Synthesis of Acetal-Containing Main Chain Degradable Type Photosensitive Polyimide

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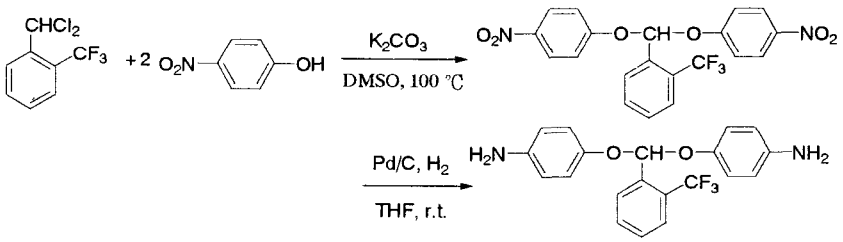
INTRODUCTION:

Photosensitive polyimides are one of the key materials for advanced microelectronics. Recently, a great deal of interest has been directed toward positive-working type polyimide resists, initially due to their workable development with water-base solution. Among them, main chain degradable positive-working photosensitive polyimides have been reported in some cases, however, most of them exhibited poor photosensitivity or hard development-conitiond. In this paper, we reported a novel main chain photodegradable polyimides containing acetal structure.

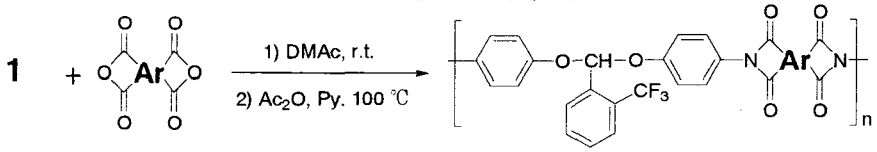
EXPERIMENTAL SECTION:

Monomer **1** was prepared by catalytic reduction of the corresponding dinitro-compound prepared by Williamson reaction of 4-nitrophenol with 2-trifluoromethyl benzal chloride.



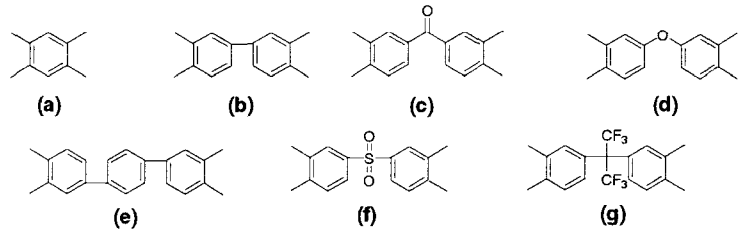
(1)

Main chain degradable polyamic acids (PAAs) containing acetal structure were prepared by polyaddition of monomer **1** with various aromatic dicarboxylic anhydrides (**2**) in DMAc. Without isolating the PAA precursors, chemical imidization was immediately carried out to yield the corresponding polyimides.



(2) **(3)**

Ar:



RESULTS AND DISCUSSIONS:

Characterization of polyimides: The polymers were successfully obtained with inherent viscosities in the range 0.29-0.34 dL/g, as shown in Table 1. The imidization was carried out by chemical reaction between polyamic acids and acetic anhydrous with high yields over 96%. The formation of polyimides was confirmed by means of ^1H NMR and IR spectroscopy. The peaks at around 10.5 ppm attributed to amide groups disappeared after imidization. Moreover, the IR spectra showed characteristic absorptions at 1785 and 1727 cm^{-1} due to the imide carbonyl group.

The thermal properties of polyimides were examined by thermogravimetry (TG) and differential scanning calorimetry (DSC). The weight loss started at about 290-300 °C both in air and nitrogen atmospheres, 10% weight loss temperatuer (T_{10}) were measured at approximately 410-450 °C. The glass transition temperature (Tg) of polyimide **3** were found to be in the range 200-230 °C.

Table 1. Preparation and Thermal Properties of Acetal-Containing Polyimides.

