Novel High Temperature Resistant Polypyrrolones with Asymmetric Biphenyl Moiety in the Main Chain: Synthesis and Characterization

Jin-gang Liu[*], Xiao-juan Zhao, Hai-xia Yang, Hong-shen Li, Lin Fan, Shi-yong Yang

Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Abstract: Two novel polypyrrolones (PPys) with asymmetric biphenyl moieties in the main chains had been synthesized from 2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA) and two aromatic tetraamines, 3,3',4,4'-tetraamino biphenyl (TABP) and 3,3',4,4'-tetraamino diphenylether (TADPE), respectively via soluble poly(amide amino acid) (PAAA) precursors, followed by thermal cyclization at elevated temperatures. The polymerization and curing conditions were studied and confirmed. Asymmetric biphenyl structures endowed the polymers with good combined properties. For example, flexible and tough PPy films with acceptable mechanical properties were obtained. Tensile strengths of higher than 70MPa and elongations at break of higher than 6% were achieved. The PPy films with final curing temperature of 350^0C exhibited good thermal stability and the 10% weight loss temperatures were 610.3^0C for PPy-I, and 607.8^0C for PPy-II. The residual weight ratios at 700^0C were higher than 80%. In addition, the PPy films showed good dielectric properties with dielectric breakdown strengths of higher than 100V/μm and dielectric constants of 3.64 for PPy-I and 3.53 for PPy-II.

Keywords: asymmetry; 2,3,3',4'-BPDA; films; polypyrrolone; thermal properties

Introduction

Aromatic polypyrrolones (PPys), characterized by possessing a rigid repeat unit of two benzene rings jointed by two fused five membered rings, are well known for their excellent thermal and environmental stabilities. [1-3] When elaborately designed, PPys could be endowed with versatile functionalities. In practice, they have found wide applications as gas permeable membranes, electron-transporting materials or conductive polymers. [4-8] The rigid molecular backbones impart good thermal stability to PPys, however, inevitably sacrifice their processability at the same time. Thus, considerable efforts have been made to modify their molecular structures aiming at increasing their solubility in organic solvents, or decreasing the strong inter- or intra-molecular interactions. But, few promising results have been reported until

---

[*] To whom correspondence should be addressed (Tel: +86-10-62529173, E-mail: liujg@iccas.ac.cn)

now. For instance, Sek and coworkers reported the processable polypyrrolones derived from commercial available tetraamines and new dianhydrides with flexible ester segments in the main chain. The poly(esterimidazopyrrolone)s were prepared by one-step high temperature polycondensation procedure due to their good solubility in *m*-cresol or *p*-chlorophenol. However, the thermal stability of the polymers was notably damaged and the temperatures of 10% weight loss were less than 350^0C. [9]

Recently, asymmetry strategy has been proved to be one of the most attractive methods to improve the processability of conventional heteroaromatic polymers while maintaining their intrinsic properties. [10] Asymmetric components, especially asymmetric biphenyl moiety, endow the polymers with non-coplanar structures and thus improve their solubility and melt-processability greatly. For example, polyimides derived from an unique asymmetric dianhydride, 2,3,3',4'-biphenyl tetracarboxylic dianhydride (a-BPDA), exhibited high solubility in organic solvents, low melting viscosity at elevated temperatures, and at the same time, high thermal stability. Thus, a-BPDA-based polyimides have been widely used as high temperature composites, [11-13] coatings, [14-15] and other functional materials in many high-tech fields. As part of our continuous work in developing high performance PPys materials for electronics, two new asymmetric PPys derived from a-BPDA and aromatic tetraamines were developed in the present work. The effects of asymmetric dianhydride moiety on the thermal and mechanical properties of the new PPys were evaluated in detail.

