

SHORT COMMUNICATIONS

**Novel Synthesis of Polyimide with Pendant
1-Phenylethyl Ester**

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Alkyl esters of polyamic acids are noted as functional precursors of polyimides such as photosensitive polymers,¹ because full-imidized polyimides show low solubility. The polymers have been synthesized by polycondensation of the corresponding half-esters of tetracarboxylic acids or their derivatives with diamines so far. However, this synthetic route is complicated.¹ Recently, we found that esterification of poly(methacrylic acid) (PMAA) with alkyl halide proceeded quantitatively using 1,8-diazabicyclo[5,4,0]undecene-7 (DBU) at room temperature.²⁻⁴ When DBU is used, the direct esterification of polyamic acid with alkyl halide can be expected to give the ester of polyamic acid.

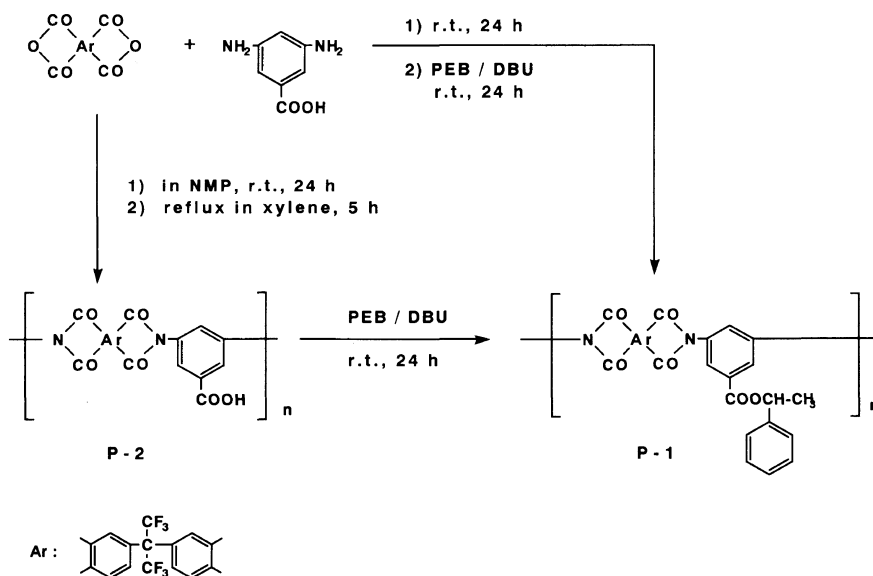
This communication reports the reaction of the polyamic acid resulting from polyaddition of hexafluoroisopropylidene-2-bis(phthalic anhydride) (6FDA) with 3,5-diaminobenzoic acid (DABA) with 1-phenylethyl bromide (PEB) using DBU in order to evaluate the reactivity of two different carboxylic acids in the polyamic acid (Scheme 1).

The model compound *N*-[*m*-(1-phenylethoxycarbonyl)phenyl]phthalimide (*Anal. Calcd* for C₂₃H₁₇NO₄: C, 74.39%; H, 4.61%; N,

3.77%. Found: C, 74.11%; H, 4.60%; N, 3.71%) was prepared in 96.7% yield from the addition of phthalic anhydride (0.741 g, 5 mmol) with *m*-aminobenzoic acid (0.687 g, 5 mmol) in dimethyl sulfoxide (DMSO, 10 ml) at room temperature for 24 h followed by reaction with 3-fold amounts of PEB and DBU at room temperature for 2 h.

A typical procedure for the synthesis of polyimide with pendant 1-phenylethyl ester (P-1) is as follows: The polyaddition of 6FDA (1.471 g, 5 mmol) with DABA (0.761 g, 5 mmol) was carried out in *N*-methyl-2-pyrrolidone (NMP, 10 ml) at room temperature for 24 h. To the resulting polymer solution was added a solution of DBU (3.43 g, 22.5 mmol) in NMP (10 ml) and PEB (4.16 g, 22.5 mmol), and the mixture was stirred at room temperature for 24 h and poured into methanol (500 ml). The resulting polymer was purified by reprecipitating twice from THF solution into methanol, and dried at 60°C *in vacuo*. The yield of P-1 was 2.97 g (89.4%). The degree of esterification was 100 mol%, calculated from the integrated ratio of ¹H NMR spectrum. Reduced viscosity, 0.15 dl g⁻¹ [0.5 g dl⁻¹ in dimethylformamide (DMF) at 30°C].

