

# Preparation and Properties of Organosoluble Montmorillonite/Polyimide Hybrid Materials

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**ABSTRACT:** Organosoluble montmorillonite/polyimide hybrids were prepared using a monomer solution intercalation polymerization method. Montmorillonite was organo-treated with *p*-aminobenzoic acid and the organosoluble polyimide was based on pyromellitic dianhydride and 4,4'-diamino-3,3'-dimethyldiphenylmethane. The particle size of montmorillonite in the hybrid containing 1 wt % of montmorillonite is about 400 nm. The strength and the toughness of montmorillonite/polyimide hybrids are improved simultaneously when the montmorillonite content is below 5 wt %. The thermal stabilities of montmorillonite/polyimide hybrids are obviously improved and their thermal expansion coefficients are reduced. When the montmorillonite content is below 5 wt %, the montmorillonite/polyimide hybrids are soluble in strong aprotic polar organic solvents. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 73: 2063–2068, 1999

**Key words:** montmorillonite; polyimide; organosoluble; hybrid; intercalation polymerization

## INTRODUCTION

Montmorillonite (MMT) is a type of clay made of silicate sheets with a thickness of about 1 nm. It has been reported that some organic compounds such as styrene, acrylic acid, and acrylnitrile may enter between the silicate sheets and undergo polymerization.<sup>1–4</sup> According to this feature, it is possible to disassociate MMT to particles of nanometer size. This may provide a novel route (intercalation method) to prepare clay/polymer nanometer composites.

In comparison with conventional polymer-matrix composites, polymer-layered silicate (PLS)

nanocomposites prepared by the intercalation method possess the following features: A very small fraction of silicate filler would give significant improvements in the strength and toughness of the materials<sup>5–9</sup>; the composites possess excellent thermal stability and size stability<sup>5–9</sup>; and the composite films possess excellent “barrier” properties because of the planar orientation of the silicate sheets.<sup>10–12</sup>

Aromatic polyimides (PIs) exhibit outstanding dielectric and mechanical properties at elevated temperature.<sup>13,14</sup> A study on MMT/PI hybrids was reported by Yano et al.<sup>5,15</sup> In their studies, a conventional aromatic PI based on pyromellitic dianhydride (PMDA) and 4,4-diaminodiphenylether (ODA) was used as the polymer matrix. This PI and the corresponding hybrids would be neither soluble nor fusible after the imidization process. This causes difficulties in fabrication and may limit their applications. In this study, an

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organosoluble PI was used as the matrix to prepare novel organosoluble MMT/PI hybrids through a monomer solution intercalation polymerization method in an attempt to obtain materials with improved thermal stability and mechanical properties and a lower thermal expansion coefficient than that of conventional PIs. The materials may find good applications in the microelectronics industry.

## EXPERIMENTAL

### Materials

Sodium montmorillonite (Na MMT) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences (China). The particle size was 40  $\mu\text{m}$ . *p*-Aminobenzoic acid (analytical reagent grade) was purchased from Beijing Chemicals Co. (Beijing, China) and used as received. PDMA (chemical reagent grade) was purchased from the Beijing Chemicals Co. and recrystallized from acetic anhydride before use. 4,4'-Diamino-3,3'-dimethyl-diphenylmethane (MMDA) was synthesized by a reaction between *o*-methylaniline and formaldehyde.<sup>16</sup> *N*-Methyl-2-pyrrolidone (NMP, analytical reagent grade), *N,N*-dimethylacetamide (DMAc, analytical reagent grade), *N,N*-dimethylformamide (DMF, analytical reagent grade), and dimethyl sulfoxide (DMSO, analytical reagent grade) were purchased from Shanghai Reagent Co. (Shanghai, China) and dried over molecular sieves before use. Common reagents, such as acetic anhydride, were used without further purification.

