Novel polyaryletherketones bearing pendant carboxyl groups and their rare earth complexes, Part I: Synthesis and characterization

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ABSTRACT

A series of novel polyaryletherketones bearing pendant carboxyl groups were synthesized via solution nucleophilic polycondensation reaction, and the rare earth ($Re^{3+} = Sm^{3+}$, Eu^{3+}, Dy^{3+} and Tb^{3+}) coordinated polymers were prepared using the polymer as macromolecular ligand and 1,10-phenanthroline (Phen), dibenzoylmethane (DBM) or 8-hydroxyquinoline (HQ) as co-ligands. Their structures were confirmed by means of FT-IR, ^1H NMR and WAXD methods. WAXD results showed that the rare earth-coordinated polymer had similar amorphous structure to the polymer matrix, whereas the diffraction peaks corresponding to rare earth salts were completely absent, indicating a homogeneous distribution of rare earth ions within the polymer hostess due to the formation of coordination bonds between rare earth ions and the carboxyl groups on the polymer backbone. The rare earth coordination polymers were soluble in polar solvents such as DMSO, DMAc, DMF and NMP, and could be easily cast into transparent tough thin films. The polyaryletherketones synthesized had high glass transition temperatures above 210 °C, and showed fairly good thermal stability with 5% thermal decomposition loss above 402 °C.

1. Introduction

The study of rare earth complexes luminescent materials has always been an active research area, due largely to their excellent luminescence characteristics, i.e., high luminous intensity, long luminous lifetime and extremely sharp emission bands from the electronic transitions between the 4f energy levels [1–4]. Some research groups have incorporated the organic low-molecular complexes into various matrixes, such as sol–gel glasses [5–11], inorganic–organic hybrid materials [12,13], polymers [12,14–19], or liquid crystals [20,21]. Among these matrixes, polymers own many advantages as rare earth ions hosts, including low cost, and convenient control of various optical parameters such as refractive index, birefringence, optical transparency bandwidth. In addition, polymers are easy to process and can be deposited onto different substrates using spin-coating or dip-coating processing techniques. Therefore, rare earth polymers have drawn much attention as new functional materials in the fields of photoluminescence, electroluminescence, optics communications, lasers, and solar-energy conversion systems [15,22–24].

At present, there are two methods of preparing rare earth polymers. The first one is the direct dispersion of rare earth in the polymer matrix, and the second method is the attachment of the rare earth ions on the polymer backbone through coordination bonds. The former approach offers the advantage of versatility since both the polymer matrix and the rare earth complexes can be chosen independently, but it is difficult to obtain rare earth polymers with the high fluorescence intensity and long fluorescence lifetime caused by the poor compatibility of the inorganic rare earth with the polymer matrix. In contrast, the coordination of rare earth ions with carboxyl, amide, amino, or sulfo groups on the polymer chain may provide the solution to the above problems. The two main routes are as follows: (i) rare earth ions coordinate with coordinatable groups attached on the polymer chain and (ii) low-molecular rare earth complexes carry out polymerization as monomer or comonomer.

There are several polymers, which are often used as the polymer matrixes, such as poly(methyl methacrylate) (PMMA) [25–27], polystyrene (PS) [28], polyacrylic acid (PAA) [19] and their copolymers [29–32]. However, their aliphatic structure of polymer backbone brings about some limitations in practical applications, such as low glass transition temperature (80–120 °C), poor thermal stability and mechanical toughness. Therefore, developments of new polymer matrix materials bearing coordinatable groups and possessing good film-formation property, high glass transition temperature, excellent thermal stability and mechanical property are strongly desirable.

Hydroquinone based polyetheretherketone (PEEK) has been noted for their excellent mechanical toughness, electrical/insulating and thermo-oxidative stability, but the highly symmetric

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Table 1
Physical characteristics and spectral data of monomers synthesized

Monomers	Yield (%)	mp (°C)	Elemental analysis (Calc., Found)		FTIR (cm^{-1})
			C (%)	H (%)	
PPL-1	84.9	237–238	74.99, 75.03	5.04, 5.11	1685 (C=O of associated carboxyl group), 1612 (Ar)
PPL-2	87.4	225–226	75.84, 75.91	5.79, 5.60	1708 (C=O of associated carboxyl group), 1609 (Ar), 2923 and 2860 (Ar–CH$_3$)
PPL-3	85.3	209–210	78.85, 78.94	6.15, 6.09	1696 (C=O of associated carboxyl group), 1620 (Ar), 2928 and 2868 (Ar–CH$_3$), 2960 (CH$_3$ of isopropyl)

structural characteristic results into its very poor solubility, insoluble even in polar aprotic solvent. This paper was undertaken to synthesize novel polyaryletherketones simultaneously bearing different alkyl substituents and carboxyl group on the polymer backbone. The twisted structure and bulky alkyl substituents may endow them good solubility, whereas the carboxyl group provides the sites to coordinate with the rare earth ions. This article describes the synthesis and characterization of polymers and their rare earth coordination polymers. The study on luminescent properties will be published subsequently in the second paper.

2. Experimental

2.1. Materials

Phenolphthalein (PPH-1), 2′,2″-dimethyl-phenolphthalein (PPH-2), 2′,2″-diisopropyl-5′,5″-dimethyl-phenolphthalein (PPH-3) and bis(4-fluorophenyl)ketone (DFDPK) were purchased from Aldrich Chemical Company. Rare earth nitrate hexahydrates (Re(NO$_3$)$_3$·6H$_2$O, Re^{3+} = Sm^{3+}, Eu^{3+}, Dy^{3+} and Tb^{3+}) were obtained from Shandong Qingda Fine Chemical Factory. 1,10-phenanthroline (Phen), dibenzoylmethane (DBM) and 8-hydroxyquinoline (HQ) were provided by Shenyang Chemical Reagent Factory. All reagents mentioned above were used without further purification. Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were dried and distilled under reduced pressure just before use. Phenolphthalein (PPL-1), 2′,2″-dimethyl-phenolphthalein (PPL-2), 2′,2″-diisopropyl-5′,5″-dimethyl-phenolphthalein (PPL-3) were prepared according to the procedure described in the literature [33]. Other chemical reagents were of analytical reagent grade and used as received.

