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ENVIRONMENTALLY STABLE POLYMERS AND COATINGS FOR SPACE APPLICATION: CH-5

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to

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from

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SUMMARY

Macromolecular research studies during the past few years at Virginia Polytechnic Institute and State University have allowed the development of considerable expertise in the synthesis and characterization of siloxane modified engineering polymers. In particular, the synthesis and characterization of novel siloxane modified polyimides has been studied quite extensively. First generation poly(imide siloxane)s, based on ODA, BTDA and PMDA, were shown to possess unique characteristics. For example, the bulk properties of the material closely resembled those of the polyimide segments, whereas the surface properties modeled those of polydimethylsiloxane. Siloxane segment microphase separation and migration to air or vacuum interfaces is responsible for this phenomenon. Thus, copolymers possessing excellent thermooxidative stability and mechanical strength combined with good resistance to atomic oxygen etching were produced. The latter characteristic was postulated as being due to the transformation of the siloxane surface layer into an organosilicate ceramic-like layer which protects the underlying organic material. The major disadvantage of these systems was the intractability and insolubility of the fully imidized products, even at high siloxane contents.

Recent efforts have been directed towards overcoming the problems associated with processability and adhesion. The results of these efforts which are described in this final report are considered to have produced second generation poly(imide siloxane) copolymers. These new copolyimides, based on meta-linked diamines and monomers containing flexible bridging units, are soluble in their imidized form and possess most of the excellent properties characteristic of their insoluble predecessors. Molecular weight control has been achieved via the use of phthalic anhydride. For example, atomic oxygen data and ESCA (XPS) surface properties reported herein, confirm

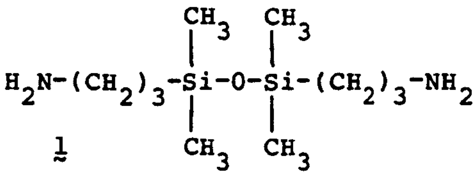
and expand previous results. These processable poly(imide siloxane)s have now also been successfully used to make strong adhesive bonds to titanium as judged by lap shear measurements and have been spray coated from NMP solutions onto various substrates such as Kapton polyimide. Significantly, the coating enhanced the composite's resistance to atomic oxygen.

In addition to the conventional bulk imidization procedures employing upper "cure" temperatures of 300°C, these materials may also be thermally imidized in solution at moderate temperatures using a novel azeotropic co-solvent system based on N-methyl pyrrolidone/N-cyclohexyl pyrrolidone (NMP/CHP). By monitoring characteristic FT-IR bands, imidization has been found to proceed to very high percent completion at 160°C using the NMP/CHP solvent-azeotroping agent system. Proton NMR estimates of residual carboxyl groups are extremely low. The resulting solution imidized poly(imide siloxane)s were transparent, creasable, and importantly, more soluble than the identical materials imidized in bulk. Physical property characterization is continuing.

BACKGROUND

Polyimides synthesized from aromatic monomers generally possess excellent thermal and mechanical properties(1-3). However, unless carefully designed these polymers are often insoluble and infusible, rendering them impossible to process by conventional methods. Therefore, much effort has been spent on synthesizing tractable polyimides that maintain reasonably high strength and thermooxidative stability. Successful efforts in this area have included the incorporation of diamines and/or dianhydrides containing flexible bridging units such as oxygen, carbonyl, sulfur, fluoroalkyl and sulfone, which impart mobility to the otherwise rigid polyimide backbone (1-3). Attempts to make soluble polyimides using aromatic monomers possessing bulky side groups have also been successful (4). The use of diamines containing meta linkages has also been shown to result in polyimides with improved solubility and processability (5,6).

The synthesis of homogeneous poly(imide siloxane) copolymers was reported in 1966 by Kuckertz (7), who reacted the simple dimer bis(aminopropyl) tetramethyl-disiloxane, 1, with pyromellitic dianhydride to produce the poly(amic acid siloxane), which was subsequently cyclized to form the imidized analog. More recently, St. Clair and coworkers (8,9) have



$$H_2N-(CH_2)_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_3-NH_2$$

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utilized the same siloxane dimer to synthesize thermoplastic siloxane modified polyimides, which were successfully used to produce high strength bonds and moldings. An alternative approach to the synthesis of soluble poly(imide siloxane) copolymers has involved the polymerization of siloxane-containing dianhydrides with various isomers of diamino-diphenylmethanes (10). In fact, many publications on siloxane-containing polyimides have shown that the incorporation of flexible siloxane segments into a polyimide backbone can permit the synthesis of soluble, processable copolyimides with fairly good thermal and mechanical properties. In addition to this, the thermally stable siloxanes can also impart a number of desirable properties such as improved impact resistance, better weatherability, and in some cases, surface modification (11). This latter property results from preferential migration of siloxane segments to the copolymer film surface.

While much of the work in the field of siloxane modified polyimides has dealt with simple bis(amino alkyl) siloxanes, some recent publications have discussed the copolymerization of functional siloxane equilibrates of higher molecular weights (11). Poly(imide siloxane)s are of interest in a wide variety of applications, including the electronics and aerospace industries (15-17). Much of the available literature on these copolymers is in the form of patents.

This report describes the synthesis of soluble, fully imidized poly(imide siloxane) segmented copolymers which may be of interest as tough environmentally stable structural matrix resins and structural adhesives. Thus, 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was reacted with various aminopropyl-terminated polydimethylsiloxane oligomers (M_n = 950 to 10,000 g/m) and a meta-substituted diamine chain-extender such as 3,3'-diaminodiphenyl sulfone (DDS) or 3,3'-diaminobenzophenone (DABP) to produce the siloxane modified poly(amic acid). Thin films were cast from the reaction mixtures and subsequent thermal dehydration produced the poly(imide siloxane) block or segmented copolymers. By varying the amount and molecular weight of the siloxane oligomer, a variety of novel copolymers of controlled composition have been synthesized. Tough, transparent, flexible, soluble films were produced by this method. Upper glass transition temperatures and mechanical properties of copolymers containing low to moderate siloxane content approach those of the unmodified controls. Solution imidization studies are also reported that show great promise for future studies.

EXPERIMENTAL

The 3,3'-diaminodiphenylsulfone (DDS) was obtained from FIC Corporation and purified by recrystallization from a deoxygenated methanol/water solution. (90% yield, m.p. 172-173°C). 3,3'-diaminobenzophenone (DABP) obtained from Ash Stevens, was also purified in high yield by similar recrystallization (m.p. 151-152°C). BTDA was obtained in high purity from the Chriskev Company and subjected to a thermal treatment prior to use. The α, ω-aminopropyl polydimethyl siloxane oligomers were synthesized in our laboratories by methods previously disclosed (11). Molecular weights were varied from about 1000 to 10,000 $\bar{M}$n, and were usually obtained by potentiometric titration of the amine end groups. All solvents were purified by vacuum distillation from calcium hydride and stored in round bottom flasks fitted with rubber septums.

The poly(amic acid siloxane) intermediates were synthesized by two methods and a representative synthetic procedure will be outlined for each method. In both cases, a poly(amic acid siloxane) sample containing 10 weight percent siloxane (Mn=950) and DDS as the chosen diamine will be discussed.

Method 1: A three neck 250 ml flask was fitted with a drying tube, nitrogen inlet and a mechanical stirrer. The nitrogen purge was started and the flask was flamed to remove moisture. Next, 1.0000 gram of ~1000$\bar{M}$n aminopropyl polydimethylsiloxane (.0010 moles) and 3.8000 grams of DDS (.0153 moles) were then added to the flask along with a cosolvent mixture of 20 mls of tetrahydrofuran (THF) and 10 mls of dimethylacetamide (DMAC). After solution had been achieved, BTDA (5.2710 grams, 0.0163 moles) was added to the reaction mixture along with 20 mls of DMAC and 10 mls of THF. A calculated quantity of recrystallized phthalic anhydride can also be added at this point to control the molecular weight of the amic acid (Figure 10). This technique was utilized to prepare resins with greater flow properties for use in adhesive applications. The reaction was allowed to proceed for eight hours during which time the solution viscosity rose steadily. A clear viscous poly(amic acid siloxane) solution was obtained which was then stored under low temperature (~-10°C) conditions before use.

Method 2: A 3 neck 250 ml flask was fitted with a drying tube, mechanical stirrer, nitrogen inlet and addition funnel. The flask was again flamed out and BTDA (5.2710 grams, 0.0163 moles) was added to the flask and rinsed in with 20 mls of DMAC and 15 mls of THF. Next, 1.0000 grams of the aminopropyl polydimethylsiloxane oligomer (.0010 moles) and 10 mls of THF were then placed in the addition funnel and added dropwise to the stirring dianhydride solution, over a 10 minute period. After stirring for an additional 20 minutes, 3.8000 grams (0.153 moles) of DDS was added as a chain extender along with 10 mls of DMAC and 5 mls of THF. The reaction was again allowed to proceed for 8 hours. The resultant clear reaction solution was again stored under low temperature (~-10°C) conditions.

Minor adjustments in both procedures were necessary to optimize each reaction for the quantities and molecular weights of the siloxane oligomers. As a general rule, a cosolvent ratio higher in THF content was needed to solvate reaction mixtures containing higher molecular weights or higher percentages of siloxanes.

A thermal procedure was initially employed to convert the poly(amic acid siloxane) intermediates to the imidized final products. Typically, a film of the amic acid solution was cast onto a glass plate at thicknesses ranging from 5 to 50 mils.; it was then placed in a vacuum oven to remove the reaction solvents. After this treatment, the film on the plate was imidized in a forced air convection oven at temperatures of 100, 200, and 300°C, each for one hour. Compositions were assessed by a variety of methods, including proton NMR.

Solution Imidization of Siloxane Modified Poly(amic acids)

Solution imidization was achieved using an N-methyl pyrrolidone/N-cyclohexyl pyrrolidone (NMP/CHP) cosolvent system (80-90% NMP) at 150-160°C. To study the rate of imidization, samples were removed from the reaction at certain time intervals during the course of the imidization and analyzed using FT-IR. Samples were cast onto glass plates and solvent removal was accomplished in a vacuum oven at 70°C for one hour. The disappearance of the amic acid band at 1546 cm^{-1} and the appearance of the imide bands at 1778 cm^{-1} and 725 cm^{-1} were monitored. These bands were found not to overlap with bands due to residual solvent and their intensities were ratioed to a reference band to normalize out film thickness. A fully imidized control was prepared by the conventional imidization method and used as a reference to determine percent imidization.

