Polymer Bulletin 47, 1–8 (2001)

Polymer Bulletin

New aromatic poly(ether-ketone)s containing hexafluoroisopropylidene groups

Corneliu Hamciuc [1](✉), **Elena Hamciuc**[1], **Maria Bruma**[1], **Markus Klapper**[2], **Tadeusz Pakula** [2]

[1] Institute of Macromolecular Chemistry, Aleea Ghica Voda 41A, Iasi, Romania
[2] Max Planck Institute for Polymer Research, Mainz, Germany
e-mail: chamciuc@poni.ichpp.tuiasi.ro, Fax: 49 (40) 32-211299

Received: 6 April 2001/Revised version: 31 July 2001/Accepted: 31 July 2001

Summary

New aromatic poly(ether-ketone)s containing hexafluoroisopropylidene groups have been prepared by aromatic nucleophylic displacement reaction of the potassium salts of aromatic dihydroxy compounds containing fluoren, 1,3,4-oxadiazole or phenylquinoxaline rings with 2,2-bis[4-(4-fluorobenzoylphenyl)hexafluoropropane. These polymers were readily soluble in various organic solvents such as N,N-dimethylformamide, pyridine, tetrahydrofuran and chloroform and gave flexible films by casting such solutions. Their glass transition temperatures (T_g) were in the range of 189-222°C and they were thermally stable up to 480°C. The polymer films displayed low dielectric constants, in the range of 2.8 – 3.2, and good mecanical properties, with tensile strength in the range of 46 – 61 MPa and elastic modulus of 1.4 – 1.6 GPa.

Introduction

High performance polymers are used in applications demanding service at enhanced temperatures while maintaining their structural integrity and an excellent combination of chemical, physical and mechanical properties. An important group of such polymers are poly(ether-ketone)s due to their unique combination of toughness, stiffness, thermooxidative stability, chemical and solvent resistance, electrical performance, and retention of physical properties at high temperature [1,2]. Despite these attributes, poly(ether-ketone)s have a relatively low glass transition temperature. The introduction of rigid units such as heterocyclic rings into the macromolecular chains of such polymers led to stiffer polymer backbone giving higher glass transition temperature and melting points. Poly(ether-ketone)s containing different heterocycles like imide [3,4], phenylquinoxaline [5], 1,3,4-oxadiazole and 1,2,4-triazole [6], benzoxazole [7], benzimidazole [8] have been prepared. Many researches have shown that the incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones increases the polymer solubility and glass transition temperature without sacrifying the thermal stability. The retention of high thermal stability is attributed to the strong C-F bonds. In addition, the 6F groups interrupt the conjugation when placed between aromatic units resulting in a decrease of colour. The bulky 6F groups also increase the free volume of the polymers, improving their electrical insulating characteristics [9-11]. Different classes of fluorinated thermostable polymers like poly(1,3,4-oxadiazole)s [12], polyphenylquinoxalines [13], polyimides [14] have been largely studied as potential candidates for practical use in microelectronics and related industries. We have designed and synthesized new fluorinated poly(ether-ketone)s by the reaction of an activated difluorinated compound containing hexafluoroisopropylidene groups with different aromatic diphenols containing preformed 1,3,4- oxadiazole, phenylquinoxaline or fluoren units. The reaction took place in polar aprotic solvents, in the presence of potassium carbonate. The properties of these polymers have been evaluated with respect to their chemical structure.

Experimental

Materials

N-Methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure. 2,2-Bis(4-carboxyphenyl)-hexafluoropropane, *p*-hydroxybenzoic acid, *p*-aminophenol, 4-hydroxybenzyl, 3,3'-diaminobenzidine, 3,3',4,4'-tetraaminodiphenylether and 9,9-bis-(*p*-hydroxyphenyl)-fluoren were provided by different commercial sources and used as received.