2.2. Measurements

Fourier transform infrared spectra (FTIR) were measured on a Nicolet 20XB FT-IR spectrophotometer in the 400–4000 cm^{-1} region. For monomers and Eu^{3+}–Phen powder samples, FTIR spectra were performed with the KBr flake. For polyaryletherketones and their rare earth coordination polymers, film samples of ca. 5-μm thickness were used, which were vacuum dried at 180 °C for at least 24 h before measurement.

Gel permeation chromatography (GPC) analysis was conducted with a PL-GPC220 system using PS as standard and tetrahydrofuran (THF) as the eluent.

Nuclear magnetic resonance proton spectra (^{1}H NMR) were recorded in deuterated dimethyl sulfoxide (DMSO-d_6) on a Varian INOVA400 spectrometer with tetramethylsilane (TMS) as internal reference.

Elemental analyses were determined with an Elementar Vario EL III elemental analyzer. The rare earth ions' contents were determined by an optimer 2000dv inductively coupled plasma (ICP).

Wide-angle X-ray diffraction (WAXD) measurements were carried out, on a D/Max-2400 X-ray diffractometer with Cu Kα$_1$ radiation ($\lambda = 1.54$ Å) over the 2θ range of 4–60°. For polymers, film

samples with thickness of ca. 40 μm were used, which were vacuum dried at 180 °C for at least 24 h prior to use. For Eu^{3+}–Phen measurement, powder sample was used. The detailed preparations are described in Section 2.3.2.

Differential scanning calorimetries (DSC) were run on NETZSCH DSC204 at the temperature of 100–400 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. The glass transition temperatures (T_g) were read at the middle of the change in the heat capacity.

Thermal gravimetric analyses (TGA) were carried out on NETZSCH TG209C under nitrogen atmosphere in the 50–700 °C region and conducted with a heating rate of 10 °C min^{-1}. The polymer films for TGA measurements were prepared in the same condition as that of WAXD.

2.3. Synthesis

2.3.1. Synthesis of polymers

A typical synthesis procedure for PEK-3 was described as follows: 8.6512 g (0.02 mol) PPL-3, 4.3640 g (0.02 mol) DFDPK, 5.5282 g (0.04 mol) anhydrous K$_2$CO$_3$, 19 ml toluene and 17 ml DMSO were added into a 150 ml three-neck round bottom flask. A slow stream of nitrogen was maintained throughout the whole reaction. The temperature was raised to 140 °C to remove water formed by azeotropic distillation with toluene for about 2 h. Then the toluene was distilled out and the temperature was raised gradually to 175 °C. It was allowed to react at this temperature for about 4 h and finally a viscous solution was obtained. After cooling, it was diluted with DMF and settled overnight. The supernatant liquid was slowly poured into a stirred mixed solution of ethanol and 0.1 N aqueous hydrochloric acid solution (v/v, 1:2) to precipitate the white polymer. The polymer was washed with deionized water to remove the inorganic salt and dried under vacuum at 100 °C for 12 h to constant weight.

The synthesis of PEK-1 and PEK-2 was similar to that of PEK-3.

2.3.2. Preparation of rare earth coordination polymers

A typical preparation procedure for PEK-3–Eu^{3+}–Phen was described as follows: 0.1800 g (2.95 mmol) PEK-3 was dissolved in 3 ml of DMF. Then a solution of 0.1315 g (2.95 mmol) Eu(NO$_3$)$_3$ and Phen (0.1753 g, 8.84 mmol) in 3 ml of dried DMF was added. The mixture solution was stirred for 2 h at room temperature. The homogeneous solutions thus obtained were used for luminescence measurement.

As a comparison, the solutions of PEK-3–Eu^{3+} and Eu^{3+}–Phen were prepared by the same molar ratio in the same solvents. The preparation procedure of other rare earth coordination polymer solutions was similar to that of PEK-3–Eu^{3+}–Phen.

The film samples of rare earth coordination polymers and non-coordinated polymers for the FTIR and WAXD measurements were obtained from their DMF solutions, which were filtered through the membrane filter and cast onto a clean glass plate at 60 °C. After 8 h, the films were transferred to vacuum oven and dried further at 150 °C for 24 h.