A Nicolet MX-1 spectrophotometer was used to obtain FTIR spectra. The samples were analyzed as thin cast films. Proton NMR spectra were obtained using an IBM 270 MHz instrument. GPC traces were obtained using Waters instrumentation. The instrument was equipped with UV and RI detectors and THF was used as the solvent.

Glass transition temperatures were determined on a Perkin-Elmer model-2 DSC or by dynamic mechanical thermal analysis (DMTA) at a frequency of 1 Hz. DSC samples were run at 10°C per minute in a nitrogen atmosphere. All samples were run at least two times to accurately determine glass transitions.

The thermal stability and thermomechanical behavior were investigated with a Perkin-Elmer system-2 thermogravimetric/thermomechanical analyzer. TGA scans were run at 10°C/min. in an air atmosphere. TGA samples were analyzed in film form. For TMA analysis a quartz penetration probe was used with a mass of 50 grams. The heating rate was again 10°C/min.

Mechanical properties were studied using an Instron model 1122. Tensile evaluations were made on dogbone shaped specimens with a gauge length of 10 mm and a gauge width of 2.76 mm. Film thicknesses ranged from 2-10 mils. The samples were deformed at a crosshead speed of 5 mm/min. and modulus values were determined by measuring the initial slope of the stress-strain curve.

Water contact angles were measured on samples prepared by spincoating the amic acid intermediates onto ferrotype plates followed by thermal imidization or by spincoating the imidized copolymer directly. 10 microliter drops were then placed on the coating and an average of 4 values was used to obtain the contact angle for each sample.

Adhesive Preparation

Single lap shear specimens were prepared by sandwiching a scrim cloth (112 E glass) coated with the poly(imide siloxane) resin betwen two primed titanium adherands. The poly(amic acid siloxane) solution (molecular weight was controlled by the addition of phthalic anhydride, Figure 10) in diglyme/THF was coated onto 112 E glass and cured in a FACO using the following schedule:

RT - 100°C, ½ HR

100 - 150°C, ½ HR

150 - 200°C, ½ HR

This procedure was repeated until an overall thickness of 9-13 mils (cloth and resin) was achieved.

The titanium adherands were sandblasted, treated with Pasa Jell 107, ultrasonically cleaned, and immediately primed with a coating of amic acid solution to preserve the surface treatment. This primer coat was imidized using the same thermal schedule as the scrim cloth.

Single lap shear specimens (½ inch overlap) were prepared by pressing the coated scrim cloth between two primed adherands using the following bonding cycle:

-- R. T. to 325°C apply 200 PSI at 280°C

-- Hold for 15 min. @ 325°C

-- Cool under pressure

XPS Surface Analysis

Samples were prepared for analysis by spin coating several layers of the amic acid in its reaction solution of DMAC/THF onto a ferrotype plate which had been washed in hexane three times prior to coating. The samples were covered with a large watchglass in order to avoid contamination and then imidized in the standard fashion in a forced air convection oven. Once imidized, the samples were washed in hexane three times and placed in clean glass containers with lids. Analyses were performed with a Kratos instrument at exit angles of 10, 30 and 90°.

Atomic Oxygen Resistance

Samples of several siloxane-polyimide copolymers were analyzed in an oxygen plasma environment for weight loss and qualitative physical degradation. The instrument was a Plasmod unit from the Tegal Corporation of Richmond, CA. Film samples were maintained in an oxygen-charged environment for 45 minutes, under a vacuum of 1.5 torr. The applied radio frequency was 50 KMz. Oxygen flow rate to the analysis chamber was approximately 30 cc/minute.

RESULTS AND DISCUSSION

Synthesis of Poly(amic acid siloxane) Intermediates

The removal of moisture from the reaction system was necessary in order to obtain high molecular weight amic acids. For this reason, monomers and solvents were dried before use and the distilled solvents were stored in sealed flasks. When needed, these solvents were handled using syringe techniques.

Maintaining solubility of the reactants throughout the polymerization was also a major factor in obtaining tough, transparent films of predictable composition. While solvents such as methylene chloride, THF, and chloroform easily solvate the polysiloxane oligomers, they do not readily dissolve aromatic monomers such as BTDA or the resultant poly(amic acid). On the other hand, dipolar aprotic solvents are good solvents for aromatic monomers, the growing polymer chain and even the aminopropyl terminated siloxane dimer. However, they are nonsolvents for siloxane equilibrates of higher (e.g. 5-10,000) molecular weight. During preliminary studies, solvents were also evaluated as possible single component polymerization media. Interestingly, diglyme was found to solvate all the monomers and siloxane oligomers sufficiently to be considered as a single solvent for the synthesis of the siloxane modified poly(amic acid) intermediates. Additionally, diglyme has been reported to yield polyimides possessing enhanced adhesive properties over those synthesized from dipolar aprotic solvents (14). Unfortunately, diglyme was not a suitable single solvent for the synthesis of the copolymers discussed in this report due to premature precipitation of the growing polymer chains. As a consequence, the resulting polyimide copolymers prepared in that manner were brittle and opaque. Based on solubility studies, a cosolvent consisting of a dipolar aprotic solvent such as NMP or DMAC along with THF was chosen to synthesize the poly(amic acid siloxane) intermediates. More recently, a cosolvent consisting of diglyme and THF has been successfully used to synthesize the poly(amic acid siloxanes), thus eliminating the need for the higher boiling dipolar aprotic solvents altogether. This was especially advantageous in preparing and evaluating adhesive bonds.

The general synthetic and imidization scheme for the siloxane modified poly(amic acid) copolymers and their conversion to the imidized form is depicted in Figure 1. These intermediates were actually synthesized by two methods. Method one modeled the way in which conventional poly(amic acid)s are produced; i.e., solid dianhydride was added to a solution of the chosen diamines. In the second method, the siloxane oligomer was capped with excess BTDA prior to chain extension with DDS or DABP.

Compared with method 2, the first method has the advantage that possible hydrolysis of the dianhydride is minimized. However, the intrinsic viscosities of the imidized copolymers (Table 1) obtained by the two synthetic methods are not significantly different, indicating that moisture effects are insignificant under our conditions. Method one was only successful when the molecular weight of the polysiloxane oligomer was less than 2100 g/m. Above this molecular weight, the solubility of all constituents could not be maintained during the polymerization and high molecular weight well defined systems were not obtained.

Mixing the reactants in a manner consistent with method 2 was successful in overcoming the solubility problem. Employing this method, siloxane oligomers with molecular weights as high as 10,000 g/m were successfully copolymerized. In this work as well as previously (11) the BTDA-capped siloxane oligomer possessed enhanced solubility in cosolvents with low THF to DMAC(NMP) ratios. Consequently, the capping method proved to be much more successful than the conventional approach. During the capping process, premature chain extension of the polydimethylsiloxane oligomer was prevented by slowly adding the siloxane oligomer to a solution of excess BTDA. The solution was then allowed to further react prior to the addition of the diamine "chain extender" to ensure that the oligomer was capped.

Analysis of Poly(imide siloxane) Copolymers

The poly(amic acid siloxane) copolymers were converted to the corresponding poly(imide siloxanes) by thermal imidization either in bulk or in solution. To insure complete bulk imidization, the films were exposed to an upper temperature of 300°C for one hour. This temperature is above the upper Tg and allowed complete imidization of the copolymers without decomposing the siloxane oligomers incorporated into the structure. All the data discussed in this report were obtained on films imidized in this manner.

Solution Imidization

Solution imidization of the amic acid siloxanes was conducted in a cosolvent consisting of NMP and CHP. CHP (cyclohexyl pyrrolidone) is an interesting solvent that becomes immiscible with water at elevated temperatures and thus acts as an effective azeotroping agent for the water of imidization. The solution imidization process allowed nearly quantitative imidization at only moderate temperatures (160°C). The imidization reaction was studied semiquantitatively using FT-IR techniques (Figure 2). The disappearance of the amic acid moiety and the appearance of the imide struc-tures were monitored over time by studying their respective bands in the IR region. The plot of this data shows that the disappearance of amic acid is closely followed by the appearance of imide, indicating the absence of side reactions. Also, imidization could be demonstrated to proceed to greater than 96% (this was a function of which band was monitored. This method shows great synthetic utility; for example, imidized oligomers capped with various functional groups may be prepared. This feature is the subject of current studies.

FT-IR spectra (Figure 3) of a poly(imide siloxane) copolymer imidized by conventional methods and containing 20 weight percent siloxane oligomer (Mn=2050 g/m) showed bands corresponding to both the aromatic imide-containing segments and the soft polysiloxane segments. The bands around 1776 and 700 cm^{-1} correspond to the imide structure, while those at 2950, 1094, and 802 cm^{-1} correspond to C-H, Si-O, and Si-C bond vibrations respectively and are characteristic of polydimethylsiloxanes. The absence of any significant bands in the area of 3300 cm^{-1} corresponding to an amide or amine type structure indicates that imidization was probably quantitative.

NMR

A proton NMR spectrum of a copolyimide containing 40 weight percent siloxane run in DMSO-D6 is shown in Figure 4. The spectrum shows the strong resonance at ~0 ppm indicative of the siloxane methyls and a series of complicated aromatic proton resonances. The absence of peaks above 10 ppm due to carboxylic acid structures also indicates quantitative imidization. The amount of siloxane in the copolymer can be determined by ratioing the peak areas of the aromatic proton region and the siloxane methyls. It was shown that the amount of siloxane charged during the copolymer synthesis agrees well with the amount actually incorporated throughout the entire copolymer composition range.

GPC

A representative GPC trace for a copolymer sample containing 60 weight percent siloxane (Mn = 950 g/m) is shown in Figure 5. The GPC chromatogram indicates the sample has a unimodal distribution. The presence of a slight low molecular weight tail may be a result of degradation during the imidization process or it may suggest a reaction time longer than 8 hours is necessary to obtain optimum degree of polymerization. Current work is emphasizing the solution imidized copolymers since they can be prepared under milder conditions.

