

Novel High- T_g , High-Strength Poly(aryl ether) Containing Quadrephenyl Unit

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ABSTRACT: A novel poly(aryl ether) was prepared by nucleophilic displacement of the fluorine atoms of a 2-perfluoro-activated bisfluoro monomer with bisphenol A. The polymer exhibited a weight average molar mass of $3.15 \times 10^5 \text{ g mol}^{-1}$ according to gel permeation chromatography. The poly(aryl ether) showed very good thermal stability, with only a 5% weight loss at 493°C according to thermogravimetric analysis under synthetic air, and it had a glass-transition temperature at 223°C according to differential scanning calorimetry and at 243°C according to dynamic mechanical thermal analysis. The polymer was soluble in a wide range of organic solvents, including CHCl_3 , tetrahydrofuran, NMP, dimethylformamide (DMF), and toluene, and was insoluble in dimethyl sulfoxide and acetone. Transparent thin films of the polymer, cast from DMF, exhibited a tensile strength of 65 MPa, a modulus of 2.62 GPa, and an elongation at break of 130%. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3149–3156, 2001

Key words: poly(aryl ether); trifluoromethyl groups; quadrephenyl unit; high glass-transition temperature (T_g); high strength

INTRODUCTION

Poly(aryl ether)s are well-recognized high-performance engineering thermoplastics. These materials have outstanding physical properties, including high modulus, toughness, high thermal stability, and chemical resistance.^{1–5} Poly(aryl ether)s are generally prepared by a step-growth polymerization of activated aryl dihalo or dinitro monomers with bisphenoxides.^{6,7} It is well known that both sulfone⁸ and ketone⁹ groups are very effective in activating aryl halides toward nucleophilic displacement. Heterocyclic rings¹⁰ and amide groups¹¹ have also been used as activating groups to produce high molar mass poly(aryl

ether)s. A common characteristic of these groups is stabilization of negative charges developed at the 2- or 4-positions of the aryl moiety in the transition state of the nucleophilic halogen displacement reaction through a Meisenheimer complex that lowers the activation energy for displacement. Labadie and Hedrick¹² reported that perfluoroalkyl groups either pendent or in the main chain activate fluoro or nitro displacement by phenoxides. Because electron-withdrawing perfluoroalkyl groups cannot participate in resonance stabilization, the activation by this group is expected because of the stabilization of the negative charges at 2- or 4-positions by hyperconjugation and/or the negative inductive ($-I$) effect. The steric congestion due to the bulky trifluoromethyl group may also facilitate the formation of a stable Meisenheimer complex with release of steric strain.¹³

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The polymers containing trifluoromethyl groups are of special interest because of their possible use as gas selective membranes, enhanced flame resistance, low dielectric constant, and remarkably low water absorption. The trifluoromethyl groups in the polymer backbone enhance polymer solubility without the forfeiture of thermal stability. They also increase the glass-transition temperature (T_g) with a concomitant decrease of crystallinity. These bulky groups also serve to increase the free volume of the polymers, thereby improving various properties of the polymers, including gas permeabilities and electrical insulating properties.^{7,14}

Because of these interesting properties of fluorinated polymers, considerable attention has been devoted to the preparation of new classes of fluorine-containing polymers. We already reported a number of semifluorinated poly(arylene ether)s containing pendent trifluoromethyl groups.^{15–19} We also reported a few polyethers containing quadraphenyl unit in the main polymer chain.¹⁹ In this article, we report a novel poly(aryl ether) and its detailed characterization, including thermal and mechanical properties.

EXPERIMENTAL

General Considerations

The elements carbon, hydrogen, and nitrogen were analyzed with a Heraeus Carlo Erba 1106 elemental analyzer. ¹H-NMR (300 MHz), ¹³C-NMR (75 MHz), and ¹⁹F-NMR (282 MHz) spectra were recorded on a Bruker ARX 300 instrument [with a reference of 0 ppm with tetramethylsilane (¹H-NMR and ¹³C-NMR) or CFC1₃ (¹⁹F-NMR)]. The IR spectrum was recorded with a Bruker IFS 55 spectrophotometer with KBr pellets. The gel permeation chromatogram was obtained with a Waters instrument equipped with ultraviolet and refractive-index detectors (Waters 510 HPLC pump, Waters 410 differential refractometer, and Waters 486 turnable detector at $\lambda = 254$ nm). Chloroform was used as an eluent at a flow rate of 0.5 mL/min, and Shodex K-802.5, K-804, and K-805 columns from Showa Denko were employed. The molecular weights and polydispersity are reported versus monodisperse polystyrene standards from Polymer Standard Service. Differential scanning calorimetry (DSC) measurements were made on a PerkinElmer DSC-7 instrument equipped with a TAC 7/DX thermal analyzer controller at a heating/cooling rate of 20 K/min under