Instrumental

Infrared spectra were recorded on a Specord M-80 Spectrophotometer using KBr pellets or polymer films with a thickness of 2-5 µm. ^{1}H NMR spectra were recorded with a Bruker AC 300 instruments, by using polymer solutions in deuterated chloroform. Gel permeation chromatography (GPC) analyses were performed with a Waters Chromatography System and a Permagel 10^3-10^6 Å column, by using polystyrene standards and tetrahydrofuran (THF) as eluent. Differential scanning calorimetry (DSC) was performed on a DSC II Metler TC 11. The samples were heated at a rate of 10°C/min under a nitrogen atmosphere. The DSC curves obtained during the second heating run were used to evaluate the glass transition. The middle point of the inflection on DSC curve was assigned as T_g of the respective polymers. Thermogravimetric analyses (TGA) were performed on a Mettler TC 10A at a heating rate of 10°C/min under nitrogen atmosphere. The onset on the TGA curve was assigned as initial decomposition temperature (IDT). The temperature at which the polymers loose 10% of their weight was also recorded. Mechanical properties of various materials have been analyzed by cold drawing of solution cast films. Mechanical testing machine Instron 6000 has been used. The samples have been drawn with the rate of 0.5/min at room temperature. The stress versus draw ratio dependencies have been recorded. The study of dielectric properties has been performed in a parallel plate capacitor under a sinusoidal voltage. Solid samples in the form of films having a thickness of 25 µm with evaporated golden electrodes (10 mm diameter) have been examined. The frequency analyzer Solartron Schlumberger 1260 (10^{-1} - 10^6 Hz) has been used. The complex dielectric permitivity (ε*), given by the equation $\varepsilon^* = \varepsilon' + \varepsilon''$ where ε’ is the real component of the dielectric constant and ε’’ is the imaginary component of the dielectric constant, has been measured as a function of frequency at constant temperature. The dielectric loss tangent was defined by $\tan\delta = \varepsilon''/\varepsilon'$ and was determined as a function of frequency. Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of Hyperchem Program, Version 4.0 [15].

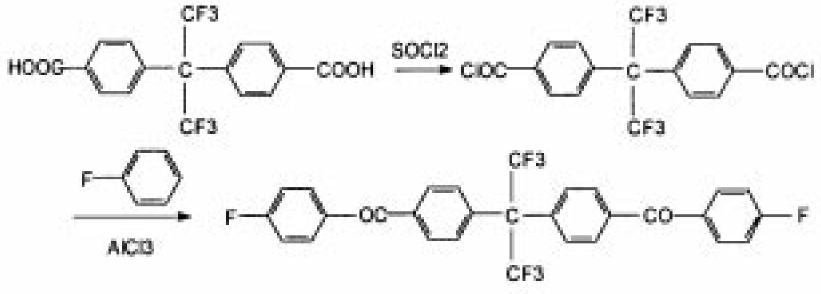
Synthesis of the monomers

2,2-Bis[4-(p-fluorobenzoyl)-phenyl]-hexafluoropropane, ***I****,* was synthesized by the Fiedel-Crafts reaction of fluorobenzene with 2,2-bis(*p*-chloroformylphenyl)-

hexafluoropropane which had been obtained by treating the corresponding diacid, 2,2-bis(*p*-carboxyphenyl)-hexafluoropropane, with thionyl chloride at reflux temperature, as shown in scheme 1 [16]. M.p.**I**: 143-144°C.

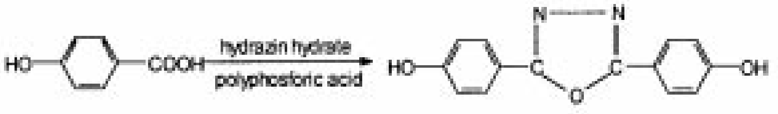
2,5-Bis(p-hydroxyphenyl)-1,3,4-oxadiazole, ***IIa***, was prepared by the reaction of *p*-hydroxybenzoic acid with hyrazine hydrate in polyphosforic acid, according to a published procedure, as shown in scheme 2 [17]. M.p. 337-339°C.