Scheme 1. The synthesis of the polymers and rare earth coordination polymers.
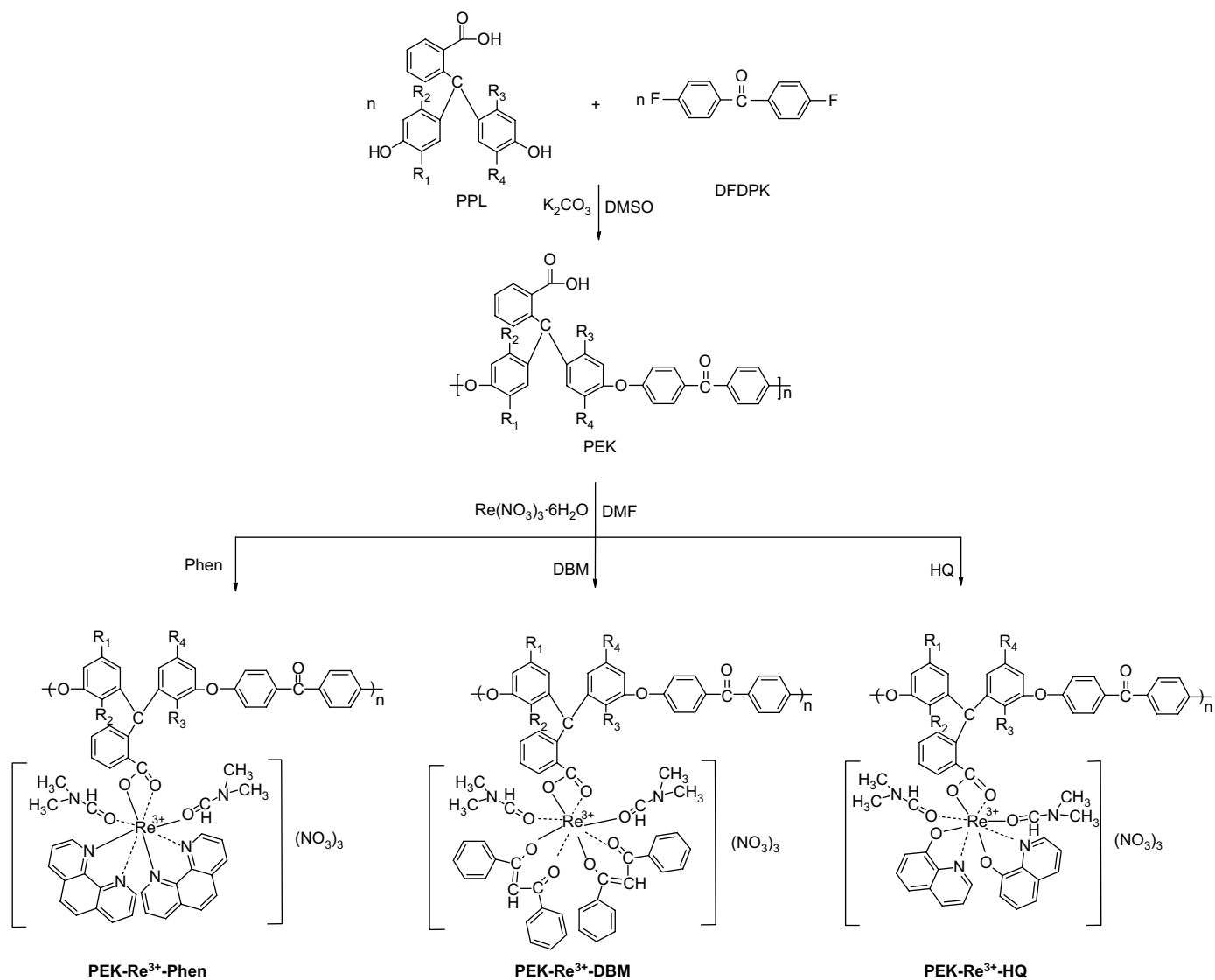
Monomer	Polymer	R_1	R_2	R_3	R_4
PPL-1	PEK-1	H	H	H	H
PPL-2	PEK-2	CH_3	H	H	CH_3
PPL-3	PEK-3	$CH(CH_3)_2$	CH_3	CH_3	$CH(CH_3)_2$

$Re^{3+} = Sm^{3+}$, Eu^{3+}, Dy^{3+} or Tb^{3+}

2.3.3. Preparation of Eu^{3+}–Phen coordination compound

Phen (0.1753 g, 8.84 mmol) was dissolved in 3 ml of dried DMF. Then a solution of 0.1315 g (2.95 mmol) $Eu(NO_3)_3$ in 3 ml of dried DMF was added. The mixture solution was stirred for 2 h at room temperature. Then, the mixture solution was slowly poured into 100 ml ethanol to obtain the light pink powder. The product was dried at 80 °C under vacuum to constant weight before FTIR and WAXD measurements.

3. Results and discussion

3.1. Synthesis of monomers, polymers and rare earth coordination polymers

Three carboxyl-containing bisphenol monomers PPL-1, PPL-2 and PPL-3 were synthesized through the reduction reaction of phenol-phthalein (PPH-1) and its derivatives 2′,2″-dimethyl-phenolphthalein
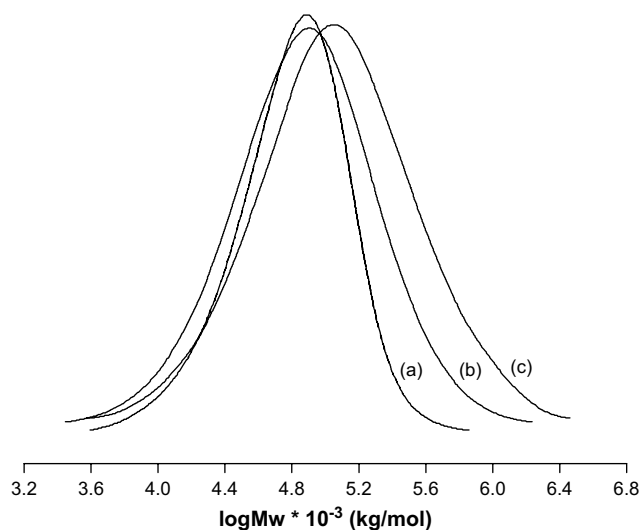
Fig. 1. GPC traces of (a) PEK-1, (b) PEK-2, and (c) PEK-3.

Fig. 2. FTIR spectra of (a) PEK-1, (b) PEK-2, and (c) PEK-3.

