Film properties and lyotropic liquid crystallinity of soluble polybenzoxazoles

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Abstract : In this report, we discuss soluble polybenzoxazoles (PBOs). Some PBOs were polymerized in polyphosphoric acid at 200°C and high inherent viscosities were obtained (> 0.8 dL/g). Particularly, fluorinated PBOs were highly soluble in NMP. For example, DHB/BIS-B-AF and ADPE/BIS-B-AF can be dissolved in NMP up to 7 wt% and 14wt%, respectively. The NMP solutions of these PBOs were cast at 60-80°C /1h, then annealed at 300°C. The DHB/BIS-B-AF PBO film showed a lower coefficient of thermal expansion (CTE = 40 ppm/K) than most of soluble PIs and also had a high Tg (340°C). On the other hand, the ADPE/BIS-B-AF film with an ether linkage showed a much higher CTE (= 57 ppm/K) and a much lower Tg at 298°C. Optical anisotropy was observed in the DHB/BIS-B-AF cast film but wasn't in the ADPE/BIS-B-AF film. This liquid crystal-like morphology is formed during solvent evaporation process.

1. Introduction: In many cases, since aromatic polyimides (PIs) are insoluble in common organic solvent, PIs films are produced through thermal imidization of as-cast PI precursor poly(amic acid) (PAA) films at high temperatures such as 300°C or higher. In this case, CTE mismatch between PI films (CTE = 50—80ppm/K in most cases) and copper substrate (CTE = 17ppm/K) causes thermal stress in the cooling process from the cure temperature to room temperature. Accordingly, if it is possible to decrease the cure temperature by addition of any catalysts for imidization, the thermal stress can be reduced. Another approach is to use of soluble PIs. A variety of organo-soluble PIs with bent/distorted chain structures and bulky sbstituents have been extensively investigated. However, soluble PIs don't have always sufficiently high Tg's and mechanical properties. The strong intermolecular interaction in PIs affects the solubility. The present work highlight PBO system without the imide carbonyl groups responsible for strong intermolecular interaction. Common PBOs are usually polymerized in polyphosphoric acid (PPA), but in most cases, they are insoluble in common organic solvents. In this study, we first investigated soluble PBO system. Good quality of PBO films were obtained for several systems by solution casting. Film properties, such as a CTE and a dielectric constant (K), were evaluated.

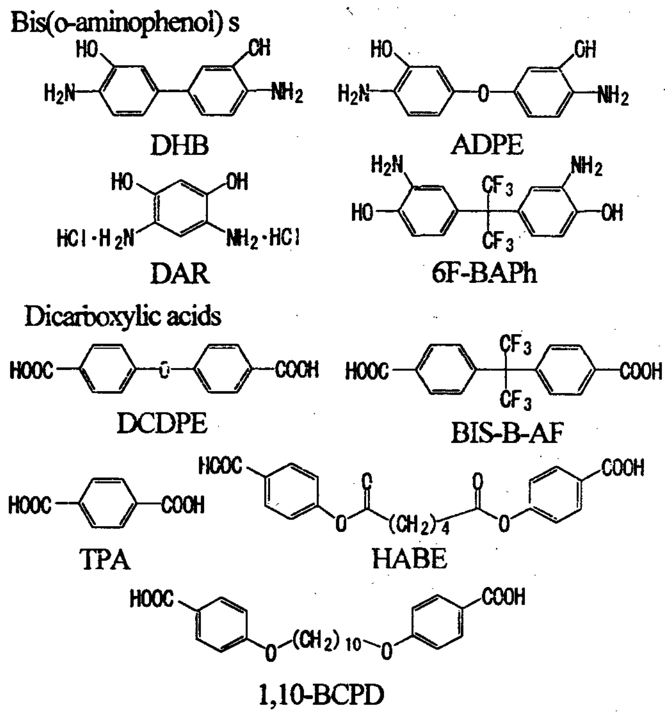

Fig. 1 Structures of monomers used.

