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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A series of high-molar-mass and controlled-molar-mass poly(arylene ether ketone)s were synthesized based on bis(*p*-fluorobenzoyl)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, which changed the exocyclic bond angle from 180° to 148° to 120°, respectively. The decrease in exocyclic bond angle decreased the glass transition temperature of the uncontrolled-molar-mass polymers from 166°C to 156°C to 154°C, respectively. The T_g of the controlled-molar-mass polymer decreased from 160°C to 147°C to 149°C for the same series, i.e. poly(1,4-BFB-BisA), poly(BFTh-BisA) and poly(1,3-BFB-BisA), respectively. The discrepancy between the two series was interpreted in terms of molar-mass differences. The thermal stability of the three polymers also decreased in the order of decreasing exocyclic bond angles. Young's modulus increased as the exocyclic bond angle was decreased, which is explained in terms of the activation theory of Eyring. These three polymers represent a new approach for the study of structure–property relationships in poly(arylene ether ketone)s.

(Keywords: poly(arylene ether ketone); thiophene; bishalide; differential scanning calorimetry; thermogravimetric analysis; dynamic mechanical spectroscopy; mechanical properties)

INTRODUCTION

The demands for thermally stable polymers as replacements for metals and ceramics in industry have significantly increased during the last decade[1]. A general class of poly(arylene ether ketone)s has received considerable attention because of their unique combination of thermal stability, mechanical properties and solvent resistance. Poly(arylene ether ether ketone) (PEEK), which represents one commercially available poly(arylene ether ketone), exhibits a high melting temperature and yet it can be processed by conventional techniques such as extrusion and injection moulding[2]. Thus, this semicrystalline polymer has been successfully applied in the areas of electrical and electronic materials, structural composites and bioengineering[3–6]. Another unique member of the high-performance poly(arylene ether ketone) family is poly(arylene 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 be able to process it. One approach used to lower the melting temperature, and yet retain the thermal stability, is to substitute monomers into the polymer structure that disrupt linearity and/or increase chain flexibility[8]. Recently, a series of amorphous, high-molar-mass poly(arylene ether ketone)s that incorporate these principles have been synthesized by DeSimone *et al.*[9]. These poly(arylene ether ketone)s can be considered as model polymers because of their unique structures, which are illustrated in *Scheme 1*. The exocyclic bond angles of the central aromatic units are 180°, 148° and 120°, corresponding to a *para*-substituted phenyl ring, a 2,5-thiophene group and a *meta*-substituted phenyl ring, respectively. Based on these structural differences, one might expect that the glass transition temperature (T_g) of poly(BFTh-BisA) is between the T_g of poly(1,4-BFB-BisA) and that of poly(1,3-BFB-BisA). The ability to introduce the 2,5-substituted thiophene ring into the polymer backbone makes it possible now to study systematically the thermal and physical properties of these high-performance polymers in terms of the influence of both geometrical and chemical variations. Preliminary d.s.c. and t.g.a. results were reported for the uncontrolled-molar-mass samples. The objective of this study is to report the effect of molar

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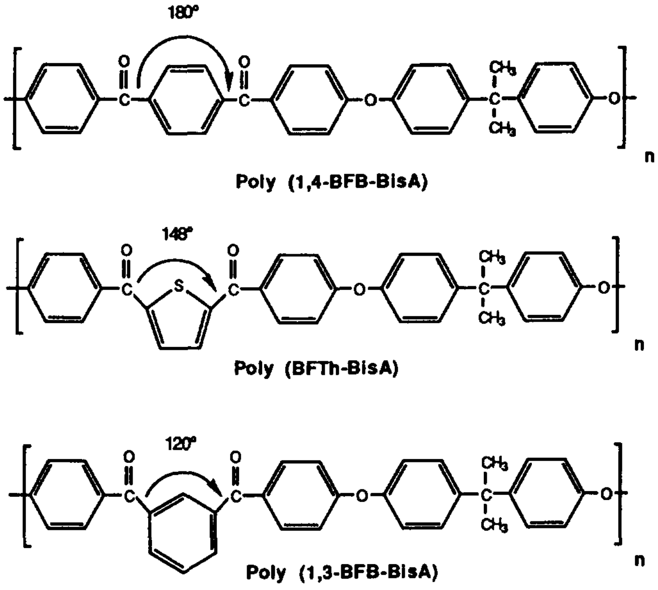
mass on thermal properties and to report for the first time the influence of the exocyclic bond angle on the mechanical behaviour of these engineering resins.

