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Synthesis and miscibility studies of rodlike/flexible polyimide molecular composites via *para–para* linked aromatic poly(amic ester) precursors

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Para–para linked aromatic poly(amic ester) precursors of rodlike polyimide (PI) BPDA-PDA and polyetherimide (PEI) HQDPA-ODA were synthesized. The *para–para* linked poly(amic ester)s were employed in this work to obtain, in theory, full-imidized polyimides. The two precursors were mixed by dissolving them in N,N'-dimethyl acetamide and subsequently coagulating in methanol. After thermal imidization, the miscibility behaviour of the resulting composites has been studied by means of dynamic mechanical analysis (d.m.a.) and differential scanning calorimetry (d.s.c.). The composites show a single glass transition temperature (T_g) at both d.m.a. and d.s.c. in which the T_g increases with increasing PI content. These T_g values are reproducible in repeated heating cycles, suggesting the true miscibility of the blends. © 1997 Elsevier Science Ltd.

(Keywords: polyimide; poly(amic ester); isomerism)

INTRODUCTION

Molecular composites based on polyimides have been prepared and characterized recently[1–4]. These are blends of a rigid polyimide as a strengthening component dispersed in a matrix of a flexible polyimide. However, such a molecular-level dispersion is very difficult to achieve because of the small entropy of mixing and high orientability of rigid-rod molecules. One approach to overcome this problem is to utilize the random coil characteristics of the precursor components. However, an additional problem arises if only poly(amic acid) precursors are employed. Since poly(amic acid)s are known to exhibit an equilibrium in solution between the polymer and its component monomers, mixing two chemically different poly(amic acid) solutions presents a real possibility for monomer interchange and thus random block copolymer formation[5–8]. For derivatized poly(amic acid)s, such as poly(amic ester)s, this equilibrium does not occur. Rodlike poly(*p*-phenylene pyromellitimide) (PMDA-PDA) composites with various flexible polyimides were previously demonstrated by the *in-situ* rod formation of its flexible poly(amic ester) precursor through thermal imidization. However, the PMDA-PDA composites exhibited phase separations with a scale larger than submicrometres[9–10].

In the present study, the approach was extended to the composite formation of rodlike poly(*p*-phenylene biphenyltetracarboximide) (BPDA-PDA) with flexible poly(bis(3,4-dicarboxyphenoxy) benzene 4,4′-oxydiphenylene bisimide) (HQDPA-ODA). It should be pointed out that poly(amic ester) and poly(amic acid) precursors which contain *meta* linkages along the polymer backbone are not well suited for this application since the conversion of this random coil structure to polyimides is difficult to realize in the solid state due to the amount of conformational change required during imidization[11,12]. A suitable starting material for molecular composite production is an all-*para* linked poly(amic ester) with extended rod characteristics. The extended conformation of all-*para* linked polymer should facilitate the conversion to polyimide, and hence, is of benefit for the formation of a good molecular composite.

EXPERIMENTAL

Materials

BPDA and HQDPA were synthesized from 4-chlorophthalic anhydride in our laboratory[13,14]. ODA and PDA were available commercially. Dianhydrides and diamines were purified by sublimation before use. Thionyl chloride ($SOCl_2$) was distilled under an inert atmosphere. THF was dried by refluxing over $LiAlH_4$. N,N'-Dimethyl acetamide (DMAc) was distilled over P_2O_5 under an inert atmosphere. Methanol was distilled under nitrogen from CaH_2.