### Preparation of Organophilic MMT

A mixture of 8.82 g (0.0584 mol) *p*-aminobenzoic acid, 4.8 mL 37% (0.0584 mol) hydrochloric acid, and 100 mL distilled water was heated to 80°C. To it, a dispersion of MMT in distilled water (heated to 80°C) was added. The mixture was agitated vigorously for 1 h. The organophilic MMT was then collected by filtration and washed with 400 mL hot water three times to remove the residual *p*-aminobenzoic acid and dried.

### Preparation of MMT/PI Hybrids

Organophilic MMT (3.14 g) was added to DMAc (90.0 g) and the mixture was heated to 90°C and agitated for 3 h. MMDA [1.017 g (0.0045 mol)] was dissolved in DMAc (18.6 g) at room temperature and to it the organophilic MMT/DMAc so-

lution was added. The mixture was stirred for 30 min before PMDA [0.982 g (0.0045 mol)] was added to it. This mixture was then stirred at room temperature for 5 h.

The obtained MMT/polyamic acid (MMT/PA) solution was cast onto glass substrates and then heated subsequently at 100°C for 6 h, 150°C for 2 h, and 270°C for 2 h under the protection of N<sub>2</sub> to obtain MMT/PI hybrids. The preparation of the hybrids is described in Scheme 1.

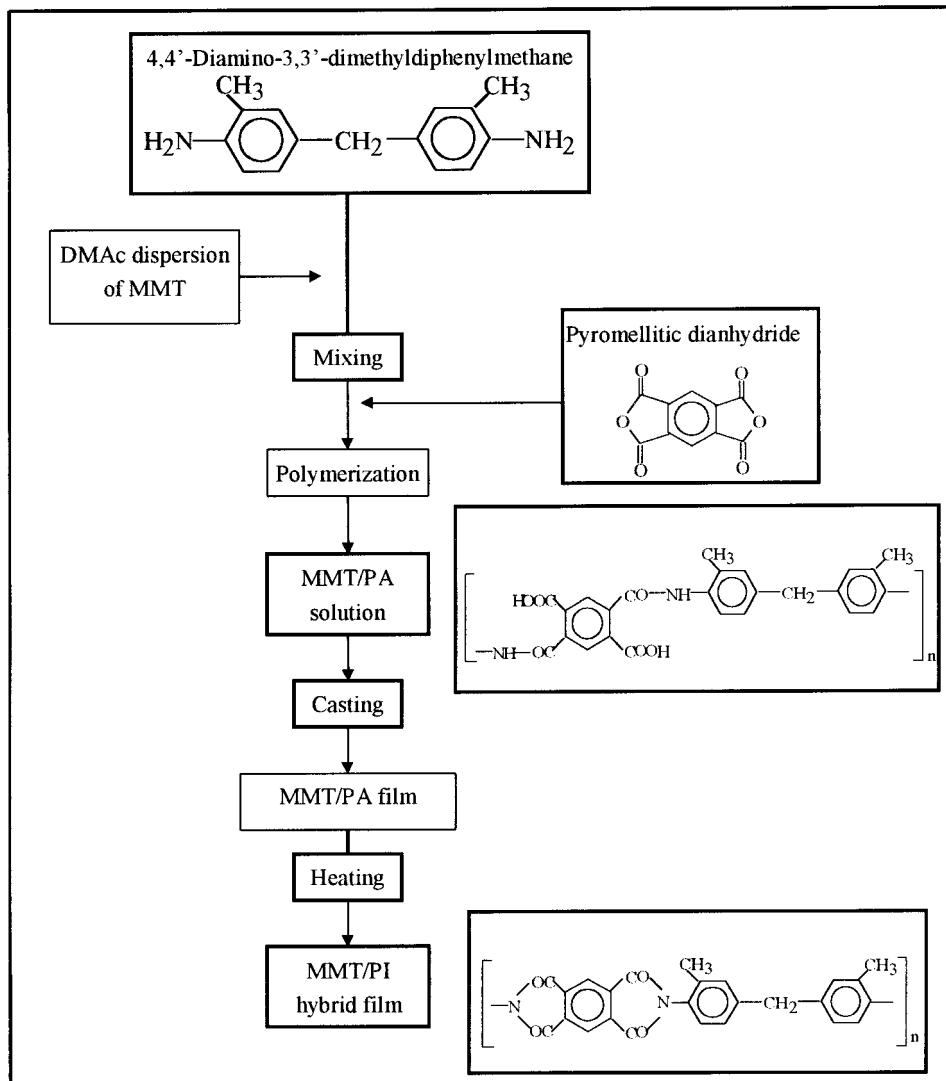
### Structure Characterization and Property Measurements of MMT/PI Hybrids

