Absorption, Fluorescence, Photoconductivity, and Thermal Properties of Alicyclic Polyimides

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1. Introduction

It is well known that intermolecular charge-transfer complexes are formed between imide and amine moieties for the usual polyimides composed of aromatic di(acid anhydride)s and aromatic diamines [1].   The formation of intermolecular charge-transfer complexes would be the reason for the coloration and the high dielectric constants of polyimides compared to other polymer films.   It may be also the reason for the low quantum yields of photosensitive benzophenone-type polyimides with ethyl-substituted aromatic diamines, PI(BTDA/DEDPM) [2].   Thus, Jin et al. [3] tried to use alicyclic diamines into the main chains of polyimides to restrain the formation of intermolecular charge-transfer complexes, to improve the transparency, and to lower the dielectric constant.   Of course, chemical thermal stability versus degradation of the polyimides composed of aliphatic diamines would be reduced, but by using the alicyclic diamines, the physical thermal stability of the polyimides such as T_g and thermomechanical properties did not show a decrease.   A photosensitive polyimide composed of BTDA with a methyl-substituted alicyclic diamine, PI(BTDA/DMDCHA), showed marked improvement in photosensitivity due to the absence of charge-transfer formation [4].

There are two methods for getting transparent polyimides without not-so-much reducing their thermal stability, the first is to introduce -C(CF$_3$)$_2$- group or other bulky substituent groups in main chains in order to avoid intermolecular aromatic interaction, and the second is to introduce alicyclic diamine or acid dianhydride in order to avoid intra- and intermolecular charge transfer formation.

In the present paper, we have prepared several highly transparent polyimides by combining 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanedianhydride (6FDA), 1,2:3,4-cyclobutanetetracarboxylic dianhydride (CBDA), and 2,3,5-tricarboxycyclopentylacetic acid dianhydride (TCAAH) with an aromatic diamine, 4,4'-diaminodiphenylmethane (DPM), a fluorinated diamine, 2,2-bis(4-diaminodiphenyl)hexafluoropropane (6FdA), and an alicyclic diamine, 4,4'-diaminodicyclohexylmethane (DCHM).   All these polyimides showed high transparency in the visible region, especially, PI(CBDA/DCHM) and PI(TCAAH/DCHM) showed absorption peaks only at 210 nm.

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A polyimide of pyromellitic dianhydride (PMDA) with an alicyclic diamine (DCHM) has shown the increase in photoconductivity compared to a usual aromatic polyimide, PI(PMDA/ODA). This unexpected phenomenon can also be explained by the existence of intra- and intermolecular charge transfer.

2. Polyimides with Alicyclic Diamines and/or Acid Dianhydride

Polyimides used in the present study for transparency are summarized in Figure 1.

Figure 2 shows the UV-Vis absorption spectra of thin films of the alicyclic polyimide, PI(6FDA/DCHM), and aromatic polyimide, PI(6FDA/PDA), which are normalized with a film thickness of 0.6 μm [5]. PI(6FDA/DCHM) and PI(6FDA/PDA) have no absorption band above 370 nm. PI(6FDA/PDA) shows a shoulder absorption at 260 nm, which is similar to that for kapton type aromatic polyimide, attributed to the intramolecular charge transfer. The introduction of 6FDA into polyimide chains weakened the intermolecular charge transfer due to the steric hindrance. On the other hand, the weak electron donating property of DCHM reduced not only intermolecular charge transfer but also intramolecular charge transfer.

UV-Vis absorption spectra of polyimide (PI) and poly(amide acid) (PAA) films composed of CBDA are shown in Figure 3 [6]. PI(CBDA/DCHM) has an absorption peak at 210 nm, and shows almost no absorption above 310 nm, which exhibits extremely transparent property in almost all ultraviolet/visible region. This can
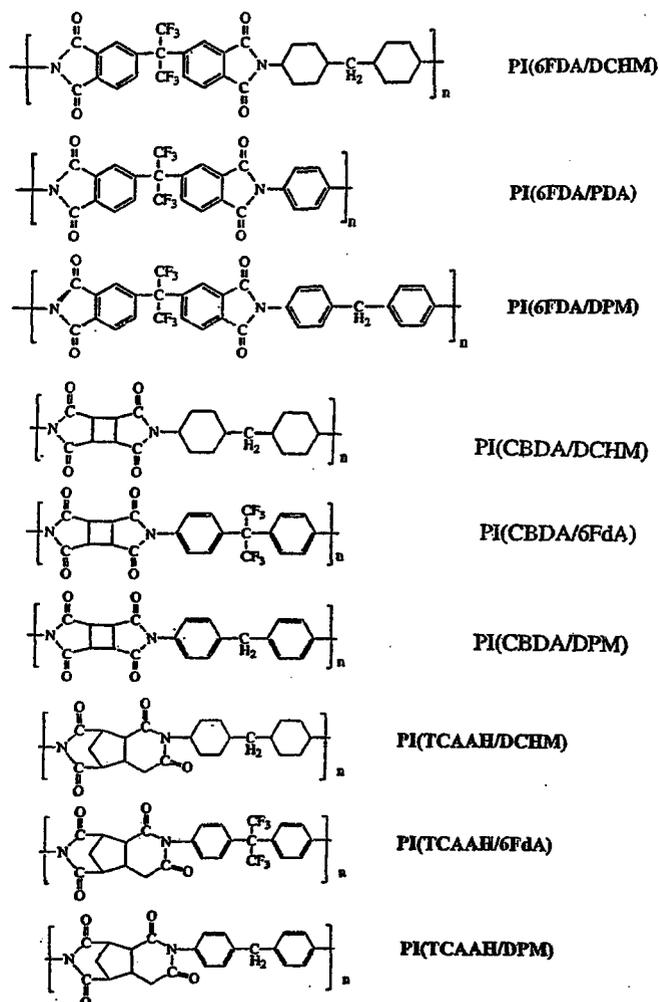

