Synthesis and Characterization of Aromatic Cyclolinear Phosphazene Polyetherketones Containing bis-Spiro-Substituted Cyclotriphosphazene Unit

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Received 9 April 2001; accepted 18 June 2001

ABSTRACT: A novel monomer, 2,2-bis-(4′-fluorobenzoylphenoxy)-4,4,6,6-bis[spiro-(2′,2″-dioxy-1′, 1′-biphenylyl)] cyclotriphosphazene, was synthesized and polymerized with 4,4′-difluorobenzophenone as a comonomer and 4,4′-isopropylidenediphenol or 4,4′-(hexafluoroisopropylidene) diphenol in *N*,*N*-dimethylacetamide at 162 °C for 4 h to give two series of aromatic cyclolinear phosphazene polyetherketones containing bis-spiro-substituted cyclotriphosphazene groups. The structure of the monomer was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR. The effect of the incorporation of the bis-spiro-substituted cyclotriphosphazene group on the thermal properties of these polymers was investigated by DSC and thermogravimetric analysis. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 2993–2997, 2001

Keywords: bis-spiro-substituted cyclotriphosphazene; cyclolinear phosphazene polymer; aromatic polyetherketone

INTRODUCTION

Aromatic polyetherketones (PEKs) are classified as engineering thermoplastics because of their excellent thermal and chemical properties. They withstand temperatures as high as 400 °C and can be used at high temperatures of about 200 °C without oxidation. PEKs display glass-transition temperature (T_g) values ranging from 100 to over 200 °C and melting temperature (T_m) values of 300–400 °C, depending on their chemical structure.[1] Two synthetic routes for producing PEKs have been reported.[1] In the nucleophilic process, activated aromatic dihalides are reacted with alkali metal bisphenolates in polar aprotic solvents to produce PEK.

The incorporation of cyclotriphosphazene groups into the polymer backbone is of considerable interest as a result of their useful thermal and chemical properties.[2] Cyclolinear phosphazene polymers in which cyclotriphosphazene rings are recurring backbone units are synthesized from substituted cyclotriphosphazene with only two reactive functional groups and bifunctional organic compounds of variable structures and properties.[3–6]

In our previous research,[7,8] we applied this concept to the preparation of aromatic PEKs containing aryleneoxy-substituted cyclotriphosphazene units in the main chain via the Friedel–Crafts acylation route. All of these amorphous polymers are relatively soluble and have T_g's ranging from 90 to 105 °C and thermal stabilities around 410 °C with 10% weight losses in nitrogen, which are nevertheless lower when compared with the wholly aromatic parent PEKs. Therefore, bis-spiro substitution through 2,2′-dioxybiphenylyl groups on the cyclotriphosphazene ring was chosen to provide a novel monomer to give PEKs with improved thermal stability and

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 39, 2993–2997 (2001)