

Introduction of Side Chains Containing Biphenyl Unit on the Crystalline Morphology and Properties of Polyimides

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ABSTRACT: Several polyimides derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,5-diaminobenzate containing various side chains with biphenyl unit through various flexible spacer were prepared by thermal imidization. By incorporating side chains, the solubility was greatly enhanced and all the polyimides with side chains showed good solubility in polar solvents. During a continuous thermal imidization procedure, the BTDA/MPDA polyimide samples formed a novel banded spherulites with not only zigzag Maltese crosses, but also distinct extinction rings, while the polyimides with side chains revealed only fine grainy crystalline particle. X-ray diffraction of BTDA/MPDA powder showed sharp diffraction peak in the X-ray diffraction and revealed the existence of highly ordered crystalline structure in polyimide, while BTDA/

PP0DA, BTDA/PP2DA, and BTDA/PP6DA polyimides with side chains revealed only a broad reflection at the low angle and demonstrated the presence of low-ordered layer structure. DSC confirmed that the introduction of side chains significantly reduced the melting points of the resulted polyimide, thus it greatly enhanced its thermal plasticity. However, the heat-resistant properties such as the thermal stability were generally decreased, and all the polyimide with side chains showed a typical two-step thermal degradation behavior relating to the pyrolysis of side chains and polyimide backbone. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2255–2260, 2006

Key words: polyimide; side chains; synthesis; properties

INTRODUCTION

In the past decade, high performance polyimides have found new applications in the fields of electronics, optical, membrane, and composite, wherein the use of fully cyclized polyimides with improved solution and melt processability is highly appreciated. Significant effort, therefore, has been spent to synthesize processable polyimides that reasonably maintain the desired mechanical properties by structural modification of polyimide macromolecular chains and high-order structure control.^{1,2} Among the various strategies, the approach of side chain modification has been adopted widely, mainly because the flexible side chains attached to a stiff polymeric backbone act much in a similar way as a solvent or plasticizer.^{3–8} In recent years, polyimides with side chains containing mesogenic unit has attracted much attention because of their promising application in high performance optic

and microelectronic applications; detailed researches were done to investigate the incorporation of side chains on the solubility, transparency, photosensitivity, liquid crystallinity, and the ability to align the liquid crystal molecules. However, the introduction of side chains on the phase behavior and crystalline morphology, which is of vital importance to such application, has rarely been reported. Kim et al.⁹ synthesized several polyimides with various side chains containing a biphenyl mesogen unit, and all the polyimide were apparently amorphous, but exhibited short-range ordering to some extent. Park et al.^{10,11} synthesized different polyimide with side chains containing stilbene mesogen, and two interesting melting peaks were observed because of the melting of side chains and main chains, respectively. Ruan systematically explored the influence of the mesogens on the packing order and physical properties of the resulting polyimides.¹² And more recently, Kim and coworkers revealed that LC pretilt angles of polyimide films with a liquid crystal structure as a side chain were $\sim 90^\circ$ when a linear and rigid polyimide main chain and a side chain of suitable length were employed.¹³

In the previous study,¹⁴ we had synthesized several novel copolyimides and studied the influence of flexible spacers with various length on the solubility and thermal mechanical properties of polyimides, and now we wish to present an extension of our earlier