(PPH-2) and 2′,2″-diisopropyl-5′,5″-dimethyl-phenolphthalein (PPH-3) with zinc powder in aqueous NaOH solution, respectively. The chemical structures of the three monomers obtained were confirmed by means of FTIR and elemental analysis methods. The measured values of C and H agreed well with the calculated values. For PPL-1, the peak at 1736 cm^{-1} corresponding to C=O stretching vibration of lactone group of PPH-1 was absent, but a new peak at 1685 cm^{-1} which is associated to C=O stretching vibration of carboxyl group of PPL-1 appeared. The similar observations were found for PPL-2 and PPL-3. This fact suggested that PPH-1, PPH-2 and PPH-3 had been completely reduced to PPL-1, PPL-2 and PPL-3, respectively. The physical characteristics and FTIR spectra data are given in Table 1.

Three new alkyl-substituted polyaryletherketones (PEK-1, PEK-2 and PEK-3) with carboxyl side group were easily prepared via solution nucleophilic polycondensation reaction from DFDPK with various bisphenol monomers, using toluene to azeotrope the water formed (Scheme 1). The number-average molecular weights (M_n) were in the range from 45.6 kg/mol to 66.4 kg/mol with the poly-dispersity indexes (PDI) from 1.8 to 3.0. The GPC measurement curves are illustrated in Fig. 1 and the detailed GPC data are listed in Table 2. Using the carboxyl-containing polyaryletherketone as macromolecule ligand, DMF and low-molecular compound (Phen, DBM or HQ) as solvent and co-ligand, rare earth coordination polymers (PEK–Re^{3+}–Phen, PEK–Re^{3+}–DBM and PEK–Re^{3+}–HQ) were prepared.

Fig. 2 shows the FTIR spectra of three polyaryletherketones. From FTIR spectra it was found that peak intensities at about 2900 cm^{-1} corresponding to alkyl substituents increased obviously from PEK-1 to PEK-3, and the C=O band of the carboxyl group was split into a doublet peak. The peak at 1720 cm^{-1} was assigned to the C=O absorption of the free carboxyl group, whereas that at lower frequency of 1698 cm^{-1} was attributed to hydrogen-bonded carboxyl group. In addition, the existence of Ar–CO–Ar peak at 1655 cm^{-1} and the ether bond absorption at 1054 cm^{-1} demonstrated that the polyaryletherketones, PEK-1, PEK-2 and PEK-3 were

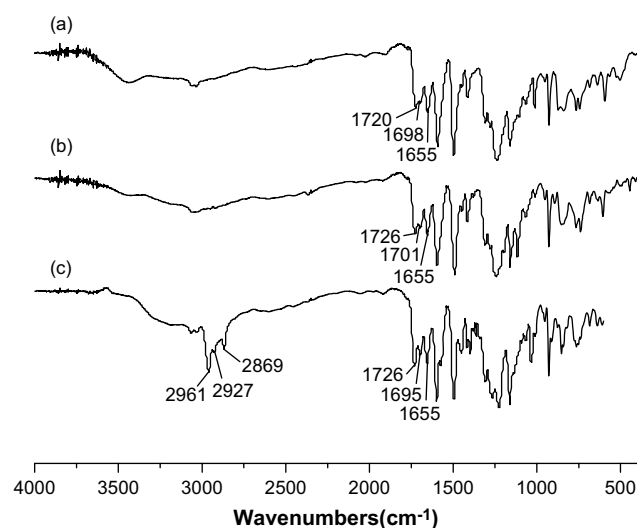indeed obtained via solution nucleophilic polycondensation reaction.

The ^{1}H NMR spectra of the polymers and their detailed assignment of proton peaks are shown in Figs. 3–5, in which chemical shifts at 12.986, 12.953 and 12.676 ppm, respectively, correspond-ing to carboxyl group proton appeared. The signal at 2.065 ppm was assigned to methyl group proton, and the signals at 2.944 and 0.899 ppm were attributed to isopropyl group protons.

Fig. 6 presents the comparison of FTIR spectra of small mole-cular ligand Phen, macromolecule ligand PEK-3, solvent DMF as well as the coordination polymer PEK-3–Eu^{3+}–Phen. From the FTIR spectra of PEK-3 and PEK-3–Eu^{3+}–Phen, it was found that the strong peak at 1725 cm^{-1} corresponding to carboxyl group in curve (c) was essentially absent in curve (d). Alternatively, the typical symmetric stretching vibration (COO$^-$) at about 1384 cm^{-1} was detected. These results suggested that coordination bonds were formed between Eu^{3+} and the oxygen atom of carboxyl group. Moreover, the Ar–CO–Ar absorption at 1655 cm^{-1} occurred at almost the same position as that in non-coordinated polymer, indicating that the carbonyls embedded into the polymer main chain could not coordinate with Eu^{3+}. However, compared to curve (a), the peak in curve (d) corresponding to carbonyl group of DMF was shifted from 1672 cm^{-1} to 1668 cm^{-1}, demonstrating that there was some interaction between carbonyl of DMF and rare earth ion, suggesting that the solvent DMF was also involved in the coordination with Eu^{3+}. The peaks at 461 cm^{-1} further confirm the occurrence of coordination reaction between Eu^{3+} and carbonyl of DMF [34]. On the other hand, the comparison of FTIR spectra of Phen (curve b) and PEK-3–Eu^{3+}–Phen (curve d) revealed that the stretching vibration of Phen at 1561 cm^{-1} and the bent vibrations at 854 cm^{-1} and 739 cm^{-1} were red shifted to 1519 cm^{-1}, 841 cm^{-1} and 730 cm^{-1}, respectively, indicating the formation of coordina-tion bonds between Eu^{3+} and nitrogen atom of Phen. Accordingly, it can be included that all of PEK-3, DMF and Phen participated in the coordination reaction with Eu^{3+}. As demonstrated in other polymer systems [35], the earth coordination polymer might own the stable eight-fold coordination structure. The possible molecular formula of rare earth coordination polymer might be depicted in Scheme 1.

