Synthesis of Thermally Cross-Linkable Fluorine-containing Poly(aryl ether ketone)s I. Phenylethynyl Terminated Poly(aryl ether ketone)s

Kunio KIMURA,[†] Ai NISHICHI, and Yuhiko YAMASHITA

*Faculty of Environmental Science and Technology, Okayama University,
3-1-1 Tsushima-naka, Okayama 700-8530, Japan*

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ABSTRACT: Fluorine-containing poly(aryl ether ketone)s (PEKs) derived from 2,3,4,5,6-pentafluorobenzoic acid (PFBA) exhibit outstanding solubility, thermal stability, low dielectric constant, low moisture absorption and high transparency. Hence, they are expected to be available for optical and electric materials. In such applications, excellent solubility is of great advantage for making thin film and coating. Contrary to this advantage, this is of disadvantage from a point of solvent resistance. Thermally cross-linkable fluorine-containing PEKs terminated with phenylethynyl moiety (PEK-PEP) are synthesized to improve the solvent resistance in this study. Cross-linking reaction occurs over 320°C and it brings about not only the outstanding solvent resistance but also the increase of T_g . Relationship between the cross-linking density and T_g can be fundamentally interpreted by configurational entropy theory. Furthermore, the cured PEK-PEPs possess excellent thermal stability with the 10% weight loss temperature in the range from 544 to 598°C.

KEY WORDS Fluorine-Containing Polymer / Poly(aryl ether ketone) / Phenylethynyl Group / Cross-Linking / Solvent Resistance / Thermal Stability /

The high-performance fluorinated polymers have been receiving considerable attention as interesting advanced materials for applications as films, coatings for optical and microelectronics device, gas separation membranes and so on.^{1–3} Recently, poly(aryl ether ketone)s (PEKs) containing 2,3,5,6-tetrafluoro-1,4-phenylene moieties were synthesized from perfluorobenzophenone.⁴

2,3,4,5,6-Pentafluorobenzoic acid (PFBA) is a valuable intermediate for pharmaceuticals, pesticides, perfumes, cosmetics and so on, and it is available as a commercial product. PFBA is a very useful raw material for making fluorine-containing PEKs. We had prepared novel fluorine-containing PEKs derived from PFBA and reported so far.⁵ These PEKs (F-PEKs) described in Scheme 1 exhibit outstanding solubility, thermal stability, low dielectric constant, low moisture absorption and high transparency. Hence, they are expected to be available for optical and electric materials. In such applications, excellent solubility is of great advantage for making thin film and coating. Contrary to this advantage, this is of disadvantage from a point of solvent resistance. Solvent resistance should be improved with keeping the good solubility and other properties. Introduction of cross-linkability into the polymer chain is one of the answers to circumvent this drawback. Numerous types of thermosets had been synthesized with terminal or pendant cross-linkable endgroups which

Scheme 1. Fluorine-containing PEKs.

were sites for network formation.^{6–15} It is of importance to design the cross-linkable moiety that cross-linking reaction should occur without the evolution of small volatile compounds to form the clear film and coating. Cross-linkable moieties that meet the required condition are phenylethynyl, cyanate, benzocyclobutane and so on.⁷

Various oligomers, such as imide, sulfone and so on, terminated by phenylethynyl moiety have been reported.^{8–14} Upon thermal curing, they undergo a complex reaction involving chain extension, branching and cross-linking to afford materials with attractive properties such as solvent resistance and thermal stability. The phenylethynyl group offers certain distinct advantages over other reactive groups.¹⁵

In this paper, we report the synthesis and characterization of fluorine-containing PEKs terminated with phenylethynyl moiety (PEK-PEP).

[†]To whom correspondence should be addressed (Tel & Fax: +81-86-251-8902, E-mail: polykim@cc.okayama-u.ac.jp).