The FTIR spectra of the MMT/PI hybrid film samples were recorded on a Perkin–Elmer 180 infrared spectrophotometer. Transmission electron microscope (TEM) photographs of ultrathin sectioned MMT/PI hybrid samples were taken on a Hitachi-800 transmission electron microscope. The thermal gravimetric analysis (TGA) of PI and the MMT/PI hybrids was conducted on a Perkin–Elmer TGA 7 thermal analyzer under the protection of N<sub>2</sub>. The scan rate was 20°C/min. The linear thermal expansion coefficients (TECs) of PI and the MMT/PI hybrids were measured on a Perkin–Elmer TMS-2 thermal mechanical analyzer. The scan rate was 10°/min. The stress–strain curves of PI and MMT/PI hybrids were recorded on an Instron-8500 universal tester at room temperature at a drawing rate of 5 mm/min. The solubilities of PI and MMT/PI hybrids were decided by the observation of the solubility of samples in various organic solvents at room temperature.

## RESULTS AND DISCUSSION

### FTIR Spectra

Figure 1 shows the FTIR spectra of MMT and MMT/PI hybrids. Spectrum a is from Na MMT, in which strong absorption bands at 1092 and 1039 cm<sup>-1</sup> correspond to the characteristic absorption bands of MMT. Spectrum b is from the MMT/PA hybrid film (before imidization) in which bands at 1720, 1660, and 1605 cm<sup>-1</sup> correspond to the stretching of the carbonyl groups. The absorption at  $\approx$  3200 cm<sup>-1</sup> is from the —COOH and —NH groups. Spectrum c is from the MMT/PI hybrid film (after imidization). The clear appearance of the bands at 1778 and 1726 cm<sup>-1</sup>, which are characteristic of C=O stretching in imide groups, and the band at 1374 cm<sup>-1</sup>, which is characteris-



**Scheme 1** Preparation of organosoluble MMT/PI hybrids.

tic of C—N stretching in imide groups, the disappearance of the 1660 and 1605  $\text{cm}^{-1}$  bands, and the decrease of the  $\sim 3200 \text{ cm}^{-1}$  band clearly indicate that the PA has been converted to PI after the thermal treatment.