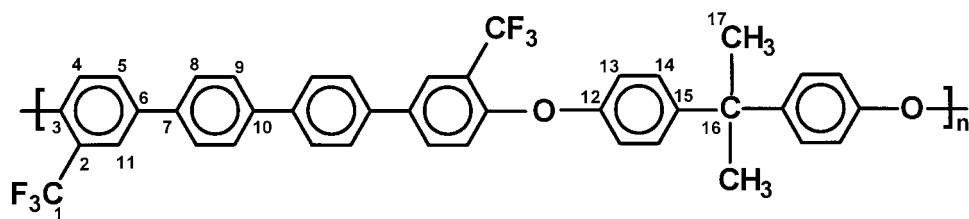
nitrogen. T_g was taken at the middle of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments TGA-2950 thermogravimetric analyzer. A heating rate of 10 K/min was used for determination of the decomposition temperature at a 5% weight loss under synthetic air. Dynamic mechanical thermal analysis (DMTA) was performed on a PL-DMTA instrument equipped with a Rheometric Scientific mechanical thermal analysis controller in the tension mode on thin-film samples with a heating rate of 2 K/min (1 and 10 Hz). Mechanical properties of the thin polymer films [cast from dimethylformamide (DMF) solutions onto glass plates, the solvent was allowed to evaporate slowly at 80°C under nitrogen for 24 h, *in vacuo* for 24 h, and at 170°C for another 24 h] were performed at room temperature on a miniature materials tester (PL Thermal Sciences) under a strain rate of 5%/min.

Starting Materials

All reagents were purchased from Aldrich, Fluka, Chempure, or Fluorochem Chemical Co. and used as received unless otherwise noted. Bisphenol A (Aldrich) was purified by recrystallization from toluene. NMP (Fluka) was purified by stirring with NaOH and distilled twice from P₂O₅ under reduced pressure. A detailed synthesis of the monomers has already been reported in a previous article.¹⁹

Polymerization

The polymerization reaction was carried out in a 100-mL, three-necked, round-bottom flask equipped with a stir bar, a Dean–Stark trap fitted with a condenser, and a nitrogen inlet. The flask was charged with an equimolar amount of the bisfluoro, K₂CO₃ (0.262 g), NMP (ca. 8 mL), and toluene (15 mL). The mixture was then heated at reflux (140–150°C) for 4–5 h, and water was removed azeotropically with toluene. After the toluene was removed from the Dean–Stark trap, the reaction temperature was increased to 180°C and maintained for 8 h. After the mixture cooled to room temperature, 10 mL of tetrahydrofuran (THF) was added to dilute the mixture, and the polymer was recovered by precipitation from about 600 mL of methanol containing a few milliliters of HCl. Fibrous solids were isolated. The product was washed several times with hot water to remove any inorganic impurities, dried *in vacuo*, dissolved in THF, reprecipitated in excess



Scheme 1

methanol, and dried *in vacuo* at 80°C for 24 h. Scheme 1 shows the polymer structure confirmed by different analytical tools.

