

**Thiophene-Based Poly(arylene ether ketone)s: 2. Thermal
and Mechanical Properties of Amorphous Systems Using
Bis(p-fluorobenzoyl)aryl Monomers.**

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ABSTRACT

A series of high molar mass and controlled molar mass poly(aryl ether ketone)s were synthesized based on bis(*p*-fluoro-benzoyl)aryl monomers and 4,4'-isopropylidenediphenol. The central aromatic unit of the activated bishalide was varied to include 1,4 phenylene, 2,5 thiophene, and 1,3 phenylene to systematically change the exocyclic bond angle from 180° to 148° to 120°, respectively. The thermal, dynamic mechanical and mechanical properties of the three polymers were determined for the controlled molar mass materials. The glass transition temperature of the controlled molar mass 2,5-thiophene based polymer was 147°C compared to 149°C for 1,3-phenylene based polymer and 162°C for the 1,4-phenylene based polymer. The thermal stability of poly(BFTh-BisA) was similar to that of poly(1,3-BFB-BisA) and poly(1,4-BFB-BisA). Two sub T_g loss dispersions were measured for each of the three polymers. The pronounced γ relaxation for poly(BFTh-BisA), poly(1,4-BFB-BisA), and poly(1,3-BFB-BisA), has an activation energy of 7.5, 9.0, and 10 kcal/mole, respectively. The activation energy of β dispersion for poly(BFTh-BisA) is 16 kcal/mole. The Young's modulus is 2.9 GPa, 3.1 GPa and 3.6 GPa for poly(1,4-BFB-BisA), poly(2,5-BFTh-BisA) and poly(1,3-BFB-BisA), respectively.

(Keywords: poly(arylene ether ketone), thiophene, bishalide, DSC, TGA, DMS, mechanical property)



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INTRODUCTION

The demands for thermally stable polymers as replacements for metals and ceramics in industry have significantly increased during last decade¹. A general class of poly(aryl ether ketone)s has received considerable attention because of their unique combination of thermal stability, mechanical properties, and solvent resistance. Poly(aryl ether ether ketone) (PEEK), which represents one commercially available poly(aryl ether ketone), exhibits a high melting temperature and yet it can be processed by conventional techniques such as extrusion and injection molding². Thus, this semicrystalline polymer has been successfully applied in the areas of electrical and electronic materials, structural composites, and bioengineering³⁻⁶. Another unique member of the high performance poly(aryl ether ketone) family is poly(aryl ether ketone ketone) (PEKK), which consists of a higher percentage of keto linkages (67%) compared to PEEK (33%)⁷. Although PEKK has most of the same advantages as PEEK, its melting temperature is too close to its decomposition temperature to process. The most common approach of lowering the melting temperature and retaining the thermal stability is to substitute monomers into the polymer structure that disrupt linearity and/or increase chain flexibility⁸. Recently, a series of amorphous, high molar mass poly(aryl ether ketone)s, that incorporate these principles, have been synthesized by DeSimone et al⁹. These poly(aryl ether ketone)s can be considered as model polymers because of their unique structures, which are illustrated in Scheme I. The exocyclic bond angles of the central aromatic units are 180°, 148°, and 120°, corresponding to 1,4 linked phenyl group, 2,5 thiophene group, and 1,3 linked phenyl group, respectively. Based on these structural differences, one might expect that the glass transition temperature of the 2,5 thiophene based polymer is between that of the 1,4 phenylene based polymer and the 1,3 phenylene based polymer. The ability to introduce the thiophene unit into the polymer backbone makes it possible to study the thermal and physical properties of

these high performance polymers in terms of the influence of both geometrical and chemical variations.

The objective of this study was to evaluate the relationships between the structures and the thermal behavior of each of the three polymers using DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis). In addition to the thermal properties, the dynamic mechanical behavior and stress-strain response were determined.

EXPERIMENTAL

The synthesis of the high molar mass poly(arylene ether ketones) was described elsewhere⁹. Controlled molar mass polymers were obtained by upsetting the stoichiometric balance, as defined by the Carother's equation, of the monomers through the addition of monofunctional tert-butyl phenol. The intrinsic viscosities are listed in Table I for the series of polymers. The first batch represents the high molecular weight polymers and the second batch represents controlled molecular weight by end capping. The number average molecular weights, listed for the controlled molar mass samples, were determined by ¹H NMR⁹.

The glass transition temperatures for all polymers were evaluated in a SEIKO DSC220C with a scan rate of 10°C/min from room temperature to 300°C in a nitrogen atmosphere maintained at a flow rate of 100 ml/min. The DSC samples were prepared by weighing 10 mg of each polymer in the aluminum pans for analysis. The instrument was calibrated with indium and tin standards. The glass transition temperature is calculated as the intermediate point of the discontinuity between two baselines in the thermograms.

The dynamic thermal stability for all polymers were determined by using a SEIKO TG/DTA320 with a heating rate of 20°C/min from room temperature to 1200°C under a nitrogen or air atmosphere. The temperature at 5% weight loss was designated the decomposition temperature ($T_d^{5\%}$).

The dynamic mechanical behavior of controlled molar mass polymers were determined with a SEIKO DMS200(FT) operated by a SEIKO SDM/5600H computer.

Because there was at least 2% residual solvent in each of the three polymers as-received, approximately 1.7 grams of each polymer was dried at 180°C under a vacuum of 28 in Hg for at least 24 hours prior to use. The DMS sample plaques were prepared in a hydrostatic hot press, which was preheated to 280°C. The lower mold plate and sample were placed on the lower heated platen and then covered with a second plate after 10 minutes. The mold was held at 280°C for 60 minutes. Pressure was applied and then slowly increased to 3200 PSI and held for 20 minutes. The power was then turned off and the samples were allowed to slowly cool to room temperature (average rate of 1°C/min) under constant pressure. Typical sample dimensions were approximately 0.3 mm thick x 7.0 mm wide x 20 mm long. The pressed films were analyzed in TG/DTA by simulating the film molding procedure. The results showed that there was less than 1% weight loss throughout the whole film stacking process.