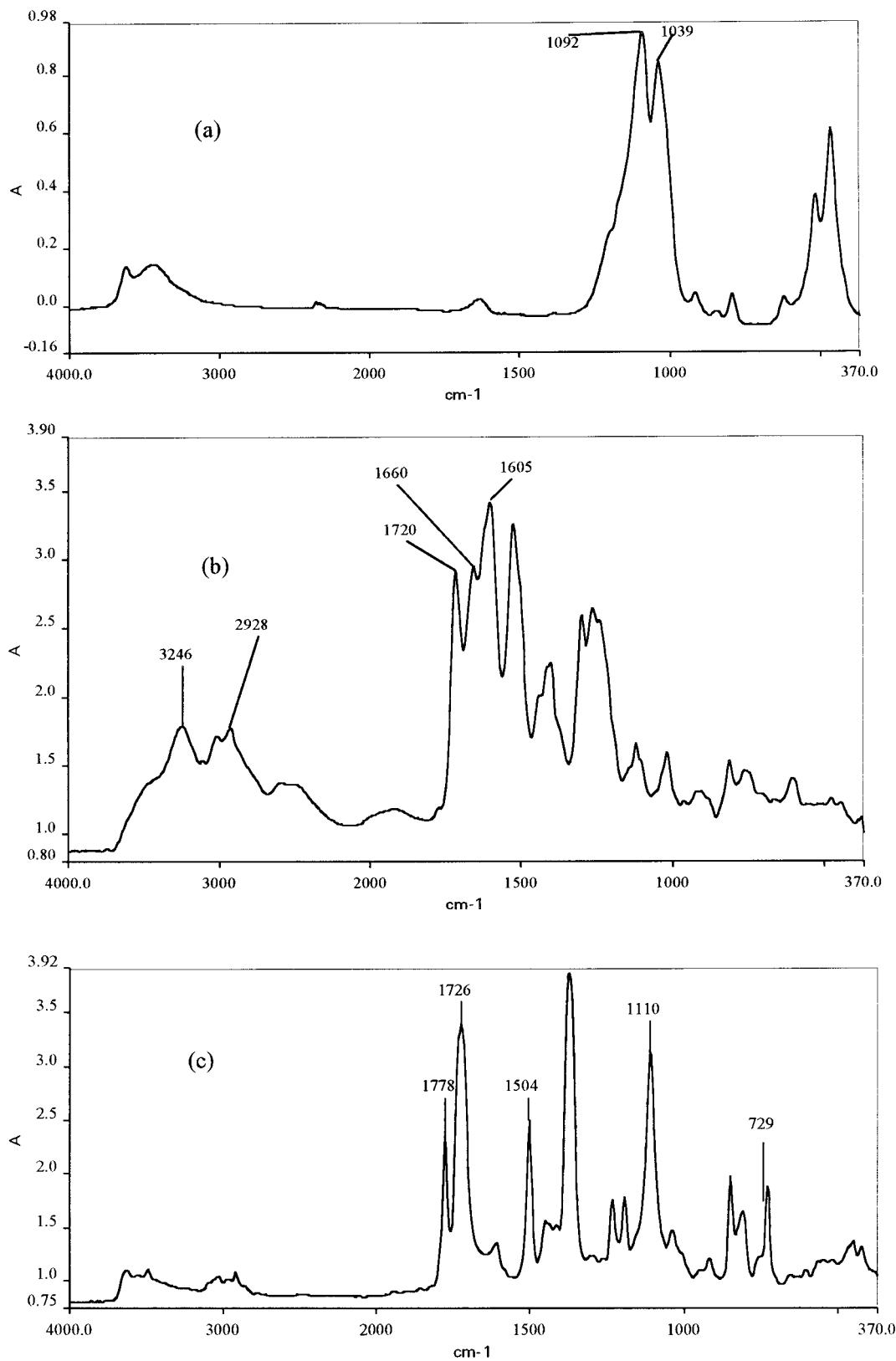
#### MMT Dispersion in PI Matrix

Figure 2 is a TEM photograph of the MMT/PI hybrid containing 1 wt % of MMT. It is observed that the MMT particle size is about 400 nm and is well dispersed. The particle size of MMT was reduced from micrometer order to nanometer order after the organo-treatment with *p*-amino benzoic acid.

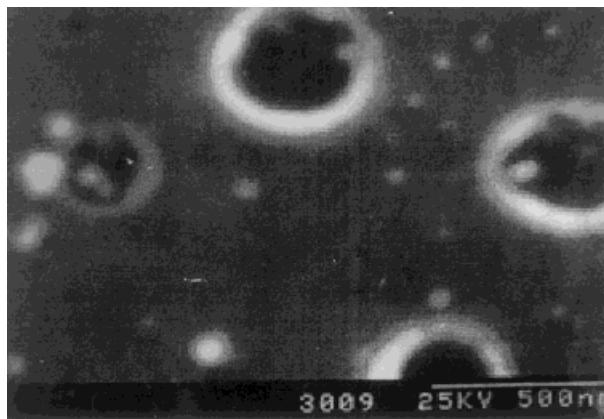
#### Thermal Properties of MMT/PI Hybrids