EXPERIMENTAL

The synthesis of the high-molar-mass poly(arylene ether ketone)s was described elsewhere[9]. Controlled-molar-mass polymers were obtained by upsetting the stoichiometric balance, as defined by the Carothers equation, of the monomers through the addition of monofunctional t-butylphenol. The intrinsic viscosities are listed in *Table 1* for the series of polymers. The number-average molar masses, listed for the controlled-molar-mass samples, were determined by ^1H n.m.r.[9].

The glass transition temperatures of all polymers were evaluated in a Seiko DSC220C at a scan rate of 10°C min^{-1} from room temperature to 300°C in a nitrogen atmosphere maintained at a flow rate of 100 ml min^{-1}. The d.s.c. samples were prepared by weighing 10 mg of each polymer into aluminium 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 the two baselines in the thermograms.



Scheme 1

The dynamic thermal stability of each polymer was determined with a Seiko TG/DTA320 at a heating rate of 20°C min^{-1} from room temperature to 1200°C under a nitrogen or air atmosphere. The temperature corresponding to a 5% weight loss was designated as the decomposition temperature ($T_d^{5\%}$).

The dynamic mechanical behaviour of each controlled-molar-mass polymer was 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 g of each polymer was dried at 180°C under a vacuum of 28 inchHg (~710 mmHg, ~95 kPa) for at least 24 h prior to use. The d.m.s. sample plaques were prepared in a hydrostatic hot press, which was preheated to 280°C. The lower mould plate and sample were placed on the lower heated platen and then covered with a second plate after 10 min. The mould was held at 280°C for 60 min. Pressure was applied and then slowly increased to 3200 psi (~22 MPa) and held for 20 min. The power was then turned off and the samples were allowed to cool slowly to room temperature (average rate of 1°C min^{-1}) 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 analysed in t.g./d.t.a. by simulating the film moulding procedure. The results showed that there was less than 1% weight loss throughout the whole film stacking process.

The d.m.s. samples, which were clamped between two heat-resistant metal chucks, were tested under the following conditions: a sinusoidal strain with a maximum amplitude of 10 μm, frequencies ranging from 0.1 to 20 Hz, temperature ranging from −150 to 250°C, a heating rate of 1°C min^{-1} and a constant nitrogen flow rate of 200 ml min^{-1}. The temperature in the d.m.s. was calibrated by using the maximum of the loss modulus peak corresponding to the T_g of standard poly(methyl methacrylate) (PMMA) samples at a heating rate of 1°C min^{-1} 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 controlled-molar-mass polymers were determined using an Instron Universal Testing Instrument (model 1122) according to ASTM D638M. The instrument was calibrated according to the manual. The dogbone specimens were prepared using an ASTM cutting die. The typical sample dimensions were 25 mm gauge length and 2.5 mm width at the

Table 1 The glass transition temperatures[e] and other thermal properties

	Poly(1,3-BFB-BisA)		Poly(BFTh-BisA)		Poly(1,4-BFB-BisA)	
	(a)	(b)	(a)	(b)	(a)	(b)
[η] (dl g^{-1})[c]	0.79	0.37	1.23	0.38	0.92	0.49
M_n (g mol^{-1})[d]	n.a.	20 000	n.a.	24 000	n.a.	23 000
D.s.c. T_g (°C)[e]	154	149	156	147	166	160
D.m.s. T_g (°C)[e]	n.a.	151	n.a.	149	n.a.	162