ELEM. ANAL. Calcd. for $(C_{41}H_{28}F_6O_2)_n$ (666.66 g mol⁻¹)_n: C, 73.86%; H, 4.23%. Found: C, 73.41%; H, 4.04%. IR (KBr, cm⁻¹): 3035, 1608, 1509, 1485, 1426, 1332, 1250, 1207, 1174, 1135, 1053, 1017, 969, 929, 814. ¹H-NMR (CDCl₃, δ, ppm): 7.85 (s, 2H, H11), 7.7–7.5 (m, 10H, H5, H8, H9), 7.18 (d, J = 8 Hz, 5H, H14 and for CDCl₃), 7.0–6.85 (m, 6H, H4, H13), 1.64 (s, 6H, H17). ¹³C-NMR (CDCl₃, δ, ppm): 155.5 (s, C3), 154.5 (s, C12), 146.9.9 (s, C7), 140 (s, C10), 138.8 (s, C6), 135.5 (s, C5), 131.8 (s, C15), 128.6 (s, C14), 127.9 (s, C8), 127.7 (s, C9), 126 (m, C11, not resolved), 121.96, 125.58 (d, J = 272.8 Hz, C1, it should be a quartet, two signals are missing), 121.6, 122.0 (d, J = 30.5 Hz, C2, it should be a quartet, two signals are missing), 119.7 (s, C4), 119.4 (s, C13), 42.7 (s, C16), 31.4 (s, C17). ¹⁹F-NMR (CDCl₃, δ, ppm): 62.24 (s, 6F, F1).

RESULTS AND DISCUSSION

Polymer Synthesis

Polymerization of the bisfluoro monomer with a stoichiometric amount of bisphenol A was carried

out in the presence of an excess of potassium carbonate as a base in NMP in a conventional polymer synthesis,¹⁷ as shown in Figure 1. The polymerization was run at solid contents of 25%, and toluene was used for the azeotropic removal of water. During the initial stage of polymerization, the reaction temperature was maintained at 140–150°C, and the water generated by deprotonation of the phenols was most effectively removed through a Dean–Stark trap. Upon completion of bisphenoxide formation and dehydration (4–5 h), the reaction temperature was raised to 180°C to effect nucleophilic displacement. High molar mass polymers were obtained within 6 h, as judged by the dramatic increase of the viscosity of the reaction medium. The resulting polymer solution was coagulated in a large excess of methanol, and fibrous solids were isolated. The product was further purified by boiling and washing several times with hot water to remove any inorganic impurities, dried *in vacuo*, and dissolved in THF, and the concentrated solution was reprecipitated in an excess of methanol. The fibrous polymer recovered by filtration was dried *in vacuo* at 50°C for 24 h. The yield of the polymer was 98% and exhibited weight-average and number-average molecular weights of 315,000 and 120,000, re-

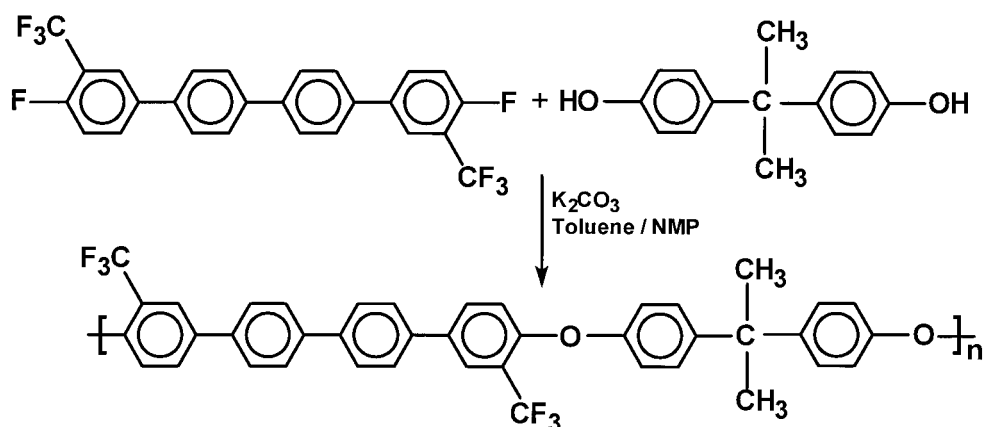


Figure 1 Reaction scheme of the synthesis of poly(aryl ether).