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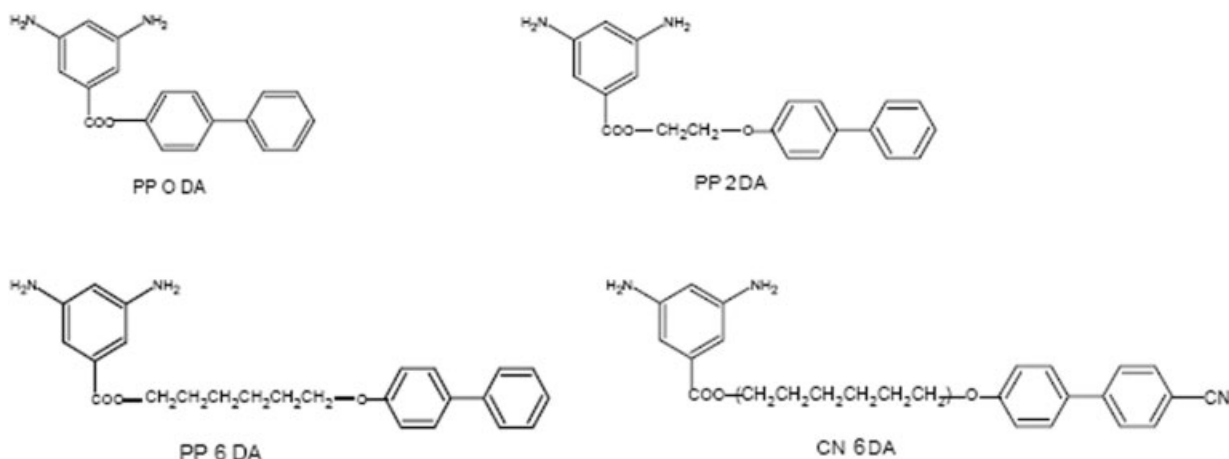


Figure 1 Diamines containing biphenyl-based side group.

works to the study of the incorporation of various side chains containing biphenyl unit on the crystalline morphology and properties of resulted polyimides. Thus four diamines, PP0DA without spacer, PP2DA with ethylene spacer, PP6DA with hexylene spacer, and CN6DA with hexylene spacer and cyano group, were synthesized. Based on these monomers, a series of novel homopolyimides were prepared by a special continuous thermal imidization procedure. As a reference, polyimides without side chains were also prepared by polycondensation of *m*-diaminobenzene with the same aromatic dianhydride. Systematic studies were carried out to investigate the effects of side chains on the density, thermal stability, and crystalline morphology and phase behavior of resulted polyimides.

EXPERIMENTAL

Materials

Reagent grade 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; Tokyo Kasei Kogyo Co., Japan) was used after drying at 150°C for 5 h under vacuum. 1,3-diaminobenzene (MPDA) (Shanghai Wulian Chem. Reagents Co., China) was used as received. Phthalic anhydride (PA) (Shanghai Wulian Chem. Reagents Co., China) as end-capper was sublimed under vacuum before use. *N*-methyl-2-pyrrolidinone (NMP; Shanghai Qunli Chemical Corp., China) was purified by vacuum distillation over phosphorus pentoxide and stored over 4-Å molecular sieves.

The diamines were synthesized via three steps using 3,5-dinitrobenzoic acid as starting material, and 4-phenylphenoxy 3,5-diaminobenzoate (PP0DA), 2-(4-phenylphenoxy)ethyl 3,5-diaminobenzoate (PP2DA), and 6-(4-phenylphenoxy)hexyl 3,5-diaminobenzoate (PP6DA) were synthesized through catalytic hydrogenation using hydrogen and 5% palladium on active

carbon as catalyst. 6-(4-Cyano-phenylphenoxy)hexyl 3,5-diaminobenzoate (CN6DA) with cyano end group was prepared through reduction using SnCl₂ in ethanol. The detailed synthesis procedure and characteristic data have been published elsewhere.^{14,15} Their structures are shown in Figure 1.

Measurements

FTIR (KBr pellet or film) spectra were recorded on a Nicolet 560 Fourier transform spectrometer. X-ray diffraction measurements were performed at room temperature using Philips X'Pert-MPD X-Ray diffractometer operated at 40 KV × 40 mA, DSC measurements were made from a TA Instruments DSC 2910 at a heating rate of 10°C/min under a nitrogen flow, and TGA thermograms were taken from a TA Instruments TGA2950 at a heating rate of 20°C/min under a nitrogen flow. An XPT-7 polarized optical microscope (POM; Jiangnan Optical Instruments Co., China) equipped with a hot stage was used in cross-polarized mode for the visual observation of mesomorphic textures. The density of polyimide film was measured by floating method using ethanol/carbon tetrachloride solution at 25°C.