(a) Uncontrolled-molar-mass polymers
(b) Controlled-molar-mass polymers
[c] Intrinsic viscosity in *N*-methylpyrrolidone at 25°C
[d] Determined by ^1H n.m.r. using end-group analysis
[e] D.s.c. T_g were obtained from the third heat at a heating rate of 10°C min^{-1} with a N_2 flow rate of 100 ml min^{-1}. D.m.s. T_g were measured at a heating rate of 1°C min^{-1} with a frequency of 1 Hz and a N_2 flow rate of 200 ml min^{-1}

centre of the specimens. Samples were tested with a typical crosshead speed of 2.5 mm min^{-1}. Five samples were analysed for each polymer film.

RESULTS AND DISCUSSION

Differential scanning calorimetry

The three traces of the relative heat flow *versus* temperature are plotted in *Figure 1* for the third heating run for each of the controlled-molar-mass polymers. Only a glass transition for each of the three polymers is apparent. The glass transition 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 d.s.c. curve is due to the non-equilibrium solid state of the glassy polymer upon cooling below the T_g (ref. 10). The excess enthalpy of the endothermic peak for each of the three polymers, as calculated by integration of the peak area, is 0.2 ± 0.1 mJ mg^{-1}. 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 bisphenol A as a repeat unit in the backbone structure. As shown in *Table 1*, 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 sample of poly(1,3-BFB-BisA). The trend in T_g measured for the controlled-molar-mass samples, with respect to the geometry of the polymer chain, suggests that by increasing the exocyclic bond angle the number of conformations available is increased. By evaluating the structures in *Scheme 1* in a three-dimensional sense, one would be able to verify this quite readily. Thus, the T_g decreases as the change in entropy from the glassy state to the liquid state increases. The inversion of this trend for the poly(1,3-BFB-BisA) and poly(BFTh-BisA) may be indicative of weaker intermolecular interactions for a thiophene–phenyl interaction *versus* a phenyl–phenyl interaction[1].

Thermogravimetric analysis

The decomposition temperatures ($T_d^{5\%}$) of the high-molar-mass samples, as listed in *Table 2*, 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 values listed in *Table 2* represent the average of a minimum of three separate runs per sample. The variation of decomposition temperatures for each analysis was typically less than or equal to 1°C. This is important in terms of the observations and conclusions made regarding the thermal stability of each polymer. The dynamic thermal decomposition profiles under a nitrogen purge are illustrated in *Figure 2* for the

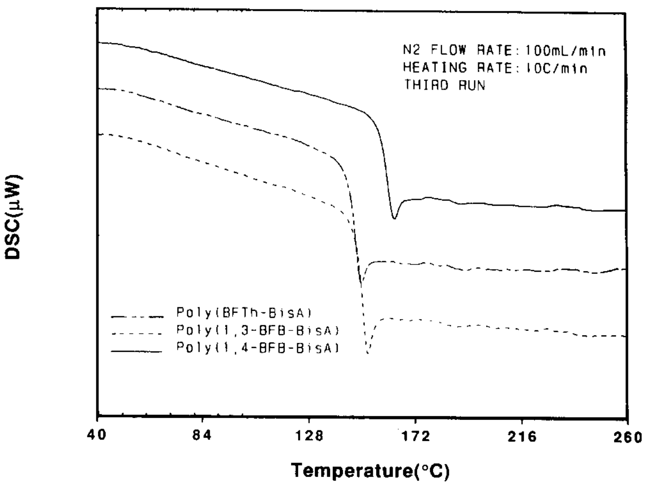


Figure 1 D.s.c. thermograms for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA) and poly(BFTh-BisA). Heating rate, 10°C min^{-1}; N_2 purge, 100 ml min^{-1}