Bis(hydroxyphenylquinoxaline)s ***IIb*** *and* ***IIc*** were synthesized by the reaction of 4-hydroxybenzyl with aromatic tetraamines such as 3,3'-diaminobenzidine or 3,3',4,4'-tetraaminodiphenylether (Scheme 3) [18]. M.p. **IIb**: 352-354°C; M.p. **IIb**: 184-185°C



I

Scheme 1. Preparation of 2,2-bis[4-(*p*-fluorobenzoyl)-phenyl]-hexafluoropropane, **I.**



IIa

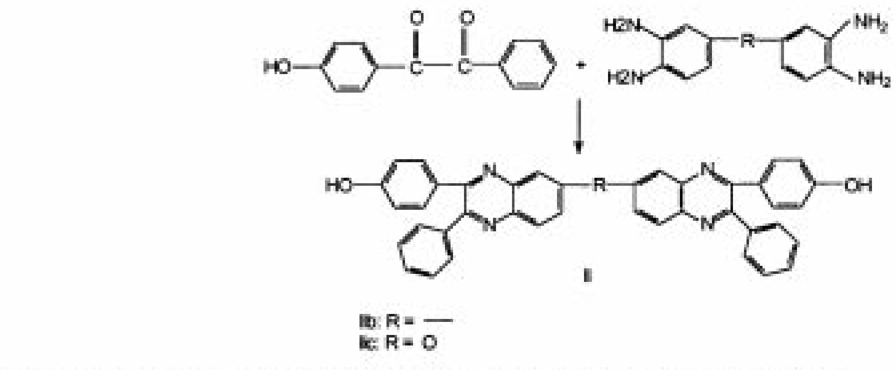
Scheme 2. Preparation of 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole, **IIa**.

Synthesis of the polymers ***III***

A typical synthesis of fluorinated poly(ether-ketone) **III** was conducted in a three-neck flask equipped with a magnetical stirrer, Dean-Stark device and condenser, under nitrogen atmosphere. The flask was charged with 2,2-bis[4-(*p*-fluorobenzoyl)phenyl]-hexafluoropropane, an aromatic diphenol, potasium carbonate, toluene and NMP as solvent. The polymers were prepared using equimolar amounts of monomers at a concentration of 15-20% (w/v) solids in NMP. An excess of potasium carbonate was used for all the polymers. The reaction mixture was heated to reflux temperature and water was removed by azeotropic distillation with toluene for 4-6 h. Toluene was then removed from the reaction flask by distillation and the reaction mixture was heated at 170-180°C for approximately 20 h. After cooling to room temperature, the viscous polymerization mixture was diluted with NMP and the polymer was precipitated by pouring in water. The polymer was filtered, washed with water and methanol, and vacuum dried.

Film casting

Dried polymer sample (0.2 g) was dissolved in 4 mL of chloroform to give 5.0% (w/v) solution which was filtered onto a glass plate and carefully spread to the edges. The films were allowed to dry slowly under a Petri dish for 24 h and then dried for 2 h in air at 130°C. The polymer films were released from the glass plates by placing them in water and used for different measurements.



Scheme 3. Preparation of bis(hydroxyphenylquinoxaline)s **IIb** and **IIc**.