Preparation of polyimides

Dianhydride (0.010 mol) was added to the solution of 0.095 mol diamine in NMP, stirring for half an hour, and then the phthalic anhydride as end capping was added to the reaction solution. The reaction flask was purged with nitrogen and then sealed tightly and stirring was continued for 12 h at ambient temperature. Solid contents of the precursor solutions were 15–20 wt %. The precursor solutions were then spin-coated on glass plates, followed by drying and imidization under specified thermal cycle as shown in

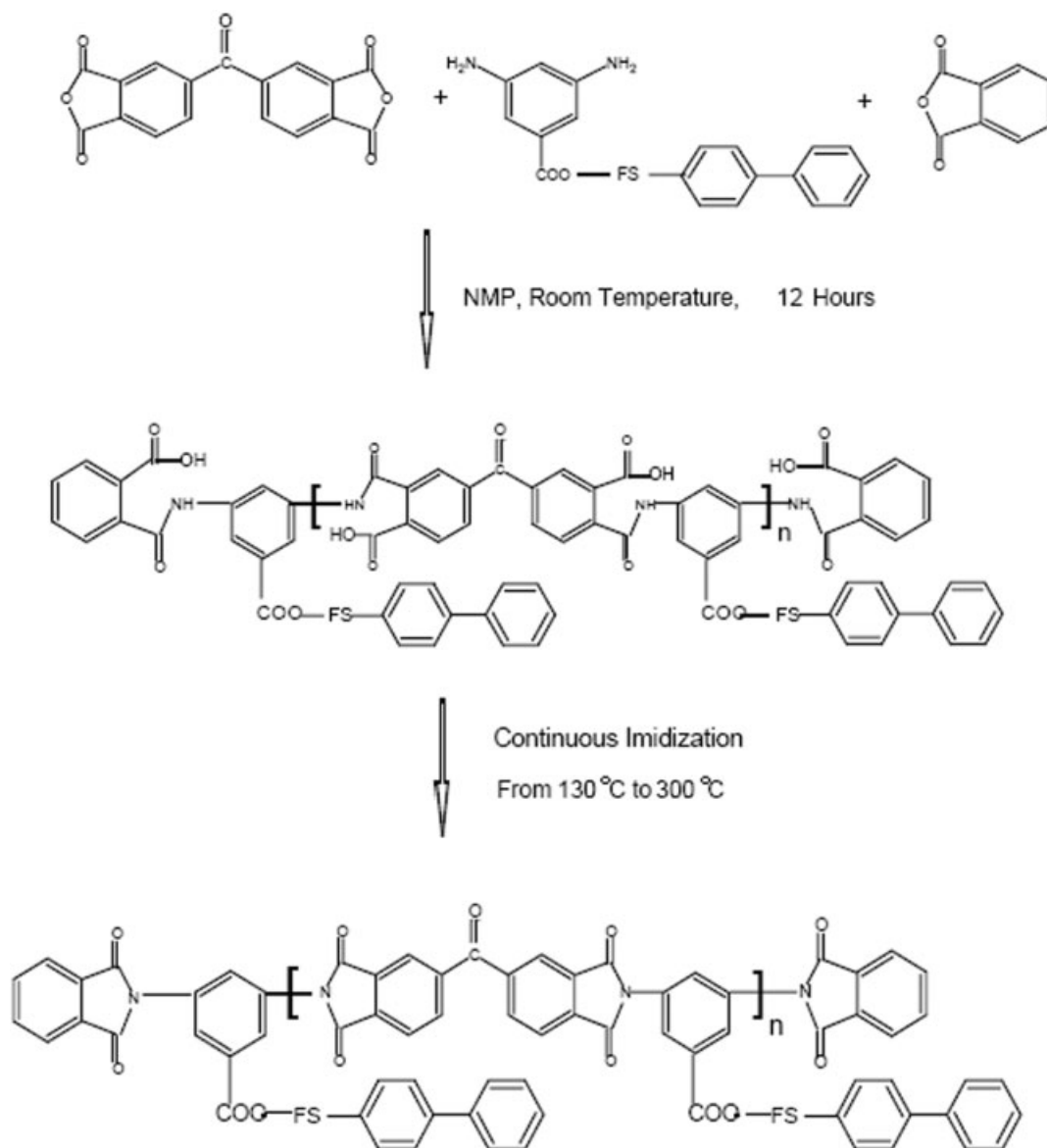


Figure 2 Preparation of poly(amic-acid)s and polyimides. FS: non, CH_2CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$.

