

Low-K and Low-CTE wholly cycloaliphatic polyimides

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ABSTRACT

Rigid wholly cycloaliphatic polyimides (PIs) possessing simultaneously a low dielectric constant (K) and low linear coefficient of thermal expansion (CTE) were molecular designed. At first, we focused on CBDA/CHDA polyimide derived from 1,2,3,4-cyclobutanetetracarboxylic dianhydride with trans-1,4-cyclohexanediamine. No polymerization proceeds in this system under any conditions owing to the formation of completely insoluble salt at the initiate stage. The in-situ silylation method made the polymerization possible when an adequate solvent was selected. Precise control of the silylation% of CHDA led to a considerably high molecular weight silylated poly (amic acid) (Si-PAA) with a good solution stability during storage at room temperature. CBDA/CHDA polyimide film showed considerably a low K (2.66) and a low CTE (26 ppm/K) simultaneously. Then we synthesized 1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride with bulky substituents which is expected to prevent the strong salt formation. In contrast to the CBDA/CHDA system, the polymerization in DMCBDA/CHDA system proceeded smoothly in DMAc without silylation of CHDA. DMCBDA/TFMB polyimide film showed a considerably low K (2.59), a low CTE (28.1ppm/K), a high Tg (341°C), and high transparency simultaneously.

INTRODUCTION

Aromatic polyimides (PIs) have been utilized in variety of industrial fields, such as electric, microelectronic, optoelectronic, and aerospace applications. In recent years, especially, polyimides used as interlayer dielectrics are demanded to decrease both the dielectric constant (K) and the coefficient of thermal expansion (CTE). But there are so far few practical low-K and low-CTE PIs. In general, the low CTE characteristics are observed in several PI systems with linear/stiff chain structures. On the other hand, the introduction of fluorine, aliphatic, and bulky groups with low polarizability per a unit molecular volume is known to be effective to decrease the dielectric constant. Our approach is to use rigid wholly cycloaliphatic monomers, that is, CHDA, CBDA and DMCBDA which are expected to show low-K and low CTE, simultaneously. The monomers used in this work are shown in Figure 1.

EXPERIMENTAL SECTION

In CBDA/CHDA system, the in-situ silylation method was applied to poly(amic acid) (PAA) polymerization to avoid salt formation. N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was used as a silylation agent. The detailed conditions of the polymerization are described later.

1,3-dimethyl-1,2,3,4-cyclobutanetetracarboxylic dianhydride (DMCBDA) was prepared by photodimerization of citraconic anhydride in dioxane in the presence of benzophenone as a sensitizer with a high pressure mercury lamp. To the dry N,N-dimethylacetamide (DMAc) solution of CHDA or TFMB, the equimolar amount of DMCBDA powder was gradually added with stirring until the reaction mixture turned to a viscous and clear solution. The PAA solutions obtained were spread on a glass substrate then, dried at 60°C for 1h. PAA films were thermally imidized at established

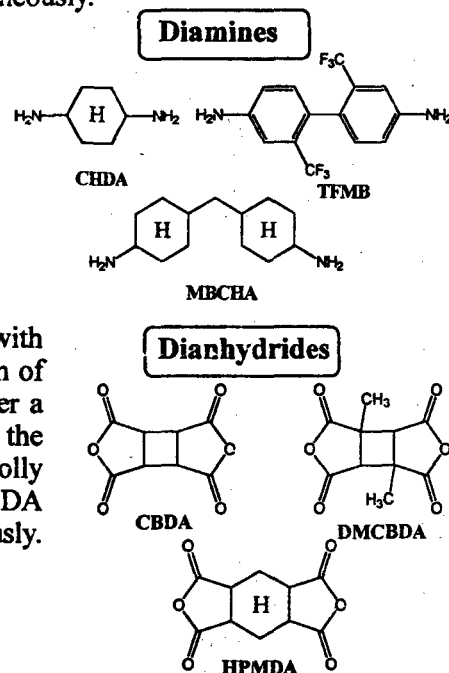


Figure 1. Structures of monomers used.

temperatures. CTE, T_g, K_{RI} (K estimated from average refractive index), 5% weight loss temperature (T_d⁵) of PI films were measured.