Preparation of aromatic diester-diacids

m,m-*Dimethyl ester of* 3,3′,4,4′-*diphenyl tetracarboxylic acid (*m,m-*BPDE).* BPDA (25 g, 0.086 mol) was refluxed with 150 mol of dry methanol under dry nitrogen in a 250 ml flask. After the reaction was complete, as indicated by dissolution of BDPA, the excess

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methanol was distilled off under vacuum, and the desired diester-diacid was obtained as an isomer mixture (30.4 g). The separation of *m,m*-BPDE isomer from a mixture of the three isomeric *meta–meta, meta–para* and *para–para* attached diester-diacids was achieved by fractional recrystallization from butylacetate three times. The yield of *m,m*-BPDE was 8.5 g (28%). Elemental analysis: Calcd for $C_{18}H_{14}O_8$: C, 60.34; H, 3.94. Found: C, 60.57; H, 4.01. ^{1}H n.m.r.: 13.04 (*s*, 2H, OH acid); 8.12 (*sd*, 2H, Hb, Hb′); 8.11 (*s*, 2H, Ha, Ha′); 7.99 (*dd*, 2H, Hc, Hc′); 3.90 (*s*, 6H, CH_3 ester). *FT*i.r. (KBr): 1730 cm^{-1} (C=O, ester), 1700 cm^{-1} (C=O, carboxylic acid).

m,m-*Dimethyl ester of 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (*m,m-*HQDPE).* HQDPA (40 g, 0.1 mol) was refluxed with 150 ml of dry methanol and dioxane (50/50, v/v) under dry nitrogen in a 250 ml flask. The dioxane was used to improve the solubility. After a clear solution was obtained, the solvents were distilled off under vacuum, and the desired diester-diacid was obtained as an isomer mixture. The separation of *m,m*-HQDPA from a mixture of the three isomeric *meta–meta, meta–para* and *para–para* attached diester-diacids was achieved by fractional recrystallization from dioxane/H_2O (1/1) twice. The yield *m,m*-HQDPE was 15.4 g (33%). Elemental analysis: Calcd for $C_{24}H_{18}O_{10}$: C, 61.81; H, 3.89. Found: C, 62.00; H, 4.02. ^{1}H n.m.r.: 7.90 (*d*, 2H, Hb, Hb′); 7.37 (*s*, 4H, phenoxy); 7.30 (*dd*, 2H, Hc, Hc′); 7.26 (*sd*, 2H, Ha, Ha′); 3.88 (*s*, 6H, CH_3 fester). *FT*i.r. (KBr): 1729 cm^{-1} (C=O ester), 1691 cm^{-1} (C=O, carboxylic acid); 1221 cm^{-1} (C–O–C).

Preparation of poly(amic ester)s

Poly(amic ester) precursors were prepared by the low temperature polymerization of a diamine and an aromatic diester-diacyl chloride in DMAc. A detailed example of the main synthetic procedure is as follows.

m,m-Dimethyl ester of biphenyl tetracarboxylic acid (3.58 g, 0.01 mol) was dissolved in thionyl chloride (30 ml) with several drops of dimethylformamide (DMF) as the catalyst in a 100 ml three-neck flask equipped with magnetic stirrer, reflux condenser and a light stream of inert gas that was bubbled through a dilute NaOH bath upon leaving the reaction system. The reaction was refluxed until there was no further gas evolution. After evaporation of excess thionyl chloride under reduced pressure, the residual thionyl chloride was removed by stripping with the added toluene and subsequent distillation of the toluene under reduced pressure. The diester-diacyl chloride obtained was used directly in the polymerization without further purification.

The above product was dissolved in THF (~8 ml) and added gradually to a DMAc (50 ml) solution containing PDA (1.08 g, 0.01 mol) and dry pyridine (1.58 g, 0.02 mol) under nitrogen. The solution was cooled to 0°C for 1 h and then slowly returned to room temperature for an additional 3 h. The resulting polymer solution was precipitated into distilled water, washed twice with ethanol, and extracted with ethyl acetate in a Soxhlet extractor for a day to remove any remaining DMAc, soluble oligomers, and side products. After vacuum drying at 80°C for 24 h, the desired polymer was obtained in the yield of 92%.