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Scheme 1. Synthesis of P-1.

Also, P-1 [0.15 dl g^{-1} (0.5 g dl^{-1} in DMF at 30°C)] was prepared in 96.3% yield by esterification of the corresponding polyimide (P-2) containing pendant carboxylic acid with PEB and DBU.⁴

RESULTS AND DISCUSSION

A model reaction of *o*-(*N*-phenylcarbamoyl)benzoic acid (amic acid) with 3-fold amounts of PEB and DBU was carried out in NMP at room temperature according to esterification of PMAA with PEB,⁴ prior to the synthesis of polymer. The IR spectrum of the product showed characteristic absorptions at 1785 and 1725 cm^{-1} due to C=O bonds of imide. Also, the ^1H NMR spectra showed no proton peak due to N-H and -COOH groups, and proton peaks at $\delta = 1.68$, 6.15 , and 7.2 – 8.2 ppm based on 1-phenylethyl groups (Figure 1). The product composed of equimolar amounts of 1-phenylethyl group and imide calculated from the integrated ratio of phenyl protons to methine or methyl protons. 1-Phenylethyl ester (I) of the amic acid was thus not obtained from the reaction in contrast

to our expectation, and the imidization of amic acid and esterification of pendant carboxylic acid proceeded simultaneously to give *N*-[*m*-(1-phenylethoxycarbonyl)-phenyl]phthalimide (II) in 96.7% yield at room temperature for 2 h. Recently, the chemical imidization of esters of amic acid and polyamic acid was investigated using bases such as DBU independently.⁵ The imidization of amic acid using the DBU-PEB mixture proceeded through the corresponding ester (I) or the transition state between the amic acid and its ester as an intermediate (Scheme 2), although the intermediate was not observed in the model reaction.

This prompted us to synthesize polyimide (P-1) containing pendant 1-phenylethyl ester. The synthesis of P-1, (polyaddition, imidization, and esterification), was carried out from 6FDA and DABA using the one-pot method. P-1 was prepared from polyaddition of 6FDA with DABA at room temperature for 24 h followed by the imidization and esterification of the resulting polyamic acid with excess amounts of PEB and DBU (Table I). The synthesis of P-1 was carried out stepwise. The corresponding polyimide [P-2; 0.13 dl g^{-1}

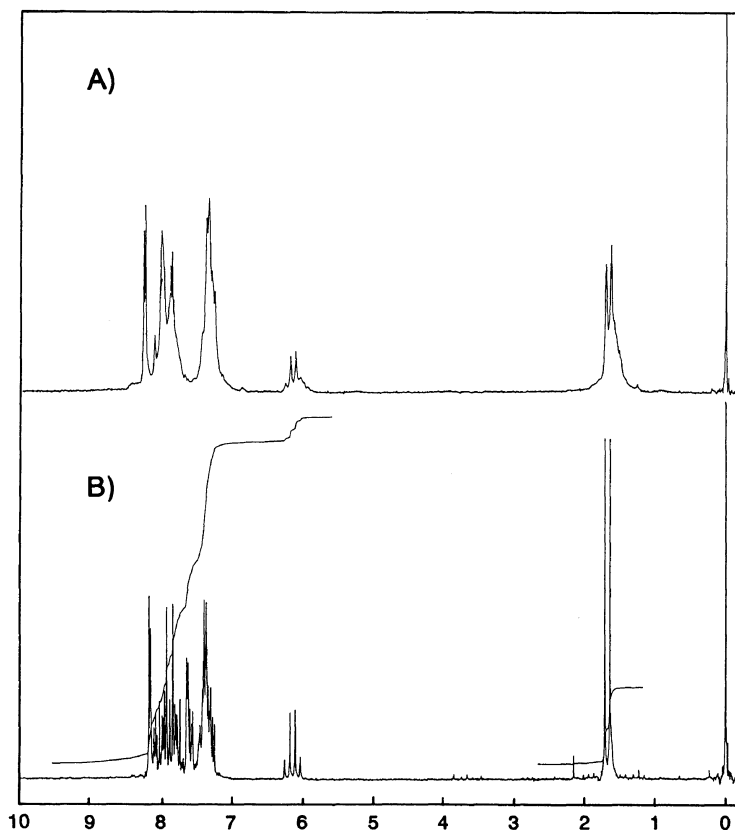
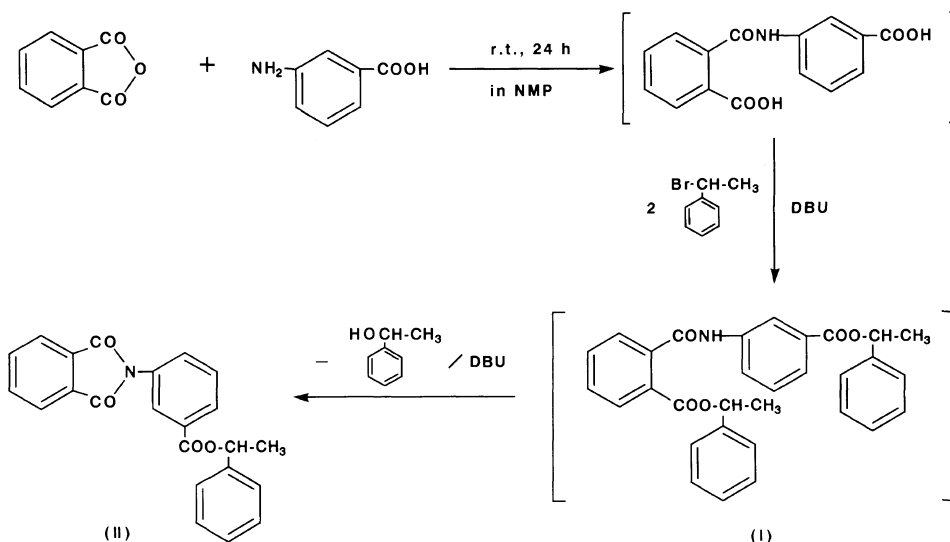