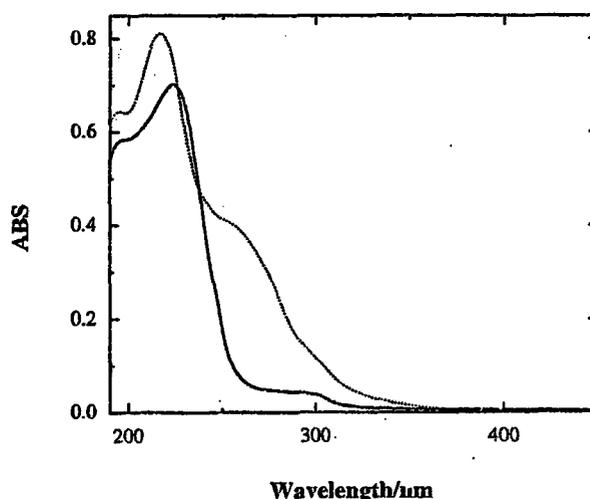Figure 1. Chemical structures of polyimides studied.

Figure 2. The UV absorption spectra of PI(6FDA/DCHM) (−) and PI(6FDA/PDA) (···) thin film of 0.6μm.

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be explained by the elimination of intra- and intermolecular charge transfer formation. PI(CBDA/DPM) and PI(CBDA/6FdA) have absorption peaks at 236 nm and 235 nm, which are due to the absorption of phenylene groups of the diamine moieties, as the dianhydride belongs to alicyclic compounds. In poly(amide acid)s, partial contribution of enolizaton of amide bond [7] (-C(OH)=N-) would extend the delocalization of electrons, which results in the red shift of the absorption spectra of PAA(CBDA/DPM) and PAA(CBDA/6FdA).

Another alicyclic acid dianhydride, TCAAH was also used for preparing transparent polyimides (Figure 4) [7]. All of the films have no absorption above 330 nm, which means all polyimides derived from the alicyclic dianhydride, TCAAH, show highly transparent properties in the visible region. PI(TCAAH/6FdA) shows an absorption peak at 248 nm, and PI(TCAAH/DPM) shows a shoulder at the same wavelength, while PI(TCAAH/DCHM) shows no absorption at this region. This suggests that theses absorption peaks at 248 nm are due to the absorption of phenylene groups of the diamine moieties.

Fluorescence spectroscopy is usually used for investigating the microstructure or aggregate structure of polymers, because it is very sensitive to the changes of microenvironments of chromophore moieties in polymer matrices. Figure 5 shows the fluorescence spectra of PI(CBDA/DCHM) film with a thickness of 50 μm [6]. When excited at 324 nm, the emission peak is observed at 424 nm. When excited at 370