EXPERIMENTAL

Materials

PFBA was a gift from Nippon Shokubai Co. Ltd. 2,2-Bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FBA), 4-bromophenol and phenylacetylene were obtained from Aldrich Chemical Co., Inc. 9,9-Bis(4-hydroxyphenyl)fluorene (HF) was obtained from Kennedy and Klim. Co., Inc. 6FBA and HF were purified by recrystallization. *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich Chemical Co., Inc. Triethylamine (TEA) and pyridine were purchased from Ishizu Co. Ltd. Pyridine was purified by distillation over potassium hydroxide. DMAc and TEA were purified by distillation over potassium hydroxide under nitrogen atmosphere with removing dissolved oxygen. NMP was used as received. Dichlorobis(triphenylphosphine)palladium(II), triphenylphosphine and copper(I) iodide were obtained from Aldrich Chemical Co., Inc.

Synthesis of Phenylethynylphenol (PEP)

The procedure of PEP was modified from the method of Lee.¹⁶ 1-Bromo-4-acetoxybenzene (BAB) was synthesized from 4-bromophenol according to the previous procedure.^{16,17}

8.0 g of BAB (37 mmol), 0.49 g of triphenylphosphine (1.9 mmol) and 14 mL of DMAc were placed in a 200 mL three-neck flask equipped with a condenser, a thermometer, an additional funnel and a nitrogen inlet tube. This solution was treated by freeze-thaw cycles to remove traces of dissolved oxygen. 0.26 g of dichlorobis(triphenylphosphine)palladium(II) (0.37 mmol) washed with 28 mL of TEA, 0.088 g of copper(I) iodide (0.47 mmol) and 28 mL of TEA were added into this solution. This mixture was treated further by freeze-thaw cycles. 4.6 g of phenylacetylene (45 mmol) and 4.7 mL of DMAc were placed into a 50 mL flask, and treated by freeze-thaw cycles. This phenylacetylene solution was added dropwise into the mixture at 70°C while stirring, and then maintained at 70°C for 24 h. After being allowed to cool, the reaction mixture was filtered to remove inorganic salts and then TEA was stripped off under reduced pressure. The obtained viscous liquid was poured into acidic water, and the organic layer was extracted with dichloromethane. The solution was dried over sodium sulfate and the dichloromethane was evaporated. The obtained brown solid was recrystallized from 2-propanol. 5.2 g of 4-acetoxy-phenylethynylbenzene was obtained (59% yield). The product characteristics were as follows; T_m : 104°C, FT-IR (KBr, cm^{-1}): 1753, 1502, 1371, 1200,

1014, 916, 849, 758, 692, 523.

Into a flask equipped with a condenser were placed 5.0 g of 4-acetoxy-phenylethynylbenzene (21 mmol), 47 mL of THF and 47 mL of methanol. 3.7 g of sodium hydroxide (93 mmol) dissolved in 31 mL of water was added to this solution. After being refluxed for 12 h with stirring, the reaction mixture was allowed to cool and poured into acidic water. The organic layer was extracted with dichloromethane and dried over sodium sulfate. After evaporating dichloromethane, the obtained solid was purified by recrystallization from the mixture of *n*-hexane and toluene. Yellow crystal of PEP was obtained at 3.3 g (80% yield). The product characteristics were as follows; T_m : 128°C (lit.¹⁷ 125°C), FT-IR (KBr, cm^{-1}): 3423, 1606, 1591, 1510, 1439, 1371, 1252, 1101, 833, 750, 688, 521, ^1H NMR (CDCl_3 , ppm): 4.93 (s, 1H, H^f), 6.80 (d, 2H, H^e), 7.30–7.34 (m, 3H, H^a , and H^b), 7.42 (d, 2H, H^d), 7.49 (d, 2H, H^c).