The DMS samples, which were clamped between two heat-resistant metal chucks, were tested under the following parameters: a sinusoidal strain with a maximum amplitude of 10 μ m, frequencies ranging from 0.1 to 20 Hz, temperature ranging from -150°C to 250°C, a heating rate of 1°C/min, and a constant nitrogen flow rate of 200 ml/min. The temperature in the DMS was calibrated by using the maximum of the loss modulus peak corresponding to the T_g of standard PMMA samples at a heating rate of 1°C/min with a frequency of 1 Hz. The activation energies of β and γ dispersions for each polymer were calculated using the Activation Energy Analysis Software from results of viscoelastic measurements which employs an Arrhenius algorithm.

The mechanical properties of the second batch of polymers were determined using an Instron Universal Testing Instrument (Model 1122) according to ASTM 638 D638M. The instrument was calibrated according to the manual. The dog bone specimens were prepared using an ASTM cutting die. The typical sample dimensions were 25 mm gauge length and 2.5 mm width at the center of the specimen. Samples were tested with a typical crosshead speed of 2.5 mm/min. Five samples were analyzed for each polymer film.

RESULTS AND DISCUSSIONS

Differential Scanning Calorimetry

The three traces of the relative heat flow versus temperature are plotted in Figure 1 for the third heat of each of the controlled molar mass polymers. Only a glass transition for each of three polymers is apparent. The glass transition temperatures and derivative DSC peak temperatures decrease with a corresponding reduction of the central unit exocyclic bond angles, which suggests that the chain mobilities increase in the order of poly(1,4-BFB-BisA) and poly(1,3-BFB-BisA) as predicted. However, poly(BFTh-BisA) does not follow this prediction, in that its glass transition temperature is lower than that of poly(1,3-BFB-BisA) which has the larger exocyclic bond angle. The small endothermic peak existing close to the final point of discontinuity on each DSC curve might be ascribed to the non equilibrium solid state of the glassy polymer upon cooling below the T_g^{10} . The excess enthalpy of the endothermic peak for each of three polymers, as calculated by integration of the peak area, is 0.2 ± 0.1 mJ/mg. There was no sign of crystallization or melting in any of the thermograms of the three polymers which is as expected for most polymers with bis(phenol A) in the backbone structure. As shown in Table I, a higher glass transition temperature was exhibited by each of the three higher molar mass polymers. However, the higher molar mass sample of poly(BFTh-BisA) has a higher T_g than that of the controlled molar mass samples of poly(1,3-BFB-BisA).

Thermogravimetric Analysis

The decomposition temperatures ($T_d^{5\%}$) of the high molar mass samples, as listed in Table II, increased in the order of poly(1,4-BFB-BisA), poly(BFTh-BisA), and poly(1,3-BFB-BisA) in both nitrogen and air atmospheres. The dynamic thermal decomposition profiles under a nitrogen purge are illustrated in Figure 2 for the high molar mass samples of the three polymers. The high molar mass samples of all three polymers are quite stable under dynamic conditions in a nitrogen atmosphere up to temperatures exceeding ca. 490°C (Table II) as indicated by the $T_d^{5\%}$. Weight loss progressively increased beyond $T_d^{5\%}$ for the three polymers up to ca. 525°C. Above

ca. 525°C, a fairly stable char forms under a nitrogen atmosphere as illustrated in Figure 2. The residue on ignition at 1200°C for the high molar mass sample of poly(1,4-BFB-BisA) was the highest at 52% compared to values of 49% and 39% for poly(1,3-BFB-BisA) and poly(BFTh-BisA), respectively. However, the controlled molar mass samples (Table I) yielded residues on ignition of 42%, 44%, and 46% for poly(1,4-BFB-BisA), poly(2,5-BFTh-BisA) and poly(1,3-BFB-BisA), respectively (Table II). Thus, there is an indication that differences in molar mass, between the controlled molar mass samples and the uncontrolled molar mass samples, may have contributed to the variation in residue on ignition for the high molar mass samples.

The weight loss of the three polymers in an air purge sharply contrasts those under nitrogen as illustrated by the thermograms in Figure 3. The initial stage of weight loss for the three polymers (Fig. 3), which begins at ca. 495°C and ends at ca. 525°C, is quite similar to the weight loss profile in a nitrogen atmosphere (Fig. 2). However, the second stage of volatilization under an air purge, i.e. ca. 525°C to 650°C, indicates different mechanisms for the degradation of poly(1,3-BFB-BisA) and poly(BFTh-BisA) compared to poly(1,4-BFB-BisA) material (Fig. 3). Poly(1,3-BFB-BisA) and poly(BFTh-BisA) exhibit a slower rate of weight loss beyond the initial stage of volatilization, whereas the weight loss of poly(1,4-BFB-BisA) proceeds quite rapidly over the same temperature range. The slower rate of volatilization of both poly(1,3-BFB-BisA) and poly(BFTh-BisA) beyond the initial stage may be due to either a cross-linking reaction and/or oxidation. This is reasonable in that degradation by chain scission would be expected to proceed at a faster rate of volatilization by formation of low molecular weight species. The results of this study are not sufficient to make this determination. However, in similar studies by Hay and Kemmish¹¹, the degradation products from the decomposition of PEEK and PEK were isolated and analyzed by mass spectroscopy. Their study demonstrated that in the thermal decomposition of PEEK and PEK, three major mechanisms were likely. The mechanisms were chain scission, cross-linking and oxidation. The study by Hay and Kemmish demonstrates that at a higher ratio of cross-linking reactions to chain scission reactions, a lower rate of volatilization would be observed. In another study,

the decomposition of poly(phenylene sulfide) (PPS) was studied by Ma et al using TGA under both nitrogen and air atmospheres¹². The well known cross-linking of PPS, in air, at temperatures exceeding 490°C were correlated with a slower rate of weight loss under air compared to nitrogen over the same temperature range¹³. Thus, it can be implied that cross-linking or oxidation must contribute to a slower volatilization of both poly(1,3-BFB-BisA) and poly(BFTh-BisA) during the second stage thermal degradation (Fig. 3). This indicates the mechanism of decomposition of the poly(1,4-BFB-BisA) material involves less cross-linking or oxidation and is dominated by chain scission over the same temperature range.