Experimental Part

Materials

2,3,3',4'-Biphenyl tetracarboxylic dianhydride (a-BPDA) was synthesized in our laboratory. 3,3',4,4'-Tetraamino biphenyl (TABP) was purchase from Acros and used as received. 3,3',4,4'-Tetraamino diphenylether (TADPE) was synthesized according to the literature. [16] N, N'-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidinone (NMP) were purified by vacuum distillation over CaH_2 and stored with 4Å molecular sieves prior to use. The other reagents were purified according to standard procedure.

Polymer synthesis

PPy-I and PPy-II (**Scheme 1**) were synthesized by similar, but a bit different polymerization procedures. For example, PPy-I was synthesized as followed experiment. Into a 250mL three-necked flask equipped with a mechanical stirrer, a dropping funnel, a dry nitrogen inlet and a thermometer was charged TABP (10.7135g, 50.0mmol) and newly distilled NMP (80mL). The reaction system was cooled with ice-salt bath and the temperature was maintained at -5^0C. When a clear tetraamine

solution was obtained, a-BPDA (14.7110g, 50.0mmol) dissolved in NMP (60mL) was added dropwise to the system over a period of 1h. Additional NMP (5mL) was added to wash the residual dianhydride solution, and at the same time adjust the solid content of the system to be 15% (wt.-%). The reaction mixture was stirred at -5^0C for 3h and then 24h at room temperature to yield a viscous poly (amide amino acid) (PAAA) solution.

PPy-II was synthesized according to a similar procedure mentioned above, except that a-BPDA was added incrementally as a solid instead of a NMP solution.

Film preparation

The deep-brown PAAA solution with a solid content of 15% (wt%) was filtered through a 0.2μm Teflon syringe filter to eliminate any particulates that might affect the quality of the cured film. The purified PAAA solution was spin-coated on a 5-inch (12.7cm) diameter Si wafer, and the thickness of PAAA coating was controlled by adjusting the spin rate. For example, the thickness of specimen for FT-IR or UV-Vis measurement was controlled to be 2-3μm by adjusting the spin rate to 1000rpm. While the specimens for mechanical and dielectric property were obtained with a thickness of about 30-50μm. PPy films were obtained by thermally curing the PAAA solution in an oven for 1h each at 80^0C, 150^0C, 250^0C, 300^0C, 350^0C, and in some cases for an additional hour at 400^0C. The PPy films, deep brown in color, were obtained by immersion the Si wafer in warm water.

Measurements

Absolute viscosity (υ) was measured with Brookfield DV-II+ viscometer at 25^0C. Inherent viscosity was measured using an Ubbelohde-viscometer with 0.5 g.dl^{-1} NMP solution at 25^0C. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrophotometer. Ultraviolet-visible (UV-Vis) spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. PPy films were dried at 100^0C for 1h before testing to remove the absorbed moisture. The wide-angle *X*-ray diffraction (XRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/K-α1 radiation, operated at 40kV and 200mA. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 10^oC /min. Isothermal aging was measured by placing the PPy films ($3.0 \times 1.0 \times 0.005 cm^3$) in an air- or nitrogen-circulating oven at 350^0C with a flow rate of 100mL/min. The samples were weighted at the scheduled aging time intervals. Mechanical properties were measured on an Instron 3365 Tensile Apparatus with $80 \times 4 \times 0.05 mm^3$ specimens

in agreement with GB1447-83 at a drawing rate of 2.0 mm/min. Dielectric properties were measured on a ZC36 Precision Resistivity Meter and the dielectric constant and dissipation factor were determined by the parallel plate method with an AS2851Q capacitance meter at a frequency of 1MHz at $25^{0}C$. Water uptakes were determined according to the following procedure: the polymer sample ($3.0 \times 1.0 \times 0.005$ cm^3) was immersed in boiling deionized water ($100^{0}C$) in a 250 ml round-bottom flask fitted with a condenser for 24hr, which was then dried immediately and weighed to determine the water uptakes.