Results and discussion

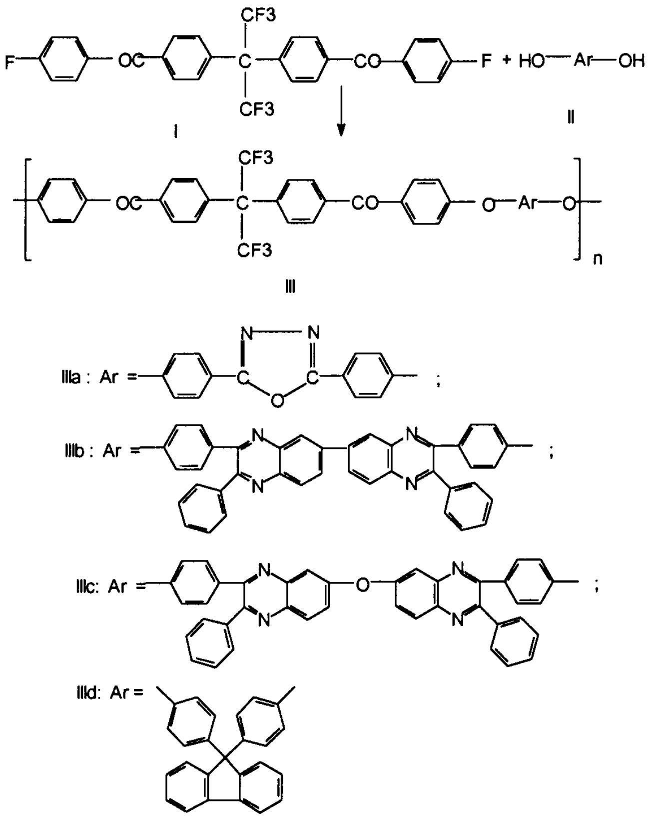
Fluorinated poly(ether-ketone)s **III** were prepared successfully by the conventional aromatic nucleofilic substitution polymerization technique of 2,2-bis[4-(*p*-fluorobenzoyl)-phenyl]-hexafluoropropane, **I,** with various bisphenols incorporating a rigid unit **II**, as shown in scheme 4. The reactions were carried out at elevated temperature in NMP, in the presence of anhydrous potassium carbonate. The yields of the polymers were always higher than 94 %.

The structure of the polymers was identified by elemental analysis, infrared and NMR spectroscopy. The elemental analysis values for carbon, hydrogen and nitrogen were in good agreement with the calculated values for all the polymers. The IR spectra of the polymers showed characteristic absorption bands at 1650 cm^{-1} due to C=O stretching of ketone groups, at 1240 cm^{-1} due to C-O-C stretching of aryl ether groups and at 1180 and 1210 cm^{-1} due to 6F groups. The IR spectrum of polymer **IIIa** showed absorption bands near 1020 and 950 cm^{-1} that are characteristic of =C-O-C= stretching in oxadiazole rings. In IR spectra of polymers **IIIb** and **IIIc** absorption peaks at 1348 and 1315 cm^{-1} were attributed to quinoxaline rings.

The ^1H NMR spectra of all the polymers confirm their structure. In figure 1 is presented the ^1H NMR spectrum of the polymer **IIIa**. The protons which are in *orto* position to oxadiazole rings, Ha, appeared as a doublet at $\delta = 8.16$ ppm; the protons in *orto* position to carbonyl groups, Hd and He, appeared as a doublet at $\delta = 7.90$ and $\delta = 7.80$ ppm, respectively. The protons in *orto* position to 6F groups, Hf, appeared as a doublet at $\delta = 7.54$ ppm and the protons in *orto* position to ether linkage, Hc and Hb, appeared as multiplet at $\delta = 7.19$ ppm.

All the polymers were soluble in N,N-dimethylformamide (DMF), pyridine (Py), tetrahydrofuran and chloroform. It was noticed that polymer **IIIc**, containing an additional ether linkage when compared with polymer **IIIb**, was soluble in benzene, as well. Polymers **IIIa** and **IIIb** were partially soluble in benzene and polymer **IIId** was insoluble. The good solubility of the polymers is due to a relatively high flexibility of the macromolecular chains which was determined by the presence of ether and ketone groups into the repeating unit. Also the 6F groups introduced a factor of asymmetry and sterical hindrance that prevent a dense packing of the chains. The same effect was produced by voluminous phenylquinoxaline rings, in the case of polymers **IIIb** and **IIIc**. This arrangement of phenylquinoxaline and 6F groups to create a distance between the chains is evidenced by molecular modelling as seen in figure 2.

The molecular weight distribution of the polymers was determined by GPC. The molecular weight values, M_w were in the range of $4.64x10^4$ - $30.9x10^4$, M_n were in the range of 1.62×10^4 - 15.2×10^4 g/mol, and M_w/M_n in the range of 2.03-2.86 (Table 1). The molecular weight distributions were essentially unimodal without evidence of significant oligomeric or unreacted species. It is mentioned here that GPC measurements by using polystyrene as standard provide only an estimation of molecular weight and not accurate evaluation.



