

PL-02

Synthesis of New Polypyromellitimides and Their Properties

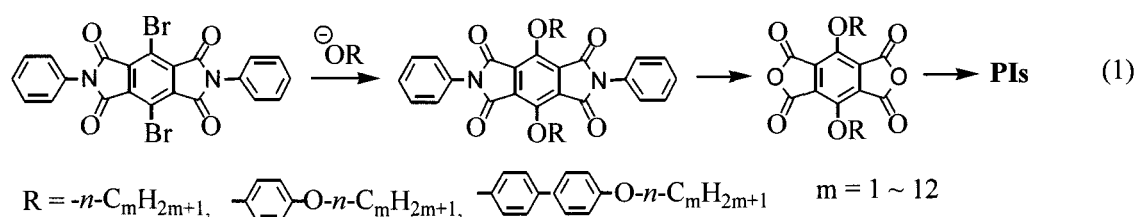
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Aromatic polypyromellitimides are certainly the most important type of polyimides considering the chain structure and performance in various properties. However, derivatization of pyromellitimide unit is considerably more difficult because only two sites of substitution are available in its ring, and most of new polypyromellitimides were prepared from pyromellitic dianhydride and new diamines.

In the present article three series of new polypyromellitimides have been prepared by aromatic nucleophilic substitution of *N,N'*-diphenyl-3,6-dibromopyromellitimide with *n*-alkoxy, 4-(*n*-alkoxy)phenyloxy and 4'-(*n*-alkoxy)biphenyloxy groups (1) and the liquid crystal aligning abilities on their thin rubbed films were investigated in terms of the pretilt angles. The substitution reaction proceeded smoothly when aromatic (*n*-alkoxy)aryloxy anions were used as nucleophiles, but in spite of various attempts aliphatic *n*-alkoxy anions were found to attack at imide C=O groups to open the ring. Therefore 3,6-di(*n*-alkoxy)pyromellitic dianhydrides had to be prepared by etherification with *n*-alkylbromides of *N,N'*-diphenyl-3,6-dihydroxypyromellitimide, which had been synthesized by oxidation of *N,N'*-diphenyl-3,6-dimethoxypyromellitimide with KMnO_4 in pyridine, followed by demethylation and deprotection. Peculiar enough, no other higher dialkoxy pyromellitimides than dimethoxypyromellitimide were stable enough against the oxidation condition.



Novel aqueous alkali-soluble polypyromellitimides were prepared by polymerization of 4-(3,6-dicarboxyphenyl)pyromellitic dianhydride with various conventional diamines. The dianhydride was synthesized by Suzuki coupling of *N,N'*-diphenyl-3,6-dibromopyromellitimide with 4-carboxyphenyldiboric acid (2). The polyimides were transformed to poly[4-(2-nitrobenzyl)pyromellitimide] by polymer-analogous reaction with 2-nitrobenzyl chloride and this new nitrobenzylated polyimide was investigated for application as novel photosensitive polyimide of non-precursor type.