The thermal properties of the MMT/PI hybrids are listed in Table I. It was observed that the thermal

resistance of the MMT/PI hybrids is obviously increased compared to the corresponding PI. The thermal decomposition temperature of an MMT/PI hybrid is increased with increase of the MMT content in the range studied. The temperature at 5 wt % loss of an MMT/PI is increased by 20°C and 36°C on the basis of PI for an MMT content of 1 and 5 wt %, respectively. This increase in the thermal stability by the introduction of MMT, first, may be caused by the “barrier” effect<sup>4</sup> of the MMT layer structure which prevents the mobility of the small molecules produced during the thermal decomposition of the PI molecules. The increase in the thermal stability of the hybrids may also result from the strong interaction between the organophilic MMT and PI molecules. This strong interaction may make MMT particles act as the crosslink points, which led to an



**Figure 1** IR spectra of (a) Na MMT, (b) MMT/polyamic acid hybrid, and (c) MMT/PI hybrid.



**Figure 2** TEM photograph of MMT/PI hybrid containing 1 wt % of MMT.

increase of the thermal stability of the hybrids with increase of the MMT content. This explanation could be further supported by the observation that the thermal stability of a Na-MMT/PI hybrid is not increased compared to the corresponding PI.

It is also observed from Table I that the TECs of the MMT/PI hybrids are effectively decreased compared to the corresponding PI. The TEC of a hybrid is decreased with increase of the MMT content. The TEC of the hybrid is decreased by about 40% and above 50% when only 1 and 5 wt % of MMT, respectively, is introduced.

#### Mechanical Properties of MMT/PI Hybrids

The tensile strength and the elongation at break of the PI and MMT/PI hybrid films are listed in Table II. It was observed that the tensile strength of the PI is clearly increased with the introduction of MMT and also with increase of the MMT content (in the range studied). However, the more interesting result comes from the observation that the introduction of 1 wt % of MMT leads to a

**Table I Thermal Properties of MMT/PI Hybrids**

Thermal Properties	MMT Content (wt %)			
	0	1	5	5 <sup>a</sup>
$T_d^b$ (°C)	510	530	546	501
$T_d^c$ (°C)	573	577	581	566
TEC ( $\times 10^{-5}$ K $^{-1}$ )	3.60	2.20	1.76	2.40

<sup>a</sup> Na-MMT/PI hybrid.

<sup>b,c</sup>  $T_d$ : decomposition temperature determined by TGA; <sup>b</sup> 5% weight loss; <sup>c</sup> 10% weight loss; scan rate: 20°C/min, N<sub>2</sub> protection.

**Table II Mechanical Properties of MMT/PI Hybrids (25°C)**

Mechanical Properties	MMT Content (wt %)			
	0	1	5	5 <sup>a</sup>
Tensile strength (MPa)	78	88	95	75
Elongation at break (%)	15	24	20	17

<sup>a</sup> Na-MMT/PI hybrid film; all hybrids were transparent.

60% increase in the elongation at break as well as a 13% increase in the tensile strength. Further increase in the MMT content would lead to a decrease in the elongation at break, even though the elongation at break of the hybrid containing 5 wt % of MMT is still much higher than that of the PI. It could be concluded from the above observation that in a certain MMT content range the introduction of MMT would lead to both the strengthening and toughening of the PI matrix. This may be regarded as a feature of a nanometer-composite.

It is observed in this study that the MMT particle size is about 400 nm when the MMT content is 1 wt % (cf. Fig. 2). The decrease in the elongation at break of the hybrid, as the MMT content is increased from 1 to 5 wt %, may be caused by the aggregation of the MMT particles. The aggregation leads to an increase in the particle size and, as a result, the disappearance of the "nanometer effect." It could be expected, therefore, that the observation of both the strengthening and the toughening effects may extend to a wider MMT content range if the aggregation of MMT can be controlled and the MMT particle size can be restricted to the nanometer range. The improvements in the mechanical properties may result from the strong interfacial interaction between PI and MMT. This explanation may be supported by the fact that no obvious improvement in the mechanical properties on the basis of the PI is observed for Na-MMT/PI.