Synthesis of 4,4'-Bis[4-(4-phenylethynylphenoxy)-2,3,5,6-tetrafluorobenzoyl]diphenyl ether

0.16 g of PEP (0.83 mmol), 0.057 g of potassium carbonate (0.41 mmol), 1.2 mL of NMP and 0.80 mL of toluene were placed into a 10 mL of flask equipped with Dean-Stark trap, a condenser and a nitrogen inlet tube. The mixture was refluxed for 3 h with eliminating by-produced water by azeotropic distillation and then toluene was distilled over. The mixture was allowed to cool and 0.23 g of 4,4'-bis(2,3,4,5,6-pentafluorobenzoyl)diphenyl ether (BPDE) (0.41 mmol) synthesized according to the previous procedure⁵ was added into the mixture. The reaction was kept at 120°C for 15 h. The reaction mixture was allowed to cool to room temperature and poured into methanol. The precipitates were collected by filtration, and washed with water containing 1% acetic acid and water. Pale brown solid of 4,4'-bis[4-(4-phenylethynylphenoxy)-2,3,5,6-tetrafluorobenzoyl]diphenyl ether was obtained at 0.27 g (71% yield). The product characteristic was as follows; Calcd for $\text{C}_{54}\text{F}_8\text{H}_{24}\text{O}_5$: C, 71.68%; F, 16.81%; H, 2.66%; O, 8.85%. Found: C, 70.94%; F, 17.11%; H, 2.94%; O, 9.01%. FT-IR (KBr, cm^{-1}): 1678, 1587, 1496, 1319, 1238, 1167, 1107, 989, 831, 692, ^1H NMR (CDCl_3 , ppm): 7.00 (d, 4H, H^e), 7.19 (d, 4H, H^g), 7.33–7.35 (m, 2H, H^a , and 4H, H^b), 7.51 (d, 4H, H^d), 7.53 (d, 4H, H^c), 7.93 (d, 4H, H^f), ^{19}F NMR (CDCl_3 , ppm): -142 (d, 4F, F^a), -130 (d, 4F, F^b).

Synthesis of Polymers

Synthesis of PEK(6FBA)-PEP_n = 20 is given as a typical example as follows.

0.090 g of PEP (0.46 mmol) was added into the solution of 0.026 g of potassium hydroxide (0.46 mmol) and 20 mL of methanol. The mixture was stirred for 1 h at room temperature. Methanol and by-produced water were evaporated and phenylethynylphenoxide was prepared.

Into a 25 mL flask equipped with Dean-Stark trap, a condenser and a nitrogen inlet tube were placed 0.43 g of 6FBA (1.28 mmol), 0.18 g of potassium carbonate (1.28 mmol), 4.7 mL of NMP and 2.4 mL of toluene. The mixture was refluxed for 3 h with eliminating by-produced water by azeotropic distillation and then toluene was distilled over. After being allowed to cool at 80°C, 0.75 g of BPDE (1.34 mmol) was added into the mixture. The polymerization was kept at 80°C for 20 h. Then 0.060 g of phenylethynylphenoxide (0.26 mmol) was added into the mixture. The reaction was kept at 120°C for 15 h. The reaction mixture was allowed to cool to room temperature and poured into methanol. The precipitated polymer was collected by filtration, and then washed with water containing 1% acetic acid and water. 0.84 g of PEK(6FBA)-PEP_n = 20 was obtained (73% yield). The product characteristics were as follows; FT-IR (KBr, cm⁻¹): 1680, 1587, 1495, 1414, 1319, 1240, 1174, 1107, 991, 874, 831, 650, ¹H NMR and ¹³C NMR were shown in Figures 4 and 5. ¹⁹F NMR (CDCl₃, ppm): -151 (d, Ar-F), -140 (d, Ar-F), -63.8 (s, CF₃).