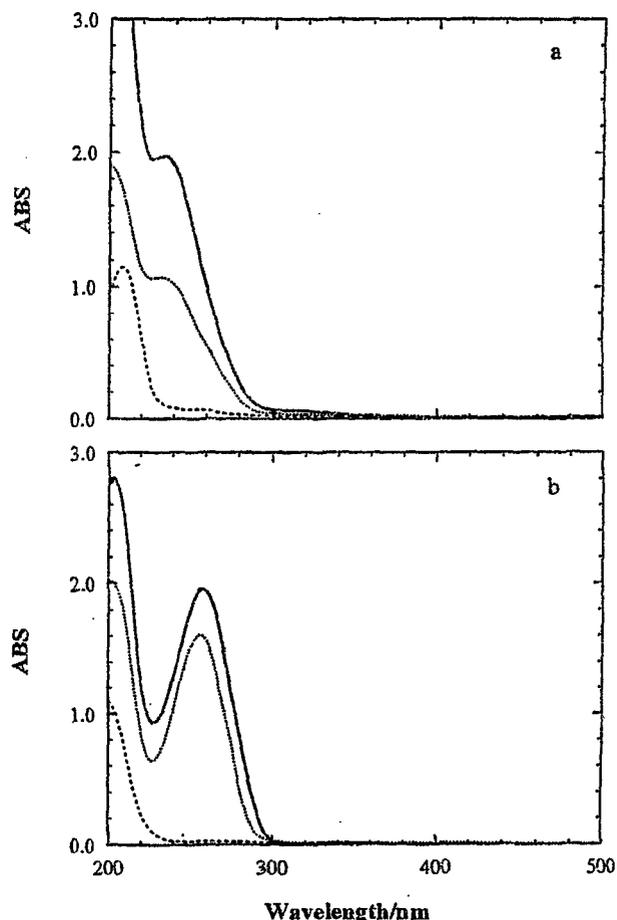Figure 3. UV absorption spectra of polyimides (a) and poly(amide acid)s (b) thin films of ca. 0.3 μm thick, (CBDA/DPM) (—), (CBDA/6FdA) (···), and (CBDA/DCHM) (---).
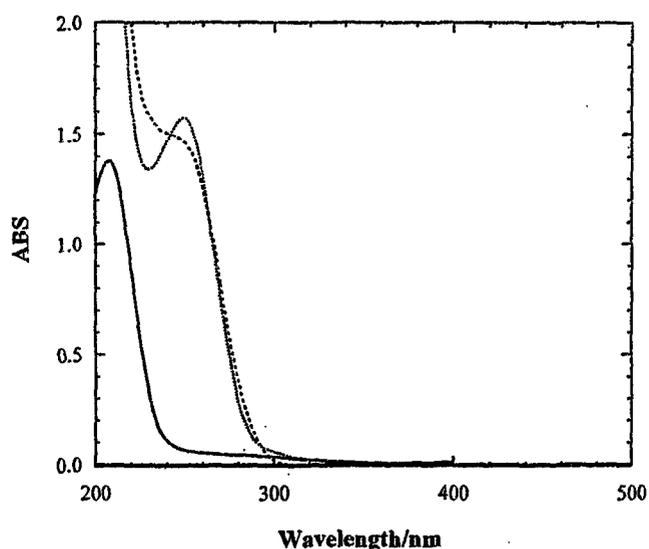

Figure 4. UV absorption specra of PI(TCAAH/DCHM) (—), PI(TCAAH/6FdA) (···), and PI(TCAAH/DPM) (---) thin films of ca. 0.3 μm thick.

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nm, 390 nm, 410 nm, 430 nm, 450 nm, 470 nm, respectively, red shifts of emission peaks from 430 nm to 524 nm are observed, showing a marked excitation-wavelength dependence of the emission peak. The excitation wavelength dependence would be due to the existence of ground-state complexes with various energy levels in the PI(CBDA/DCHM) film. The observation of excimer fluorescence at the same wavelength for three model compounds suggests that the head-to-tail overlap is favorable to the intermolecular dimer interaction between alicyclic imide moieties. By considering these results, the packing arrangement of

Figure 5. Fluorescence spectra of PI(CBDA/DCHM) film (50 μm thick) imidized at 160 °C, 200 °C, and 240 °C. — : emission spectra excited at (a) 240 nm, (b) 280 nm, (c) 324 nm, (d) 370 nm, (e) 390 nm, (f) 410 nm, (g) 430 nm, (h) 450 nm, and (i) 470 nm, respectively; ····: excitation spectra monitored at (a) 424 nm, (b) 450nm, (c) 480 nm, and (d) 500 nm, respectively.

PI(CBDA/DCHM) could be proposed as a mixes layer packing with the head-to-tail stacking of imide rings of one polymer backbone with that of another polymer backbone. The excitation wavelength dependence has been observed for all polyimides presently studied shown in Figure 1, suggesting the less-ordered packing structure compared to usual aromatic polyimides.

