Journal of Fluorine Chemistry 144 (2012) 176–181

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Soluble copoly(aryl ether ether ketone ketone)s containing xanthene and hexafluoroisopropylidene moieties

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ARTICLE INFO

Article history:
Received 27 June 2012
Received in revised form 9 September 2012
Accepted 11 September 2012
Available online 3 October 2012

Keywords:
Fluoropolymer
Poly(aryl ether ketone) copolymers
Xanthene unit
Trifluoromethyl group
Soluble

ABSTRACT

Several new copoly(aryl ether ether ketone ketone)s (PEEKKs) containing xanthene and hexafluoroisopropylidene moieties were prepared *via* nucleophilic substitution polycondensation of 1,4-bis(4-fluorobenzoyl)benzene with 9,9-bis(4-hydroxyphenyl)xanthene (BHPX) and 4,4′-hexafluoroisopropylidenediphenol (6F-BPA) by varying mole proportions of BHPX to 6F-BPA (5/95–75/25) in tetramethylene sulfone in the presence of anhydrous potassium carbonate. These polymers with weight-average molecular weights of 78,900–81,500 and number-average molecular weights of 38,500–40,800 were all amorphous and soluble in organic solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF), and even in THF and chloroform at room temperature. The copolymers showed glass transition temperatures (T_g's) between 180 and 216 °C, and the T_g values increased with increase in concentration of the BHPX units in the polymer. Besides, all the polymers were stable up to 470 °C with 5% weight loss temperatures ranging from 525 to 544 °C, and char yields of 58–64% at 800 °C in nitrogen. These copolymers could be cast into transparent, strong, and flexible films with tensile strengths of 52.4–75.1 MPa, elongations at break of 8–13%, and tensile moduli of 2.05–2.55 GPa. Their films had low dielectric constants of 2.58–2.84 (1 MHz) and low water absorptions in the range of 0.24–0.38%, and high transparency with an ultraviolet–visible absorption cut-off wavelengths in the 356–376 nm range.

1. Introduction

Aromatic poly(ether ketone)s (PEKs), known as high performance engineering plastics, have received considerable attention from industry and academy, due to their high mechanical properties, excellent thermooxidative stability and chemical resistance [1]. Among them, two of the most prominent examples, poly(ether ether ketone) (PEEK) and poly(ether ketone ketone) (PEKK) have achieved significant commercial importance as matrices for carbon fiber composites in aerospace, industrial and automotive applications and as dielectrics in the micro electronics field [1]. They are semicrystalline polymers with melting temperatures around 340–360 °C and glass transition temperatures (T_g's) around 140–160 °C. Moreover, they are generally insoluble in organic solvents at ambient temperature. As a result, these polymers cannot be processed by the casting method and require a high molding temperature resulted from their high melting temperatures. Additionally, the T_g's of these polymers are relative low, which leads to a low dimension stability [1]. Therefore, many efforts have been directed toward synthesizing soluble PEKs with enhanced processability, while keeping their desired properties. It has been proposed that introduction of pendant groups, heterocyclic moieties, asymmetry or noncoplanar structures into the polymeric chains of PEKs could improve the processability and/or glass-transition temperature [2–13]. Another successful approach to increasing solubility and processability of PEKs without an extreme loss of their outstanding properties is the introduction of a bulky cardo group into the polymer backbones. It has been demonstrated that the incorporation of cardo groups [14–19] into the backbone of PEKs results in polymers with enhanced solubility, processability, and good thermal stability. On the other hand, fluorine-containing polymers are currently of special interest because of their unique properties and high temperature performance. In general, the incorporation of fluorinated substituents into PEKs will decrease the dielectric constants, moisture absorption, and refractive index and increase the free volume, solubility, and thermal stability [15,20–24]. In particular, the polymers containing hexafluoroisopropyl moieties have been exploited for applications as optical wave-guide materials, microelectronic devices, and gas-separation membranes. Recently, our groups have prepared xanthene-based cardo poly(arylene ether ketone)s [25] with enhanced solubility, processability, and good mechanical strengths and thermal properties, as well as glass transition temperature above 210 °C.

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http://dx.doi.org/10.1016/j.jfluchem.2012.09.007

Table 1
Synthetic data and some physical properties of the polymers.

Polymer	Yield (%)	η_{inh} (dL/g)[a]	M_w (g/mol)[b]	M_n (g/mol)[b]	M_w/M_n
Pa	97	0.75	78,900	38,500	2.05
Pb	98	0.80	80,800	39,900	2.03
Pc	97	0.77	79,700	40,600	1.96
Pd	97	0.82	81,500	40,800	2.00
Pe[c]	96	0.77	80,400	40,500	1.98

[a] Measured at a polymer concentration of 0.5 g/dL in NMP at 30 °C.
[b] Determined by GPC in tetrahydrofuran with polystyrene as standard.
[c] Derived from BFBB with BHPX in the literature [25].

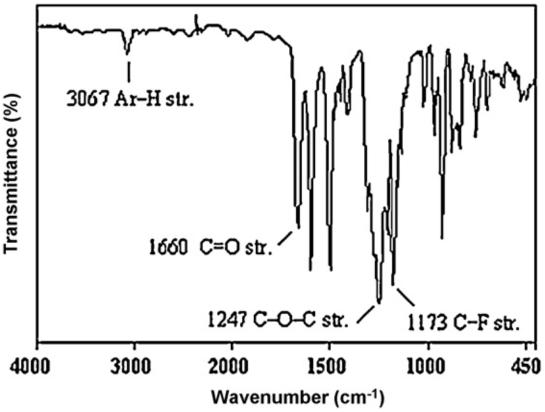


Fig. 1. FTIR spectrum of the PEEKK copolymer **Pc**.

