UV absorption spectra of polyamide acids and their amine salts

Qinghua Li, Takashi Yamashita, Kazuyuki Horie
Department of Chemistry and Biotechnology,Graduate school of Engineering,
University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

A series of polyamide acids and polyamide acid amine salts PMDA-PDA, BPDA-PDA, BTDA-PDA were prepared and UV absorption properties were studied.

Introduction

With superior thermal and mechanical properties and low dielectric constant, polyimides have been widely used in the electronics industry.[1] Being insoluble in most common solvents, polyimides are usually processed in the form of their precursors, polyamide acids, which are then thermally converted to the imide structure. However, most polyamide acids are soluble only in strongly polar solvents which need careful handling. In our previous study,[2] it was found that the amine salts of polyamide acids are soluble in water, and that their color is different from the original polyamide acids.

In this report, several polyamide acid amine salts were prepared and their UV absorption spectra were studied. Also, we will discuss the factors which affect their absorption with model compounds.

Experiments

A series of polyamide acids were prepared by the ordinary process, with pyromellitic dianhydride(PMDA), 3,4,3',4'-biphenyltetracarboxylic dianhydride(BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride(BTDA), as dianhydrides, and p-phenylene-diamine(PDA) as a diamine. Polyamide acid amine salts(PASs) were prepared by mixing an equimolar ratio of polyamide acids and triethanolamine in dimethylacetamide(DMAc). The UV absorption spectra of both PAAs and PASs were measured with a Jasco-660 UV/VIS spectrophotometer in dimethylformamide(DMF) and in water solution.

Triethanolamine $(COH)CH_2CH_2)_3N$

Results and discussion

In order to elucidate the relationship between molecular structure and absorption properties, we selected three kinds of aromatic tetracarboxylic dianhydride PMDA, BPDA, BTDA to react with PDA to form polyamide acids and their amine salts in this research.

All the samples of these polyamide acid amine salts are soluble in water. According to IR spectra, we could say all the polyamide acids were converted to polyamide acid amine salts completely because of the disappearance of C=O absorption peak in 1710cm^{-1} in the absorption spectra of the amine salts.

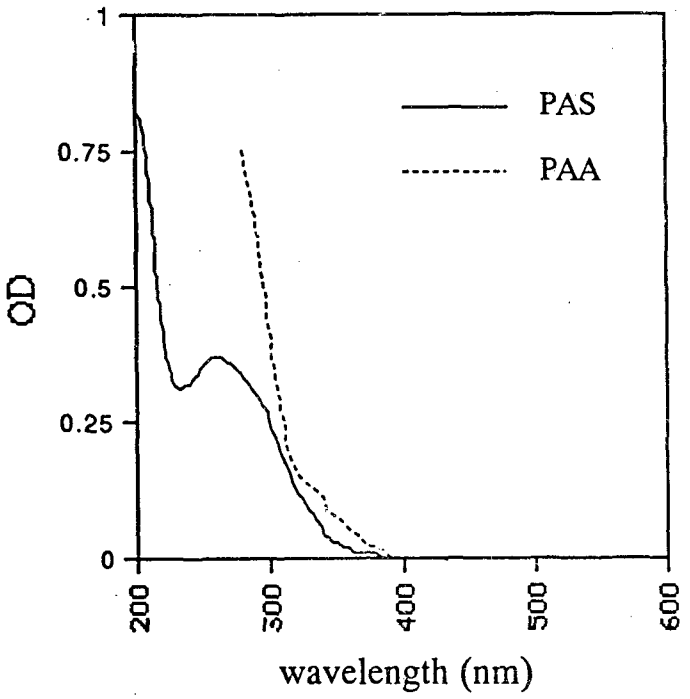

Fig.1. The UV absorption spetra of PAA(PMDA/PDA)(1.0×10^{-5} M) and PAS(PMDA/PDA)(1.71×10^{-5} M)

Fig.1.is the UV absorption spectra of PAA and PAS of PMDA/PDA . As can be seen, the absorption of PAS is smaller than PAA. Table 1. is the summary of molar extinction coefficient of polyamide acids and their amine salts in DMF solution and water solution at 300 nm. As shown in Table 1., the value of ε of PAS(PMDA/PDA) in H_2O is smaller than PAA(PMDA/PDA) in DMF. On the other hand, the value of ε of PAS(BTDA/PDA) is bigger than PAA for BTDA/PDA.

Table 1. Molar extinction coefficient of PAAs and PASs at 300nm

ε ($M^{-1}cm^{-1}$)	PMDA/PDA	BPDA/PDA	BTDA/PDA
PAA in DMF	4.30×10^4	3.72×10^4	2.14×10^4
PAS in H2O	1.52×10^4	3.45×10^4	2.71×10^4

In aromatic polyamide acids, charge transfer complex (CTC) between dianhydride and

diamine moieties is known to exist. The CTC is one of the factors which affects the color of polyamide acids.[3] When PAS are formed, the charge transfer interaction would be weakened by the ion pair between amine and carboxylic group. At the same time, polarity of the solvent, and the degree of conjugation between the dianhydrides and diamines through the amide bond have also an important effect on determining their color. So we will report in more detail with some model compounds.

Reference

(1). K.L.Mittal, Polyimides, plenum press, NewYork, 1984

(2). H.Yoshimoto, Thesis for the degree of bachelor, 1993; T.Yamashita et al., Polymers for Microelectronics, 837(1990)

(3). E.D. Wachsman and C.W.Frank, Polymer, 29, 1191(1988)