Thermal properties of these transparent polyimides [5, 6, 7] are summarized in Table 1, where the results for PMDA-containing polyimides [3] are also given as references. Glass transition temperature, T_g, measured with DSC or TMA does not decrease appreciably for polyimides containing either alicyclic diamine or alicyclic acid dianhydride compared to the corresponding aromatic polyimides. Thus transparent polyimides can be realized without any loss of their physical thermal stability. However T_g for polyimides composed of both alicyclic diamine and acid dianhydride showed a decrease by 80 °C compared to corresponding aromatic polyimide, probably due to the drastic change in packing structure.
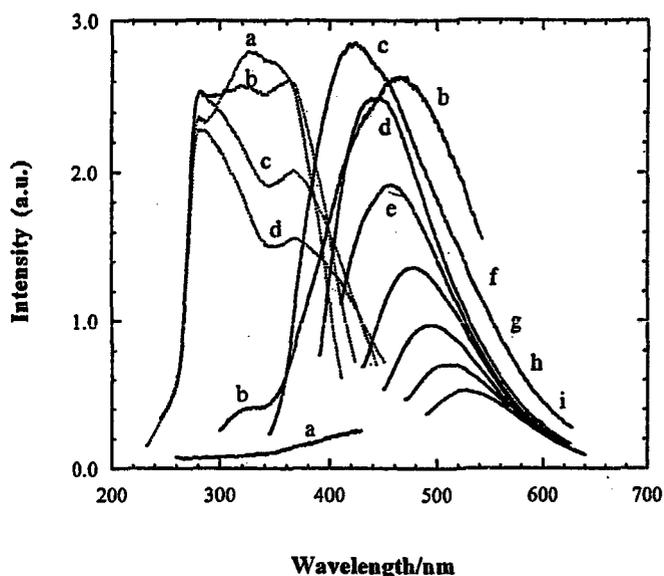
Table 1. Thermal Properties of Polyimides Studied

Polyimides	T_g (°C) by DSC	T_{id} (°C) by TG	T_d (°C) by TG	T_g (°C) by TMA
PI(6FDA/DCHM)	260		458	251
PI(6FDA/DPM)	292		526	-
PI(6FDA/PDA)	344		541	252
PI(CBDA/DPM)			454	360
PI(CBDA/6FdA)			441	349
PI(CBDA/DCHM)			440	277
PI(TCAAH/DPM)		365	447	336
PI(TCAAH/6FdA)		350	457	328
PI(TCAAH/DCHM)		340	427	251
PI(PMDA/DPM)	330		>500	336
PI(PMDA/DCHM)	325		450	315

Note: T_{id}: initial decomposition temperature; T_d: main decomposition temperature; T_g: glass transition temperature.

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3. Photoconductivity of a Polyimide with an Alicyclic Diamine

Photoconductivity of a polyimide with an alicyclic diamine, PI(PMDA/DCHM), and an aromatic polyimide, PI(PMDA/ODA) (Figure 6), was investigated by the addition of an electron donor, N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) [9]. The addition of the electron donor increase the photocurrent generation of two polyimide films by about three orders of magnitude (Figure 7) shifting to longer wavelength (Figure 8) by forming intermolecular charge-transfer complex in the ground state of the polyimide films. The polyimide with the alicyclic diamine doped with the electron donor showed a larger enhancement of photocurrent probably due to the existence of only intermolecular charge-transfer complex in the polyimide film which would be effective for photoconductivity.
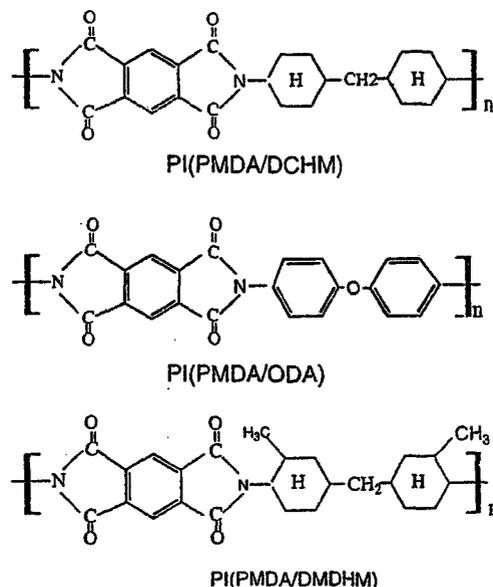

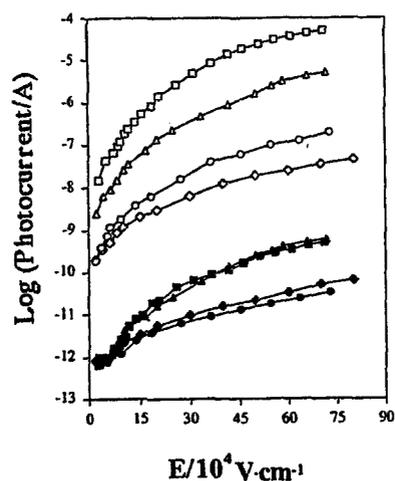Figure 6. Chemical structure of polyimides used for photoconductive study.