The results of elemental analysis of three coordination polymers PEK-1–Eu^{3+}–Phen, PEK-2–Eu^{3+}–Phen and PEK-3–Eu^{3+}–Phen were conducted using an Elementar Vario EL III elemental analyzer and an optimer 2000dv inductively coupled plasma (ICP). The measured values of H, N and Eu^{3+} agreed well with the calculated values, but the values of C showed some deviation from the

Table 2
GPC data of the polymers synthesized

Polymer	M_n (kg/mol)	M_w (kg/mol)	PDI
PEK-1	45.6	82.1	1.8
PEK-2	46.1	117.8	2.6
PEK-3	66.4	199.4	3.0

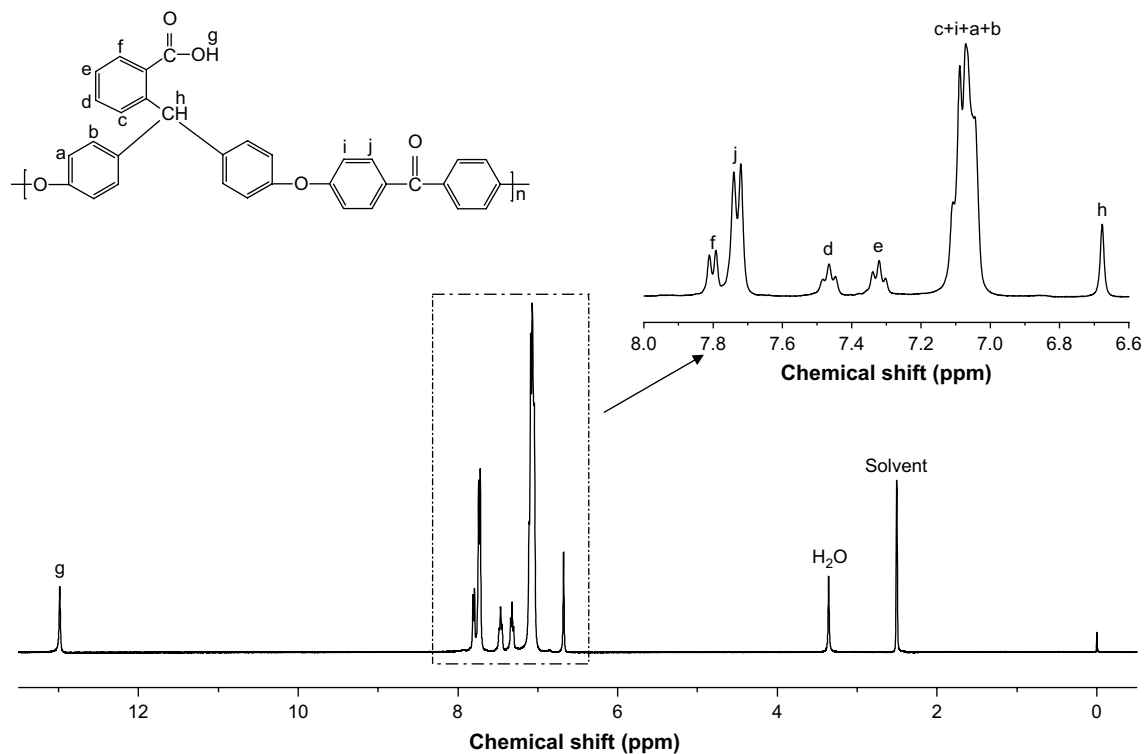**Fig. 3.** Chemical structure and ^{1}H NMR spectra of PEK-1.

measured ones (Table 3). For PEK-1–Eu^{3+}–Phen and PEK-2–Eu^{3+}–Phen, there was a position deviation in the found C content. On the contrary, for PEK-3–Eu^{3+}–Phen, a negative C content deviation was observed. The possible reason was assumed that, compared with PEK-1 and PEK-2, the bulky isopropyl substituents

on the phenylene ring of PEK-3 resulted into serious steric hindrance and lowered mobility ability, as demonstrated by its increased glass transition temperature. These structural factors led to PEK-3 the relatively lower coordination ability. Accordingly, the content of small molecular ligands Phen and DMF in
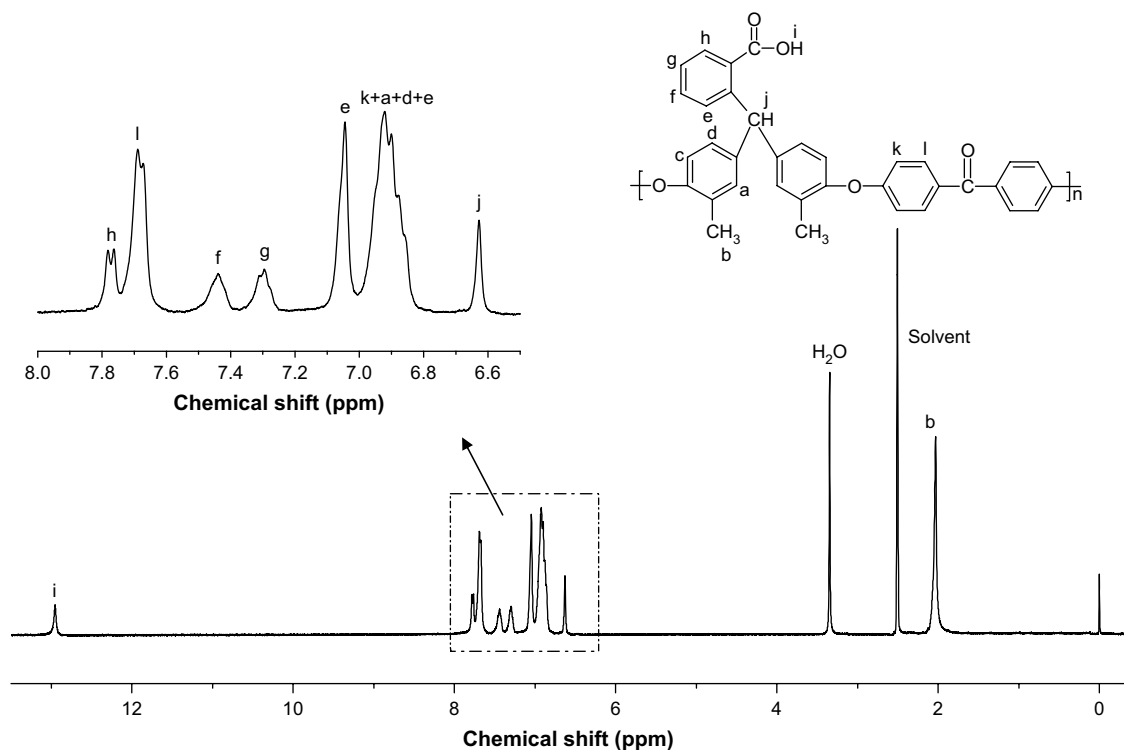