The thermal degradation of the end capped polymers offers some further insight into this behavior. The decomposition temperatures of the controlled molar mass polymers in air are 12°C, 10°C, and 3°C higher than that in nitrogen each for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA), respectively (Table II). Thus, since the presence of oxygen would provide for oxidation, this data supports the previous argument. An example of this behavior is given by the two thermograms illustrated in Figure 4 for the controlled molar mass sample of poly(BFTh-BisA) in both air and nitrogen. The overall profiles are similar to those of the uncontrolled molar mass illustrated in Fig 2 and 3. The apparent higher stability of these materials in an air atmosphere are most likely associated with the use of tert-butyl phenol as the end capping monomer to control the molar mass. The $T_d^{5\%}$ is relatively the same for all three polymers of controlled molar mass in a nitrogen gas stream or an air purge. This is attributed to the end capping that yielded three polymers of nearly equivalent molecular weight and thus an equivalent number of end groups.

Dynamic Mechanical Spectroscopy

The storage modulus (E'), loss modulus (E''), and $\tan \delta$ are plotted as a function of temperature in Figure 5 for the uncontrolled molar mass samples of poly(1,4-BFB-BisA), poly(BFTh-BisA), and poly(1,3-BFB-BisA), measured at a frequency of 1 hz. The storage moduli (Figure 5a) for all three polymers is approximately 3 GPa at a temperature of -150°C and begins to decrease slowly as the temperature of the

experiment is increased up to the onset of the glass transition. A drop of nearly three orders of magnitude occurs at the glass transition temperature followed by a stable region for all three polymers. The T_g was 149°C, 151°C, and 162°C for the poly(BFTh-BisA), poly(1,3-BFB-BisA) and poly(1,4(BFB-BisA) samples, respectively. The samples underwent considerable deformation beyond the T_g . The storage modulus reflects a small drop at sub ambient temperatures associated with two dispersions detected for each of the polymers. The loss modulus and $\tan \delta$ (Figures 5b and 5c, respectively) illustrate the nature of these transitions more clearly. The first relaxation is detected around -120°C to -90°C with a maximum loss modulus at -102°C for poly(1,4-BFB-BisA), -99°C for poly(1,3-BFB-BisA) and -91°C for poly(BFTh-BisA). These low temperature relaxations are normally attributed to local oscillations in the polymer backbone. The γ relaxation for poly(BFTh-BisA), poly(1,4-BFB-BisA), and poly(1,3-BFB-BisA) has an activation energy of ca. 7.5, 9.0, and 10 kcal/mole, respectively. In the case of other poly(arylene ether)s and poly(phenylene sulfide), Eisenberg et al.¹⁴ reported that a β relaxation for poly(p-phenylene oxide) (PPO) at -113°C has an activation energy of 12 kcal/mole and was probably due to hindered oscillatory motions of the backbone phenyl groups. Others have shown that these low temperature relaxations are sensitive to the level of moisture in polymers with a phenyl ether linkage^{15, 16, 17}. In preparation of our samples, every effort was made to insure dry samples, yet it is possible that the dispersions at near -100°C are partially the result of adsorbed moisture.

The next loss dispersion, referred to as the β relaxation, which was detected in the plot of the loss modulus and $\tan \delta$ of these materials is not clearly separate from the lower temperature γ relaxation. It is, however, apparent from examination of the profiles in Figs. 4b and 4c, that the β relaxation for the poly(BFTh-BisA) material is most prominent with a maxima at ca. -38°C. The β relaxation found for poly(BFTh-BisA) has an apparent activation energy of ca. 16 kcal/mole.

Mechanical Properties

The plot of engineering stress versus elongation for representative samples of

all three polymers are illustrated in Figure 6. The modulus of the three polymers decrease slightly in the order of 3.58 GPa for poly(1,3-BFB-BisA), 3.13 GPa for poly(BFTh-BisA), and 2.92 GPa for poly(1,4-BFB-BisA) (Table III). This suggests that poly(1,3-BFB-BisA) is the stiffest material among the three polymers which is reflected both in these measurements and the storage modulus at room temperature (Fig 4a). The poly(1,4-BFB-BisA) is the most ductile material with a maximum elongation of 66% compared to the brittle poly(1,3-BFB-BisA) with a maximum elongation of 5.33%. One might offer as an explanation for the observed trend the effect of molecular structure. Poly(1,4-BFB-BisA), which contains a central unit with a 180° bond angle, favors chain movement during a cold flow process. However, poly(1,3-BFB-BisA), has a 120° central unit bond angle and thus kinks the main chain, hindering chain movement and results in its brittle material behavior. This also may be the reason that the modulus, stress and strain at yield, and stress and strain at break of poly(BFTh-BisA) are intermediate between poly(1,4-BFB-BisA) and poly(1,3-BFB-BisA). It is apparent from the results that the differences in overall mechanical properties are slight, but that the trend exists.

CONCLUSIONS

The three new poly(aryl ether ketone)s have quite unique structures which give rise to different thermal and physical properties. The glass transition temperature of controlled molar mass poly(BFTh-BisA) is 147°C compared to 149°C for the poly(1,3-BFB-BisA) and 162°C for poly(1,4-BFB-BisA). All three polymers are thermally stable under dynamic conditions up to temperatures up to ca. 490°C in nitrogen and temperatures up to nearly 480°C in air. A higher thermal stability in air measured for the controlled molar mass samples is tentatively assigned to oxidation or cross linking of the tert-butyl phenol end group at temperatures greater than 475°C. Two low temperature dispersions are found for each of the polymers. The pronounced γ relaxation for poly(BFTh-BisA), poly(1,4-BFB-BisA), and poly(1,3-BFB-BisA), has an activation energy, respectively, of ca. 7.5, 9.0, and 10 kcal/mole. The storage modulus at room temperature and the Young's modulus decrease in the order of

poly(1,3-BFB-BisA), poly(BFTh-BisA) and poly(1,4-BFB-BisA) which correlates to a decreasing exocyclic bond. The overall properties of the thiophene containing poly(arylene ether ketone) are comparable to the two poly(arylene ether ketone)s described in this report.