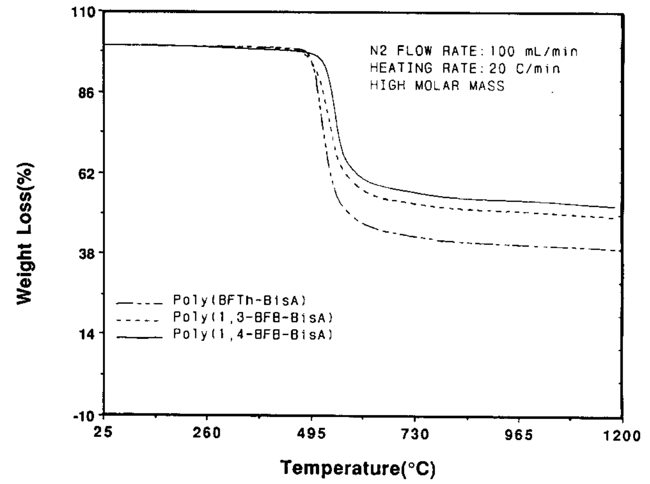


Figure 2 T.g.a. thermograms for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA) and poly(BFTh-BisA). Heating rate, 20°C min^{-1}; N_2 purge, 100 ml min^{-1}

Table 2 The decomposition temperatures[c]

		Poly(1,3-BFB-BisA)	Poly(BFTh-BisA)	Poly(1,4-BFB-BisA)
T_d (°C) at 5% weight loss (N_2)	(a)	495	496	521
	(b)	489	488	478
T_d (°C) at 5% weight loss (air)	(a)	475	481	513
	(b)	499	491	490
Total weight loss in N_2 (%)	(a)	51	61	48
	(b)	54	58	56

(a) Uncontrolled-molar-mass polymers
(b) Controlled-molar-mass polymers
[c] Gas flow rate, 100 ml min^{-1}; heating rate, 20°C min^{-1}; temperature ranging from 25 to 1200°C

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 2*) 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 2*) yielded residues on ignition of 44%, 42% and 46% for poly(1,4-BFB-BisA), poly(BFTh-BisA) and poly(1,3-BFB-BisA), respectively (*Table 2*). Thus, the large difference in molar mass between the uncontrolled-molar-mass samples of poly(BFTh-BisA) and poly(1,3-BFB-BisA), i.e. intrinsic viscosities of 1.23 and 0.79 dl g^{-1}, respectively, invalidates any difference in thermal stability. However, the controlled-molar-mass samples are equivalent in molar mass and are therefore a better indication of any trends that relate to the exocyclic bond angle of the central aromatic unit.

The weight loss of the three uncontrolled-molar-mass polymers in an air purge sharply contrasts with those under nitrogen, as illustrated by the thermograms in *Figure 3*. The initial stage of weight loss for the three polymers (*Figure 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 (*Figure 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 (*Figure 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 crosslinking reaction and/or oxidation. It is reasonable that degradation by chain scission would be expected to proceed at a faster rate of volatilization by formation of low-molar-mass species. The results of this study are not sufficient to make this determination. However, in similar studies by Hay and Kemmish[11], the degradation products from the decomposition of PEEK and PEK were isolated and analysed 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, crosslinking and oxidation. The study by Hay and Kemmish demonstrated that, at a higher ratio of crosslinking reactions to chain scission reactions, a lower rate of volatilization would be observed. In another study, the decomposition of poly(phenylene sulphide) (PPS) was studied by Ma *et al.* using t.g.a. under both nitrogen and air atmospheres[12]. The well known crosslinking of PPS at temperatures exceeding 490°C was correlated with a slower rate of weight loss under air compared to nitrogen over the same temperature range[13]. Thus, it can be implied that crosslinking 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 (*Figure 3*). This indicates that the mechanism of decomposition of the poly(1,4-BFB-BisA) material involves less crosslinking or oxidation and is dominated by chain scission over the same temperature range.