Solubilities of the poly(imide siloxane) copolymers were evaluated in a variety of solvents at a concentration of 1-2 percent (w/v) (Table 2). Dipolar aprotic solvents such as NMP and DMAC completely dissolved all of the copolymers tested while the unmodified controls showed only partial solubility. Also, copolymer solubility in these solvents improved with increasing polydimethylsiloxane content. Copolymers containing higher percentages of siloxanes were soluble in a wide range of solvents such as THF, diglyme and methylene chloride which suggests the possibility of spray coating. Intrinsic viscosities of the copolymers were determined in NMP and the results obtained for the series employing DDS as the chain extender are tabulated in Table 1. These values range from 0.51 to 0.84 dl/gm, indicating that the goal of synthesizing high molecular weight copolymers has been achieved over the entire composition and segment molecular weight range examined.

Upper glass transition temperatures of the poly(imide siloxane)s were determined using differential scanning calorimetry (DSC) at a scanning rate of 10°C per minute or by dynamic mechanical thermal analysis (DMTA) at a frequency of 1 Hz. Again, the values obtained for the series employing DDS as the chain extender are listed (Table 3). All of the copolymers listed in the table were synthesized by method 2. In many cases, the copolymer's Tg is only slightly lower than the value for the unmodified control, indicating that good microphase separation was achieved in the copolymers. Generally, the upper copolymer Tg is observed to decrease with both decreasing siloxane oligomer molecular weight and with increasing siloxane weight percent.

TGA scans of selected copolymers run under a flowing air atmosphere are shown in Figure 6. It is evident that as siloxane content is increased, the onset of copolymer degradation occurs at lower temperatures. However, the samples maintained good thermal stability even at siloxane levels of 60 weight percent. The char yield at high temperatures was also found to be proportional to siloxane content. It is suggested that a silicate-type structure is the principal degradation product in an air atmosphere.

Copolymer thermal stability also varied with the molecular weight of the siloxane oligomer, Figure 7. Thermal stability increased with increasing siloxane molecular weight (weight percent siloxane held constant). From this observation it may be concluded that degradation begins at the aliphatic n-propyl segments linking the siloxane oligomers to the polyimide matrix. As the siloxane oligomer molecular weight is increased, the concentration of n-propyl linkages in the copolymer backbone decreases, thus increasing overall thermal stability. Future research will investigate the possibility of wholly aromatic amine end groups.

TMA traces for a series of copolymers having the same siloxane molecular weight are shown in Figure 8. As expected, samples containing higher amounts of siloxane show decreased resistance to probe penetration. The traces indicate, however, that the copolymers possess fairly high modulus values at elevated temperatures.

Mechanical Property Analysis

The effect of siloxane content on the mechanical behavior of the copolyimides was briefly investigated and is illustrated in Figure 9. Mechanical properties proved to be highly dependent upon siloxane content. While copolymers containing low to moderate amounts of siloxane maintained good rigidity and ductile mechanical properties, a large drop in modulus was observed for copolymers containing high amounts of siloxane. This decrease in modulus was accompanied by a significant increase in percent elongation. These observations no doubt reflect the fact that the siloxane microphase is continuous in these latter cases.

Water content angle measurements and water absorption measurements are listed in Table 4. A significant increase in contact angle is observed between the unmodified control and copolymer samples containing only 5-10 weight percent siloxane. In fact, the copolymer contact angles approach those of pure polydimethylsiloxane. The water absorption is also significantly reduced upon siloxane incorporation. Both of these properties are attributed to the hydrophobicity of siloxanes.

Adhesive Results

Preliminary adhesive data on controlled molecular weight copolymers are shown as lap shear strengths in Table 5. Although our values are not as high as those reported in the literature, one important trend is noted. The incorporation of low to moderate amounts of siloxane (M_n = 950 g/m) does not significantly alter the adhesive characteristics of the material. Only at high levels of siloxane do the lap shear strengths fall below 2000 psi (~14 MPA), indicating the potential utility of these materials as atomic oxygen resistant structural adhesives. The effect of increasing the siloxane oligomer molecular weight on adhesion is being studied currently to determine if the release agent qualities of siloxanes are more pronounced at these compositions.

XPS Analysis of Siloxane-Modified Polyimide Copolymers

Since the surface composition of these macromolecular materials is directly related to such properties as coefficient of friction and atomic oxygen stability, X-ray photoelectron spectroscopy (XPS or ESCA) was employed in order to characterize the surface composition of the siloxane-modified polyimide copolymers (Figure 11). By varying the angle of the sample relative to the analyzer, different depths of the polymer were sampled, such that 15° grazing take-off angle characterizes molecules from the uppermost surface more so than molecules from the bulk. The 90° take-off angle, on the other hand, yields compositional information more characteristic of the sub-surface regions.

The results of the XPS experiments are listed in Table 6. The results conclusively demonstrate that the siloxane component dominates the surface of the copolymer. Furthermore, the extent of domination is independent of the weight percent of the siloxane incorporated into the copolymer. Thus, one is able to achieve a surface characteristic of the siloxane component while tailoring the physical properties which are characteristic of the bulk.

These results are supported by the data obtained earlier by contact angle measurements. Unlike XPS, however, contact angle measurements provide no direct quantitative information regarding either surface or bulk compositions.

Initial Studies of Atomic Oxygen Stability

The copolymers examined were based upon BTDA-PSX-DDS as well as their oxydianiline (ODA) analogue, and had siloxane contents of 30 and 50 weight percent and siloxane segment molecular weights of 1000. Results obtained thus far are listed in Table 7. In every run, the DDS-based 50 weight percent siloxane samples lost no weight after exposure to the oxygen environment and their ODA analogues performed similarly well, showing only 0.25% weight loss. Interestingly, the ODA-based systems seemed to perform somewhat less successfully than the DDS-based copolymers. Additionally, the 30 weight percent siloxane copolymers lost more weight during exposure than the 50 weight percent siloxane analogues, in both the DDS and ODA systems. Consistently, Kapton lost more weight than either the DDS or ODA based siloxane-modified polyimides, and coating Kapton with the DDS-based copolymers enhanced the stability of the Kapton film under the aggressive environment for both the 30 and 50 weight percent siloxane levels. Under these latter conditions, the performance of the Kapton-coated film resembled the performance of the siloxane-modified polyimides which constituted the coated layer.

CONCLUSIONS

New, high molecular weight, randomly coupled poly(imide siloxane) soluble block copolymers have been synthesized from bis(amino propyl) polydimethylsiloxane equilibrates of various molecular weights, aromatic meta-linked diamines, and BTDA. Two synthetic procedures were successfully used to synthesize the poly(amic acid siloxane) intermediates. For both synthetic procedures, a cosolvent system was employed to achieve complete solvation of all components throughout the polymerization. A thermal procedure was used to convert the poly(amic acid siloxane) intermediates to the corresponding polyimides, essentially quantitatively. A novel solution imidization procedure was developed based upon the co-amide solvent NMP/CHP reacted at 150-160°C. FT-IR studies of the imidization suggested that nearly complete cyclization was achieved. The poly(imide siloxane)s produced by this method were flexible, tough, transparent, soluble and are possible candidates for environmentally stable structural matrix resins and structural adhesives. Upper glass transition temperatures of many copolymers approach those of the unmodified controls, (~272°C) indicating good microphase separation. Lap shear strengths achieved against surface treated titanium showed that relatively good adhesion could be achieved under practical bonding conditions. Moreover, the values were basically unchanged as a function of siloxane content at low (e.g., 10-15%) siloxane levels. Photoelectron spectroscopy (XPS or ESCA) demonstrated the top surface (~10Å) is dominated by the siloxane. Additional "ashing" experiments in oxygen plasma reconfirm that weight loss is definitely reduced by this feature.

REFERENCES

1. H. D. Burks and T. L. St. Clair in "Polyimides: Synthesis, Characterization, and Applications", Vol. 1, K. L. Mittal Ed., Plenum, NY, 1984, pp. 117-135.
2. P. R. Young and N. T. Wakelyn, proceedings from the Second International Conference on Polyimides. Ellenville, NY, 1985, pp. 414-425.
3. J. P. Critchley and M. A. White, J. Polym. Sci., Polym. Chem. Ed., 10, 1809 (1972).
4. F. W. Harris, S. O. Norris, L. H. Lanier, B. A. Reinhardt, R. D. Case, S. Varaprath, S. M. Padaki, M. Torres, and W. A. Feld in "Polyimides: Synthesis, Characterization, and Applications", Vol. 1, K. L. Mittal Ed., Plenum, NY, 1984, pp. 3-14.
5. A. K. St. Clair, T. L. St. Clair and E. N. Smith, Polymer Preprints, 17, 359 (1976).
6. T. L. St. Clair and D. A. Yamaki in "Polyimides: Synthesis, Characterization, and Applications", Vol. 1, K. L. Mittal Ed., Plenum, NY, 1984, pp. 99-116.
7. J. H. Kuckertz, Makromol. Chem., 98, 101 (1966).
8. S. Maudgal and T. L. St. Clair, Int. J. Adhesion and Adhesives, 4(2), 87 (1984).
9. S. Maudgal and T. L. St. Clair, Proceedings from the Second International Conference on Polyimides, Ellenville, NY, 1985, pp. 47-73.
10. G. N. Babu in "Polyimides: Synthesis, Characterization, and Applications", Vol. 1, K. L. Mittal Ed., Plenum, NY, 1984, pp. 51-66.
11. B. C. Johnson, I. Yilgor and J. E. McGrath, Polymer Preprints, 25(2), 54 (1984); B. C. Johnson, Ph.D. Thesis, VPI and SU 1984; B. C. Johnson, J. D. Summers. and J. E. McGrath, J. Poly. Sci., in press, 1987; J. E. McGrath, P. M. Sormani, C. S. Elsbernd and S. Kilic, Makromol. Chemie, accepted, 1986; P. M. Sormani, R. J. Minton and J. E. McGrath, in "Ring Opening Polymerization: Kinetics, Mechanisms and Synthesis", J. E. McGrath, Editor, ACS Symposium Series No. 286 (1985), Chapter 11, p. 147-161.
12. R. Edelman, Proceedings from the Second International Conference on Polyimides, Ellenville, NY, 1985, pp. 182-185.
13. C. S. Sroog, J. Polym. Sci., Macro. Rev., 11, 161 (1976).
14. T. L. St. Clair and D. J. Progar, Polymer Preprints, 16(1), 538 (1975).
15. C. L. Lee, "High Performance Silicone-Imide Copolymers", SAMPE Symposium No. 30, p. 52-63 (1985).
16. A. Berger, "Modified Polyimides by Silicone Incorporation", SAMPE Symposium No. 30, p. 64-73 1985.
17. G. Davis, Photosensitive Polyimide-Siloxanes, in "Polymers in Electronics", T. Davidson, Editor, ACS Symposium Series No. 242, 1984, p. 259-272.