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FIGURE CAPTIONS

- Figure 1 - DSC thermogram for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA). Heating rate = 10°C/min; N₂ purge = 100 ml/min
- Figure 2 - TGA thermogram for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA). Heating rate = 20°C/min; N₂ purge = 100 ml/min
- Figure 3 - TGA thermogram for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA). Heating rate = 20°C/min; Air purge = 100 ml/min
- Figure 4 - TGA thermogram controlled molar mass sample of poly(BFTh-BisA) in air and nitrogen atmospheres. Heating rate = 20°C/min; purge = 100 ml/min
- Figure 5 - a) Storage modulus for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA); b) Loss Modulus for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA); c) Tan Delta for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA). Frequency = 1 Hz; Heating rate = 1°C/min; N₂ purge = 100 ml/min.
- Figure 6 - Engineering stress versus elongation for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA), and poly(BFTh-BisA).

Table I - The Glass Transition Temperature[†]

	Poly(1,3-BFB-BisA)		Poly(BFTh-BisA)		Poly(1,4-BFB-BisA)	
$[\eta]$ (dL/g) [‡]	0.79 ^a	0.37 ^b	1.23 ^a	0.38 ^b	0.92 ^a	0.49 ^b
Mn (g/mol) [*]	NA	20,000	NA	24,000	NA	23,000
DSC T _g (°C)	154	149	156	147	166	160
DMS T _g (°C)	NA	151	NA	149	NA	162

[†] DSC T_g were obtained from the third heat at a Heating rate of 10°C/min with a N₂ flow rate of 100 ml/min. DMS T_g were measured at a heating rate of 1°C/min with a frequency of 1 Hz and a N₂ flow rate of 200 ml/min.

[‡] Intrinsic viscosity in NMP @ 25°C.

^{*} Determined by ¹H NMR using end group analysis.

^a uncontrolled molar mass

^b controlled molar mass

Table II - The Decomposition Temperature[†]

	Poly(1,3-BFB-BisA)	Poly(BFTh-BisA)	Poly(1,4-BFB-BisA)
T _d (°C) at 5% Weight Loss (N ₂)	495 ^a	496 ^a	521 ^a
	489 ^b	488 ^b	478 ^b
T _d (°C) at 5% Weight Loss (Air)	475 ^a	481 ^a	513 ^a
	499 ^b	491 ^b	490 ^b
Total Weight Loss in N ₂ (%)	51 ^a	61 ^a	48 ^a
	54 ^b	58 ^b	56 ^b

[†] Gas flow rate: 100 ml/min, Heating rate: 20°C/min, Temperature ranging from 25°C to 1200°C.

^a The first batch polymers.

^b The second batch polymers.

Table III. Mechanical Properties[†]

	E' (GPa)	Stress at Yield (MPa)	Strain at Yield (%)	Stress at Break (MPa)	Strain at Break (%)
Poly(1,3-BFB-BisA)	3.58 (0.2)	86.4 (0)	3.43 (0)	83.9 (12)	3.73 (0.8)
Poly(BFTh-BisA)	3.13 (0.2)	75.6 (2.3)	3.69 (0.1)	65.0 (6.8)	20.6 (11)
Poly(1,4-BFB-BisA)	2.92 (0.4)	70.3 (5.5)	3.41 (0.1)	63.4 (6.9)	40.0 (25)

[†] The data were obtained from the average values of five dog bone samples.