E/10^{4}V·cm^{-1}

Wavelength/nm

Figure 7. Photocurrent generation as a function of applied field for 1 μm undoped polyimide films and 1 μm TMPD-doped polyimide films. Films were photoirradiated with the intensity of 3 mWcm^{-2} at 350 nm for PI(PMDA/DCHM) (O), at 400 mn for PI(PMDA/DCHM)/TMPD (□), at 420 nm for PI(PMDA/ODA) (◇), and at 460 nm for PI(PMDA/ODA)/TMPD (△) where optical density is 0.3-0.5. Filled symbols denote darkcurrents for corresponding system.
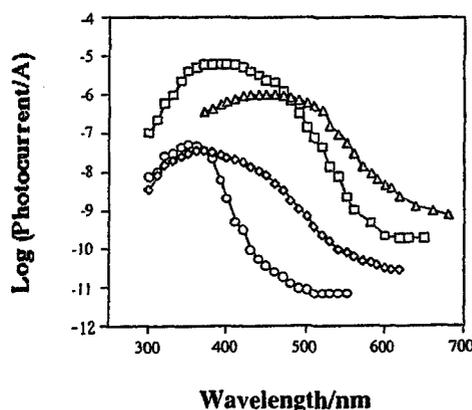
Figure 8. Action spectra of the photocurrent under an electric field of 5.0 x 10^5 Vcm^{-1} for 1μm undoped polyimide films and 1 μm TMPD-doped polyimide films. Undoped polyimide films; PI(PMDA/DCHM) (O), PI(PMDA/ODA) (◇), and TMPD-doped polyimide films; PI(PMDA/DCHM)/TMPD (□), PI(PMDA/ODA)/TMPD (△).

Photoconductivity of PI(PMDA/DCHM) depends upon the degree of molecular packing between polymer backbones, since PI(PMDA/DMDHM) has no photoconductivity probably due to a barrier to their intermolecular packing by the existence of two methyl

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phospholene-1-oxide (PMO) was purchased from Aldrich Chemical Co. Ltd. and used without further purification. Other reagents and solvents were obtained commercially and used as received.

Measurement. The infrared spectra were recorded on a JASCO FT/IR-230 FT-IR spectrophotometer. The NMR spectra were obtained on a JEOL JNM LA-400 (400 MHz) spectrometer. Thermal analyses were performed on a SEIKO SSS 5000-TG/DTA 200 instrument at a heating rate of 10 °C/min for TG , SEIKO SSS 5000 DSC220 at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) under nitrogen and a SEIKO SDM 5600H DMS210 at a heating rate of 5 °C/min (10Hz) for dynamic mechanical analysis (DMA). Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using TOSO HPLC 8120 system equipped with TOSO GMH-HR and G2000H-HR column at 40 °C in THF. The dielectric constants were measured by a HP 4284A Precision LCR meter at a frequency of 1 MHz and a temperature at 25 °C.

RESULTS AND DISCUSSION

Preparation of Poly(carbodiimide)s (PCDs).[5] The most commonly used aromatic PCDs are prepared from tolylene 2,4-diisocyanate (TDI) or 4,4'-methylenebis(phenyl isocyanate) (MDI) because these diisocyanate are easily available in the polyurethane industries. On the other hand, over the past several years, a considerable amount of research has been directed toward the synthesis of fluorine-containing polymers, particularly those incorporating hexafluoroisopropylidene (6F) groups. The incorporation of fluorine groups into polymer backbones increases the solubility, thermal stability, and environmental stability, and decreases the dielectric constant and the moisture absorption.
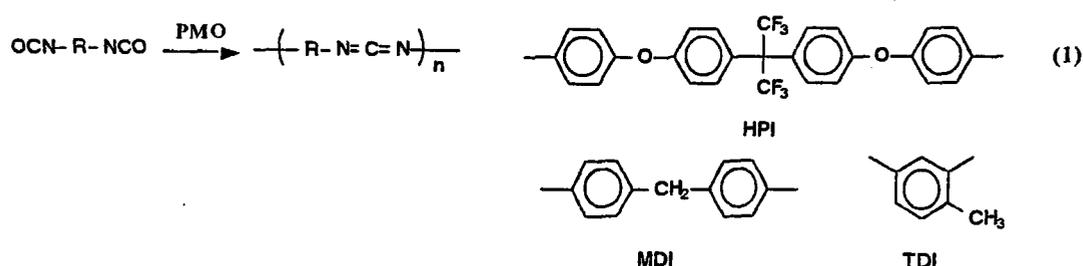
Table 1 Preparation of various PCDs

Type	Yield (%)	IR. (cm^{-1}) (C=N)	Molecular weight		
			Mn	Mw	Mw / Mn
HPI	96	2140	8400	26100	3.11
MDI	98	2130	7600	24700	3.22
TDI	86	2120	5000	18800	3.79

The synthesis of PCDs from diisocyanates including HPI, TDI and MDI was carried out in THF in the presence of PMO. The polycondensations proceeded in homogeneous solutions and gave viscous polymer solutions. After the polycondensations, the solutions were poured into *n*-hexane and the precipitated polymers were collected and dried *in vacuo*. The polymer was soluble in common organic solvents such as toluene or dichloromethane. A transparent film was cast from its toluene solution. The molecular weight of the polymer was determined by GPC. The chromatogram indicated that the relative Mn and Mw values was 8400, and 26100, respectively, for standard polystyrene.