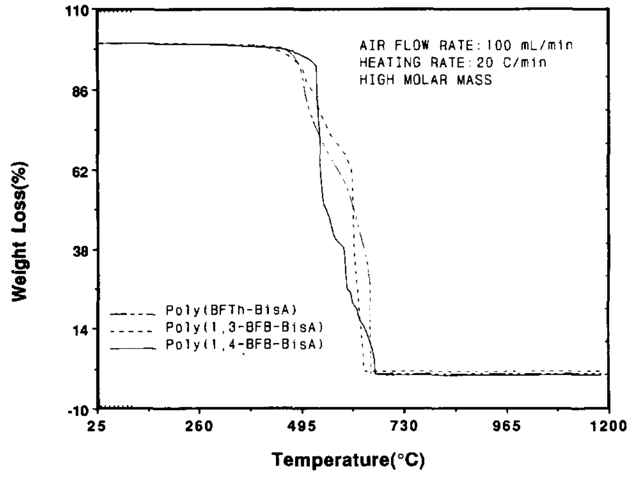


Figure 3 T.g.a. thermograms for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA) and poly(BFTh-BisA). Heating rate, 20°C min^{-1}; air purge, 100 ml min^{-1}

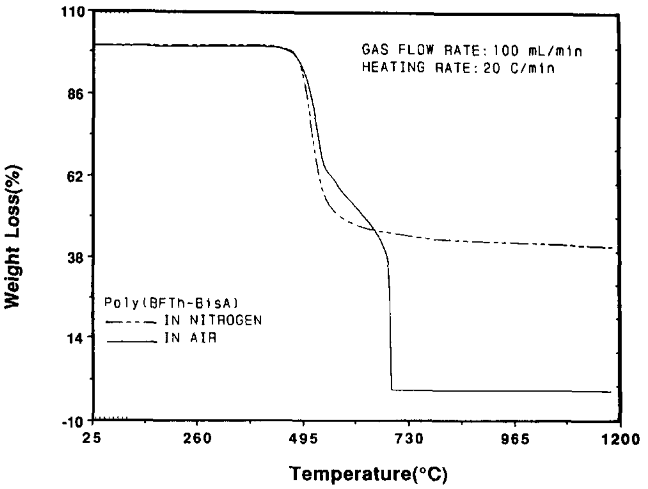


Figure 4 T.g.a. thermograms of controlled-molar-mass sample of poly(BFTh-BisA) in air and nitrogen atmospheres. Heating rate, 20°C min^{-1}; purge, 100 ml min^{-1}

The thermal degradation of the end-capped polymers offers some further insight into this behaviour. The decomposition temperatures of the controlled-molar-mass polymers in air are 12°C, 10°C and 3°C higher than that in nitrogen for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA) and poly(BFTh-BisA), respectively (*Table 2*). Thus, since the presence of oxygen would provide for oxidation, these data support the previous argument. An example of this behaviour 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 polymers illustrated in *Figures 2* and *3*. The apparent higher stability of these materials in an air atmosphere is most likely associated with the use of t-butylphenol as the end-capping monomer to control the molar mass; however, further studies are necessary to verify this. The $T_d^{5\%}$ for all three polymers of controlled molar mass in a nitrogen gas stream or an air purge differ by no more than ca. 10°C. This is attributed to the end-capping that yielded three polymers of nearly equivalent molar mass and thus an equivalent number of end-groups.

Dynamic mechanical spectroscopy

The storage modulus (E'), loss modulus (E'') and $\tan\delta$ are plotted as functions of temperature in *Figure 5* for the controlled-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 modulus (*Figure 5a*) of each polymer, approximately 4 GPa at a temperature of −150°C, decreases 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-T_g 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 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 mol^{-1}, respectively. In the case of other poly(arylene ether)s and poly(phenylene sulphide), Eisenberg *et al.* reported that a β relaxation for poly(*p*-phenylene oxide) (PPO) at −113°C has an activation energy of 12 kcal mol^{-1} and was probably due to hindered oscillatory motions of the backbone phenyl groups[14]. Others have shown that these low-temperature relaxations are sensitive to the level of moisture in polymers with a phenyl ether linkage[15–17]. In preparation of our samples, every effort was made to assure dry samples, yet it is possible that the dispersions 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 *Figure 5b* and *5c* that the β relaxation for the poly(BFTh-BisA) material is most prominent with a maximum at ca. −38°C. The β relaxation found for poly(BFTh-BisA) has an apparent activation energy of ca. 16 kcal mol^{-1}.