Figure 1. ^1H NMR spectra: A) P-1; B) model compound (II).

(0.5 g dl^{-1} in DMF at 30°C)] containing pendant carboxylic acid was prepared by the polyaddition of 6FDA with DABA in NMP followed by azeotropic imidization of the polyamic acid in xylene for 5 h under reflux conditions. The esterification of the pendant carboxylic acid in P-2 with PEB proceeded quantitatively to give P-1 [0.15 dl g^{-1} (0.5 g dl^{-1} in DMF at 30°C)] by the esterification of PMAA with PEB.⁴ The IR spectrum of the obtained polymer showed strong absorptions at 1785 and 1730 cm^{-1} ($\text{C}=\text{O}$ stretching of imide and ester). The ^1H NMR spectra of the polymer showed signals of methyl protons at $\delta=1.67\text{ ppm}$, methine proton at $\delta=6.1\text{ ppm}$, and aromatic protons at $\delta=7.0\text{--}8.3\text{ ppm}$. The IR and ^1H NMR spectra were exactly consistent with those of a polymer prepared

using the one-pot method, and resembled very well those of the model compound (Figure 1). Therefore, the reaction of polyamic acid with PEB gave P-1 in the presence of DBU, although quantitative imidization of polyamic acid was required for 24 h at room temperature. A mixture of acetic anhydride-pyridine has been used for the chemical imidization of polyamic acid as dehydration reagent and solvent.⁶ This method needs to isolate unstable polyamic acid from the polymer solution prepared by the polyaddition of tetracarboxylic dianhydride with diamine, while polyaddition and imidization can be carried out in a one-pot using the DBU-PEB mixture. In addition, the esterification of pendant carboxylic acid with PEB occurred simultaneously to give P-1 from the starting materials in the one-pot when the



Scheme 2. Model reaction of amic acid with PEB using DBU.

Table I. Synthesis of P-1

Dianhydride	Solvent	Yield	DE ^a	η_{sp}/C^b
		%	%	dl g ⁻¹
6FDA	DMSO	66.6	100	0.31
	DMAc	89.9	100	0.11
	DMF	86.6	100	0.12
	NMP	89.4	100	0.15

^a Degree of esterification.^b Measured at 0.5 g dl⁻¹ in DMF at 30°C.

DBU-PEB mixture was used. These results suggest that this method is simpler and more convenient than other methods for the synthesis of polyimide. The obtained polymer was soluble in many solvents such as THF, chloroform, and cyclohexanone, and stable under 200°C without any acid catalyst. The addition of an acid catalyst caused the deesterification of P-1 to occur at the lower temperature. Therefore, 1-phenylethyl ester in P-1 is available as an acid sensitive protecting

group.

Further studies on the synthesis and acid-catalyzed deesterification of polyimide containing 1-phenylethyl ester are now in progress.

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