Polyimide	$[\eta]$ [d] (dL/g)	Tg (°C) [a]	Decomposition Temperature T_1 (°C) [b]		T_{10} (°C) [c]	
			in air	in N_2	in air	in N_2
3a	0.31	232	290	302	414	414
3b	0.34	214	333	335	437	440
3c	0.29	202	318	317	426	415
3d	0.31	198	321	319	425	419
3e	0.31	217	337	338	462	456
3f	0.29	220	315	318	415	418
3g	0.32	221	316	316	438	434

[a] Determined by DSC at a heating rate of 20 °C/min in nitrogen.
[b] 1% weight loss determined by TG at a heating rate of 10°C/min .
[c] 10% weight loss temperature.
[d] Measured at a concentration of 0.5g/dL in DMAc at 30 °C.

The solubility of polyimides **3** was studied qualitatively and was summarized in Table 2. All of the polyimides showed excellent solubility not only in aprotic solvents but also in non-polar solvents, which is probably due to the $-CF_3$ substituent and acetal structure.

Table 2. The solubility of acetal-containing polyimides [a]

Polyimide	Solubility						
	NMP	DMAc	DMF	DMSO	THF	Chloroform	*m*-Cresol
3a	++	++	++	++	+	+	+
3b	++	++	++	++	±	+	+
3c	++	++	++	++	+	++	+
3d	++	++	++	++	+	++	+
3e	++	++	++	++	±	+	+
3f	++	++	++	++	+	++	+
3g	++	++	++	++	++	++	++

[a]: ++ soluble at room temperature; + soluble at heating
± part soluble

All of the polyimide films showed good transparecy. The UV-visible spectrum of polymer **3d** was shown in Figure 1. The transmittance of polyimide **3d** film (1 μm thick) was 91% at 365 mn and 98% at 436 nm, respectively, which suggested the photochemical reactions of PAG in the polyimide film could occur smoothly.

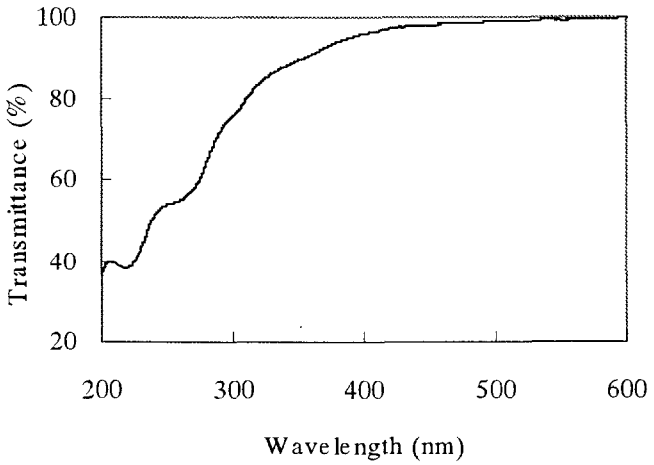
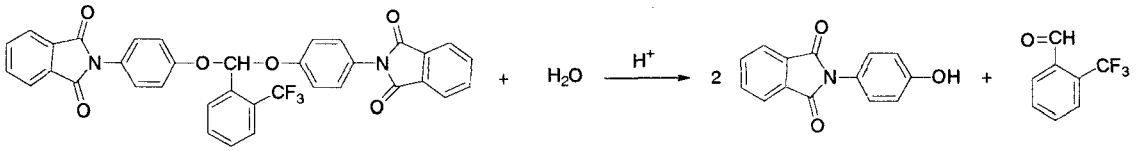


Figure 1. UV-visible spectrum of polyimide film **3d**.

Model Reactions: In order to investigate the acid-catalyzed degradation behavior of the acetal unit in polyimides **3**, the model reaction of the compound **4** with *p*-toluenesulfonic acid was carried out under various conditions.



(4)