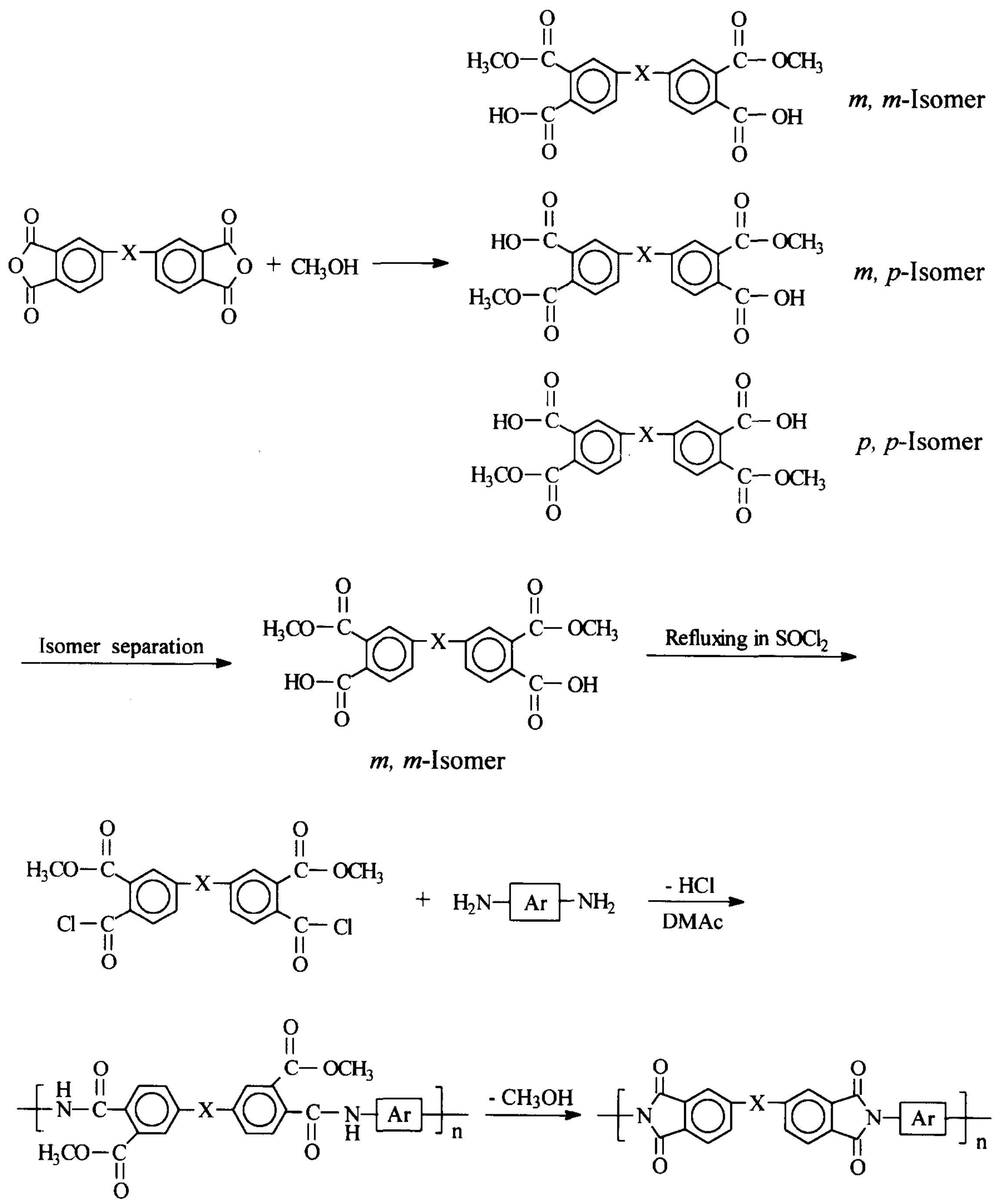
The precursor polymers were blended at various compositions (100/0, 80/20, 60/40, 40/60, 20/80, 0/100 in w/w) in DMAc for 1 day, and solutions of various compositions were coagulated in methanol. The precipitates were washed copiously with methanol to remove residual solvent and then dried at 50°C in a vacuum oven for over 1 day. Additionally, the dried precursor mixtures were thermally imidized at 350°C for 1 h under vacuum for analysis.