1. Only second batch polymers were tested.

2. Gauge length: 25 mm; Crosshead speed: 2.5 mm/min; Room Temperature

FIGURE 1

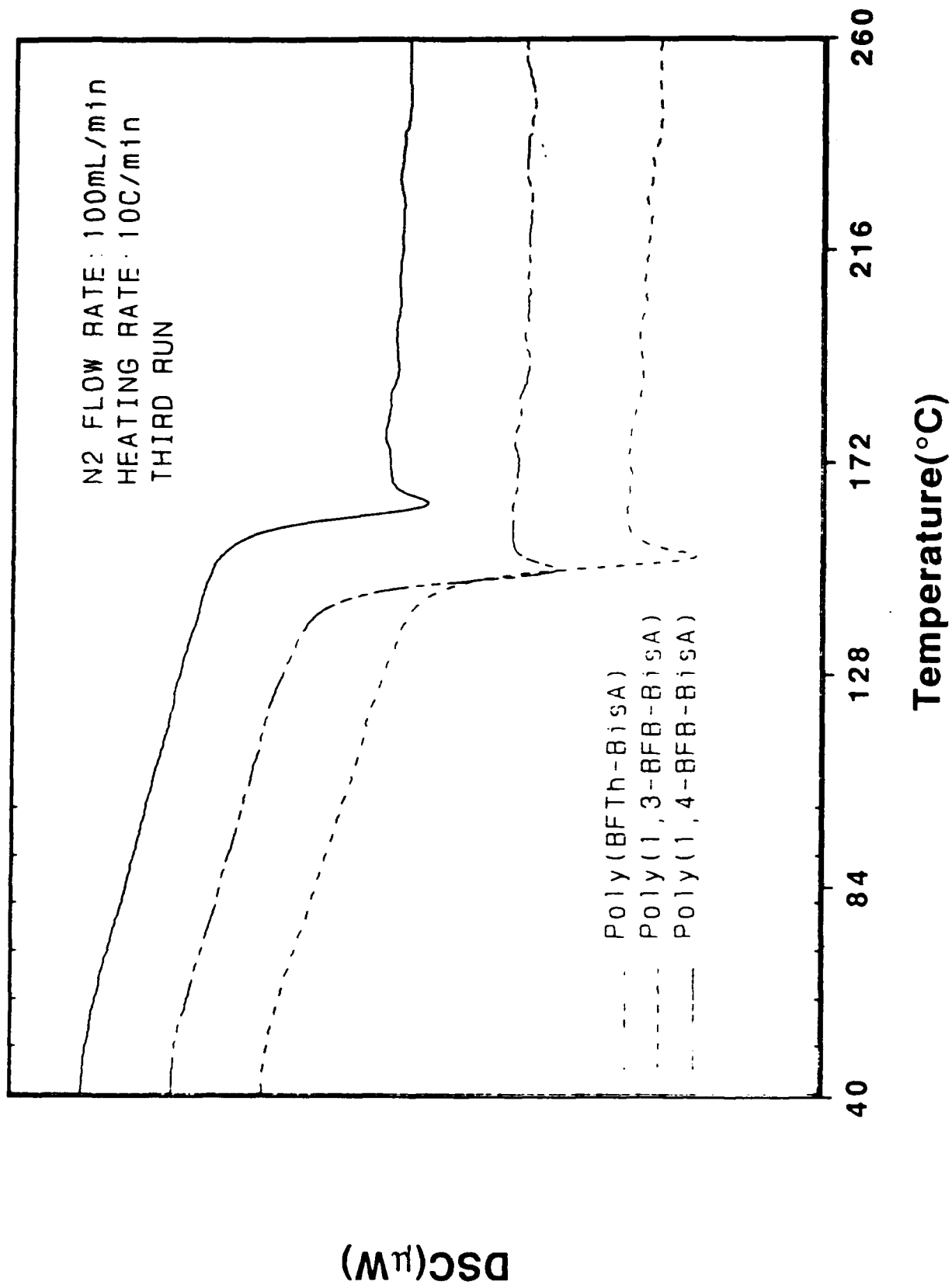


FIGURE 2

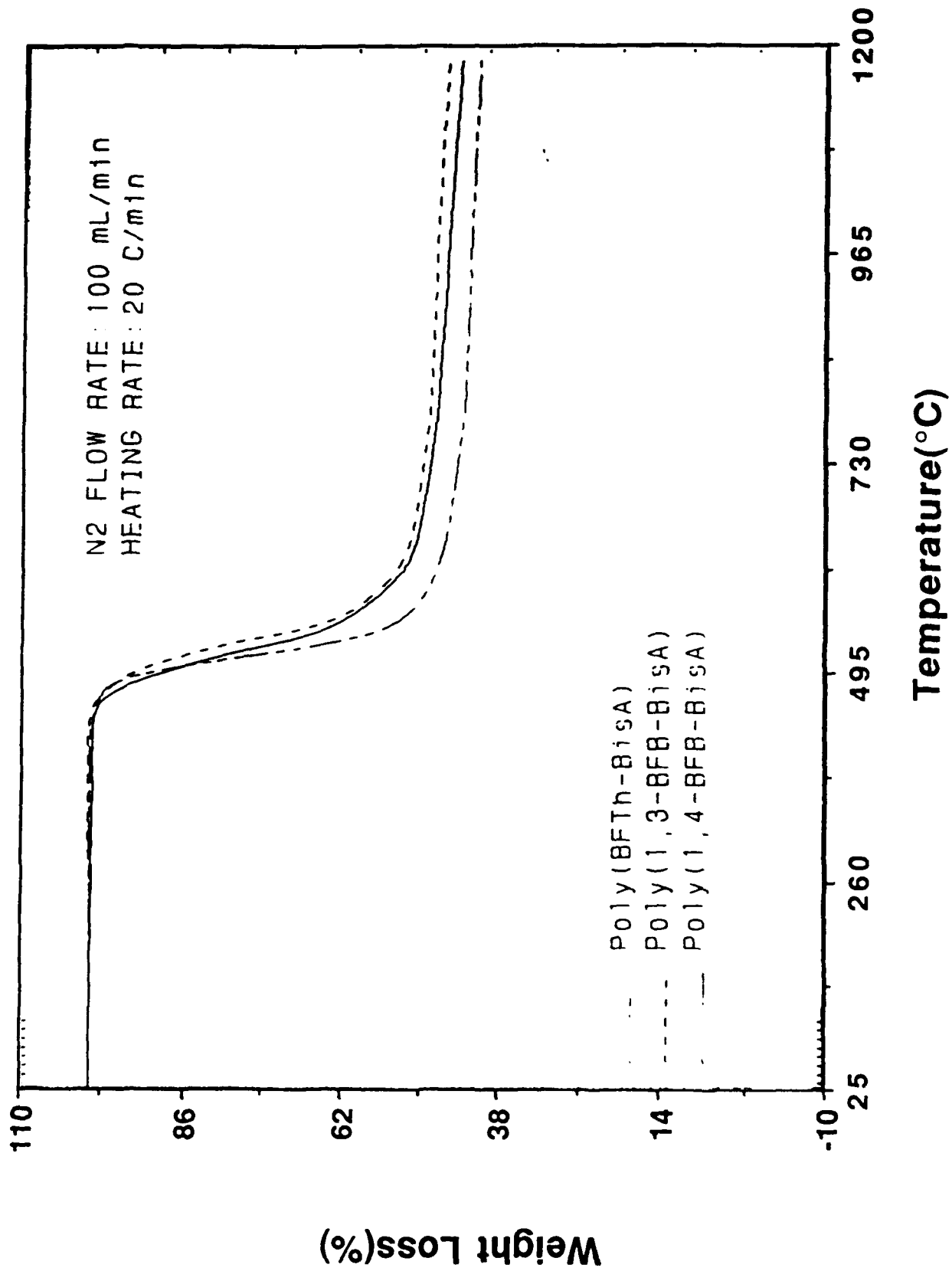


FIGURE 3