Figure 2. The thermal imidization of poly(amic-acid) precursor was monitored by Fourier transform infrared spectra; all the resulted polyimides showed a similar pattern. FTIR spectra show no trace of amine and acid peaks, indicating the polyimides were fully imidized. This was also confirmed by the peaks at 1780 and 1710 cm^{-1} ascribed to the stretching of carbonyl group and at 1380 cm^{-1} ascribed to $\text{C}-\text{N}-\text{C}$ stretching.

RESULTS AND DISCUSSION

General principle of continuous thermal imidization procedure

The most important method for polyimide synthesis has been the "two-step" method involving a poly-

(amic acid) (PAA) precursor, which is subsequently cast from solution and thermally imidized in a form of film. A widely employed laboratory thermal cycle conducted under vacuum or nitrogen to remove water and to prepare bubble-free films is as follows: RT for 1 h, 100°C for 1 h, 200°C for 1 h, and 300°C for 1 h. For the BTDA/MPDA, sample imidized through this process is semicrystalline, and no sharp diffraction peak in the X-ray diffraction revealed the lack of highly ordered crystalline structure in polyimide. According to our previous study,¹⁶ as the initial processes of imidization and crystallization take place simultaneously, thus the crystal structure should better be formed before vitrification. We choose a relatively high heating rate to promote the formation of crystalline order in the early stage of imidization process,

and the optimum experimental conditions for developing highly crystalline polyimides was revealed as follow: sample were prepared by casting a drop of the 20% NMP solution of poly(amic-acid) between two glass slide, the sample was then put on the hot stage preheating to 130°C, followed by drying and imidization at a heating rate of 5°C/min up to 300°C, and held at this temperature for an hour to complete the imidization. Under such a specified continuous thermal imidization condition, BTDA/MPDA polyimide sample showed sharp diffraction peak in the X-ray diffraction and revealed the existence of highly ordered crystalline structure in polyimide. (See Fig. 6 sample BTDA-MPDA)

Effect of side chains on the density and solubility of polyimides

The density of polyimides was measured by floating method. Polyimides generally have a relatively high density of about 1.28–1.48 g/cm³ at room temperature. It can be seen that BTDA/MPDA without side chains was measured to be 1.4258 g/cm³, the introduction of side chains generally decreased the density of polyimides BTDA/PP0DA, BTDA/PP2DA, BTDA/PP6DA, and BTDA/CN6DA, and revealed the density of 1.3744, 1.3627, 1.3602, and 1.3726, respectively. The density of polyimide decreased with the introduction of side chains and it was further lightly decreased with the increase in length of flexible spacer. Which means that the introduction of side chains interrupted the dense packing of polyimide molecular chains and thus lowered the density of the resulted polymers. The solubility of polyimides was tested qualitatively to study the improvement of the solubility of polyimides through the introduction of bulky side chains. It is obvious that the solubility of polyimides was considerably enhanced by the incorporation of side chains containing biphenyl unit. BTDA based polyimide without side chains showed no solubility in any of these polar solvent, while all the polyimides with side chains showed good solubility in *m*-cresol, NMP, and DMAC. This is understandable from the viewpoint that biphenyl side chains providing a molecular irregularity and separation of chains very beneficial in terms of free volume increase, thus significantly enhanced the solubility of the resulted polyimides.

Introduction of side chains on crystalline morphology of polyimides

In recent years, the study of crystalline behavior and morphological features of polyimides became particularly attractive, and the introduction of side chains on the crystalline morphology of the resulted polyimide was examined by means of polarized optical microscopy.