Measurements

High resolution ^{1}H n.m.r. spectra were recorded with a Varian Unity-400 spectrometer. The ^{1}H chemical shift were read directly from internal tetramethylsilane (TMS). The solvent for all samples was dimethyl sulfoxide-d_6 (DMSO-d_6). High performance liquid chromatography (h.p.l.c.) was performed on a GILSON HPLC system with a GILSON model 306 pump. A 250 × 4.6 mm i.d. reverse phase column (Spherisorb ODS-2) was used. The solvent system was 25/75 acetonitrile/buffer (pH = 3.0) solution[15]. Dynamic mechanical analysis (d.m.a.) was carried out with a Du Pont 982 DMA at a heating rate of 5°C min^{-1} from room temperature to 400°C. The specimens used for d.m.a. were prepared by supporting the polymer on a glass braid and being imidized at 350°C for 1 h under vacuum. D.s.c. experiments were carried out on a Perkin–Elmer DSC-7 system at a heating rate of 20°C min^{-1} under nitrogen.

RESULTS AND DISCUSSION

The synthetic procedure for *para–para* linked poly(amic ester) precursors and the respective polyimide for the present study are shown in *Scheme 1*. The initial step for the synthesis of poly(amic ester) precursors involves the esterification of aromatic dianhydrides. Since the alcohol can attack either of the anhydride carbonyl groups, it results in the formation of three isomers of aromatic diester-diacids for bridged dianhydrides. H.p.l.c. study of all the as-prepared esterified products furnished three perfectly defined peaks, corresponding to the three isomers in *Scheme 1*. The isomer ratio of *meta–meta, meta–para* and *para–para* attached diester-diacid isomers, quantified from their respective chromatographic peak integrations were 0.35/0.44/0.21 for mixed-BPDE, and 0.62/0.32/0.06 for mixed-HQDPE, respectively. The separation and purification of *meta–meta* attached aromatic diester-diacid isomer (*m,m*-isomer) can be achieved by taking advantage of its lower solubility in organic solvents. ^{1}H n.m.r. is used to determine the isomer structure by comparing the spectrum of *m,m*-isomer to that of the corresponding unseparated isomer mixture. The examination of the aromatic region furnishes valuable data for the structural study. In the case of *m,m*-isomer and *p,p*-isomer, which has a centre of symmetry, one single peak and two double peaks should be expected, while *m,p*-isomer was expected to give two single peaks and four double peaks. The proton signals predicted for *m,p*-isomer would each be expected due to their similar chemical environments to superimpose with their counterparts in *m,m*-isomer and *p,p*-isomer. The assignments of ^{1}H n.m.r. spectra was facilitated by comparing the spectra of the isomer mixture to that of pure isomer. The lower field single peak is attributed to *p,p*-isomer and one of the protons of *m,p*-isomer due to a proton situated *ortho* to a



Scheme 1 Synthesis of *para–para* linked poly(amic methyl ester)s and their polyimides

carboxylic acid group[17,18]. The spectra are shown in *Figures 1* and *2*. H.p.l.c. study indicated that both *m,m*-BPDE and *m,m*-HQDPE were pure. The *para–para* linked poly(amic ester)s were synthesized from the respective diester-diacid chlorides and corresponding diamine in low-temperature solution polycondensations with polar aprotic solvents. Inherent viscosities of BPDA-PDA and HQDPA-ODA poly(amic ester)s are 0.45 dl g^{-1} and 0.56 dl g^{-1} in DMAc at 30°C, respectively.

After blending the BPDA-PDA and HQDPA-ODA poly(amic ester)s at various composition in DMAc solution, the resulting precursor mixtures were thermally imidized at 350°C for 1 h so that the flexible BPDA-PDA poly(amic ester) is converted to the rodlike polyimide whereas the flexible HQDPA-ODA poly(amic ester) is changed to the flexible poly(ether imide). The miscibility behaviour of the resulting BDPA-PDA/HQDPA-ODA (PI/PEI) was explored using d.m.a. and d.s.c.