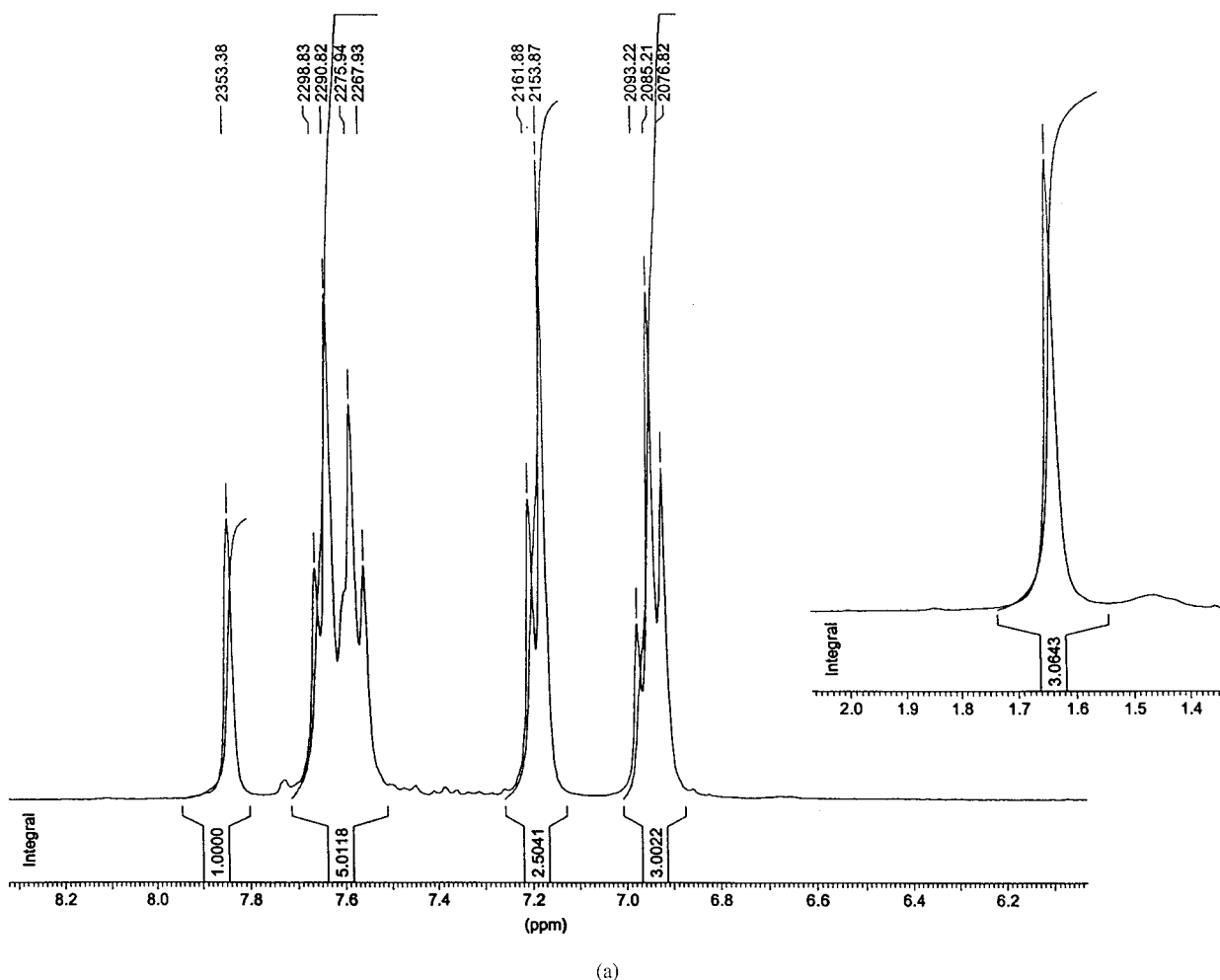


Figure 2 (a) $^1\text{H-NMR}$ and (b) $^{13}\text{C-NMR}$ spectra of poly(aryl ether).

spectively, according to gel permeation chromatography (GPC). These results prove that the 2-perfluoroalkyl activation of fluoro displacement is sufficient to obtain high molecular weight polyethers.^{19,20}

Polymer Properties and Characterization.

The prepared poly(aryl ether)s exhibited good solubility in common organic solvents such as NMP, DMF, THF, toluene, and chloroform but were insoluble in dimethyl sulfoxide (DMSO) and acetone. It is somewhat surprising that toluene appears to be a fairly good solvent despite its low polarity in comparison with the solvents commonly used for poly(aryl ether)s. It is more surprising that DMSO is a nonsolvent (even on refluxing) for this type of poly(aryl ether),^{17,19} despite its polarity being similar to the polarities of DMF and NMP. We believe that polarity alone is not a sufficient parameter for selecting a polymer solvent.