TABLE 1

INTRINSIC VISCOSITIES OF POLY(IMIDE SILOXANE) COPOLYMERS (3,3'-DDS BASED)

SILOXANE WT%	SILOXANE Mn	SYNTHETIC METHOD	$[\eta]$ 25°C, NMP
10	950	1	0.62
10	950	2	0.69
10	2,100	2	0.66
10	5,000	2	0.71
10	10,000	2	0.73
20	950	1	0.78
20	950	2	0.84
20	2,100	2	0.79
20	5,000	2	0.51
40	950	2	0.55
60	2,100	2	0.57

TABLE 2

SOLUBILITIES OF POLY(IMIDE SILOXANE) COPOLYMERS (3,3'-DDS BASED)(A)

		(WEIGHT % PSX)				
SOLVENT	CONTROL	5	10	20	40	60
NMP	SW	SW	S	S	S	S
DMAC	SW	SW	S	S	S	S
DMF	SW	SW	SW	SW	S	S
DIGLYME	I	I	I	I	SW	S
THF	I	I	I	I	SW	S
CH_2Cl_2	I	I	I	I	SW	S
$CHCl_3$	I	I	I	I	SW	S

S=SOLUBLE
I=INSOLUBLE
SW=PARTIALLY SOLUBLE / SWELLING

(A) Mn OF PSX RANGED FROM 1,000 - 10,000 g / m

TABLE 3

UPPER GLASS TRANSITION TEMPERATURES POLY(IMIDE SILOXANE) COPOLYMERS (3,3'-DDS BASED)

SILOXANE WT%	SILOXANE Mn	SYNTHETIC METHOD	Tg (°C) DSC	DMTA (1 Hz)
CONTROL		1	272	
10	950	1	252	
10	950	2	256	260
10	2,100	2	267	267
10	5,000	2	264	
10	10,000	2	264	266
20	950	1	246	
20	950	2	246	248
20	2,100	2	259	
20	5,000	2	262	
40	950	2	*	225

* NO TRANSITION DETECTED IN DSC SCAN

TABLE 4

WATER ABSORPTION AND WATER CONTACT ANGLES OF 3,3'-DDS BASED POLY(IMIDE SILOXANE) COPOLYMERS

SAMPLE (PSX wt.% / PSX Mn)	WATER CONTACT ANGLE (DEGREES)	WATER UPTAKE (%) (1 week soak)
CONTROL	68	1.1
5 / 950 (2)	92	~0.0
10 / 950 (1)	99	↓
10 / 950 (2)	98	
10 / 2,100 (2)	100	
10 /5,000 (2)	98	
10 / 10,000 (2)	100	
20 / 950 (1)	102	
20 / 950 (2)	101	
20 / 2,100 (2)	102	
20 / 5,000 (2)	102	
40 / 950 (2)	106	
40 / 950 (2) (recast)	105	
60 / 2,100 (2)	106	

contact angle samples were prepared by spin coating the amic-acids onto ferrotype plates followed by thermal imidization

TABLE 5

PRELIMINARY ADHESIVE RESULTS

SILOXANE WT. %	SILOXANE Mn	$[\eta]$ 25° C NMP	LAP SHEAR STRENGTH (PSI)
CONTROL	-	INSOLUBLE	4650*
CONTROL	-	INSOLUBLE	2510
5	950	INSOLUBLE	2480
10	950	.40	2360
20	950	.36	2110
40	950	.34	1860

RESIN COATED 112 E-GLASS (SCRIM CLOTH) WAS PRESSED BETWEEN TWO PRIMED TITANIUM ADHERANDS (.5 inch overlap) USING THE FOLLOWING BONDING CYCLE:

R.T. TO 325 °C, APPLY 200 PSI AT 280 °C
HOLD FOR 15 MIN.
COOL UNDER PRESSURE

*T. L. ST.CLAIR AND D. A. YAMAKI IN "POLYIMIDES: SYNTHESIS, CHARACTERIZATION, AND APPLICATIONS", VOL 1, K. L. MITTAL ED., PLENUM, NY, 1984, PP.99-116.

TABLE 6

XPS ANALYSIS OF SILOXANE - MODIFIED POLYIMIDE SURFACES

(3, 3' DDS-BASED)

SAMPLE (WT % PSX-PSX M_n)	TAKE-OFF ANGLE	WT% SILOXANE AT SURFACE
5% - 950	15°	85
5% - 950	90°	34
10 % - 950	15°	77
10 % - 950	90°	35
10 % - 10,000	15°	87
10 % - 10,000	90°	39
20 % - 950	15°	87
20 % - 950	90°	53
40 % - 950	15°	86
40 % - 950	90°	63

TABLE 7

OXYGEN PLASMA STABILITY OF SILOXANE-MODIFIED POLYIMIDES

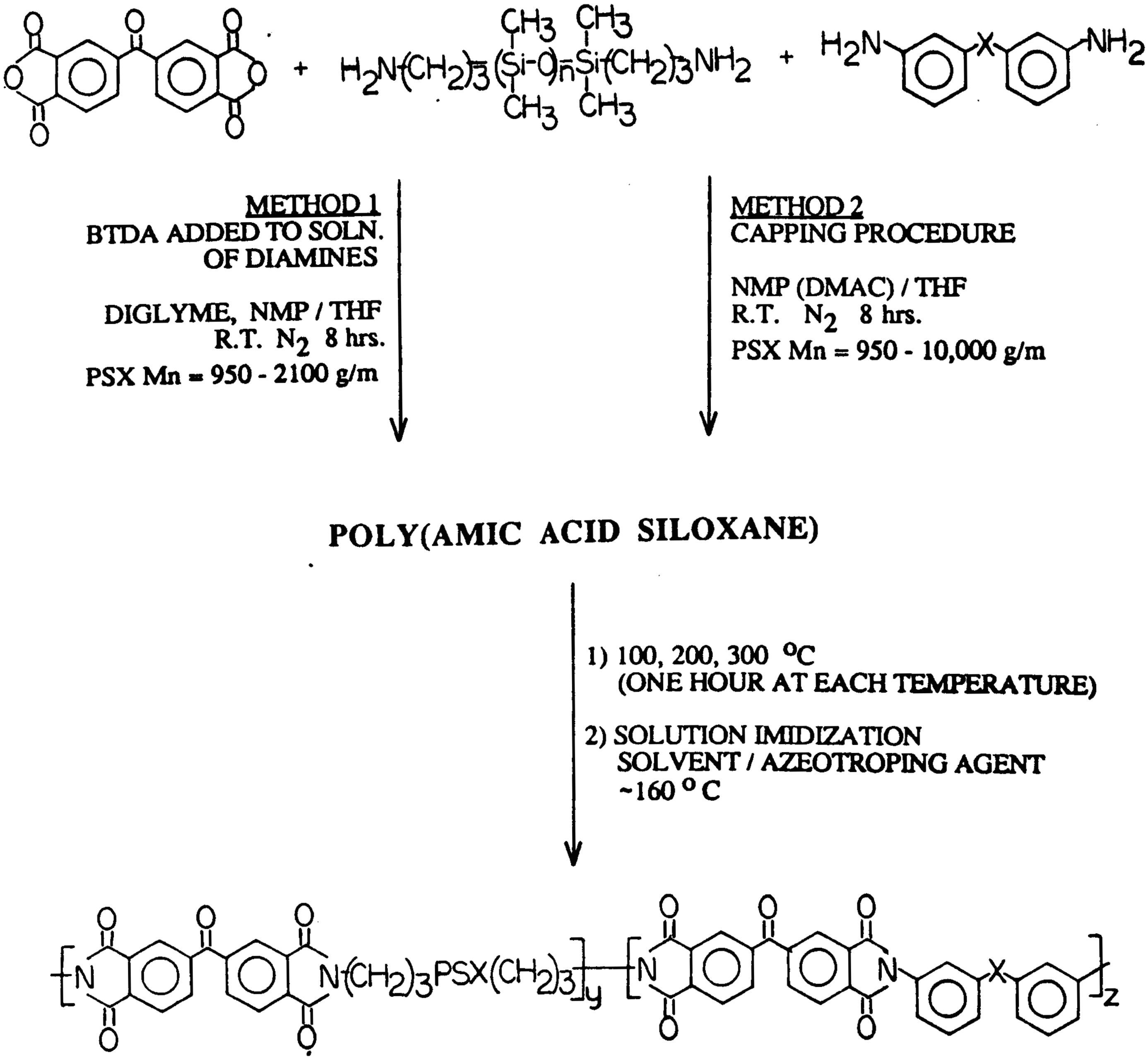
(BASED UPON EITHER 3,3'-DDS OR 3,3' ODA WITH SILOXANE MW 1000)

SAMPLE	WEIGHT LOSS, % [(a)]
KAPTON	3.55
DDS-CONTROL	2.05
DDS-CONTROL	3.74
DDS-30% PSX	1.21
DDS-CONTROL	2.80
DDS-30% PSX	0.51
DDS-CONTROL	3.88
DDS-30% PSX	1.43
DDS-CONTROL	2.19
DDS-50% PSX	0.0
DDS-CONTROL	3.27
DDS-50% PSX	0.0
DDS-CONTROL	5.23
DDS-30% PSX ON KAPTON	2.33
DDS-CONTROL	3.20
DDS-50% PSX ON KAPTON	0.86
ODA-CONTROL	5.83
DDS-CONTROL	2.62
ODA-CONTROL	6.56
DDS-CONTROL	2.33
ODA-CONTROL	4.97
ODA-30% PSX	1.44
ODA-CONTROL	8.78
ODA-50% PSX	0.25

(a) 45 minute exposure (see experimental)