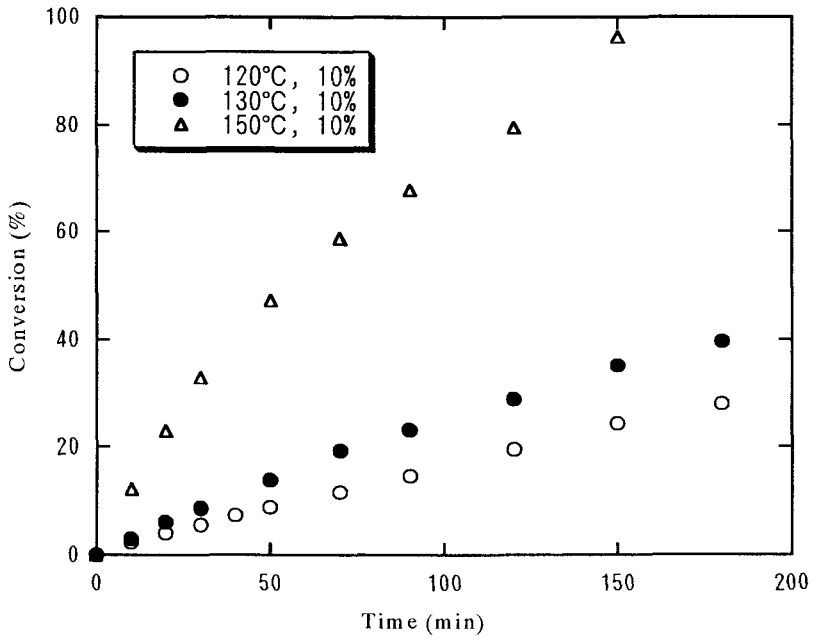


Figure 2. Relationship between conversion and reaction time for the model reaction. The amount of *p*-toluenesulfonic acid: 10 mol%

Figure 2 showed the relationship between the conversion and reaction time for acid-catalyzed degradation of compound **4** under different temperature, while the amount of the acid catalyst kept to be constant (10 mol%/ 3 wt%). All of the acetal unit decomposed within 180 min at 150 °C. However, the conversion decreased to about 40% at 130 °C.

The degradation behavior of polyimide **3d** was investigated also with *p*-toluenesulfonic acid as a catalyst. The relationship between the inherent viscosity of polymer **3d** and the reaction time was shown in Figure 3. The inherent viscosity of polymer **3d** (0.31 dL/g) decreasd with the reaction time. In ^{1}H NMR for the sample reacted for 180 min, the peak associated with a phenolic proton was clearly observed. It is clear that acid-catalyzed main chain degradation occurred for polymer **3d**, similar to the model reaction.

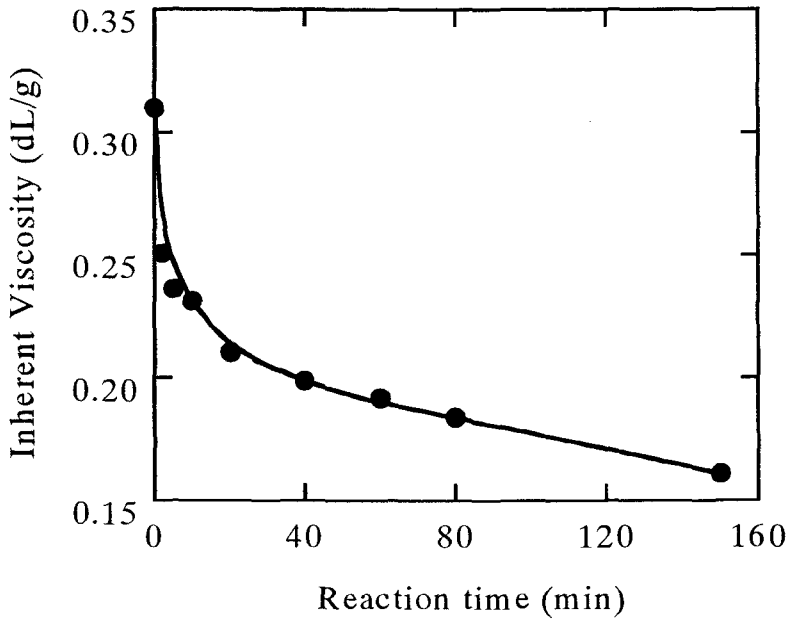


Figure 3. Relationship between [η] of polyimide **3d** and reaction time at 130 °C with 10 mol% of *p*-toluenesulfonic acid.

CONCLUSIONS:

Main chain degradable polyimide **3**s were synthesized by polyaddition of monomer **1** with various aromatic tetracarboxylic anhydrides followed by chemical imidization. These polyimides showed excellent transparency in UV region, and also better solubility in common organic solvents. Acid-catalyzed degradation behavior was confirmed by the model reaction and polymer **3d**. These data suggested the possibility of the polyimides **3**s for the application of chemically amplified photoresist materials.