Spectroscopic data from FTIR and $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and $^{19}\text{F-NMR}$ support the structure of the poly(aryl ether). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of this polymer are shown in Figure 2(a,b), respectively. The integrated peak areas, for different protons in the $^1\text{H-NMR}$ spectrum, match very well, as expected theoretically for the polymer structure, shown in Figure 2, except for the H14 protons. One extra proton is coming from the NMR solvent (CDCl_3). It was not possible to resolve this proton (at 7.18 ppm) from the four H14 protons that appeared as doublets in the region of 7.13–7.26 ppm. The detailed peak assignment is given in the Experimental section. In the $^{13}\text{C-NMR}$ spectrum, C1 and C2 carbons were expected to show a quartet due to coupling with three fluorine atoms.^{17,19} However, only doublets were observed, with coupling constant values of 272.8 and 30.5 Hz as expected for C1 and C2 carbon atoms, respectively. No signal corresponding to

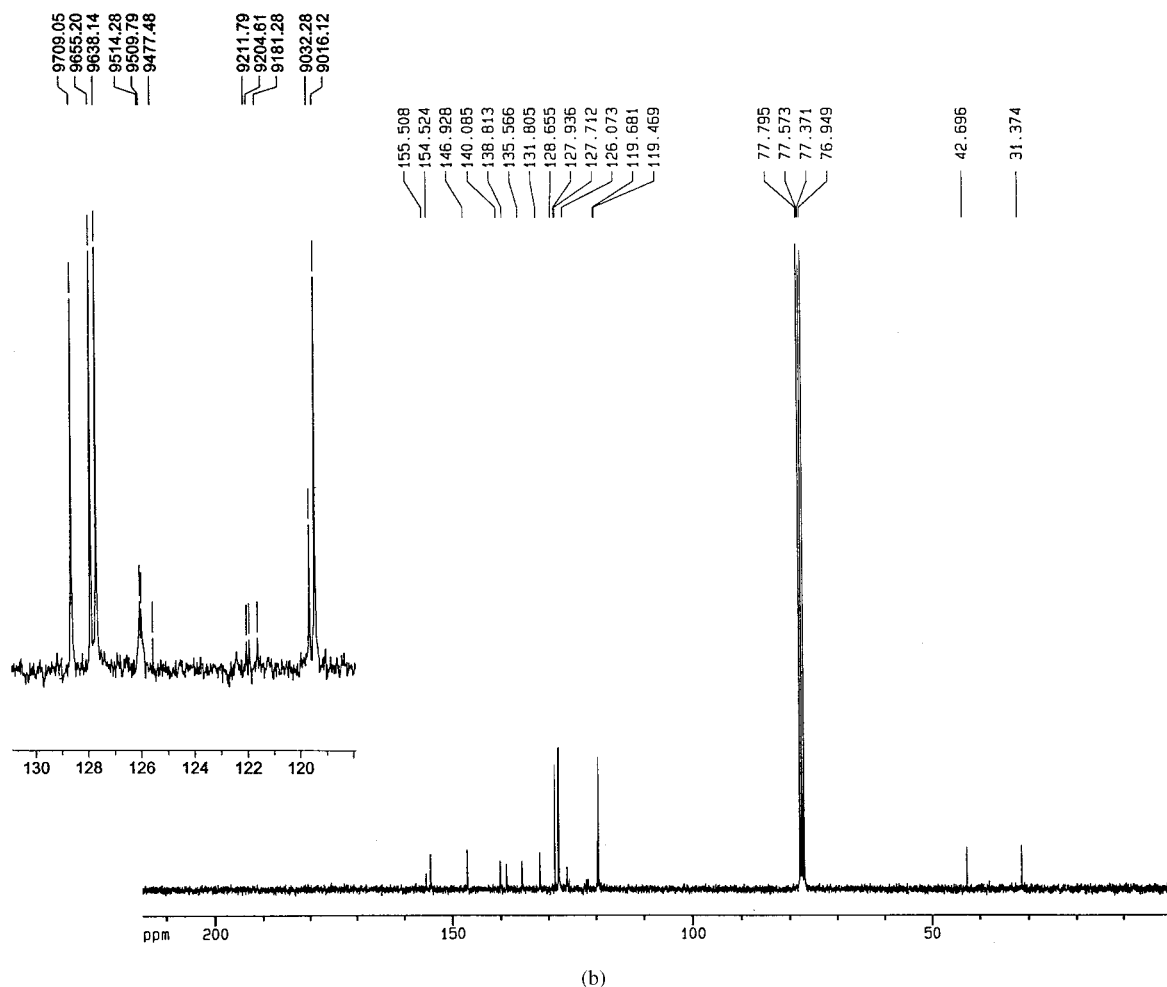