2. Experimental section: The structures of the monomers used are shown in Figure 1; bis(o-aminophenol)s: 3,3'-Dihydroxydenzibine (DHB), 3,3'-Oxybis[4-aminophenol] (ADPE, supplied from Nihon Kayaku Co. Ltd.), 4,6-Diaminoresorcinol dihydrochloride (DAR) and 2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6F-BAPh, supplied from Central Glass Co. Ltd.) and dicarboxylic acid: 2,2'-Bis(carboxyphenyl) hexafluoro-propane (BIS-B-AF, supplied from Central Glass Co. Ltd.), 4,4'-Dicarboxydiphenyl ether (DCDPE), Terephthalic acid (TPA), Hexanedioic acid bis(4-carboxyphenyl) ester (HABE), 1,10-Bis (4-carboxyphenoxy) decane (1,10-BCPD). An equimolar amount of bis(o-aminophenol)s and dicarboxylic acid was dissolved in PPA, in a nitrogen stream, then heated to 200°C and maintained for several hours. The reaction mixtures were reprecipitated in water, and washed with methanol. The precipitated polymer was vacuum-dried at 100°C for 24h. The inherent viscosity was measured at 30°C at 0.5wt% in NMP. Some of them were dissolved in NMP. The NMP solutions of PBOs were doctor-bladed on a glass substrate at 60—80°C for 1 h. PBO films were cast at 60°C /1h then annealed at 250—400°C 1 h. CTE, Tg, and the 5% weight loss temperature (Td^5) were measured. The refractive index and birefringence were measured on an Abb's refractometer. The dielectric constant ($K=1.1n_{av}^2$) was estimated from the average refractive index (n_{av}).

Result and discussion

1. Polymerization reactivity: Polymerization results are shown in Table 1. No polymerization proceeded when HABE and 1,10-BCPD were used as dicarboxylic acids components owing to their poor solubility in PPA even at 200°C. Other dicarboxylic acids, TPA, BIS-B-AF and DCDPE were so soluble in PPA at 200°C that they were allowed to react with bis(o-aminophenol)s to form high molecular weight of PBOs (see Table 1). The ADPE/DCDPE and DHB/DCDPE systems showed a considerable high reactivity from the fact that the viscosity of the reaction mixture increased abruptly in 10 min and almost leveled off. On the other hand, the 6F-BAPh/DCDPE system was less reactive (it needs a much longer reaction time). The inherent viscosities of NMP-soluble systems ranged 0.87—1.46 dl/g as listed in Table 1. Although other systems gave highly viscous PPA solutions, which suggest the formation of high molecular weight PBOs, they were insoluble in NMP, so that the inherent viscosities were not measured.

Table 1 Polymerization conditions and reactivity.

System	Reaction temperature (°C)	Reaction time (min)	Reactivity	η_{red}(dl/g)
ADPE/BIS-B-AF	200	70	○	1.46
ADPE/DCDPE	190	10	◎	0.872[a)]
DHB/BIS-B-AF	200	120	○	1.31
6F-BAPh/DCDPE	200	180	△	0.891[b)]
DHB/DCDPE	190	10	◎	—
DAR/BIS-B-AF	200	120	○	—
DAR;DHB/BIS-B-AF	200	120	○	—
DAR;ADPE/BIS-B-AF	200	60	○	—
DHB/TPA;BIS-B-AF	200	120	△	—
ADPE/TPA; BIS-B-AF	200	120	△	—
DAR/HABE	130	240	×	—
DAR/1,10-BCPD	200	390	×	—

[a)]0.5wt% in m-cresol [b)]0.5wt% in THF: NMP (v/v) =1:1

2. Solubility: The solubility of the precipitated PBOs is shown in Table 2. The fluorinated DHB/BIS-B-AF, ADPE/BIS-B-AF, 6F-BAPh/DCDPE systems and the ether-containing ADPE/DCDPE system were soluble in several organic solvents. In order to prepare cast PBO films from the NMP solutions, DHB/BIS-B-AF and ADPE/BIS-B-AF were dissolved in NMP at 7wt% and 14wt%, respectively by heating at 120°C. However, the PBO solutions were not so stable at room temperature, and gelation was observed in the DHB/BIS-S-AF and ADPE/BIS-B-AF systems at room temperature after three days and six days, respectively. Therefore, the cast PBO films were prepared immediately after dissolution. All the obtained PBO films were highly tough. The 6F-BAPh/DCDPE film was almost transparent without coloring.

