

# Synthesis and Characterization of Aromatic Poly(ether ketone)s Containing Cyclotriphosphazene Units

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**ABSTRACT:** Bis(4-oxybenzoic acid) tetrakis(phenoxy) cyclotriphosphazene (IUPAC name: 4-[4-(carboxyphenoxy)-2,4,6-tetraphenoxy-1,3,5,2λ<sup>5</sup>,4λ<sup>5</sup>,6λ<sup>5</sup>-triazatriphosphinin-2-yl]oxy-benzoic acid) was synthesized and direct polycondensed with diphenylether or 1,4-diphenoxybenzene in Eaton's reagent at the temperature range of 80–120°C for 3 hours to give aromatic poly(ether ketone)s. Polycondensations at 120°C gave polymer of high molecular weight. Incorporation of cyclotriphosphazene groups in the aromatic poly(ether ketone) backbone greatly enhanced the solubility of these polymers in common organic polar solvents. Thermal stabilities by TGA for two polymer samples of polymer series ranged from 390 to 354°C in nitrogen at 10% weight loss and glass transition temperatures ( $T_g$ ) ranged from 81.4 to 89.6°C by DSC. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 1227–1232, 1998

**Keywords:** cyclotriphosphazene; aromatic poly(ether ketone)

## INTRODUCTION

Aromatic poly(ether ketone)s (PAEK)s are classified as high-performance plastics because of their good mechanical properties and thermooxidative stability. Two synthetic routes for producing aromatic PAEKs have been described in literature.<sup>1</sup> One involves nucleophilic displacement and the other electrophilic condensation. In the latter case, an aromatic carboxylic acid or acid chloride is polycondensed with an aromatic ether using various type of catalysts.<sup>2</sup> Although PAEKs are opaque, tough engineering thermoplastic showing excellent high temperature resistance, they have proved difficult to synthesize and process because of their lack of solubility in common organic solvents. In this point of view, most structural modifications have been carried out to improve the properties of PAEK type polymers introducing the functional groups in<sup>3</sup> or onto<sup>4</sup> the polymer backbone.

Cyclotriphosphazene groups show useful thermal and chemical properties such as self-extinguishability and flame retardancy, which are generated basically by the presence of nitrogen and phosphorus elements in the ring.<sup>5</sup> Although several linear poly(phosphazenes) have been reported in literature,<sup>6</sup> there are also a large number of papers regarding the polymers with cyclotriphosphazene units obtained from addition<sup>7</sup> or step polymerization.<sup>8</sup>

In the present paper, we describe the synthesis and characterization of novel PAEKs containing tetrakisphenoxy substituted cyclotriphosphazene units containing. PAEKs were prepared by direct polycondensation of bis(4-oxybenzoic acid) tetrakis(phenoxy) cyclotriphosphazene (**1**) with diphenylether or 1,4-diphenoxybenzene using Eaton's reagent<sup>9</sup> as condensing agent and solvent.

## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene (Fluka), ethyl *p*-hydroxybenzoate (Fluka), phenol (Fluka), diphe-

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