Figure 2 (Continued from the previous page)

terminal —OH and —F groups in the $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ spectra indicates a high conversion. These characterization methods, as well as elemental analysis, do not indicate degradation of trifluoromethyl groups.

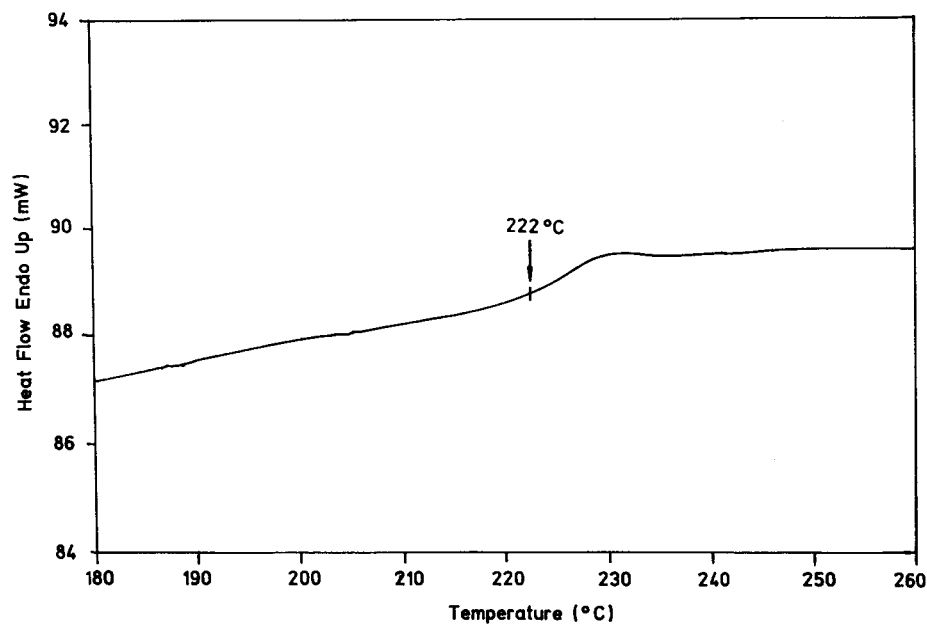
This polymer is amorphous in nature. DSC and DMTA measurements of this polymer are shown in Figure 3(a,b), which shows thermal transitions at 223 and 243°C, respectively, typical of a glass transition. The storage modulus plot shows very little loss of modulus before T_g . A secondary relaxation at -60°C was also observed, typical of many other engineering plastics.²⁰ This polymer showed very good thermal stability: only a 5% weight loss took place up to 493°C at a heating rate of 10 K/min in air. The thermogravimetric analysis (TGA) plot of this polymer is shown in Figure 3(c).

Figure 4 shows the stress-strain behavior of the poly(aryl ether). Films of the polymer were cast from DMF solutions onto glass plates; the