Results and Discussion

Polymer synthesis

PPy-I and PPy-II (**Scheme 1**) were synthesized by standard two-step procedure via soluble poly(amide amino acid) (PAAA) precursors. A bit different polymerization conditions were utilized for PPy-I and PPy-II, respectively, which was mainly attributed to the different reactivity of the two tetraamine monomers. The amino groups in TABP showed higher reactivity than those in TADPE. Thus, lower polymerization temperature (below minus $5^{0}C$) was utilized to avoid undesirable side-reactions, such as gel, branch and so on. At the same time, dianhydride was added as a solution in NMP. Attempts had ever been made to add the solid a-BPDA
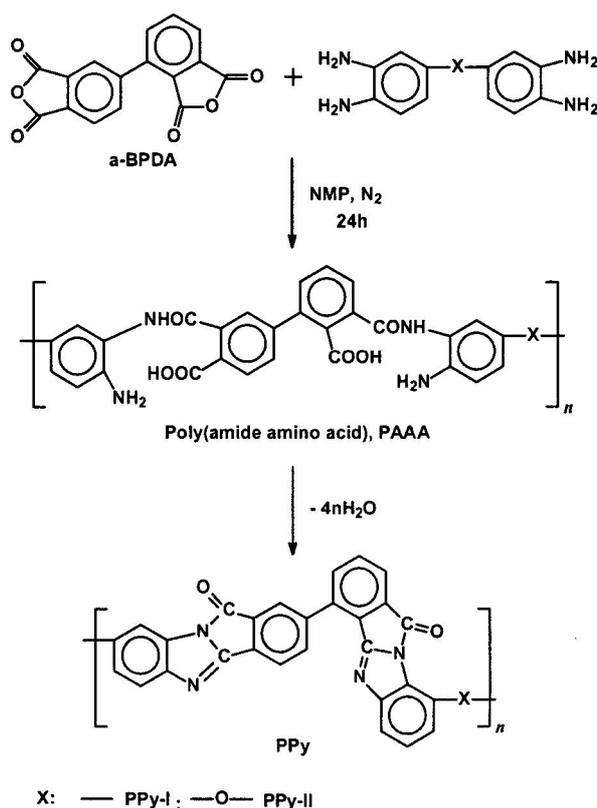
Scheme 1. Synthesis of PPy via two-step procedure

during the synthesis of PPy-I. But, in most cases, gelation inevitably occurred. However, in the case of PPy-II synthesis, polymerization reaction progressed smoothly, even the solid a-BPDA was utilized.

Both of the two different procedures resulted in viscous PAAA solution, whose absolute viscosity (Brookfield, 25^0C) was 789cp for PAAA-I and 622cp for PAAA-2 (**Table 1**). The inherent viscosities of PAAA solutions measured by Ubbelohde viscometer with 0.5 g/dL NMP solution at 25^0C were in the range of 0.68–0.72dL/g, which indicated the moderate molecular weight of the polymers. The inherent viscosity of PPy-II prepared from TADPE was lower than that of PPy-I, which was mainly attributed to the relative lower reaction activity of TADPE under the polymerization condition. The polymer films exhibited water uptakes of 1.42% for PPy-I and 1.51% for PPy-II, a bit higher than that of a-BPDA-based polyimide, [17] which might be attributed to the larger free volumes of the fused molecular chains of PPys.

Table 1. Structural analysis of the polypyrrolones

Polymer	η_a [a] (mPa·s)	η_{inh} [b] (dL/g)	Elemental analysis (%, Founded/Calculated values)		
			C	H	N
PPy-I	789	0.68	76.82/77.06	2.87/2.77	12.53/12.84
PPy-II	622	0.72	73.98/74.33	2.82/2.67	12.25/12.38

[a] Absolute viscosity measured with PAAA solution in NMP at 15% solid content at 25^0C.

[b] Inherent viscosity measured with PAAA solution in NMP at a concentration of 0.5g/dL at 25^0C.