Scheme 4. Synthesis of fluorinated poly(ether-ketone)s **III.**

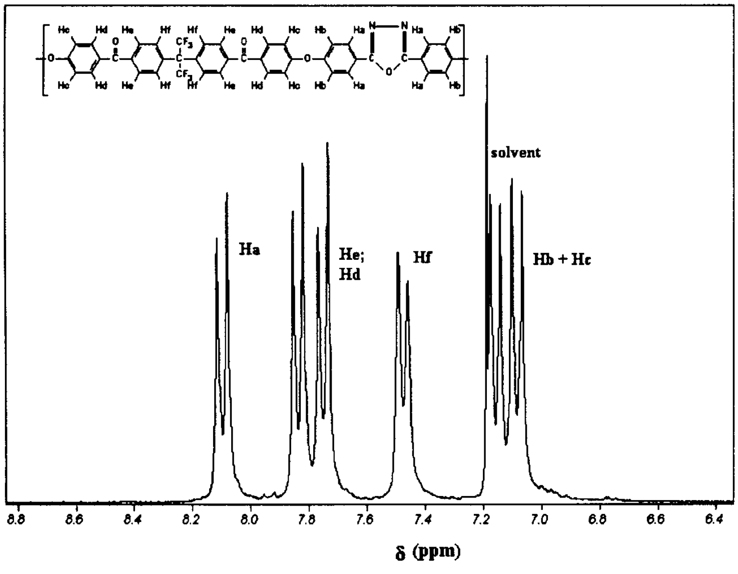


Figure 1. The ^{1}H NMR spectrum of fluorinated poly(ether-ketone) **IIIa**.

The thermal stability was investigated by TGA. TGA curves show that the polymers do not loose weight bellow 480°C. They start to decompose in the range of 510-530 °C and show 10 % weight loss in the range of 520-540°C (Table 1). These values illustrate the high thermal stability of the polymers.

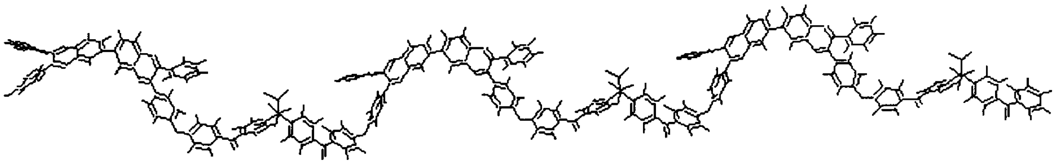


Figure 2. Molecular model of a fragment incorporating 3 repeating units of the polymer **IIIb.**

Table 1. Properties of the fluorinated poly(ether-ketone)s **III**.

Polymer	M_w (g·mol^{-1})	M_n (g·mol^{-1})	M_w/M_n	IDT(1 (°C)	T_{10}(2 (°C)	T_g (°C)
IIIa	4.64x10^4	1.62x10^4	2.86	510	520	222
IIIb	8.58x10^4	4.19x10^4	2.04	520	540	209
IIIc	4.79x10^4	2.07x10^4	2.31	515	530	189
IIId	30.9x10^4	15.2x10^4	2.03	530	540	211

(1 Initial decomposition temperature = onset of TGA curve.

(2 Temperature of 10% weight loss.

The DSC measurements showed no evidence of crystallization or melting which proves an amorphous morfology. The glass transition temperatures (T_g) of the fluorinated poly(ether-ketone)s **III** were in the range of 189-222°C (Table 1). The polymers had higher glass transition temperature when compared with similar polymers not containing any rigid unit in the bisphenol segment, having T_g in the range of 150-180°C [16]. Also, a fluorinated poly(ether-ketone) derived from the same difluorinated compound 2,2-bis[4-(4-fluoro-benzoylphenyl)-hexafluoropropane and 4,4-(hexafluoroisopropylidene)-diphenol had T_g = 180°C [16]. The higher T_g of the present polymers is due to the presence of voluminous heterocyclic rings or fluoren units which increase the rigidity of the macromolecular chains. A decrease of T_g with about 20°C was observed for the polymer **IIIc** when compared to the polymer **IIIb** which has similar structure but does not contain any ether linkages between phenylquinoxaline rings of bisphenol segment. There is a large interval between T_g and decomposition temperature of all these polymers which could be advantageous in their processing by thermoforming techniques.