FIGURE 1

SYNTHETIC SCHEME



METHOD 1
BTDA ADDED TO SOLN. OF DIAMINES

DIGLYME, NMP / THF
R.T. N_2 8 hrs.
PSX Mn = 950 - 2100 g/m

METHOD 2
CAPPING PROCEDURE

NMP (DMAC) / THF
R.T. N_2 8 hrs.
PSX Mn = 950 - 10,000 g/m

POLY(AMIC ACID SILOXANE)

1) 100, 200, 300 °C
(ONE HOUR AT EACH TEMPERATURE)

2) SOLUTION IMIDIZATION
SOLVENT / AZEOTROPING AGENT
~160 °C

X = SO_2, CO

ALL FILMS ARE TRANSPARENT AND CREASABLE

FIGURE 2

SOLUTION IMIDIZATION OF POLY(IMIDE SILOXANE) SEGMENTED COPOLYMER (3,3'-DDS BASED)

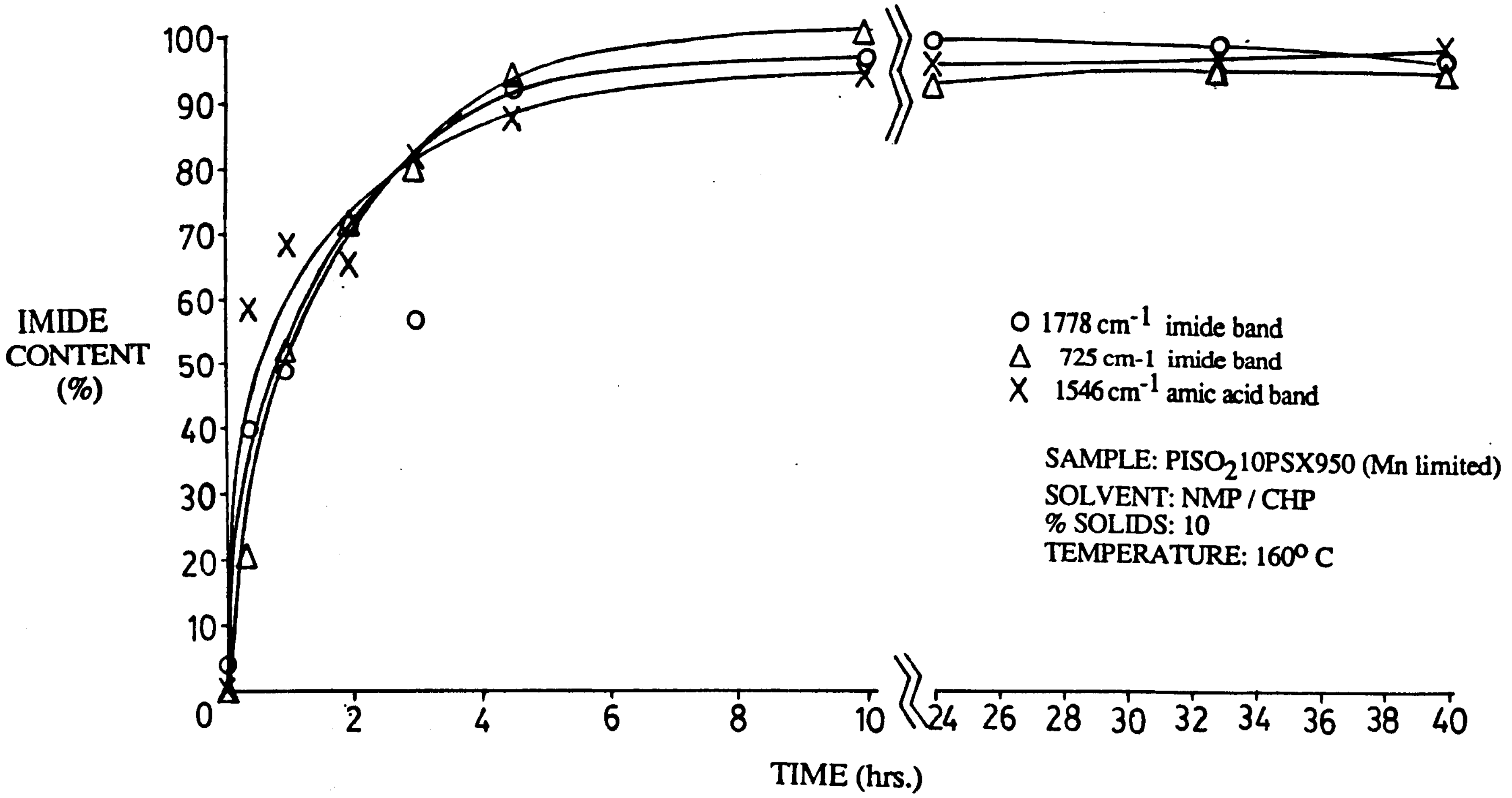


FIGURE 3

FT-IR SPECTRUM OF A POLY(IMIDE SILOXANE) BLOCK COPOLYMER
(DDS BASED) PSX CONTENT = 20 %, PSX Mn = 2,100 g/m

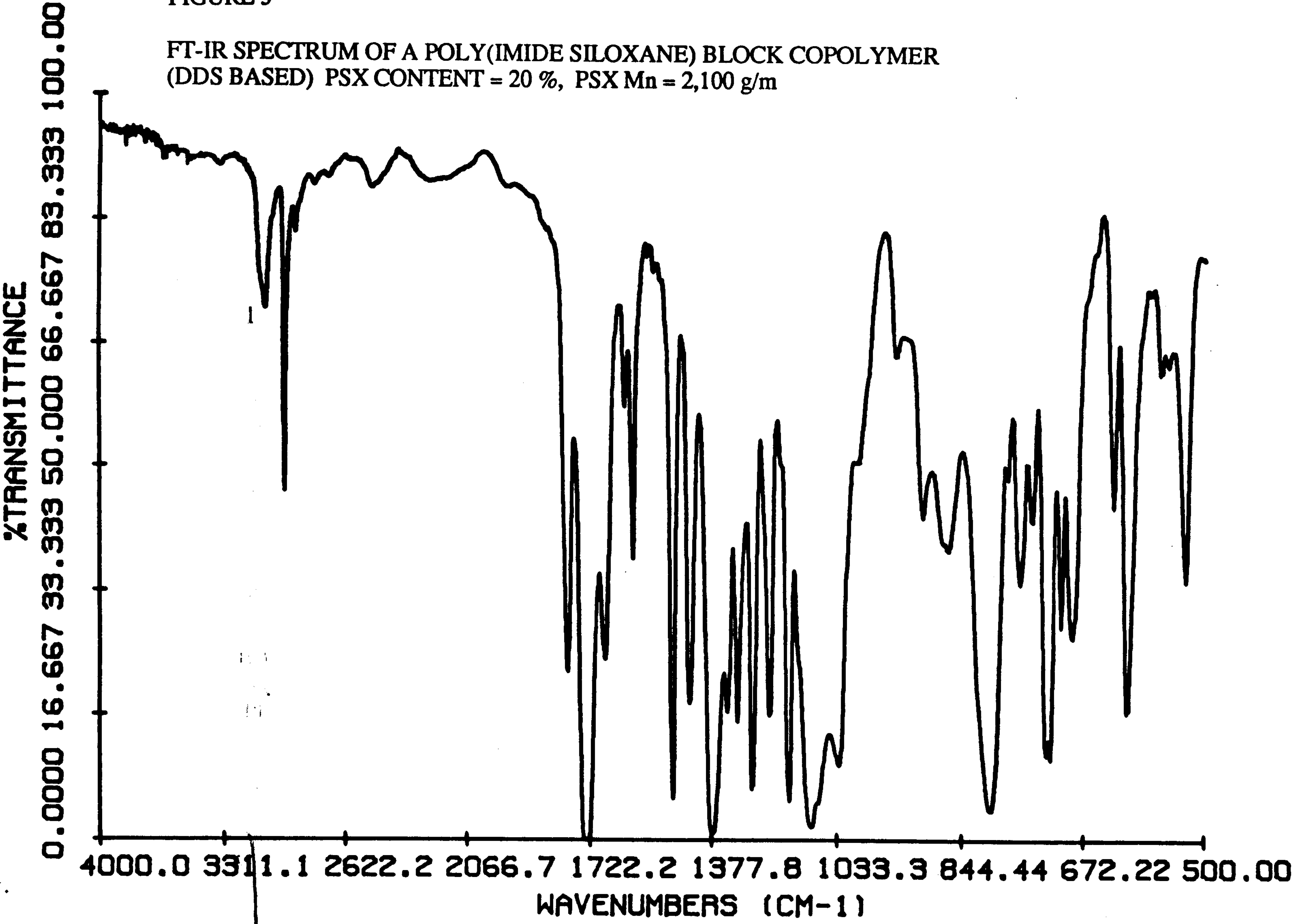


FIGURE 4

PROTON NMR SPECTRUM
POLY(IMIDE SILOXANE) BLOCK COPOLYMER
40 wt. % PSX (Mn = 950 g/m)