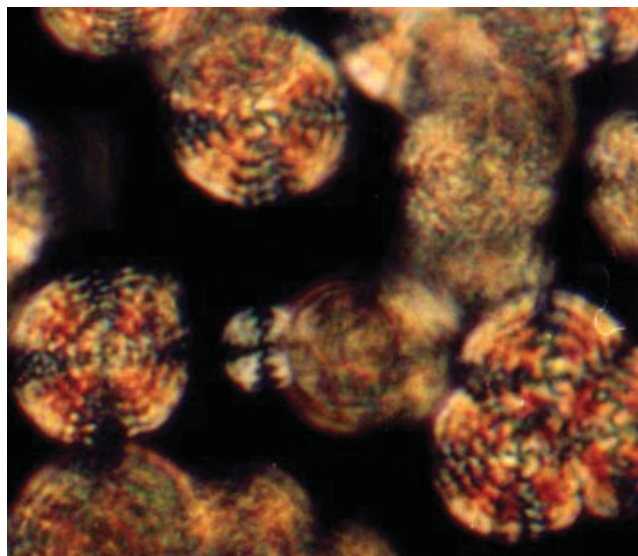


Figure 3 POM of BTDA+PA/mPDA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

For BTDA/MPDA polyimide sample, in the initial stage of thermal imidization, the PAA films looked totally dark under polarized light. With the increase of temperature, many spherulites formed in a relatively short time; instead of the fine grainy particle seen under classical thermal cycle, complicated spherulitic morphological feature was clearly observed under the continuous thermal imidization. In addition to the zigzag Maltese cross, the spherulites also showed concentric extinction rings, see Figure 3, which are the characteristics of banded spherulite, and insertion of a sensitive tint plate along the 45° direction leads to an identification of negative birefringence. The introduction side chains significantly inhibited the formation of perfect spherulite morphology. Under continuous thermal imidization condition, BTDA/PP0DA, BTDA/PP2DA, and BTDA/PP6DA formed only fine grainy crystalline particle, and a typical polarized micrograph is shown in Figure 4. While for polyimide with cyano-biphenyl side chains no crystalline can be seen under polarized light. The phase transition of polyimides was measured by DSC and the results are shown in Figure 5. The BTDA/MPDA polyimide showed no melting transition even after heating up to 400°C, while the polyimides with side chains showed a melt transition between 320 and 350°C. The significant decrease of melting temperature with the introduction of side chains is of special interest and deserves some comments. The introduction of side chains into the backbone acted as a bounded solvent or internal plasticizer and provided considerable lower molecular order and less CTC interaction, hence markedly increased the melting temperature of polyimides.

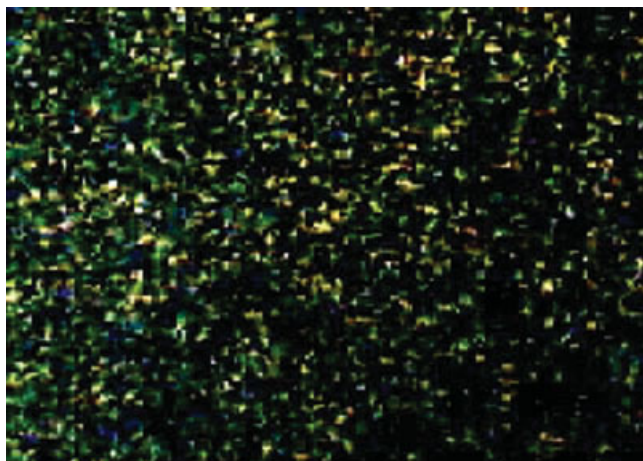


Figure 4 POM of BTDA/PP0DA with side chains. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of side chains on the phase structure of polyimides

The structures of polyimide films prepared were examined by X-ray diffraction measurement. The ob-