D.m.a. is a sensitive method for detecting the transition behaviour and miscibility of polymer blends. *Figure 3* shows the d.m.a. traces (flexural loss modulus vs temperature) of the PI/PEI blends, which clearly show that there are two transitions above room temperature, α and β, in the blends as well as in the components. The α relaxation is the glass transition, while the β relaxation is related to the rotation of rigid segments composed of *p*-phenylene and imide groups around the hinges in the diamine[16]. The single glass transition is evident in all compositions, suggesting that these blends are completely miscible.

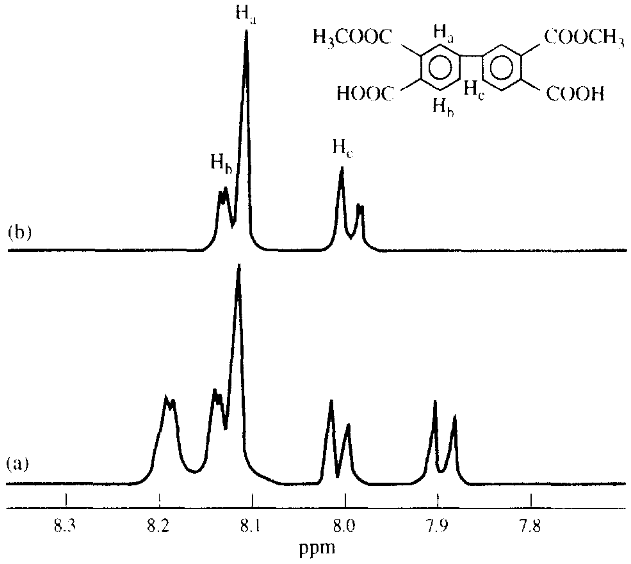


Figure 1 ^1H n.m.r. spectra of aromatic region of BPDA esterified derivatives: (a) isomer mixtures; (b) *m,m*-isomer

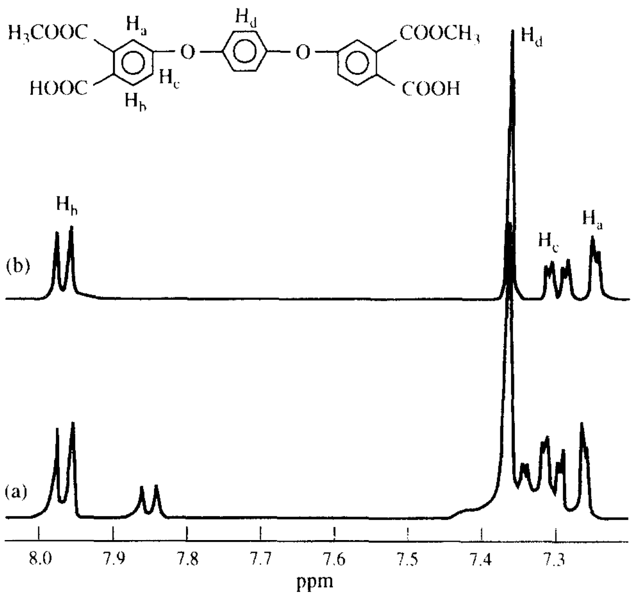


Figure 2 ^1H n.m.r. spectra of aromatic region of HQDPA esterified derivatives: (a) isomer mixtures; (b) *m,m*-isomer

The miscibility between PI and PEI was further verified by a d.s.c. method. A single glass transition is observed in all compositions, which is in good accord with the d.m.a. results. The reproducibility of the T_g values in repeated d.s.c. heating runs is a signature of the true miscibility in the PI/PEI.

Plots of the dependence of the α and β transition temperatures as well as T_g obtained from d.s.c. of the blends are shown in *Figure 4*. It can be seen that the transition temperatures increase progressively with increasing PI content, indicative of miscible character. However, the T_gs of the blends are much lower than predicted by the Fox equation, this was also found in other polyimide blends reported by us and others[17,18]. Higher glass transition temperature values in the d.m.a. relative to the d.s.c. studies are simply due to the frequency effect.