The tensile properties of some polymer films are summarized in table 2. The meaning of the parameters determined is illustrated in figure 3. Elastic modulus (E) and the coordinates of the yield point (ε_Y, σ_Y) as well as of the point of fracture (λ_B, σ_B) have been determined as averages of 3-5 independent drawing experiments. The parameters determined for these averaged curves are shown in table 2. All materials have shown similar type of behavior with the elastic deformation range at small strains up to λ = 1.03, with the yield point indicating the beginning of plastic flow range and finally with a ductile fracture in some cases after weak strain hardening. The values of elastic modulus are in the range of 1.4-1.6 GPa and the values of tensile strength vary in the range of 46 – 61 MPa, which shows that these polymers have good mechanical properties.

Table 2. Mechanical properties of studied films on the basis of the cold drawing experiments.

Sample	E (GPa)	σ_y (MPa)	$\varepsilon_y = \lambda_y - 1$	σ_B (MPa)	λ_B
IIIa	1.46	53.1	0.0518	48.0	1.36
IIIb	1.56	52.8	0.0565	61.0	1.93
IIIc	1.60	51.3	0.0538	46.5	1.76
IIId	1.63	44.2	0.0329	48.3	1.04

E = modulus; σ_y =yield stress; ε_y =yield strain; σ_B = tensile strength; λ_B =draw ratio at break

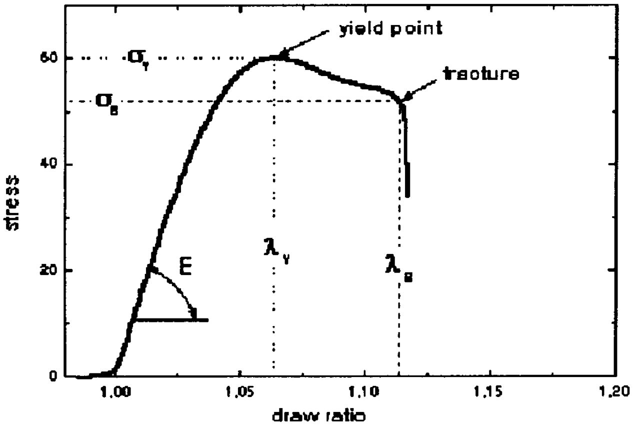


Figure 3. Schematic stress-strain dependence with the parameters characterizing the elasticity at small deformation as well as the yield and the break points.

The dielectric constant and dielectric loss tangent of polymer films are displayed from 10^{-1} - 10^{6} Hz. In figure 4 is presented the dependence of real dielectric constant values (ε') to frequency. In figure 5 is presented the dependence of loss tangent (tan δ) to frequency. The frequency dependencies are similar for all the polymers. By increasing the frequency a small monotonic decrease in ε' appeared. The dielectric loss tangent values are very small due to a very small values of ε'' in the equation of complex permitivity. The dielectric constants for all the polymers at 100 Hz, 10 KHz and 1 MHz are listed in table 3. The values of dielectric constants at 1 MHz were in the range of 2.8 – 3. 1. The low dielectric constant values of the polymer films are due to the presence of hexafluoroisopropylidene groups and voluminous phenylquinoxaline or fluoren units which increase the free volume of the polymers and reduce the humidity absorption improving the electroinsulating properties. These values are lower than that of "H Film", a polyimide which is prepared from pyromellic dianhydride and 4,4'-diaminodiphenylether, which is one of the most prefered high performance dielectrics in microelectronic applications, having a dielectric constant of 3.5 [19]. The low values of dielectric constant of these polymers make them desirable candidates for high-temperature processing of high speed integrated circuits.

Table 3. Dielectric constant at selected frequencies for poly(ether-ketone)s **III**.