The polymer was obtained in white powder state and was confirmed to be the corresponding 6FPCD by FT-IR, ^{13}C-NMR spectroscopy, and elemental analysis. The FT-IR spectra exhibited characteristic absorptions at 2140 cm^{-1} due to the carbodiimide linkage. Elemental analysis also supported the formation of expected polymer.

Conventional types of PCDs were also prepared from TDI and MDI to compare their thermal properties to that of 6FPCD.

Properties of 6FPCD.[5] Thermal behaviors of MDI-PCD moldings are reported in literature and cross linked PCDs are formed by dimerization and trimerization of carbodiimide moieties through thermal treatment[3]. Therefore, thermal properties of 6FPCD were investigated.

Figure 1 shows the dynamic mechanical behavior for the 6FPCD films cured at 200 °C and 250 °C for 1 h, respectively. Tgs of the films increased with increasing the cure

Figure1. Dynamic mechanical analysis of 6FPCD

temperature due to the cross-linking reaction of carbodiimide moieties.

Storage modulus (E') of films after thermal treatment at 250 °C for 1 h was more than 10^8 Pa. at 250 °C while PCD films prepared from MDI and TDI melted down at 250 °C. Furthermore, DMA measurements of conventional PCD films cured at 250 °C were impossible because films were changed to dark colored brittle films.

The detailed comparison of thermal and dielectric properties of the 6FPCD with those of the conventional PCDs is summarized in Table 2. The 6FPCD exhibited a lower dielectric constant (2.98 at 1MHz) compared to the conventional PCDs and an excellent thermal stability. The lower dielectric constant of 6FPCD is attributable to the introduction of fluorine atoms with the low polarizability.

The solubility of 6FPCD before and after thermal treatment was studied. The 6FPCD showed the excellent solubility toward a wide range of common organic solvents and was soluble even in toluene and dichloromethane. On the other hand, the cured 6FPCD at 200 °C for 30 min was insoluble in all solvents. Therefore, the 6FPCD is a very useful polymer which can undergo thermal cross-linking reaction to form an insoluble and thermal stable polymer with higher Tg.
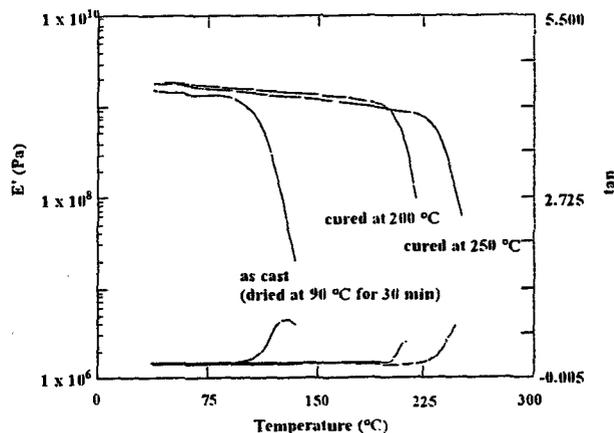
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Table 2 Properties of various PCDs

Monomer type	Powder			Film				
	Tg (°C)	Tc (°C)	TG10 [a]	Cure Temp. [b]	Flexibility [c]	E'(Pa) [d]	e	tanδ
HPI	235	380	500	200	F	1.5×10^9	2.98	0.0013
				250	F	1.5×10^9		
MDI	200	290	490	200	F	1.1×10^9	3.50	0.0019
				250	B	. [e]		
TDI	160	310	460	200	F	5.2×10^7	3.30	0.0022
				250	B	. [e]		

a) Temperature at which 10 % weight loss was recorded with TGA at heating rate of 10 °Cmin^{-1} in Air