3. Film properties and lyotropic liquid crystallinity: To remove residual NMP from PBO cast films, the films were annealed above 250°C in vacuum for measurements of the film properties. The DHB/BIS-B-AF system showed a low K (3.0) and a comparatively low CTE (40ppm/K) comparable to KAPTON in addition to the highest Tg (= 340°C) among the soluble PBOs shown in this work. On the other hand, ADPE/BIS-B-AF system exhibited 40°C lower Tg (= 300°C) and a much higher CTE (~60ppm/K). The decreased Tg is due to the flexible ether linkage in the ADPE unit. Table 3 also shows an effect of annealing temperature on the properties. With an increase in annealing temperature, Tg increased gradually for both systems, but CTE decreased as a result of orientational relaxation corresponding to a gradual decrease in bifringence.

Optical anisotropy was observed in the DHB/BIS-B-AF film cast at 80°C and 6F-BAPh/DCDPE film cast at 60°C but was not in the ADPE/BIS-B-AF film cast at 60°C. The results indicate that a lyotropic liquid crystal-like morphology was formed during solvent evaporation in the casting process. Particularly, 6F-BAPh/TPA in m-cresol solution displayed a clear droplet texture in POM photograph in Fig. 2.

Table 2 Solubility of PBOs.

System	DMAc[a)]	NMP[a)]	m-cresol[a)]	HMPA[a)]	THF[b)]	1,4-dioxane[b)]	DMSO[a)]	γ-butyrolactone[a)]
ADPE/BIS-B-AF	×	○	○	○	○	×	×	×
ADPE/DCDPE	×	×	○	×	×	△	△	×
DHB/BIS-B-AF	×	○	○	○	△	×	×	×
DHB/DCDPE	×	×	×	×	×	×	×	×
DAR/BIS-B-AF	×	×	×	×	×	×	×	×
DAR;DHB/BIS-B-AF	×	△	△	△	×	×	×	×
DAR;ADPE/BIS-B-AF	×	△	△	×	×	×	×	×
DHB/TPA;BIS-B-AF	△	△	△	△	△	×	△	×
6F-BAPh/DCDPE	△	○	○	○	○	○	×	×

○···soluble (>1wt%) △···partially soluble ×···insoluble

a) heated at 150°C for a minute then cool down at room temperature.

b) heated at 60°C for a minute then cool down at room temperature.

Table 3 Properties of PBO films.

	Annealing temperature(°C)	CTE (ppm/K)	Tg (°C)	Td^5, N_2(°C)	Td^5, air(°C)	n_{av}	Δn	ε_{cal}
DHB/BIS-B-AF	250	41	338	525.5	518.6	1.6665	0.0479	3.06
	300	40	340	528.7	524.3	1.6683	0.0545	3.06
	350	42	338	525.7	523.0	1.6634	0.0441	3.04
	400	51	343	531.3	521.4	1.6599	0.0340	3.03
ADPE/BIS-B-AF	250	58	293	527.3	511.7	1.6195	0.0207	2.89
	300	57	298	527.7	517.4	1.6215	0.0156	2.89
	350	63	303	527.9	519.3	1.6249	0.0062	2.90
	400	63	310	530.0	520.1	1.6265	0.0017	2.91

Tabiel 4 Optical anisotropy of PBO cast films.

DHB/BIS-B-AF	○
ADPE/BIS-B-AF	○
ADPE/DCDPE	×
6F-BAPh/DCDPE	○

Fig. 2 POM photograph of 6-FBAPh/TPA in m-cresol at 20wt% at room temperature (×180).