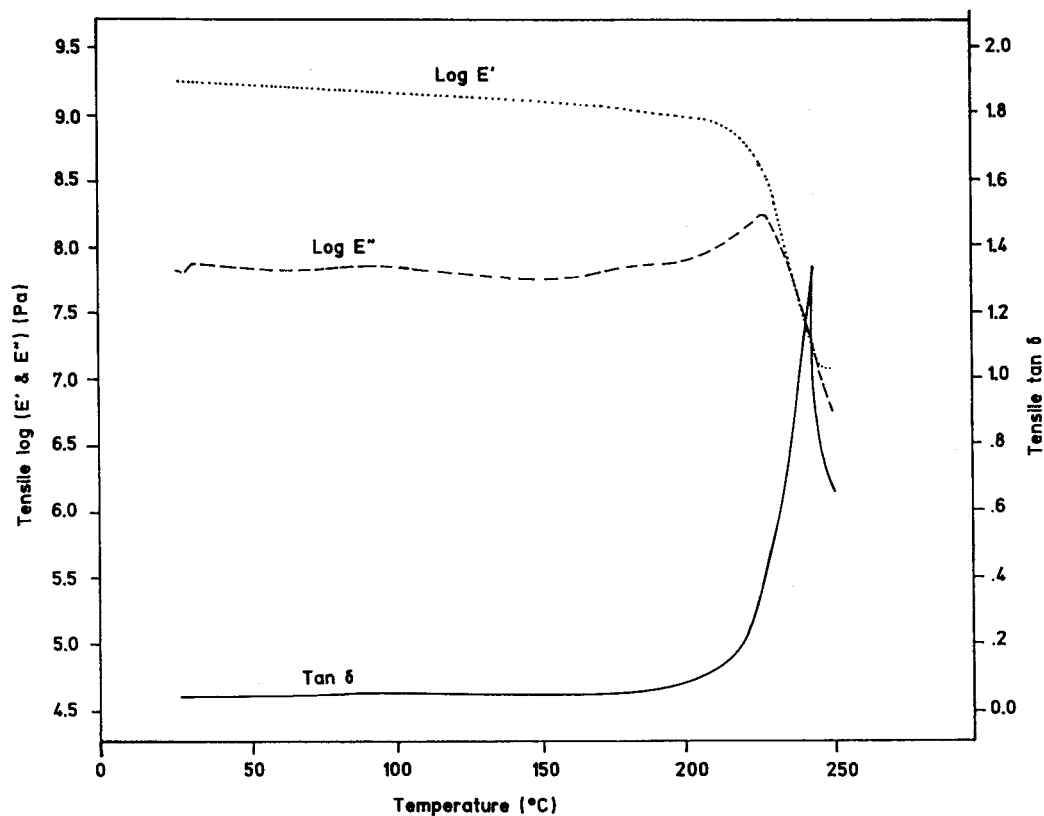
solvent was allowed to evaporate slowly at 80°C under nitrogen for 24 h, *in vacuo* for 24 h, and at 170°C for another 24 h for its complete removal, which was confirmed by IR spectroscopy (no amide stretching corresponding to DMF was observed) and TGA. The polymer films exhibited tough ductile mechanical behavior with a very high elongation of 130% and a tensile strength of 67 MPa. The polyether exhibited yield points with necking and drawing typical of those of many other ductile engineering plastics.

CONCLUSION

A novel poly(arylene ether) containing quadraphenyl elements in the polymer backbone was prepared. The resulting polymer exhibited a weight average molar mass of $3.15 \times 10^5 \text{ g mol}^{-1}$ according to GPC. The poly(aryl ether) showed very good thermal stability, with only a



(a)