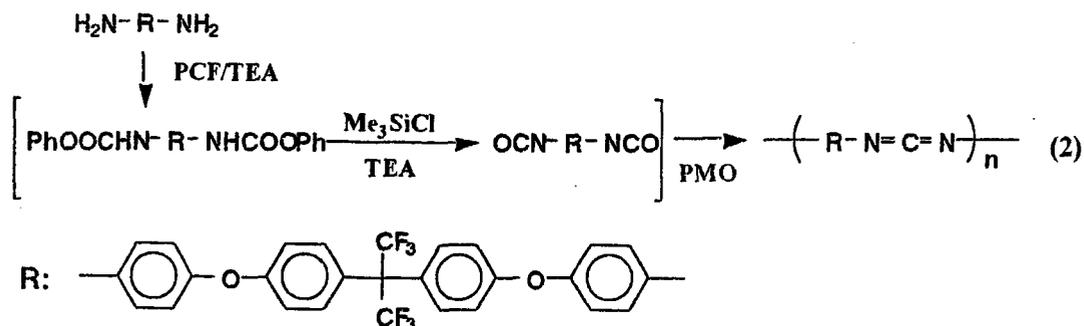b) performed at the temperature for 1hr after pre-heating at 90°C for 30 min.

c) F; flexible, B:brittle

d) value at 200 °C

e) too brittle to measure

One-pot synthesis of PCD.[6]

PCDs are usually prepared by the polycondensation reaction of diisocyanates in the presence of phospholene compounds as a catalyst. Phosgenation of diamines is a commercially adopted route for the synthesis of diisocyanate. However, phosgene is a highly toxic reagent. Furthermore, this polycondensation reaction of diisocyanates is still have some limitations such as the isolation of moisture sensitive diisocyanates that further causes unfavorable side reactions during PCD forming process. Thus, we decided to take another route for making PCD in place of conventional process.

Therefore, we investigated the synthesis of PCD by the one-pot synthesis of aromatic polycarbodiimide through *in-situ* activation of the corresponding diamine using phenylchloroformate (PCF), and then trimethylsilylchloride (TMSC)-triethylamine (TEA), followed by polycondensation of the generated diisocyanate in the presence of 1-phenyl-3-methyl-2-phosphreneoxide (PMO) as a catalyst. The method fall into three steps (eq. 2): (i) dicarbamate is formed from diamine and PCF; (ii) diisocyanate is formed by the treatment of dicarbamate with TMSC-TEA; (iii) polycondensation of the generated diisocyanate produces PCD in the presence of PMO. The progress of one-pot synthesis of 6FPCD from 6FPA was followed by FT-IR spectroscopy (Figure 2). 6FPA (Figure 2-a) was converted to dicarbamate (Figure 2-b) exhibited a characteristic absorption at 3320 cm^{-1} due to the N-H stretching and a strong carbamate carbonyl absorption at 1720 cm^{-1}.

$$H_2N-R-NH_2$$
$$\downarrow \text{PCF/TEA}$$
$$\left[PhOOCHN-R-NHCOOPh \xrightarrow[\text{TEA}]{Me_3SiCl} OCN-R-NCO \right] \xrightarrow{PMO} -\left(R-N=C=N\right)_n \quad (2)$$

R:

Subsequent addition of TMSC-TEA to the solution of dicarbamate and heating the resulting mixture at 80 °C formed diisocyanate and 6FPCD (second step). In Figure 2-c, two strong absorptions at 2270 and 2140 cm^{-1} that are assigned to the -N=C=O and -N=C=N- groups appeared in a few minutes. After additional 3h, no absorption of the -N=C=O group was detected (Figure 2-d)(third step). These results clearly supported the formation of each active intermediate at each step. The overall yield of this polycondensation is up to 90 %, which is very high compared to that of the conventional method because of no isolation and purification process of active intermediates.
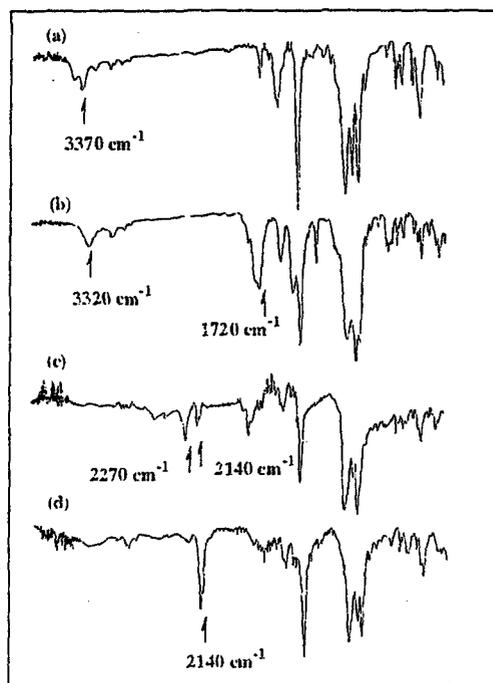

Figure 2. Progress of one-pot synthesis of 6FPCD from the corresponding diamine followed by FT-IR.