38 wt. % PSX INCORPORATED BY NMR

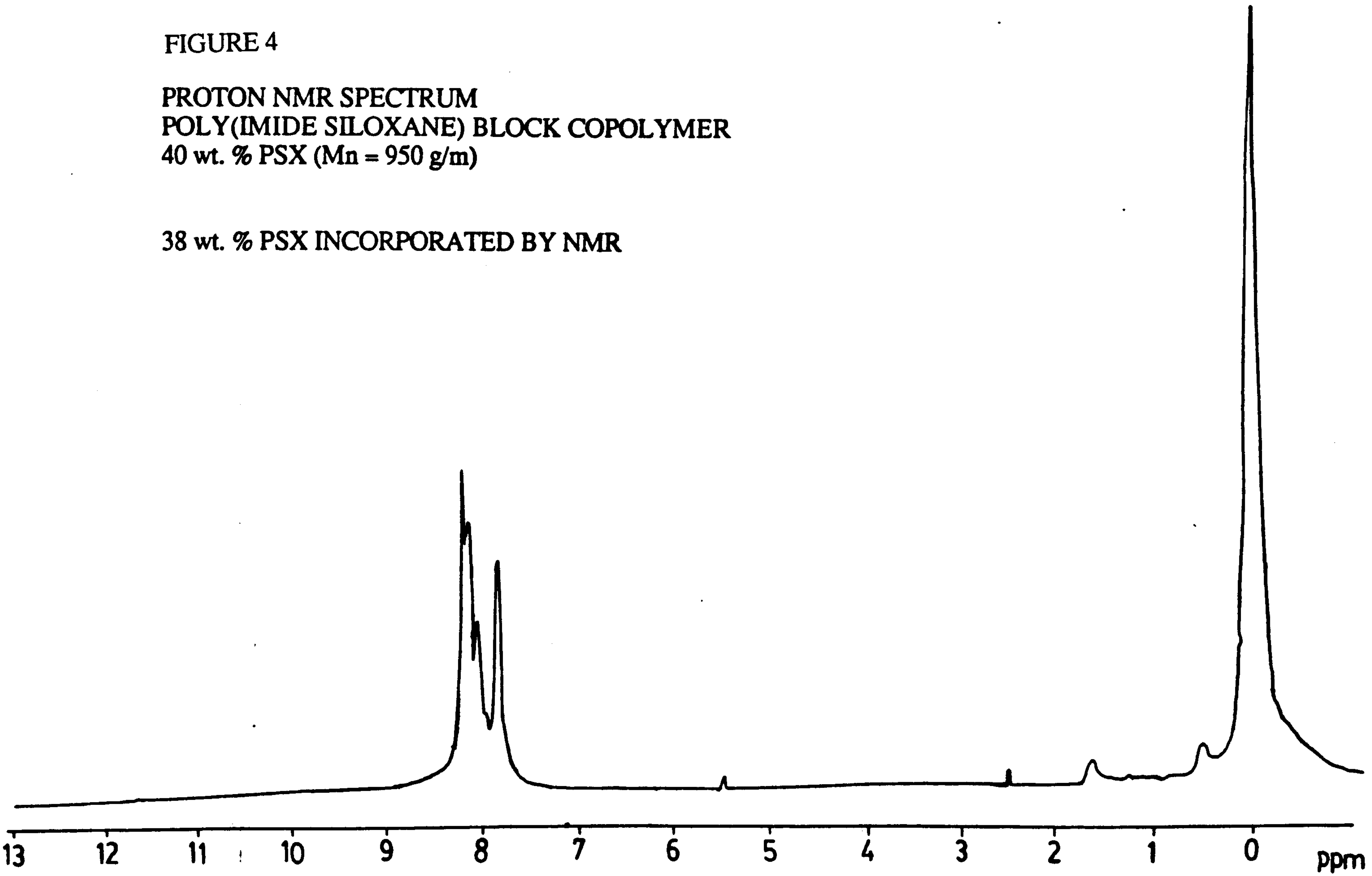


FIGURE 5

GPC TRACE
POLY(IMIDE SILOXANE) BLOCK COPOLYMER
60 wt. % PSX (Mn = 950 g/m)

SOLVENT: THF
DETECTOR: UV

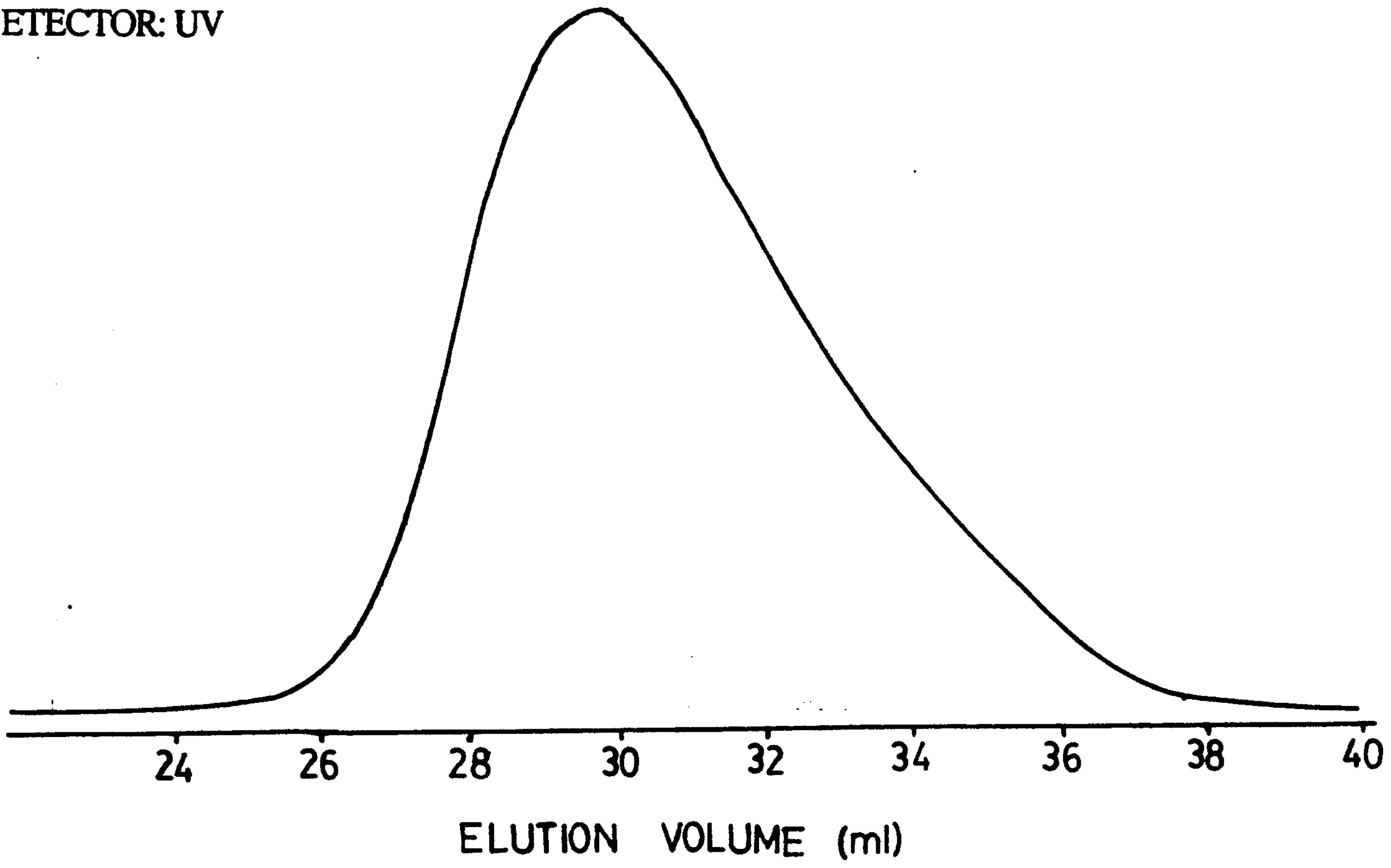


FIGURE 6

THERMOGRAVIMETRIC ANALYSIS OF
POLY(IMIDE SILOXANE) COPOLYMERS
(3,3'-DDS BASED)

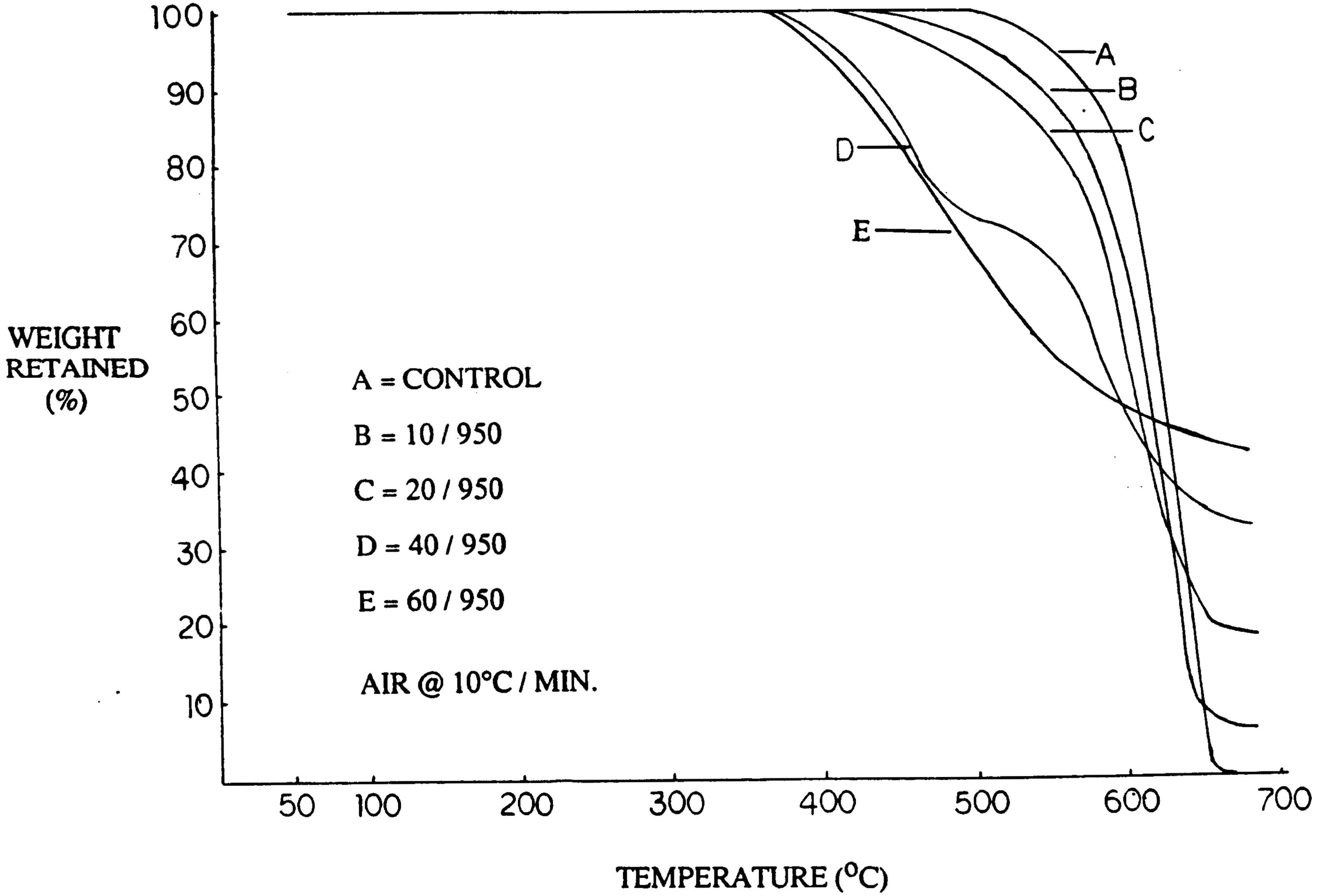


FIGURE 7

THERMOGRAVIMETRIC ANALYSIS OF
POLY(IMIDE SILOXANE) COPOLYMERS
(3,3'-DDS BASED)