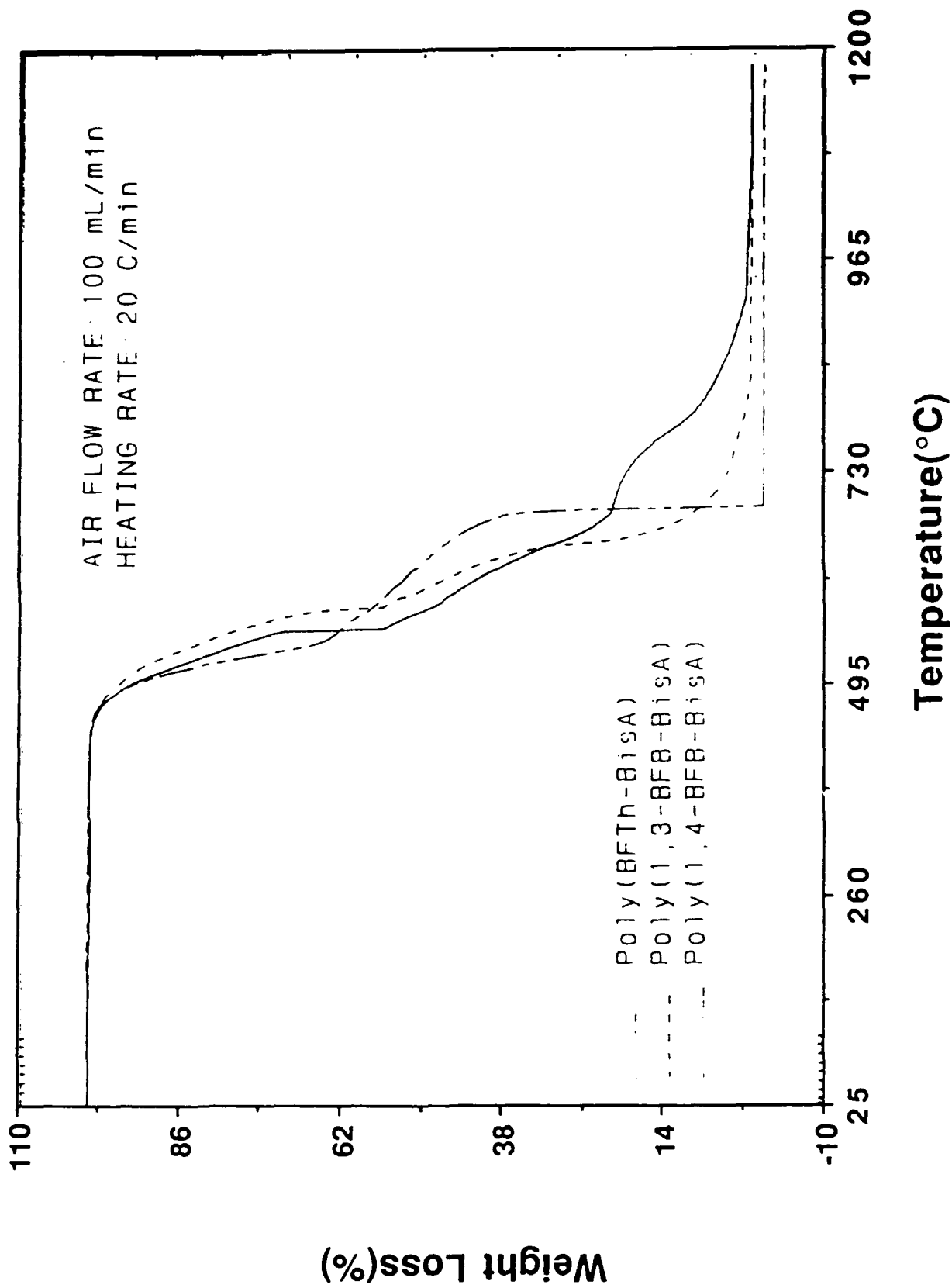


FIGURE 4

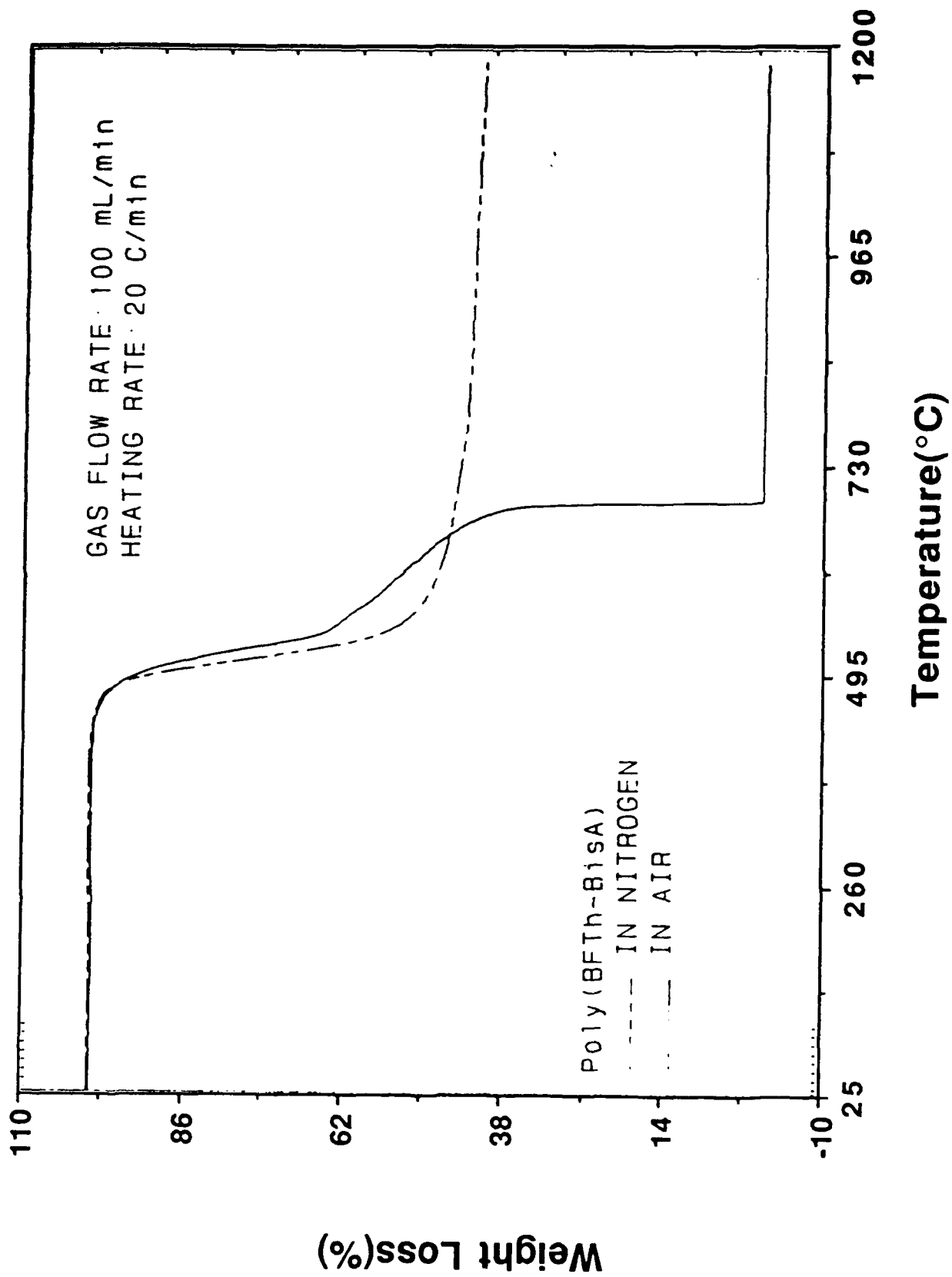


FIGURE 4a

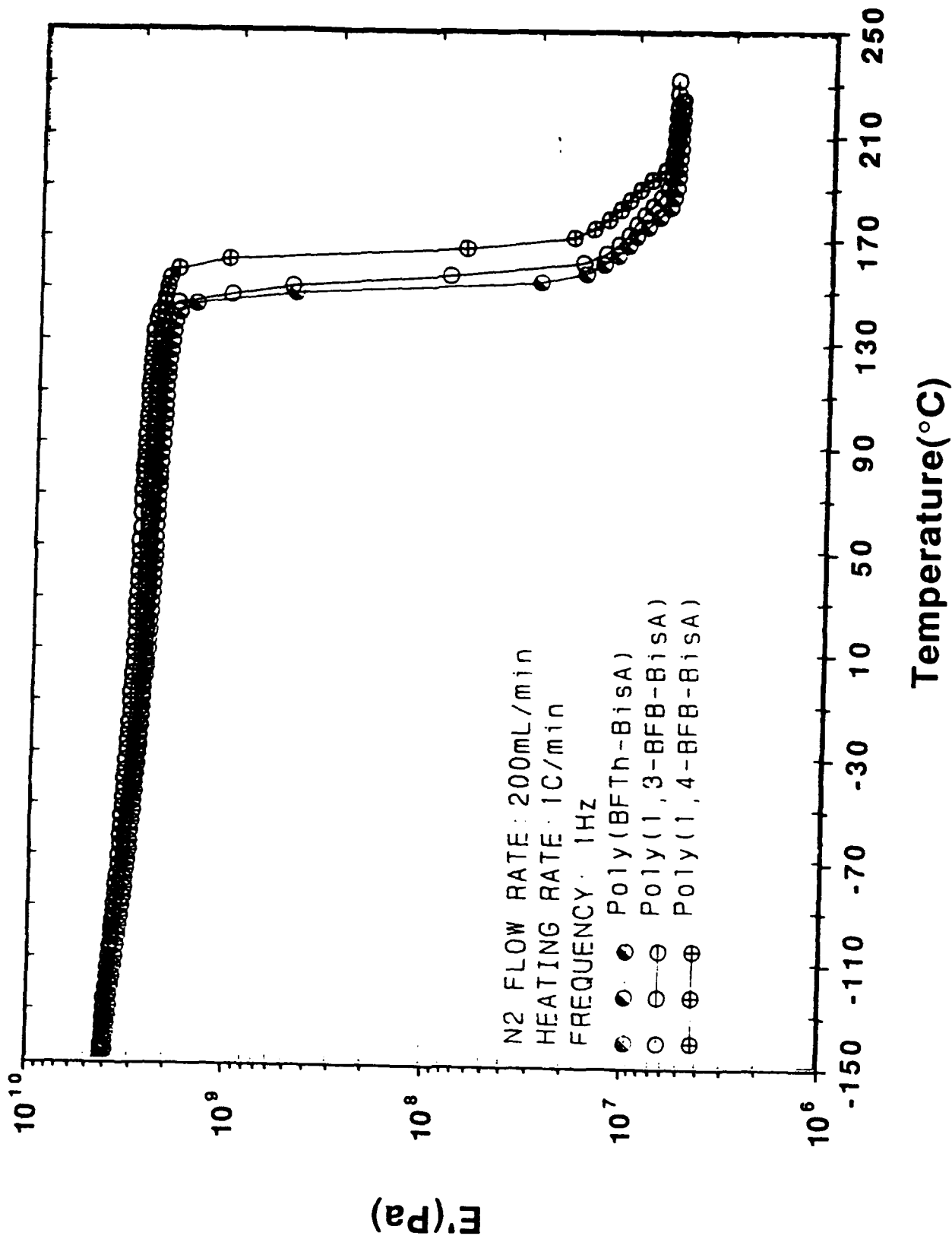


