In Situ Polymerization of Aromatic Polyamic acid-esters and Analysis of Polymerization Mechanism

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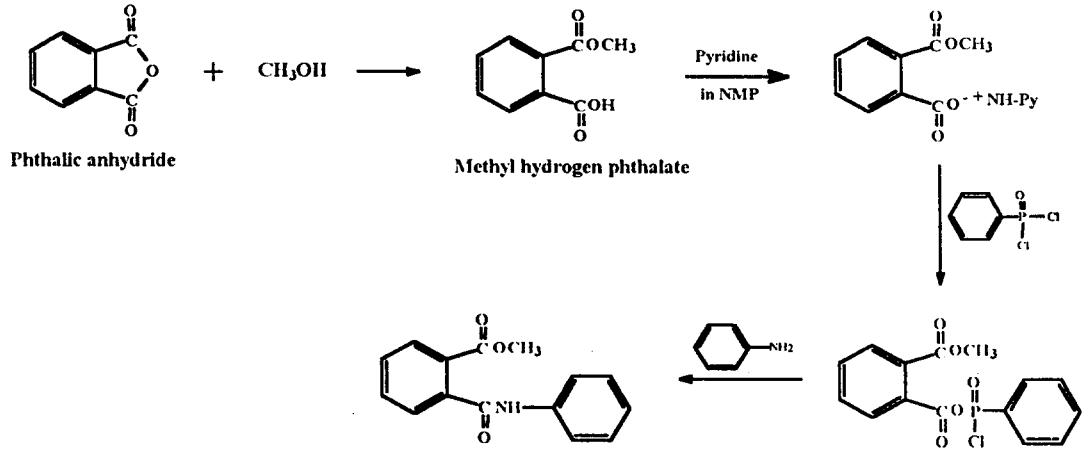
The *in situ* polymerization of aromatic diester-diacid monomers with aromatic diamines using phosphorus activating agents and tertiary amines was conducted and polymerization mechanism was investigated using model compounds. Pyromellitic dianhydride(PMDA) was heated at reflux in methyl alcohol to obtain dimethyl ester-diacid of PMDA(PMDE). PMDE was reacted with the phosphorus compound to form the activated anhydride intermediate and then the product was characterized by ^{31}P NMR and ^{1}H NMR spectroscopy. The polymerization proceeded via the nucleophilic substitution reaction according to the amidation reaction as showed in Scheme 1 using model compounds.

So far as the degree of polymerization, phenyl phosphonic dichloride and pyridine were superior to any other activating agents and tertiary amines (Table 1). The *in situ* polymerization of various dimethyl ester-diacid of aromatic dianhydrides with aromatic diamines was examined.



Scheme 1. Amidation reaction between aromatic acid and amine

Table 1. Polymerization of PMDE and 4,4′-oxydianiline with various phosphorus activating agents in NMP at a room temperature for 24h in the presence of various tertiary amines

Tertiary amine (pk_a)		η^{a}_{inh} of polyamic acid ester				
		$POCl_3$	$PhOPOCl_2$	$PhPOCl_2$	$(PhO)_2POCl$	$(C_2H_5O)_2POCl$
Pyridine	(5.23)	0.25	0.20	0.32	d	d
α-Picoline	(5.97)	0.12	0.16	0.16	d	d
2,6-Lutidine	(6.99)	b	b	b	b	b
Imidazole	(7.12)	0.18	0.23	0.24	d	d
Isoquinoline	(8.60)	c	c	c	c	c
Triethyl amine	(11.0)	c	c	c	c	c

[a]Measured at a concentration of 0.5g/dl in NMP at 25℃. [b]Precipitated when tertiary amine was introduced. [c]Precipitated when activating agent was introduced. [d]Polymer was not precipitated in methyl alcohol.