Characterization

NMR spectra were recorded on a Varian Unity-500 operating at 500 MHz (¹H), 75 MHz (¹³C) and 470 MHz (¹⁹F). CDCl₃ was used as the measuring solvent. FT-IR measurements were performed on JASCO FT-IR 350. Glass transition temperature (*T*_g) and decomposition temperature were measured on Perkin-Elmer DSC 7 and TGA 7 at a scanning rate of 20°C min⁻¹ in nitrogen atmosphere. Softening temperature (*T*_s) was measured on a Yanaco MP-500D. *T*_s was defined as the temperature at which the polymer began to soften. Thermal analyses were performed with powder samples. Molecular weights were measured on TOSO 8020 GPC. NMP was used as an eluent and column temperature was 40°C. Molecular weight was calcu-

lated with polystyrene standard. Dynamic mechanical measurement was performed on Orientech Rheovibron DDV-II -EP at 110 Hz with a scanning rate of 2°C min⁻¹. The mode of measurement was stress. The measured samples were films of which the average thickness was 37 μm. Solvent resistance was estimated by weighing insoluble part of the film after soaking for 1 d at room temperature in toluene. Crystallinity of the film was measured by WAXS diffractometer of Rigaku Gaiger flex (Cu-K_α λ = 1.5418 Å). UV spectra of the films were measured on JASCO V-570. The film thickness was 2 μm.

RESULTS AND DISCUSSION

Cross-Linking Behavior of Model Compound

4,4'-Bis[4-(4-phenylethynylphenoxy)-2,3,5,6-tetrafluorobenzoyl]diphenyl ether was synthesized from BPDE and PEP as a model compound to know the thermally cross-linking behavior of phenylethynyl moiety. The synthetic procedures of this model compound are shown in Scheme 2. The thermally cross-linking reaction of this model compound was followed by isothermal curing on DSC at 330, 340, and 360°C. The exothermic peak was observed due to cross-linking reaction as shown in Figure 1. Conversion of cross-linking was calculated on the basis of the heat content of the exothermic peak. The cross-linking reaction of the model compound obeys the first-order reaction kinetics as shown in Figure 2. The first-order rate constants at 330, 340, and 360°C are estimated as 0.79 × 10⁻³ sec⁻¹, 1.35 × 10⁻³ sec⁻¹, and 3.41 × 10⁻³ sec⁻¹, respectively. From the temperature dependence of rate constant, the activation energy (*ΔE*_a) for thermally cross-linking of phenylethynyl moiety can be calculated as 156 kJ mol⁻¹. *ΔE*_a of this model compound is in good agreement with that of phenylethynyl terminated imide oligomers which is 153 kJ mol⁻¹ as reported.¹⁸

The structural change of model compound during curing was followed by FT-IR. The spectra of uncured and cured model compound have no difference in except for wavenumber around 1650 cm⁻¹ and the spectrum of the model compound cured at 320°C for 2 h is shown in Figure 3. Previous study has reported that phenylethynyl moiety turns thermally into chain extension, branching and cross-linking through the formation of C=C double bond and that the structure of cross-

Figure 1. DSC trace of model compound at 330°C.

Figure 2. Conversion of cross-linking reaction of model compound at 330°C applied to primary reaction formula.

links were polyene, aromatic ring and so on.¹¹ The carbonyl stretching vibration is observed at 1680 cm^{-1} in both spectrum of the uncured and cured compound. This peak has a shoulder at *ca.* 1650 cm^{-1} and so it is resolved into several peaks by Lorentz function. In the spectrum of the uncured compound a peak except for 1680 cm^{-1} appears at *ca.* 1650 cm^{-1} to be assigned to overtone or combination peak of aromatic ring. After curing, a new peak appears at 1640 cm^{-1} . This peak is able to be assigned to C=C double bond stretching vibration. The appearance of this peak strongly suggested that C $\equiv$ C triple bond in phenylethynyl group undergoes the cross-linking reaction through the conversion into C=C double bond.

Figure 3. IR spectra of model compound (a) uncured and (b) cured at 320°C for 2 h.