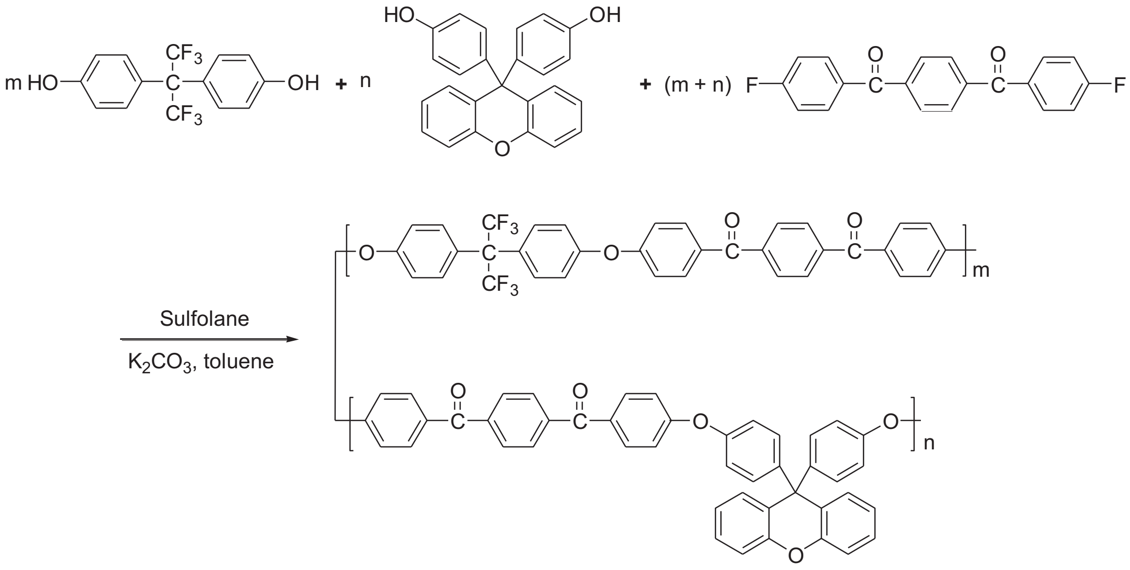
As part of an ongoing research program focused on the introduction of xanthene cardo group into the high-performance engineering thermoplastics, we here have developed several novel fluorinated PEEKK copolymers containing xanthene and hexafluoroisopropylidene moieties, which were prepared by an aromatic nucleophilic substitution reaction of 9,9-bis(4-hydroxyphenyl)xanthene (**BHPX**), 1,4-bis(4-fluorobenzoyl)benzene (**BFBB**) and 4,4′-hexafluoroisopropylidenediphenol (**6F-BPA**) in tetramethylene sulfone in the presence of potassium carbonate as an acid acceptor. In this paper, the solubility, tensile property, crystallinity, thermal property, water absorption, dielectric constant, as well as optical transparency of all the obtained polymers were investigated.

2. Results and discussion

2.1. Polymer synthesis

As outlined in Scheme 1, several PEEKK copolymers with xanthene and hexafluoroisopropylidene units were prepared by aromatic nucleophilic polycondensation of **6F-BPA**, **BHPX** and **BFBB** by varying the mole ratio of **BHPX** to **6F-BPA** (5/95–75/25) with potassium carbonate as the base, tetramethylene sulfone as a solvent and toluene as azeotropic solvent for removal of water. The reaction system was heated to a reflux temperature to promote phenolate formation. Subsequently, the polymerization was conducted at 200 °C after completely removing toluene. In the experiment, the viscosity of the reaction systems was increased dramatically only about 0.5 h, and high molecular weight polymers were obtained readily in 2.5–3 h after the completion of bisphenolate formation. Furthermore, it was found that the existence of bulky pendant xanthene groups in the monomer did not have a significant effect on the polymerization reaction. The inherent viscosity values and some physical properties of the resulting PEEKKs based on different ratios of monomers were given in Table 1. These copolymers were obtained in almost quantitative yields, with inherent viscosities in the range of 0.75–0.82 dL/g in NMP. At the same time, their gel permeation chromatography (GPC) data showed that the number-average molecular weights (M_n's) were in the range of 38,500–40,800 g/mol, and the polydispersity values of these copolymers ranged from 1.96 to 2.05, using polystyrene as a standard, indicating that all the copolymers had sufficiently high molecular weights to permit the casting of tough and flexible films.

The FTIR spectra of all the polymers supported their structures. All polymers exhibited characteristic absorption bands around 1660 cm^{-1} corresponding to aryl carbonyl groups, around 1247 cm^{-1} due to aryl ether linkages, along with the characteristic absorption bands of C–F stretching near 1174 cm^{-1}. Fig. 1 displayed the typical FTIR spectrum of the PEEKK copolymer **Pc**.



Pa: m = 23.75 mmol, n = 1.250 mmol; **Pb**: m = 18.75 mmol, n = 6.250 mmol
Pc: m = 12.50 mmol, n = 12.50 mmol; **Pd**: m = 1.250 mmol, n = 23.75 mmol

Scheme 1. Preparation of fluorinated (aryl ether ether ketone ketone) copolymers.