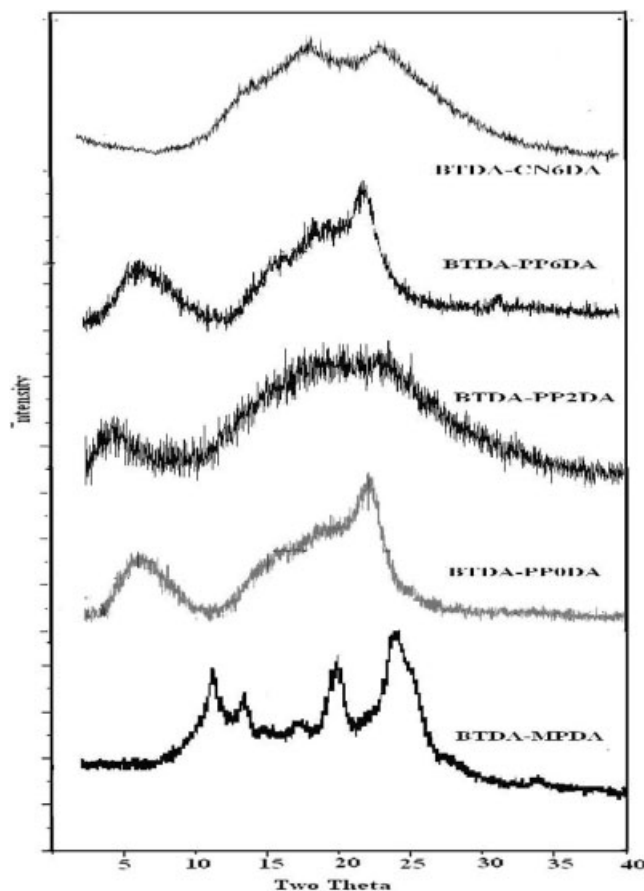


Figure 6 WAXD of fully imidized polyimides.

tained diffraction patterns are illustrated in Figure 6. The high crystallinity of polyimide BTDA/MPDA without side chains was confirmed by wide-angle X-ray diffraction, and the presence of sharp and well-resolved peaks is consistent with the well-organized

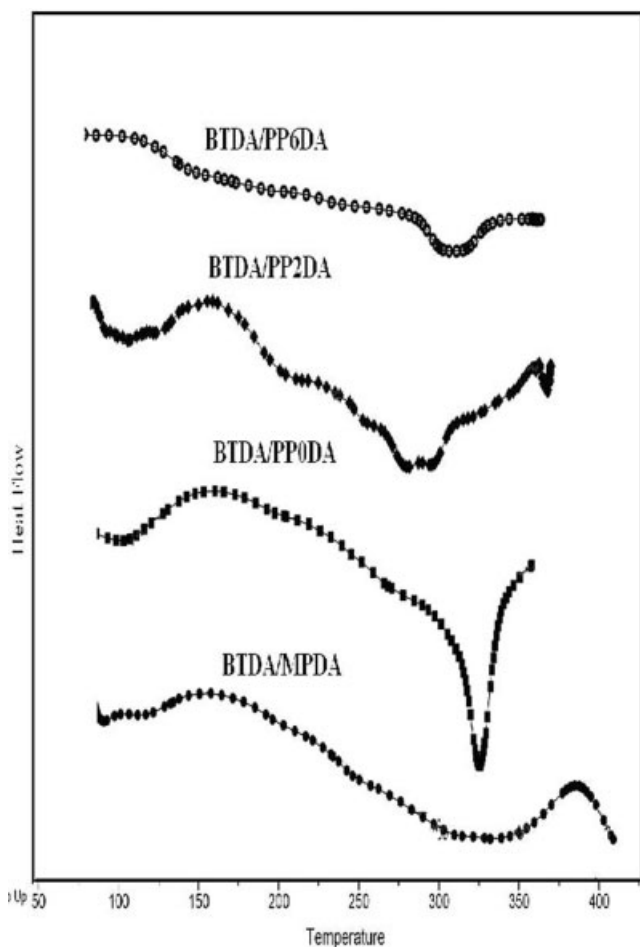


Figure 5 The DSC of fully imidized polyimides.