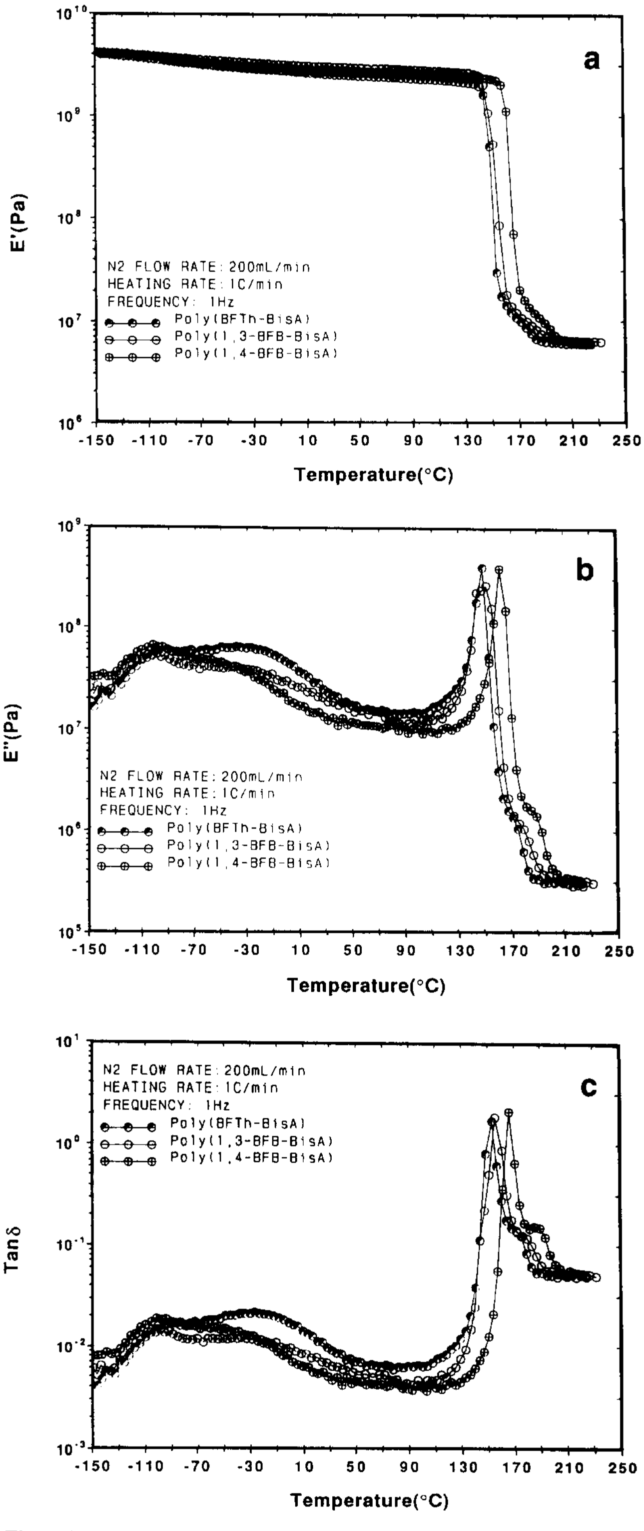


Figure 5 (a) Storage modulus, (b) loss modulus and (c) $\tan\delta$ for poly(1,4-BFB-Bis-A), poly(1,3-BFB-BisA) and poly(BFTh-BisA). Frequency, 1 Hz; heating rate, 1°C min^{-1}; N_2 purge, 200 ml min^{-1}

Mechanical properties

The plot of engineering stress *versus* elongation for representative samples of all three polymers are illustrated in *Figure 6*. Young's modulus decreased 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 3*). This suggests that poly(1,3-BFB-BisA) is the stiffest material among the three polymers, which is reflected in both these measurements and the storage modulus at room temperature (*Figure 5a*). The poly(1,4-BFB-BisA) is the most ductile material with a maximum elongation of 66% compared with the brittle poly(1,3-BFB-BisA) with a maximum elongation of 5.3%. There are a number of possible explanations for these trends. The modulus of a material is dependent upon a number of factors other than experimental, which are constant for this series, such as the chemical nature of the structure, van der Waals interactions, bond energy and conformational or entropic energy. As noted previously, the most significant difference in these materials is the