Application of PCD to the photosensitive Polymer.[7] PCDs are chemically quite inert in the solid state, however, in the solution state these polymers react with active hydrogen compounds such as carboxylic acid or amine to give the polymers having another back bone, for example polyguanidine.[2]

Previously, we reported that {[(4,5-dimethoxy-2-nitrobenzyl)oxy]carbonyl}-2,6-dimethyl piperidine (1) act as PAG in a polyisoimide (PII) film and PII containing 10 wt% of 1 functioned as a photosensitive resist, when it was postbaked at 150 °C for 5 min after exposure to UV (365 nm) light.[8] This finding prompted us to employ a new approach for development of a photosensitive polymer material having high thermal stability and processability. Before the reaction of PCD and amine, a model reaction was studied in order to clarify the reactivity of secondary amine toward carbodiimide. Thus, we investigated the reaction of piperidine with dicyclohexylcarbodiimide (DCC) in isopropyl alcohol (IPA) (eq. 3). Dicyclohexyl piperidino guanidine (PIG) was obtained in quantitative yield without the side reaction between IPA and DCC.
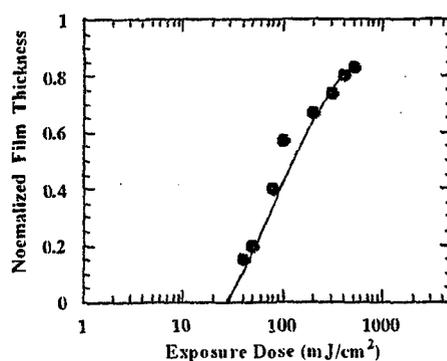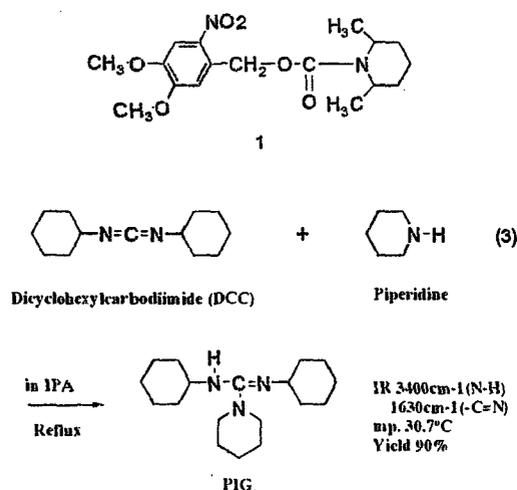

Figure3. Exposure characteristic curve for the system of PCD and 10 wt% of APG

This result indicate that PCD will react with secondly amines such as piperidine to provide a guanidine base. Furthermore, the generated guanidine parts which have active hydrogen N-H bonds, would be expected to react with another carbodiimide bonds in the PCD film, producing cross-linking polymers by the thermal treatment. A clear yellowish solution of TDI-PCD and 1 (10 wt%) was spin coated on silicon wafer and dried at 60 °C for 10 min. The film was exposed to 365 nm UV-light and post exposure bake (PEB) was performed at 120 °C for 5 min and developed with toluene at 25 °C. The sensitivity curve for 3 μm-thick PCD film shown in Figure 2 indicates that the sensitivity ($D^{0.5}$) was 100 mJ/ cm^2. The mechanism of a negative pattern formation is outlined in eq. 4. A photogenerated base reacts with carbodiimide linkages to give guanidine bonds, which undergo further addition reactions to PCDs by PEB.
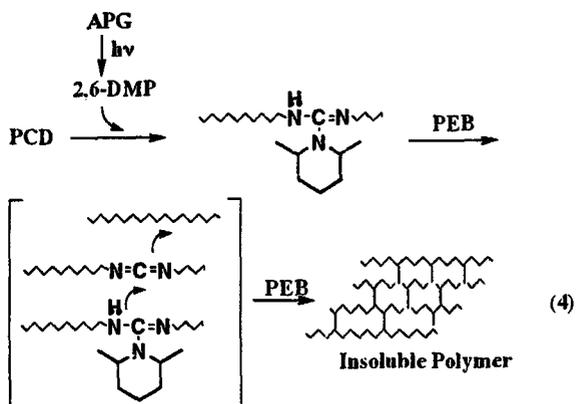
SUMMARY

The new 6FPCD was successfully prepared by polycondensation of HPI in the presence of PMO. 6FPCD has a linear structure having excellent solubility in a wide range of organic solvents. Thermal treatment of 6FPCD provides cross-linked film with excellent solvent resistance. The 6FPCD was directly synthesized by *in-situ* activation of the corresponding diamine and the simultaneous polycondensation. PCD containing 10 wt% of 1 functioned as a negative type photosensitive polymer with high sensitivity. This chemistry would be expected to open a new methodology in the design of thermal stable imaging materials.

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