RESULT AND DISCUSSION

Polymerization in the CBDA/CHDA system

We first attempted the polymerization in various solvents (DMAc, NMP, DMF, DMSO, THF/MeOH, etc.) at varying temperatures (20-150°C) in a wide range of monomer concentration (1-15wt%). But strong salt formation at the initial stage prevented completely the polymerization. In order to avoid the salt formation, CHDA was completely silylated (100%) before the addition of CBDA. However, unexpectedly, no polymerization took place in any solvents except for in a mixed solvent (DMAc/HMPA) by stirring for 3 months. Fortunately, we found out that a partial silylation (50%) of CHDA of in DMAc/HMPA(1:3vol%) led to a formation of a high molecular weight ($\eta_{red}=4.4\text{dL/g}$) Si-PAA as listed in Table 1. The obtained Si-PAA solution was highly stable during storage at room temperature. This is probably attributed to the presence of an adequate content of the carboxy groups, which contribute to solvation, on the partially silylated PAA chains.

Table 1 Reduced viscosities of Si-PAA obtained and polymerization conditions in CBDA/CHDA system.

Solvent	Solid content/wt%	Silylation/%	$\eta_{red}/\text{dL/g}$
DMAc	9.9	60	—
NMP	14.4→9.4	50	—
DMF	14.1→9.1	50	—
THF/MeOH 4:1/wt%	15	0	—
DMAc/HMPA 1:3/vol%	13.4→7.4	50	2.72
"	9.3	50	4.4
"	13.4→7.4	70	1.03
"	9.3	100	0.63

Thermal imidization of the Si-PAA film cast from the DMAc/HMPA solution led to black-colored brittle films. This result is probably due to residual HMPA. Then, the cast film was immersed in MeOH to remove residual HMPA before thermal imidization. This procedure allowed to form a good quality and highly tough films. The properties of CBDA/CHDA polyimide film are shown in Table 2. CBDA/CHDA film showed a considerably low K (2.66) and a low CTE (26 ppm/K) simultaneously. However, when was used MBCHA instead of CHDA, polymerization proceeded smoothly in DMAc without silylation. The CBDA/MBCHA film did not show low CTE (>50ppm/K) owing to the bent structure at the methylen linkage of MBCHA.

Table 2 Properties of CBDA/CHDA polyimide films.

Ti(°C)	T _g (°C)	CTE(ppm/K)	n_{in}	n_{out}	Δn	K _{RI}	ϵ'	Td ⁵ (°C)N ₂	Td ⁵ (°C)air
300	ND	26.1	1.5645	1.5367	0.0278	2.66		427	391
340	ND	25.7	1.5614	1.5415	0.0199	2.66	2.8546(1MHz) 2.6501(10MHz)	437	397

If bulky substituents can be introduced on the CBDA unit, it is expected to be obtained a high molecular PAA without the use of HMPA and silylation agent. In fact, the PAA of DMCBDA/CHDA was polymerizable on the common procedure in DMAc at room temperature. In contrast to the CBDA/CHDA system, the formed salt was not so tough in DMCBDA/CHDA. The properties of DMCBDA/CHDA film are shown in Table 3. A lower K was obtained by introduction of the bulky methyl groups, although low CTE characteristic was not attained. The film properties of other wholly and semi-cycloaliphatic PIs will be also reported.

Table 3 Properties of PI films for DMCBDA systems.

	T _g (°C)	CTE(ppm/K)	n_{in}	n_{out}	Δn	K _{RI}	Td ⁵ (°C)N ₂	Td ⁵ (°C)air	cut off/nm
DMCBDA/TFMB	341	28.1	1.5509	1.5007	0.0502	2.59	434	423	284
DMCBDA/CHDA	360	42.8	1.542	1.5395	0.0025	2.61	428	377	262