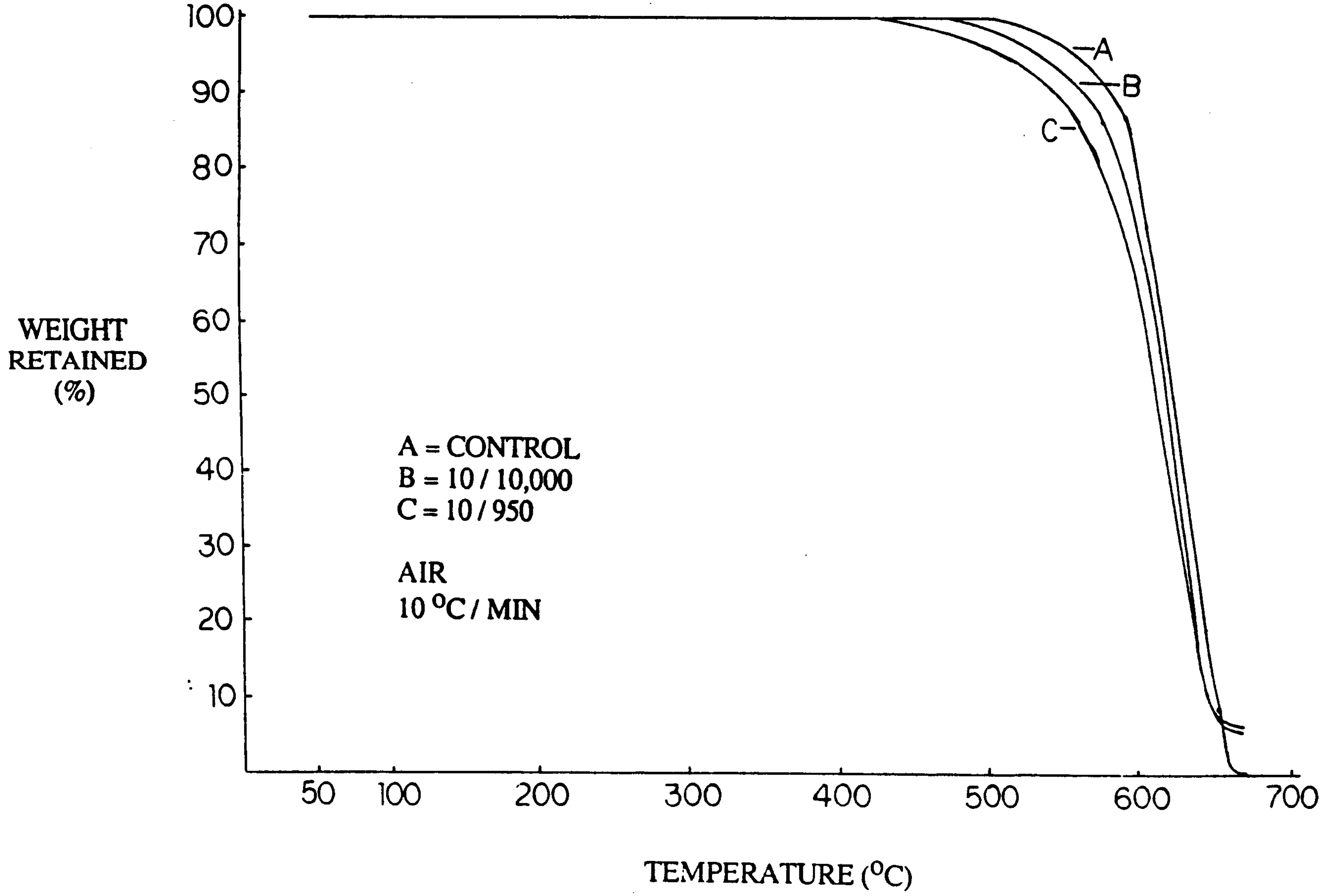


FIGURE 8

TMA PENETRATION CURVES FOR POLY(IMIDE SILOXANE) COPOLYMERS (3,3'-DDS BASED)

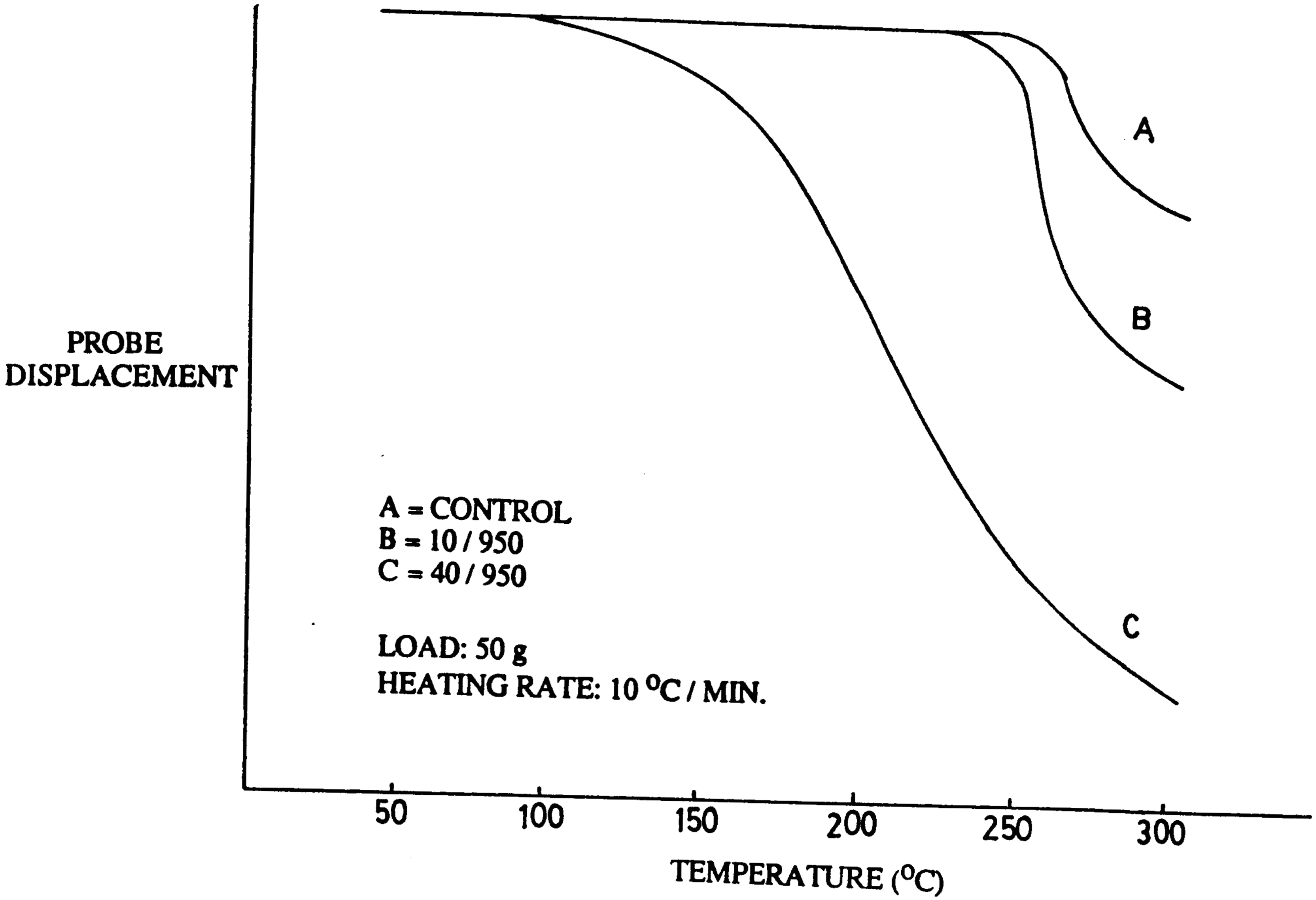
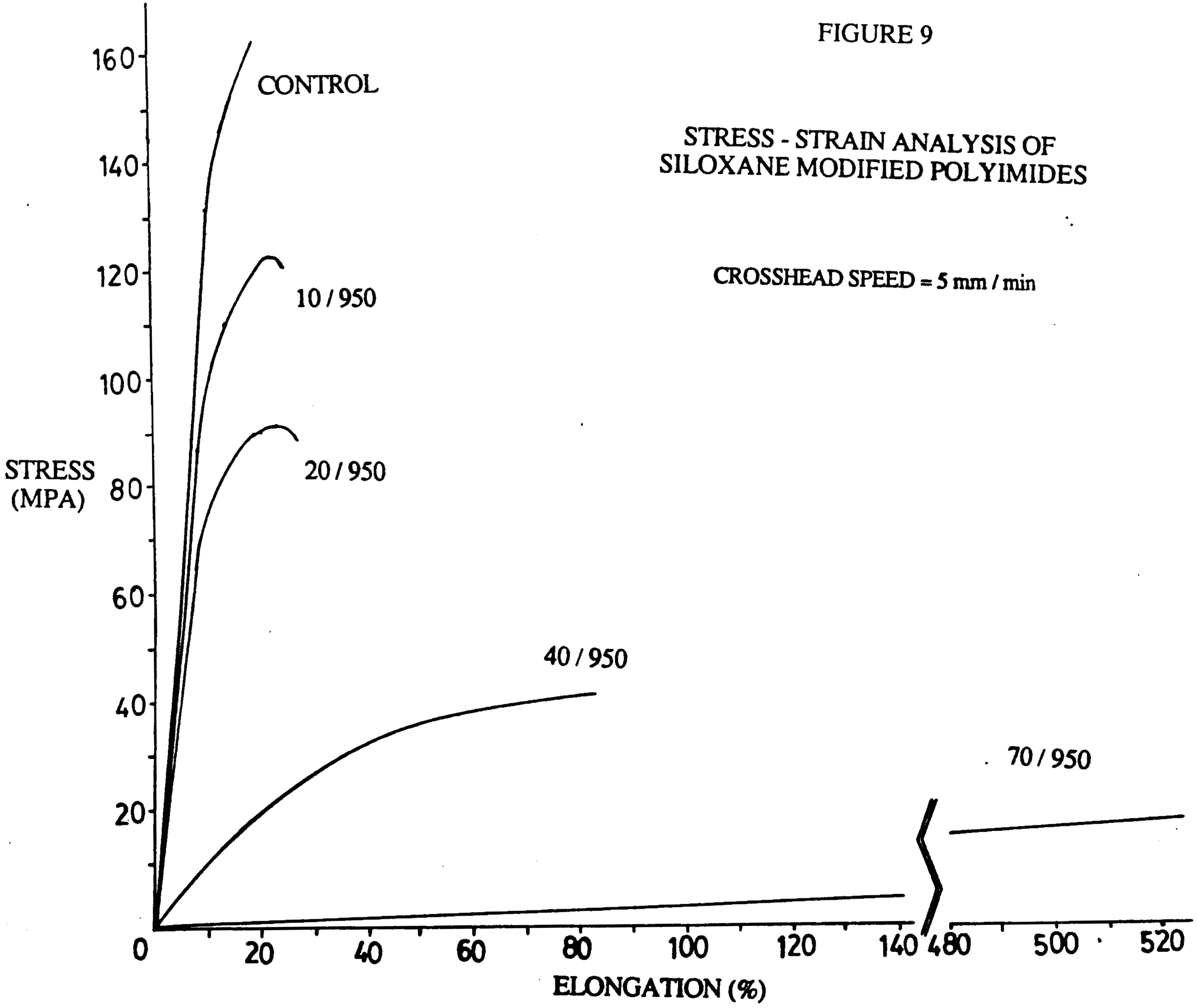