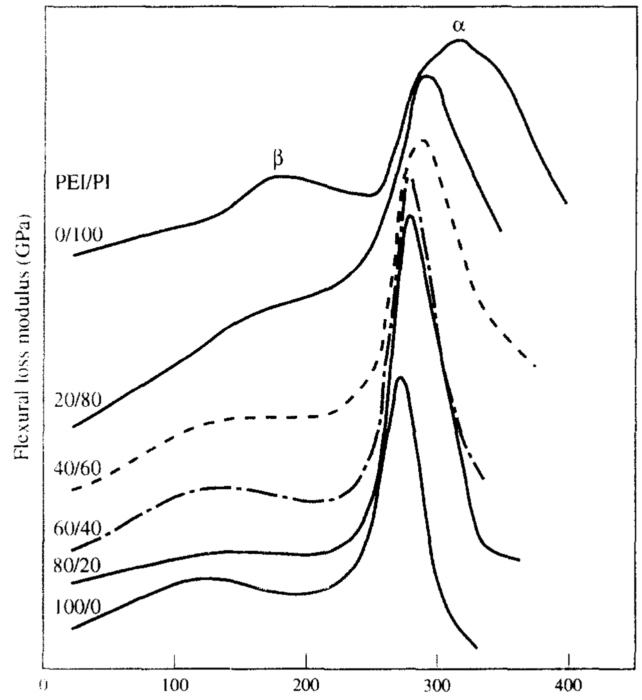


Figure 3 D.m.a. curves of BDPA-PDA/HQDPA-ODA blends (compositions are given as weight ratios)

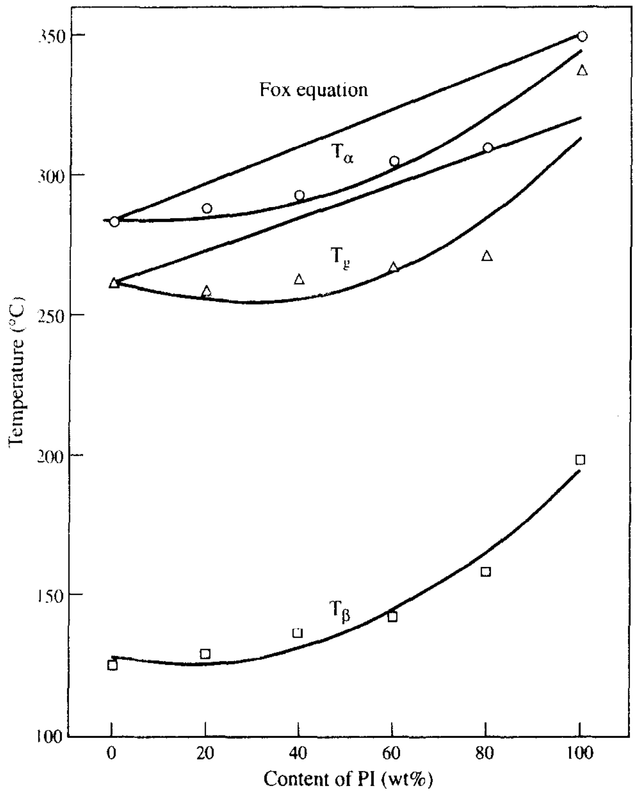


Figure 4 T_α (d.m.a.), T_β (d.m.a.) and T_g (d.s.c.) as a function of the composition of BPDA-PDA/HQDPA-ODA

The mixtures of rodlike polyimide BPDA-PDA and flexible polyimide HQDPA-ODA show a single glass transition temperature (T_g) in both d.m.a. and d.s.c. in all compositions in which the T_g increases with the increase in rodlike polyimide content. These T_g values are reproducible in repeated heating cycles, suggesting that no large scale phase separation exists and the blends of rodlike polyimide from *m*-BPDE/PDA and flexible polyimide from *m*-HQDPA/ODA are truly miscible. Our goal is to develop high performance molecular composite films with high ductility, high modulus, high strength, low thermal expansion and so on. The mechanical properties of these molecular composites are being investigated and the rodlike/flexible polyimide molecular composites based on the other systems are also in study.

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