Polymer Synthesis

PEK-PEPs were synthesized as shown in Scheme 3. 6FBA and HF were used as bisphenols. The degree of polymerization was adjusted by the feed ratio between BPDE and bisphenol. Polymer codes were named according to the bisphenol and the number-average degree of polymerization (DP_n) calculated from the feed ratio. For instance PEK(6FBA)-PEP_n = 20 in which

Scheme 3. Synthesis of cross-linkable fluorine-containing PEKs.

Figure 4. ^1H NMR spectrum of PEK(6FBA)-PEP $_n = 20$.

6FBA describes the used bisphenol and $n = 20$ stands for the calculated DP_n . The chemical structure of PEK-PEPs is confirmed by FT-IR, ^1H and ^{13}C NMR. ^1H and ^{13}C NMR spectra of PEK(6FBA)-PEP $_n = 20$ are shown in Figures 4 and 5. In Figure 4, there exists two unassignable signals at 6.8 and 8.1 ppm of which the in-

tensities are very weak. They might be signals of contaminants. In this case, DP_n calculated from the NMR result is 24.

Table I summarized the results of PEK-PEPs synthesis. Molecular weight can be controlled by the feed ratio between BPDE and bisphenol. T_g of uncured PEK-

Figure 5. ^{13}C NMR spectrum of PEK(6FBA)-PEP $n = 20$.

Table I. Synthesis of PEK-PEP

Polymer code ^a	M_n^b $\times 10^{-3}$	M_w $\times 10^{-3}$	M_w/M_n	T_g^c $^{\circ}\text{C}$	T_s^d $^{\circ}\text{C}$	Yield %
PEK(6FBA)-PEP $n = 10$	5.69	8.30	1.46	145	152	40.1
PEK(6FBA)-PEP $n = 20$	13.6	22.7	1.67	179	182	72.5
PEK(6FBA)-PEP $n = 40$	26.6	44.1	1.66	181	197	67.3
PEK(HF)-PEP $n = 20$	10.7	21.0	1.96	210	216	66.5

^aPolymer code was showed in Scheme 3. ^bDetermined by GPC calibrated with polystyrene standard eluted with NMP at 40°C . ^cGlass transition temperature was measured by DSC at a heating rate of $20^{\circ}\text{C min}^{-1}$. ^dSoftening temperature was measured by optical microscope equipped with hotting stage.

PEP is dependent on not only the molecular weight but also the structure of bisphenol. T_g of PEK(6FBA)-PEP increases with the molecular weight from 145 to 181°C . T_s has the same tendency as T_g . Concerning to the structure of bisphenol, HF leads to higher T_g due to the bulky cardo structure.

Cross-Linking Behavior of PEK-PEP

The cross-linking behavior of PEK-PEP was also followed by isothermal curing on DSC measurement at 320°C . The exothermic peak was observed which is attributed to the cross-linking reaction as well as the model compound. The cross-linking reaction of PEK-PEP does not obey the first-order reaction kinetics differed from the model compound as described above. In

Table II. Thermal properties of PEK-PEP

Polymer code ^a	$T_g^b / ^\circ\text{C}$		$T_s^c / ^\circ\text{C}$		$T_d 10^d / ^\circ\text{C}$
	Uncured	Cured ^e	Uncured	Cured ^e	Cured ^e
PEK(6FBA)-PEP $n = 10$	145	170	152	ND ^f	544
PEK(6FBA)-PEP $n = 20$	179	186	182	ND	559
PEK(6FBA)-PEP $n = 40$	181	192	197	ND	558
PEK(HF)-PEP $n = 20$	210	223	216	ND	598

^aPolymer code was showed in Scheme 3. ^bGlass transition temperature was measured by DSC at a heating rate of $20^\circ\text{C min}^{-1}$. ^cSoftening temperature was measured by optical microscope equipped with hotting stage. ^dTemperature of 10% wt loss was measured by TGA at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen. ^eCured at 320°C for 2 h. ^fNot detected under the decomposition temperature.

the case of the cross-linking reaction of polymer end groups, the mobility of polymer chain decreases with increasing conversion of the cross-linking reaction, and thereby this results in the decrease of the reaction rate.