Table 3 Mechanical properties[a]

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

[a] The data were obtained from the average values of five dogbone samples. Only controlled-molar-mass polymers were analysed. Gauge length, 25 mm; crosshead speed, 2.5 mm min^{-1}; room temperature

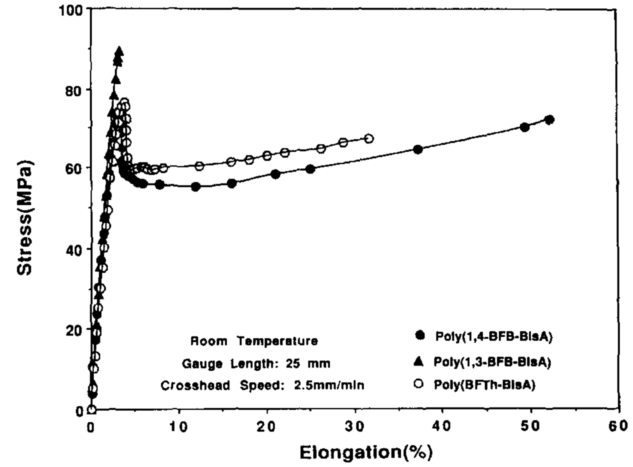


Figure 6 Engineering stress *versus* elongation for poly(1,4-BFB-BisA), poly(1,3-BFB-BisA) and poly(BFTh-BisA)

exocyclic bond angle and its influence on chain conformation. The change in the exocyclic bond angle from 180° to 148° increases the number of conformations per chain, but also decreases the effective radius of the chain by shifting the central aromatic ring into a non-symmetric position along the backbone, i.e. a kink is formed. This would be expected to decrease the packing efficiency of the chain containing the 1,3-substituted phenylene ring and the 2,5-substituted thiophene ring. In terms of Eyring's theory, the increase in the exocyclic bond angle effectively decreases the activation volume for deformation, which results in a higher modulus, higher yield stress and lower elongation at break[18]. A second possible explanation for the trends in mechanical properties is differences in molar mass. However, this seems unlikely in view of the observed trends. Further studies are in progress to measure the molar mass as a function of processing of these poly(arylene ether ketone)s. These remarks are considered valid for these three polymers, which represent the only systematic evaluation of geometric effects on mechanical properties for amorphous poly(arylene ether ketone)s.

CONCLUSIONS

Three new poly(arylene ether ketone)s have been synthesized such that the exocyclic bond angle of the central aromatic unit was systematically changed from 180° to 148° to 120°. This represents a unique approach to the study of structure–property relationships in this important class of amorphous polymers. The glass transition temperature of controlled-molar-mass poly(BFTh-BisA) is 147°C compared to 149°C for poly(1,3-BFB-BisA) and 160°C for poly(1,4-BFB-BisA). All three polymers are thermally stable under dynamic conditions to temperatures of ca. 490°C in nitrogen and ca. 480°C in air. A higher thermal stability in air measured for the controlled-molar-mass samples is tentatively assigned to oxidation or crosslinking of the t-butylphenol end-group at temperatures greater than 475°C. Two low-temperature dispersions are found for each of the polymers. A pronounced γ relaxation for poly(BFTh-BisA), poly(1,4-BFB-BisA) and poly(1,3-BFB-BisA) is believed to be due to the presence of adsorbed water. 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 with an increasing exocyclic bond. The overall elongation of these materials decreased also as the polymeric chain was effectively kinked by decreasing the exocyclic bond angle, whereas the inverse relationship was measured for the yield stress. Chain geometry was directly correlated with trends in glass transition temperature and mechanical properties.

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