FIGURE 9

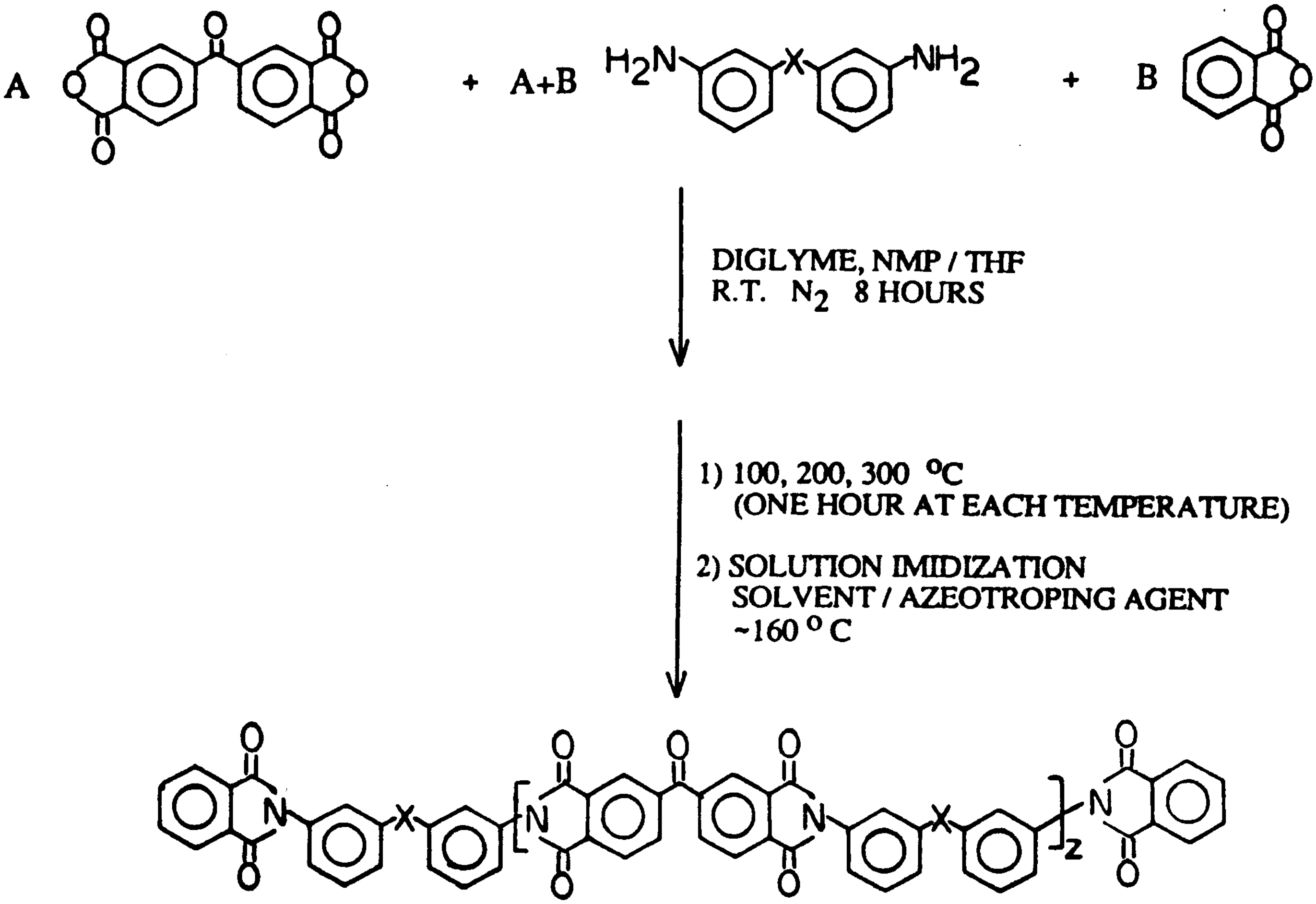


STRESS - STRAIN ANALYSIS OF
SILOXANE MODIFIED POLYIMIDES

CROSSHEAD SPEED = 5 mm / min

FIGURE 10

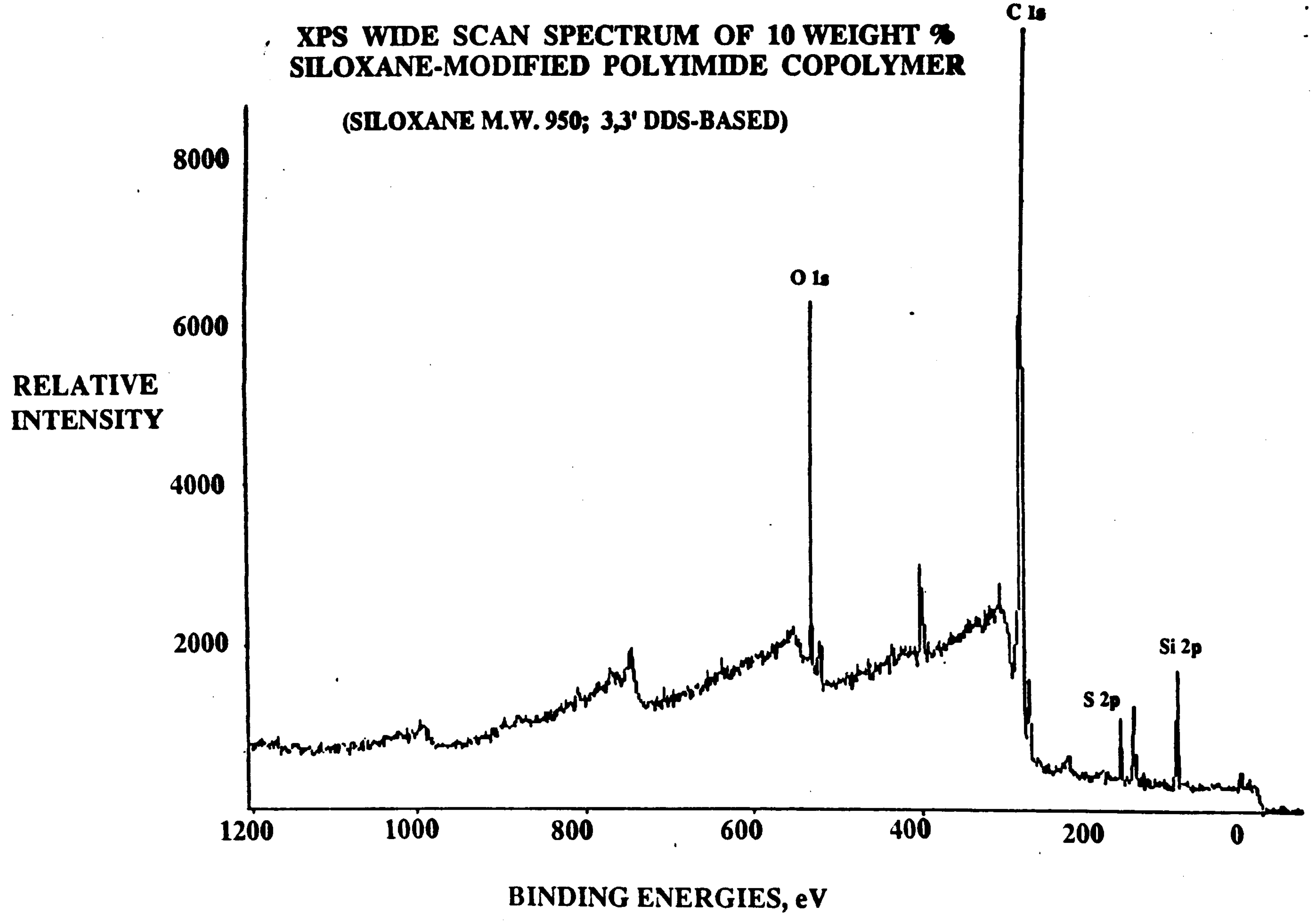
MOLECULAR WEIGHT AND END GROUP CONTROL IN THERMOPLASTIC IMIDE (CO)POLYMERS



X = SO_2, CO

- * CONCENTRATION OF "3" CONTROLS Mn AND END GROUP
- * SILOXANE SEGMENTS MAY BE INCORPORATED, IF DESIRED

FIGURE 11



XPS WIDE SCAN SPECTRUM OF 10 WEIGHT %
SILOXANE-MODIFIED POLYIMIDE COPOLYMER

(SILOXANE M.W. 950; 3,3' DDS-BASED)