Thermal properties of PEK-PEPs are shown in Table II. Curing at 320°C leads to a drastic increase of T_g . T_s of cured PEK-PEPs is not observed under their thermal decomposition. T_g of uncured PEK-PEPs is dependent on not only molecular weight but also the structure of bisphenol as described above. T_g of cured PEK-PEPs is also dependent on the structure of bisphenol. Figure 6 plots the increase of T_g against the density of cross-linking for PEK(6FBA)-PEP $n = 20$ and PEK(HF)-PEP $n = 20$ during curing at 320°C . The density of the cross-linking is estimated from conversion of the cross-linking reaction. T_g increases linearly with the density of the cross-linking in both polymers. The relation between T_g and cross-linking density for rubber had been proposed, so-called configurational entropy theory as described below.¹⁹

$$\begin{aligned} \{T_g(X) - T_g(0)\} / T_g(0) &= (KM X / \gamma) / (1 - KM X / \gamma) \\ &= \alpha X / (1 - \alpha X) \\ \therefore T_g(0) / T_g(X) &= -\alpha X + 1 \end{aligned}$$

where $\alpha = KM / \gamma$

Here, $T_g(X)$ is the glass transition temperature with degree of cross-linking.

$T_g(0)$ is the glass transition temperature uncross-linked.

X is number of cross-links per gram.

M is molecular weight of a residue.

γ is number of flexible bonds per residue.

K is constant.

The change of T_g of PEK-PEPs is analyzed according to this theory assuming that one cross-link is made from three PEP end groups, which is borne out by the results of FT-IR as mentioned above, and $\gamma = 13$. The

Figure 6. Relationship between T_g and cross-linking density (Dash-lines show the calculated lines Circles show the measured values).

following equations are obtained.

$$\text{PEK(6FBA)-PEP}n = 20$$

$$T_g(0) / T_g(X) = -426X + 1$$

$$\text{PEK(HF)-PEP}n = 20$$

$$T_g(0) / T_g(X) = -793X + 1$$

The obtained lines are also showed in Figure 6. The increase of T_g during curing seemed to be accounted for by the configurational entropy theory. However, K constant of PEK-PEP is quite different from that of rubber reported. The cross-linking reaction leads to the increase of molecular weight of PEK-PEPs and this brings about the increase of T_g . The contribution to the increase of T_g caused by molecular weight is not involved in this theory, and hence this may be a main reason for the large difference on the K constant.

Table III. Solvent resistance of PEK(6FBA)-PEPn=20

Curing time ^a min	Conv. ^b %	Insoluble part into toluene ^c wt%
0	0	0
30	21	69
60	52	80
120	91	100
200	100	100

^aCured at 320°C. ^bConversion of cross-linking was estimated from heat content of exothermic peak measured on DSC.

^cEstimated by weighing the film after soaking for 1 d at room temperature.

Table IV. Solubility of PEK-PEP

Solvent	Uncured	Cured ^a
NMP	S ^b	I ^b
DMAc	S	I
Chloroform	S	I
THF	S	I
Toluene	S	I

^aCured at 320°C for 2 h. ^bS: soluble, I: insoluble at 25°C.

Characterization

Solvent resistance of PEK-PEP was firstly evaluated by the qualitative solubility test in excess of toluene. The thin film of PEK(6FBA)-PEPn = 20 was prepared by casting of toluene solution and cured at 320°C. Insoluble part in toluene increases with curing time as summarized in Table III, that is to say, solubility decreases with the conversion of cross-linking reaction. After curing for 120 min, the film gets completely insoluble in toluene. Table IV shows the results of the solubility test in several solvents for the uncured and cured PEK(6FBA)-PEPn = 20 at 320°C for 120 min. The uncured PEK(6FBA)-PEPn = 20 possesses the outstanding solubility into many solvents. On the other hand, the cured PEK(6FBA)-PEPn = 20 is completely insoluble in even polar aprotic solvent such as DMAc and NMP. Thermal cross-linking reaction affords PEK-PEP with the excellent solvent resistance.