The mechanism of pyrrolonization during transition of PAAA to PPy has been well studied in our previous study. [18-19] Similar results were obtained to the present asymmetric PPys. **Figure 1** illustrated the FT-IR spectra of PPy-II thermally cured at different temperatures. It could be seen that when the curing temperature was lower than 180^0C, the characteristic absorptions of imide carbonyl (>C=O, about 1780cm^{-1} and 1720cm^{-1}) and amino (about 3330cm^{-1}) were observable, demonstrating that amino-substituted polyimide was the major curing product. When the curing temperature was higher than 200^0C, the imide characteristic absorptions disappeared gradually and a new absorption band at about 1760cm^{-1} appeared, which was assigned to the characteristic stretching vibration of >C=O in pyrrolone groups. [20] However, the absorptions of imide carbonyl and amine haven't disappeared completely until the curing temperature reached 300^0C. This change indicated that a second thermal cyclization between the imide groups and the α-NH$_2$ in the aromatic rings occurred when the temperature was higher than 200^0C, and pyrrolone segments
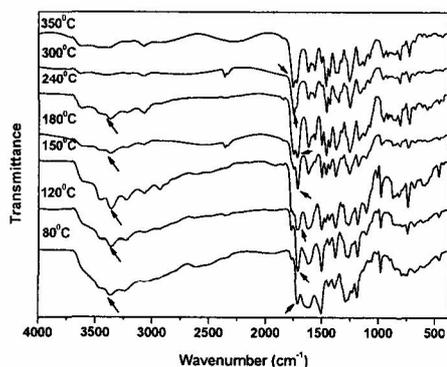
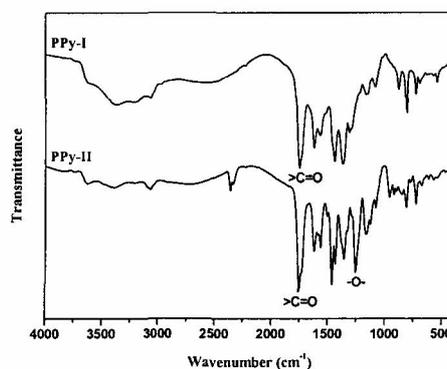Figure 1. Cyclization mechanism of
PAAA-II (film samples, 3μm)

Figure 2. FT-IR spectra of PPy films
(film sample, 10μm)

were produced. On the other hand, 350^0C of curing temperature was necessary to insure the complete pyrrolonization. FT-IR spectra of PPy-I and PPy-II cured at 350^0C were shown in **Figure 2**. Characteristic absorptions of pyrrolone carbonyl and ether bond, and phenyl indicated successful transition of PAAA precursor to PPy, which could further be confirmed by elemental analysis data listed in **Table 1**. The measured percentage of C, H, and N elements agreed well with the calculated ones.

Wide-angle X-ray diffraction patterns of PPy films shown in **Figure 3** indicated that the polymers were amorphous, which could be attributed to the reduction of crystallinity of the polymer chains caused by the presence of non-coplanar biphenyl moiety. In addition, flexible ether group in PPy-II also reduced the rigid of the polymer chain. The amorphous natures of the PPy films could also be identified by the DSC measurement discussed below. No crystalline melting phenomena were found during the measurement.