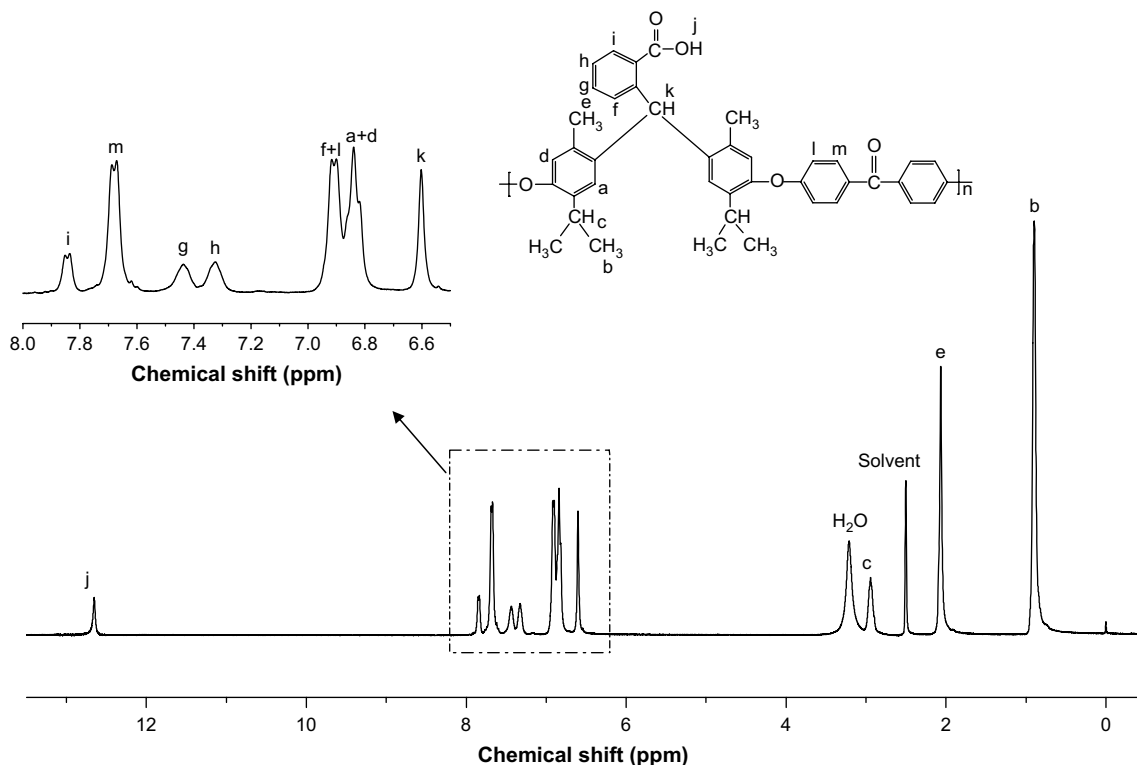**Fig. 4.** Chemical structure and ^{1}H NMR spectra of PEK-2.

Fig. 5. Chemical structure and ^{1}H NMR spectra of PEK-3.

PEK-3–Eu^{3+}–Phen might be higher than that in PEK-1–Eu^{3+}–Phen and PEK-2–Eu^{3+}–Phen to some extent, exhibiting a negative deviation of C content from the calculated value.

As shown in Fig. 7, the WAXD patterns of PEK-1, PEK-2 and PEK-3 displayed the amorphous characteristic due to the effects of twisted bisphenol structure and alkyl substituents. The wider hump of PEK-3 than PEK-1 and PEK-2 suggested that the packing regularity of PEK-3 decreased greatly with the increase of number and volume of alkyl substituents. The WAXD measurements of PEK-1–Eu^{3+}–Phen and Eu^{3+}–Phen were also carried out and illustrated in Fig. 8. The Eu^{3+}–Phen (curve b) showed extremely strong diffraction peaks at 2θ angles of 9.84, 10.78, 12.52 and 24.84°, indicative of Eu^{3+}–Phen

the perfect crystal lattice structure. However, in the WAXD pattern of PEK-1–Eu^{3+}–Phen (curve a), all the sharp peaks corresponding to Eu^{3+}–Phen disappeared and only showed the amorphous structure, which proved that the rare earth ions were not simply doped in PEK-1 system, but coordinated with the carboxyl groups on the polymer backbone, leading to a homogeneous distribution of rare earth ions within the polymer hostess. This WAXD finding was well consistent with the FTIR analysis result that the coordination bonds formed between Eu^{3+} and O or N atom in the rare earth-coordinated polymer system.