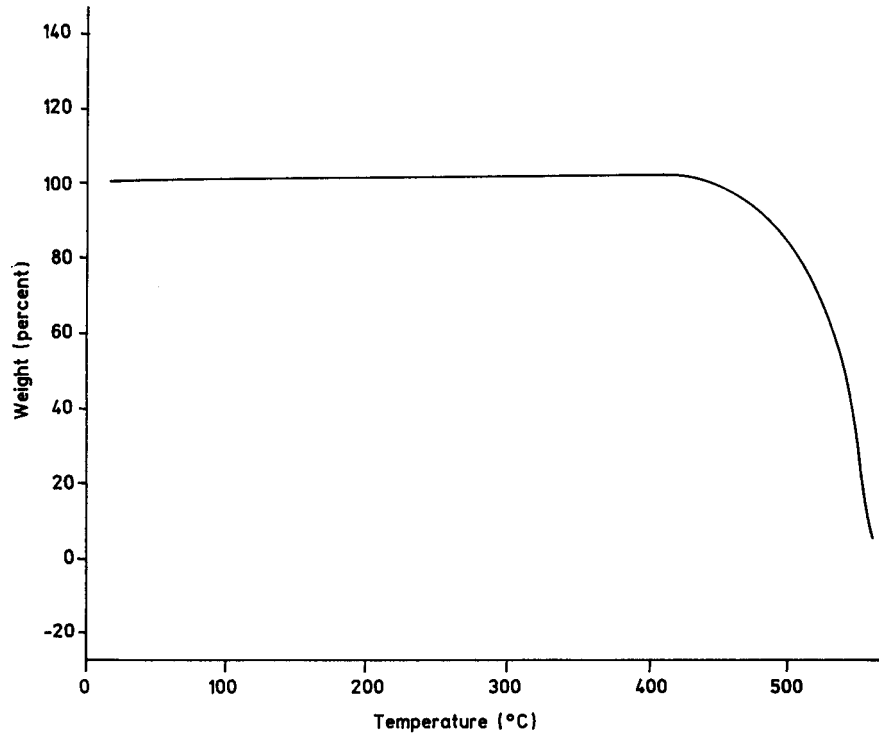


(b)

Figure 3 (a) DSC, (b) DMTA, (c) and TGA plots of poly(aryl ether).

5% weight loss up to 493°C according to TGA under synthetic air at a heating rate of 10 K/min, and it had a T_g at 223°C according to

DSC and at 243°C according to DMTA. The polymer was soluble in a wide range of organic solvents, including CHCl_3 , THF, NMP, DMF,



(c)

Figure 3 (Continued from the previous page)

and toluene. Transparent thin films of the polymer, cast from DMF, exhibited a tensile strength of 65 MPa, a modulus of 2.62 GPa, and

an elongation at break of 130%. It is anticipated that this polymer will exhibit a low dielectric constant.¹⁶

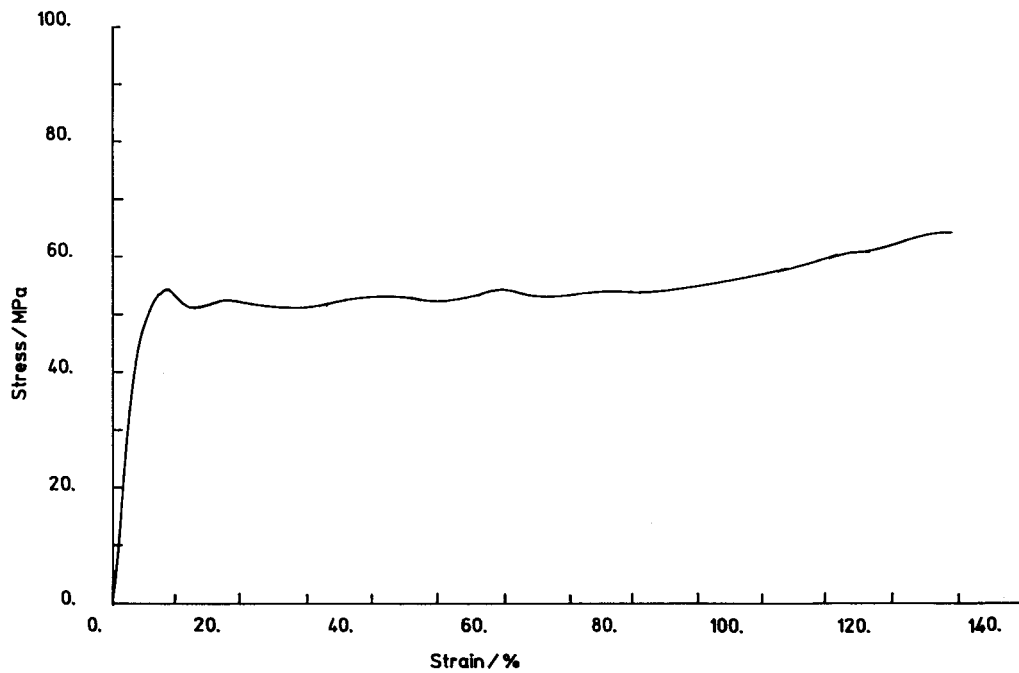


Figure 4 Stress-strain plot of poly(aryl ether).

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