FIGURE 4b

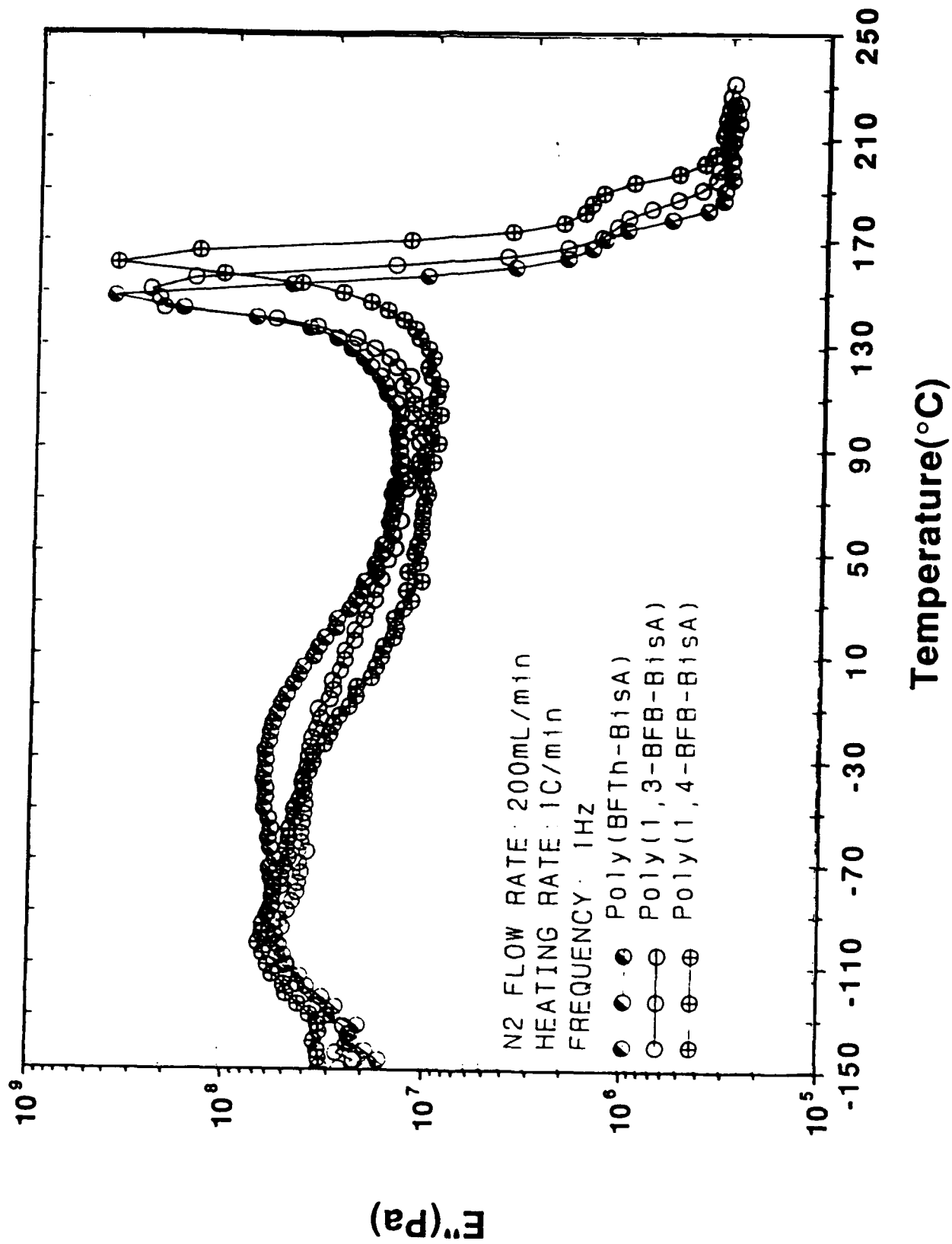


FIGURE 4c

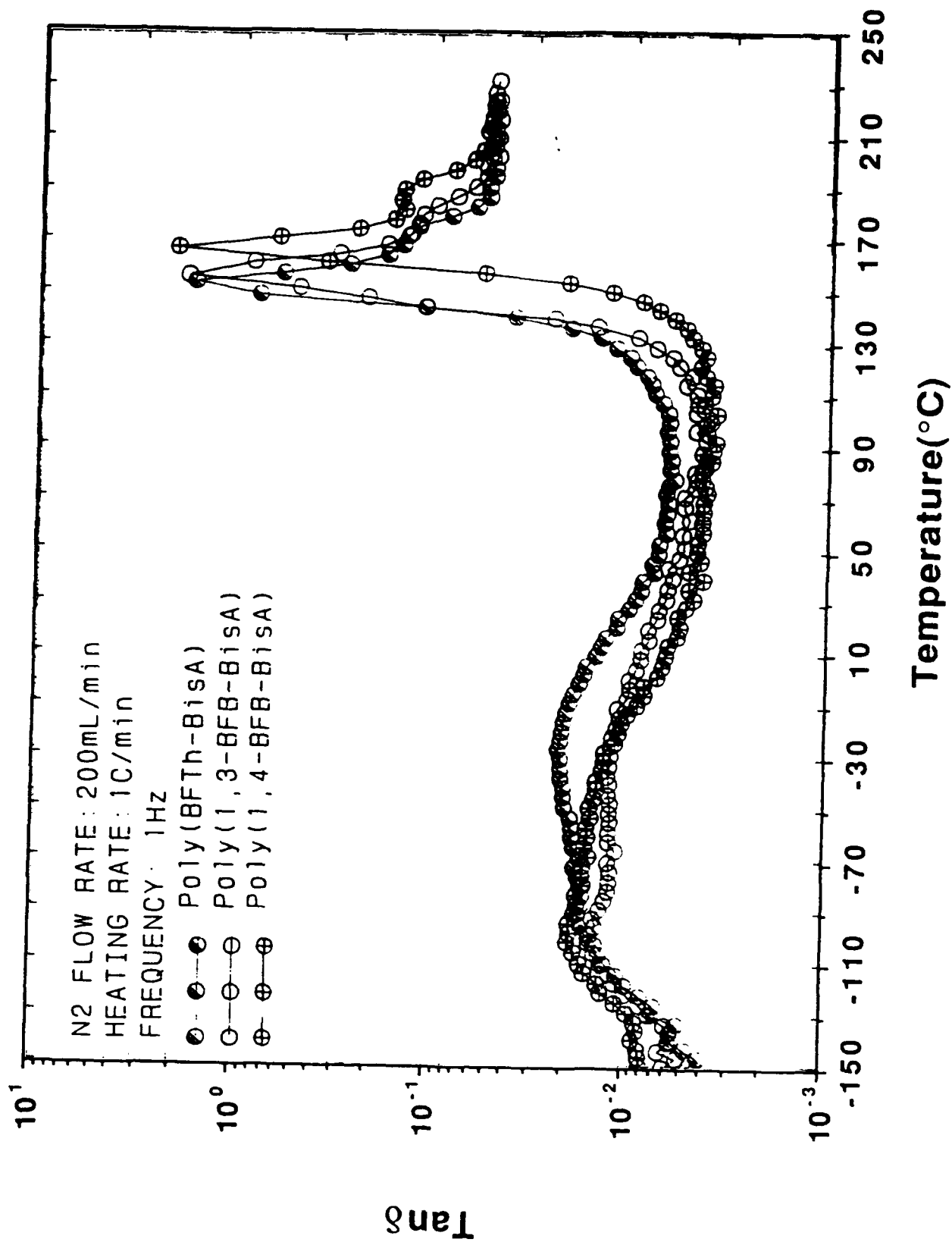


FIGURE 5