3.2. Physical properties of polymers and rare earth coordination polymers

The solubility data in Table 4 showed that all polymers were soluble in high polar solvents such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-dimethlyacetamide (DMAc), N-methylpyrrolidone (NMP), tetrahydrofuran (THF) at the room

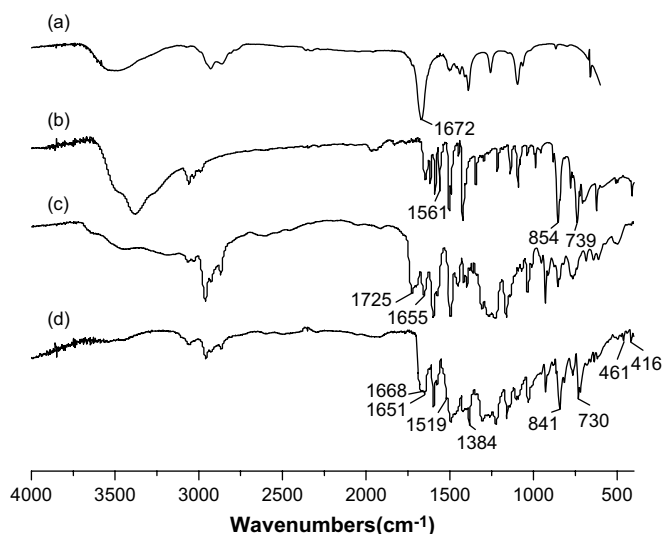**Fig. 6.** FTIR spectra of (a) DMF, (b) Phen, (c) PEK-3, and (d) PEK-3–Eu^{3+}–Phen.

Table 3
Elemental data of rare earth coordination polymers

Complexes	Element	Found	Calc.
PEK-1–Eu^{3+}–Phen	C	58.68	56.38
	H	3.47	3.83
	N	9.46	9.39
	Eu	11.25	11.32
PEK-2–Eu^{3+}–Phen	C	59.68	56.98
	H	3.74	4.05
	N	9.11	9.20
	Eu	10.46	11.09
PEK-3–Eu^{3+}–Phen	C	58.64	60.78
	H	4.64	4.33
	N	8.67	7.73
	Eu	10.45	10.38

All the values given are in percentages.

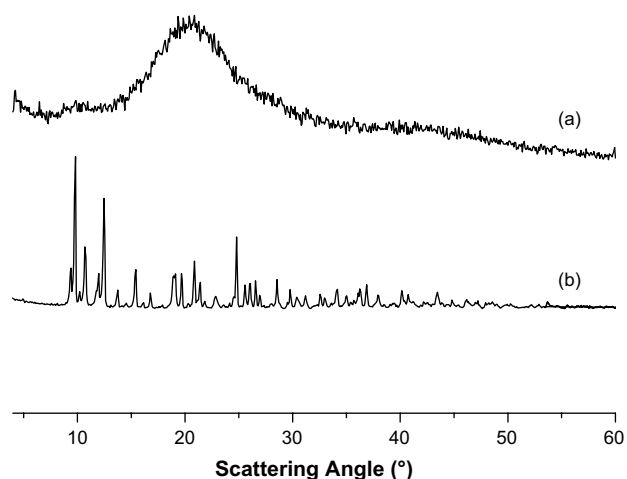**Fig. 7.** WAXD patterns of (a) PEK-3, (b) PEK-2, and (c) PEK-1.

Fig. 8. WAXD patterns of (a) PEK-1–Eu^{3+}–Phen, and (b) Eu^{3+}–Phen.

Table 5
DSC and TGA data of polymers and PEK-3–Eu^{3+}–Phen

Samples	T_g/°C	T_5/°C	T_{10}/°C	T_{30}/°C	RW/%
PEK-1	228	426	451	546	58
PEK-2	210	421	432	474	54
PEK-3	232	402	411	427	23
PEK-3–Eu^{3+}–Phen	–	256	292	429	44

T_5, T_{10} and T_{30} are referred to the temperature at 5%, 10% and 30% weight loss, respectively; RW is referred to the residual weight percentage at 700 °C.

PEK-3–Re^{3+}–Phen bearing bulky isopropyl substituents showed quite good solubility in less polar solvent at elevated temperature, such as THF. Therefore, transparent and uniform films of rare earth coordination polymers can be obtained in the different solvents by spin-coating or solution-casting method. The thickness of the films can be controlled by changing the concentration of rare earth coordination polymer solution in order to meet the requirement of practical application.

The thermal properties of these polymers and rare earth coordination polymers were evaluated by DSC and TGA in N$_2$ atmosphere. The influences of alkyl substitutions, carboxyl group and co-ligands on the glass transition temperature and thermal decomposition weight loss are summarized in Table 5. In general, there are two main effects caused by introduction of alkyl substituents on the phenylene. One is the increase of steric hindrance of the polymer segmental chain motion, and the other is the enlarged chain spacing, which will be favorable for the drop of interaction between polymer chains. As shown in Fig. 9, relative to PEK-1 ($T_g = 228$ °C), PEK-2 displayed a lower T_g (210 °C), probably due to that the wide chain spacing caused by the introduction of the dimethyl groups led to the easy chain mobility of the polymer segments. However, PEK-3 with dimethyl and diisopropyl substitution simultaneously on the phenylene showed the highest T_g (232 °C). This might be attributed to the fact that the effect of steric hindrance played the dominating role on the polymer chain motion. Of interest was the observation that, for PEK-3–Eu^{3+}–Phen, no glass transition was detected in a temperature measurement range. The possible reason could be explained that, the bulky rare earth-coordinated side group and the enhanced interchain interaction due to the ionic character of rare earth carboxylate seriously inhibited the mobility ability of polymer chain, leading to an increased glass transition temperature beyond the measurement range.