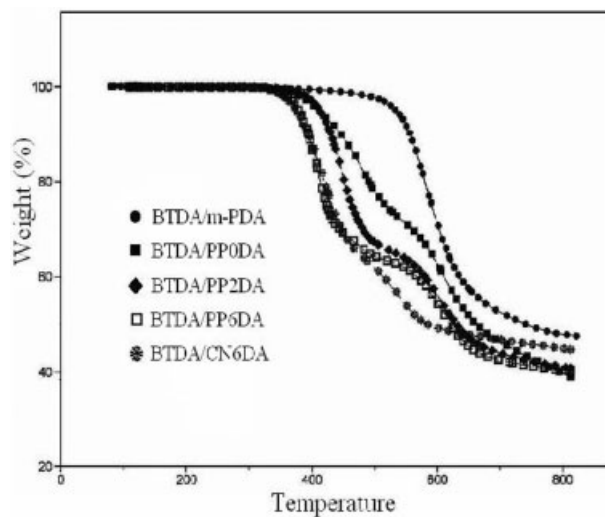


Figure 7 The TGA curve of BTDA based polyimides.

spherulitic morphology obtained through POM. The introduction of side chains significantly reduced the degree of crystallinity of polyimides, and BTDA/PP0DA, BTDA/PP2DA, and BTDA/PP6DA showed only a broad crystalline peak at about 23° (2θ). The introduction of side chains also changed the crystalline structure of polyimide. No peaks can be identified in the small-angle region for BTDA/MPDA, while for BTDA/PP0DA, BTDA/PP2DA, and BTDA/PP6DA, polyimides with side chains, a broad peak located in the small-angle was clearly identified. This may indicate that a layer-like crystalline structure was formed where the polyimides main chains formed separated layers and the disordered side chains occupy the space between the main chain layers. The peak centered at 7° (2θ) can be attributed to the layer spacing between the main chain layers. However, the reflection is so broad that the layer crystalline structure must be only loosely developed.

Effect of side chains on thermal properties of polyimides

Thermal stability of polyimides with side chains was investigated by thermogravimetry under a nitrogen atmosphere. The results are shown in Figure 7. It can be concluded that the polyimides with side chains showed a relatively low thermal stability and a distinct two-step weight loss behavior. Generally in the heating run, the weight drops markedly first over the range of 360 – 500°C , and the weight losses at this step were almost equivalent to the weight of the side chains, which indicate that the thermally unstable ester side chains first degraded at about 380°C , and then followed by an large weight loss at about 600°C with the increase of temperature. The weight loss at the second step occurred almost over the same temperature ranges, as the polyimides have similar main chain structures; this suggests that the second weight loss is due to the degradation of polyimides main chains.

CONCLUSIONS

A series of polyimides derived from BTDA and 3,5-diaminobenzate containing various side chains were prepared by special continuous thermal imidization. By incorporating side chains, the solubility was greatly enhanced and all the polyimides with side chains showed good solubility in polar aprotic sol-

vents such as *m*-cresol, NMP, and DMAC. Further study revealed that the incorporation of side chains considerably affected the crystalline morphology and structure development of aromatic polyimides; the BTDA/MPDA polyimide samples formed novel banded spherulites with highly crystallinity, while the polyimides with side chains revealed only fine grainy crystalline particle with lower ordering. The crystalline structure was also changed; no peaks can be identified in the small-angle region for BTDA/MPDA, while for BTDA/PP0DA, BTDA/PP2DA, and BTDA/PP6DA, polyimides with side chains, a broad peak located in the small-angle was clearly identified, which indicated that a low ordered layer structure was formed. Polyimide bearing cyano-biphenyl side chains showed only amorphous peak. However, the incorporation of side chains deteriorate the heat-resistant properties such as the thermal stability and glass transition temperature, and all the polyimide with side chains showed a typical two-step thermal degradation behavior relating to the pyrolysis of side chains and polyimide backbone.

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