Polymer	Dielectric constant at:		
	100 Hz	10 kHz	1 MHz
IIIa	2.88	2.86	2.82
IIIb	3.23	3.13	3.06
IIIc	3.17	3.15	3.08
IIId	2.89	2.85	2.81

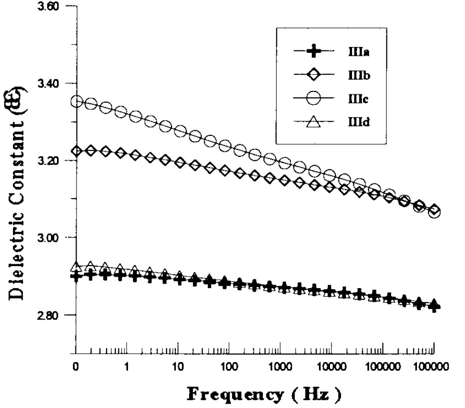


Figure 4. Dielectric analysis plot showing the real dielectric constant versus frequency for polymers **III.**

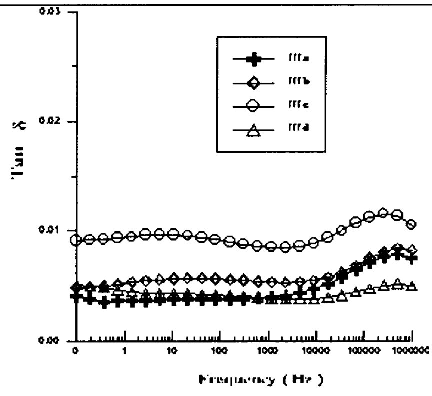


Figure 5. Dielectric analysis plot showing the loss tangent versus frequency for polymers **III.**

Conclusions

By introducing hexafluoroisopropylidene groups together with fluoren, 1,3,4-oxadiazole or phenylquinoxaline rings into the repeating unit of poly(ether-ketone)s, polymers with good thermal properties and high T_g values were obtained. The polymers were soluble in organic solvents such as DMF, Py, THF or chloroform and were easily processable from solutions into transparent films having tough mechanical properties and low dielectric constant.

Acknowledgements. We acknowledge with great pleasure the financial support provided to Corneliu Hamciuc by DAAD (Deutscher Akademischer Austauschdienst) in Bonn and Max Planck Institute for Polymer Research in Mainz, Germany.

References

1. Hergenrother PM, Jensen BJ, Havens SJ (1988) Polymer 29: 358
2. Rao VL (1995) J Macromol Sci Rev Macromol Chem Phys C35: 661
3. Matsuo S, Mitsuhashi KI (1994) J Polym Sci Part A Polym Chem 32: 1969
4. Zheng HB, Wang ZY (1999) J Polym Sci Part A Polym Chem 37: 3227
5. Hedrick JL, Labadie JW (1990) Macromolecules 23: 1561
6. Connell JW, Herghenrother PM, Wolf P (1990) Polym Mater Sci Eng 63: 366
7. Smith JGJr, Connell JW, Herghenrother PM (1991) Polym Prep 32: 646
8. Smith JGJr, Connell JW, Herghenrother PM (1991) Polym Prep 32: 193
9. Bruma M, Fitch J, Cassidy P (1996) J Macromol Sci Rev Macromol Chem Phys C36: 119
10. Hougham G, Tesoro G, Shaw J (1994) Macromolecules 27: 3642
11. Mercer FW, Fone MM, McKenzie MT (1997) J Polym Sci Part A Polym Chem 35: 521.
12. Thaemlitz CJ, Cassidy P (1993) Polymer 33: 206
13. Bruma M (1997) Polyphenylquinoxalines. In: Olabisi O (ed) Handbook of Thermoplastics. Dekker, New York, pp 771-798
14. Huang SJ, Hoyt AE (1995) Trends Polym Sci 3: 262
15. Hypercube Inc Ontario (1994) Hyperchem Version 4.0
16. Tullos G, Cassidy P, Clair AKSt (1991) Macromolecules 24: 6059
17. Siegrist AE, Maeder E, Dunnenberger N (1965) Swiss Pat 383985; Chem Abst 62: 14867c
18. Korshak VV, Belomoina NM, Jedlinski Z, Raubach H (1988) Acta Polym 39: 413
19. Sroog CE (1991) Prog. Polym. Sci: 561