The TGA curves of polymers and rare earth-coordinated polymers are illustrated in Fig. 10. For non-coordinated polymers, the decomposition temperature was in the order of PEK-1 > PEK-2 > PEK-3, indicating that there was a decrease with the introduction of alkyl groups. The 5% weight loss of all the three polymers took place at the temperatures above 400 °C, showing good thermal stability. However, the rare earth-coordinated polymers displayed different thermal decomposition behaviors. For example, the TGA curve of PEK-3–Eu^{3+}–Phen (curve c) had obvious three thermal decomposition steps. The first weight loss took place from 202 to 300 °C, which was attributed to the decomposition of Phen

temperature. Moreover, PEK-3 could even dissolve in acetone, indicating that the existence of the twisted bisphenol structure and bulk alkyl substituents were highly effective in reducing the packing density of the polymer chain and thus improved the polymer solubility. On the other hand, the enhancement of interaction between polymer chain and rare earth ion made the diffusion of solvent molecules between the polymer chains more difficult. As a result, relative to the non-coordinated polymer, the rare earth-coordinated polymers displayed the decreased solubility, but they still could dissolve in DMSO, DMF and NMP for PEK-1–Re^{3+}–Phen and PEK-2–Re^{3+}–Phen at elevated temperature and for PEK-3–Re^{3+}–Phen at room temperature. Moreover,

Table 4
Solubilities of polymers and rare earth coordination polymers

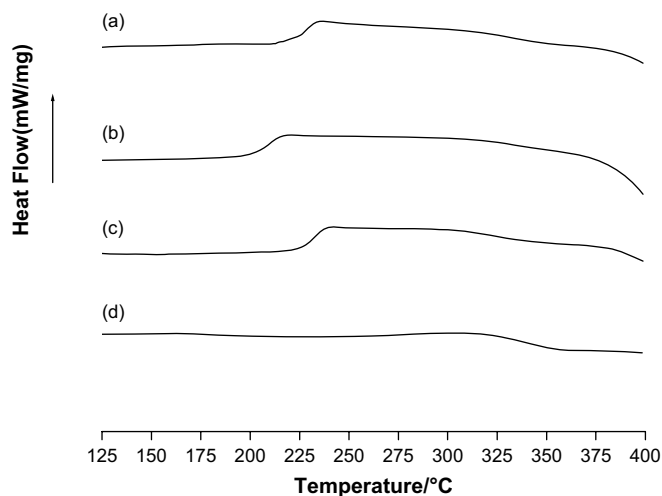| Solvent	PEK-1	PEK-1–Re^{3+}–Phen	PEK-2	PEK-2–Re^{3+}–Phen	PEK-3	PEK-3–Re^{3+}–Phen
DMSO	+	+ −	+	+ −	+	+
DMAc	+	+ −	+	+ −	+	+
DMF	+	+ −	+	+ −	+	+
NMP	+	+ −	+	+ −	+	+
THF	+	−	+	−	+	+ −
Acetone	−	−	−	−	+	−
Ethanol	−	−	−	−	−	−

+, Soluble; −, insoluble; + −, soluble on heating.

Fig. 9. DSC curves of (a) PEK-1, (b) PEK-2, (c) PEK-3, and (d) PEK-3–Eu^{3+}–Phen.
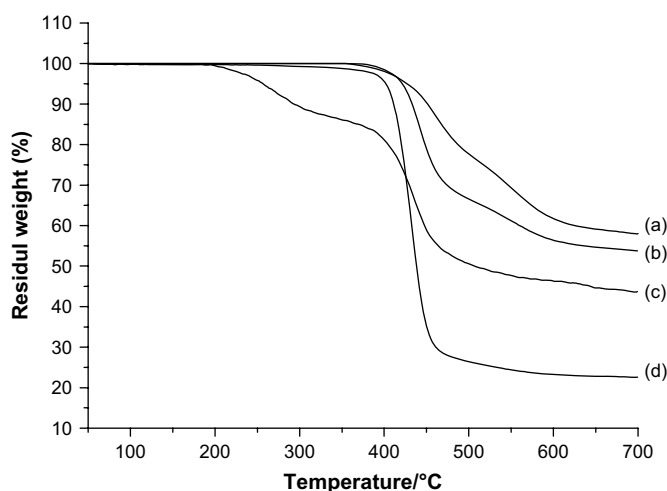

Fig. 10. TGA curves of (a) PEK-1, (b) PEK-2, (c) PEK-3–Eu^{3+}–Phen, and (d) PEK-3.

molecules. A slight weight loss in a temperature range of 300–392 °C may be attributed to the loss of DMF molecules. The similar observations were also reported in other rare earth-coordinated polymeric systems [11,36]. The boiling point of Phen is higher than that of DMF, but the loss of Phen first occurred in the TGA curve of PEK-3–Eu3+–Phen. The reason for this phenomenon is that, for coordination complex, the removal sequence of the ligands mainly depends on the coordination ability of the ligands, but not on the boiling point. The oxygen atom of DMF has stronger coordination ability with rare earth ions than the nitrogen atom of phen. Accordingly, in the TGA curve, the elimination temperature of DMF is higher than that of Phen. The steep and large weight loss that started at 392 °C should be ascribed to the decomposition of the polymer main chain.

4. Conclusions

Carboxyl-containing polyaryletherketones with different alkyl substituents were successfully obtained by the nucleophilic polycondensation reaction from newly synthesized bisphenol monomers with bis(4-fluorophenyl)ketone. Then, using these polymers as macromolecule ligands, a number of low-molecular weight compounds as co-ligands, a series of rare earth coordination polymers were prepared by the simple method of rare earth ions coordination with polymers. The structures of polymers and rare earth coordination polymers were studied by FTIR, ^{1}H NMR, elemental analysis and WAXD. The rare earth coordination polymers could easily dissolve in various polar solvents and be cast into transparent films, displaying potential application in flexible large area displays and light-emitting device fields.

Acknowledgment

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