field strength and decrease in thickness dependence was observed. The embedding of the electrode in an epoxy resin was performed to suppress partial discharges. Consequently, the embedding of the electrode in an epoxy resin or a change in the immersion medium from transformer oil to one of higher permittivity leads to the same

results, i.e., to a suppression of partial discharges and an increase in breakdown field strength.

The reasonably good agreement between the dc data and the ac DBP data times the square root of two suggests that there are similarities between the breakdown processes under ac and dc conditions.

CONCLUSIONS

Aromatic polyimides have been synthesized and characterized. The imidization process have been investigated and the influence of structure dependent differences in the reactivity of polyamic acids on the degree of imidization have been shown.

The evaluation of the electric insulating properties have revealed the following:

Under ac conditions with transformer oil as surrounding medium, the breakdown field strength of polyimides follows a power-law dependence on the film thickness. This behavior is not affected by molecular mass of the polymer but changes with the degree of imidization.

Under ac conditions with DPB as the surrounding medium, an increase in breakdown field strength was observed and no thickness dependence was seen up to 60 μm film thickness. No significant influence of the chemical structure was observed.

Under dc conditions, high breakdown field values were obtained and no thickness dependence was investigated. The dc breakdown field data show good agreement with the field peak values of the ac measurements in DBP.

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