Thermal stability estimated by TGA is also shown in Table II. Temperatures of 10% weight loss in nitrogen (Td10) of cured PEK-PEP are quite high, which is in the range from 544 to 598°C. We have reported that Td10 of the F-PEKs which do not possess the phenylethynyl moiety ranges from 499 to 553°C.⁵ Compared with these Td10s, thermal stability of PEK-PEP is improved by about 40°C due to the cross-linking. The TGA curve of the cured PEK-PEP is shown in Figure 7 with that of F-PEK. It is particularly noteworthy that the cured PEK-PEP exhibits very high char yield at high temperature.

Dynamic mechanical scans of the uncured and cured

Figure 7. TGA thermo-grams of cured PEK(6FBA)-PEPn = 20 and F-PEK(6FBA). **Figure 8.** Dynamic mechanical scan for PEK(6FBA)-PEPn = 20 (a) uncured and (b) cured at 320°C for 2 h at 110 Hz and heating rate of 2°C min⁻¹. Film thickness was 37 μm.

PEK(6FBA)-PEPn = 20 film are shown in Figure 8. Dynamic modulus at 25°C of the uncured and cured PEK-PEP are 1.42×10^{10} dyne cm⁻² and 1.30×10^{10} dyne cm⁻², respectively. Though the modulus of the uncured PEK-PEP decreases gradually over 160°C, that of cured PEK-PEP is kept up to 200°C due to the shift of α relaxation toward higher temperature correspond-

Figure 9. WAX intensity profiles of PEK(6FBA)-PEPn = 20 (a) uncured and (b) cured at 320°C for 2 h.

Figure 10. Absorption spectrum of PEK(6FBA)-PEPn = 20 (a) uncured and (b) cured at 320°C for 2 h. Film thickness was 2 μ m.

ing to glass transition. β relaxation is observed at *ca.* 30°C in the uncured PEK-PEP. This lower relaxation is attributed to the conformation change of the diphenyl ether moiety.²⁰ In the scan of the cured PEK-PEP, the β relaxation disappears, though diphenyl ether moiety does not take part in the cross-linking reaction. The complete disappearance of β relaxation also shows that the mobility of polymer chain is restricted by cross-linking.

Crystallinity was measured by WAXS diffractometer. The WAXS patterns of the uncured and cured PEK(6FBA)-PEPn = 20 film are shown in Figure 9. Any diffraction arose from the crystallite is not observed at all and only the broad halo arose from amorphous region is observed in both the films. Both the uncured and cured PEK-PEP films are not crystalline and show excellent transparency.

Though uncured PEK-PEP film was almost colorless, cured one was slightly yellow. Absorption spectra of uncured and cured film of PEK(6FBA)-PEPn = 20 are shown in Figure 10. These films exhibit $\pi - \pi^*$ absorption at 298 nm. The serious difference is not observed between uncured and cured films and the red shift of $\pi - \pi^*$ absorption is not occurred. The formation of

the aromatic ring or polyene structure is confirmed by IR as described, whereas these cross-linked structures do not affect the absorption spectrum due to the low concentration.

CONCLUSION

Cross-linkable fluorine-containing PEKs are synthesized by introducing phenylethynyl end group. Cross-linking reaction occurs over 320°C and it brings about not only the outstanding solvent resistance but also the increase of T_g . Relationship between the cross-linking density and T_g can be fundamentally interpreted by configurational entropy theory. Furthermore, the cured PEK-PEPs possess excellent thermal stability with the 10% weight loss temperature in the range from 544 to 598°C.

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