#### Solubility of MMT/PI Hybrids

Because of the high aromaticity and rigidity of the PDMA moiety, the conventional PIs based on PMDA are neither soluble nor fusible and are difficult to process. In this study, 4,4'-diamino-3,3'-dimethylidiphenylmethane (MMDA) was used to prepare PI with PMDA. The incorporation of the two substituent methyl groups leads to an increase in

**Table III** Solubility of MMT/PI Hybrids (25°C)

MMT Content (wt %)	MMT/ PA		MMT/PI			
	0	5	0	1	5 <sup>a</sup>	
NMP	+	+	+	+	+-	-
DMAc	+	+	+	+	+-	-
DMF	+	+	+	+	+-	-
DMSO	+	+	+	+	+-	-

+: soluble; +-: partially soluble; -: insoluble.

<sup>a</sup> Na-MMT/PI.

the free volume and a decrease of the molecular packing. The steric hindrance from the methyl groups may also lead to distortion of the conjugation of the PI backbones. For the above reasons, PI based on PMDA and MMDA is organosoluble.<sup>16</sup>

The solubilities of MMT/PI hybrids before and after the imidization process are listed in Table III. It is observed that the solubility of the MMT/PA hybrids is basically unaffected by the introduction and the content of MMT. The MMT/PI hybrids also exhibit good solubility in strong aprotic polar solvents such as NMP, DMAc, DMF, and DMSO as the MMA content is below 5 wt %. It is also observed that the solubility of the MMT/PI hybrids is even better than that of the PI when the MMT content is 1 wt %. This improvement in the solubility may be caused by the existence of small amounts of nanometer-size MMT particles, which reduce the strong intermolecular interactions between the PI molecules and, as a result, increase the solubility.

## CONCLUSIONS

Organosoluble MMT/PI hybrids have been successfully prepared using the monomer solution intercalation polymerization method. The size of the MMT particles was reduced from micrometer order to nanometer order in the preparation process. The particle size of MMT in a hybrid containing 1 wt % of MMT is about 400 nm. The

strength and the toughness of MMT/PI hybrids are improved simultaneously in a certain MMT content range. The thermal stability of MMT/PI hybrids is clearly improved and their thermal expansion coefficients are effectively reduced. When the MMT content is below 5 wt %, the MMT/PI hybrids are soluble in strong aprotic polar solvents.

## REFERENCES

- Giannelis, E. P. *Adv Mater* 1996, 8, 29.
- Shi, H. Z.; Lan, T.; Pinnavaia, T. J. *Chem Mater* 1996, 8, 1584.
- Akelah, A.; Moet, A. *J Appl Polym Sci* 1994, 55, 153.
- Wang, F. S.; Qi, Z. N. In Proceedings of the 1997 Chinese National Symposium on Polymers, Hefei, Oct. 1997; p. f97.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A Polym Chem* 1993, 31, 2493.
- Kojima, Y.; Usuki, A.; Kawasmi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A Polym Chem* 1993, 31, 983.
- Kojima, Y.; Usuki, A.; Kawasmi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1993, 49, 1259.
- Kojima, Y.; Fukumori, K.; Usuki, A.; Kawasmi, M.; Okada, A.; Kurauchi, T. *J Mater Sci Lett* 1993, 12, 889.
- Kojima, Y.; Usuki, A.; Kawasmi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
- Ke, Y. C.; Qi, Z. N. In Proceedings of the 1997 Chinese National Symposium on Polymers, Hefei, Oct. 1997; p. f101.
- Ke, Y. C.; Long, C. F.; Qi, Z. N. In Proceedings of the 1997 Chinese National Symposium on Polymers, Hefei, Oct. 1997; p. f103.
- Ke, Y. C.; Qi, Z. N. In Proceedings of the 1997 Chinese National Symposium on Polymers, Hefei, Oct. 1997; p. f107.
- Sroog, C. E. *Prog Polym Sci* 1991, 16, 561.
- Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Plenum: New York, 1990.
- Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Part A Polym Chem* 1997, 35, 2289.
- Lu, Q.; Yin, J.; Xu, H.; Zhang, J.; Sun, L.; Zhu, Z.; Wang, Z. *J Appl Polym Sci*, in press.