The transparency of PPy films was evaluated by UV-Vis spectra measurement. Generally, the strong conjugation interactions between the fused benzene and pyrrolone ring were propitious for the formation of charge transfer complexes (CTC), [21] which resulted in strong absorption of the polymer in the visible light region. As expected, from the UV-Vis spectra shown in **Figure 4**, cutoff wavelengths of 482nm and 454nm were obtained for PPy-I and PPy-II, respectively, which were 100nm higher than that of PI (a-BPDA/4,4'-ODA). The transmittances of the PPy films at 450nm were lower than 2.2%, whereas 78.5% for PI film. With the increase of the wavelength, the transmittance of PPy films increased. For example, at 600nm, the transmittances of PPy films were higher than 87% (**Table 2**). The good light-absorbing properties of the present PPy films made them potential candidates for
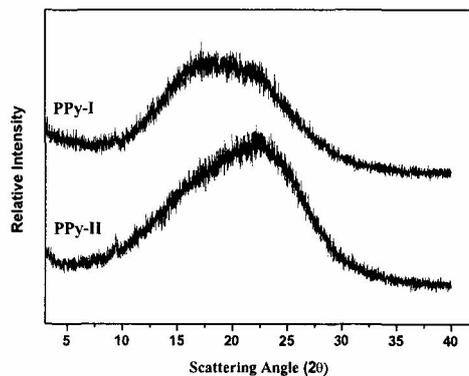
high performance light-shielding materials in some fields.
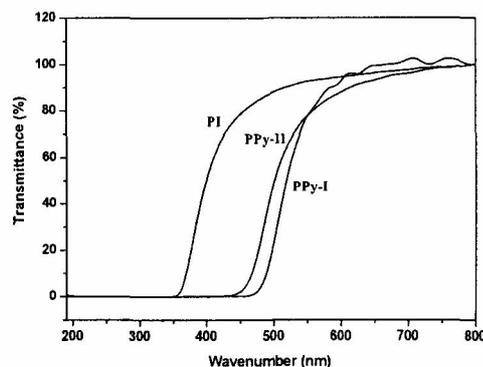

Figure 3. X-ray diffraction patterns of PPy films

Figure 4. UV-Vis spectra of PPy films (thickness: 10μm)

Table 2. Optical properties of PPy and PI films (10μm)

PPy	λ_{cutoff} [a] (nm)	T_{450nm} [b] (%)	T_{500nm} (%)	T_{550nm} (%)	T_{600nm} (%)
PPy-I	482	0.2	23.5	77.5	92.7
PPy-II	454	2.2	49.2	77.7	87.9
PI[c]	356	78.5	88.1	92.7	94.5

[a] λ_{cutoff}: UV cutoff wavelength.

[b] T_{450nm}: transmittance at 450nm.

[c] Polyimide derived from a-BPDA and 4,4'-oxydianiline

Thermal properties

Thermal properties of PPy films were investigated by TGA and DSC measurements, and the results were summarized in **Table 3**. Both the PPy exhibited good thermal stability and the initial thermal decomposition temperatures (T_d) exceeded 500^0C. PPy-I showed better thermal stability than that of PPy-II, which could be interpreted as the more rigid molecular chains of the former. **Figure 5** showed the thermal decomposition behaviors of PPy films cured at different temperatures, 300^0C, 350^0C, and 400^0C in air. It could be seen that higher curing temperatures were necessary to improve the thermal stability of the polymers. For example, to PPy-I, the 10% weight loss temperatures ($T_{10\%}$) of the polymer cured at 300^0C, 350^0C, and 400^0C were 568.6^0C, 610.3^0C, and 637.3^0C, respectively. The residual weight ratio at 700^0C also increased from 80% to 84%. It could also be found that the improvement of thermal stability from 300^0C to 350^0C was more evident than that from 350^0C to 400^0C. Furthermore, it was found that the mechanical properties of PPy films deteriorated apparently when the curing temperature exceeded 450^0C in air. Therefore, combined

with the pyrrolonization mechanism research shown in Figure 1, 350°C of final curing temperature was confirmed in the present work. The glass transition temperatures (T_gs) were determined by DSC measurements, and the results were listed in **Table 3**. PPy-II showed T_g of 368.6°C, whereas PPy-I didn't exhibit any glass transition up to 450°C.

Thermal and thermo-oxidative stabilities of PPy films were evaluated by isothermal aging at 350°C in nitrogen and flowing air, respectively. **Figure 6** illustrated the isothermal aging curves. It could be seen that the weight losses of PPy films increased with the increasing of aging time. After 300h, PPy-I lost 1.49% of its original weight in nitrogen, which is a bit lower than that of PPy-II (1.64%). In air, the similar results were obtained, and the weight loss was 2.73% for PPy-I and 2.85% for PPy-II. Therefore, PPy-I had better thermal and thermo-oxidative stabilities than those of PPy-II, which was mainly attributed to the more rigid molecular structures of the former.
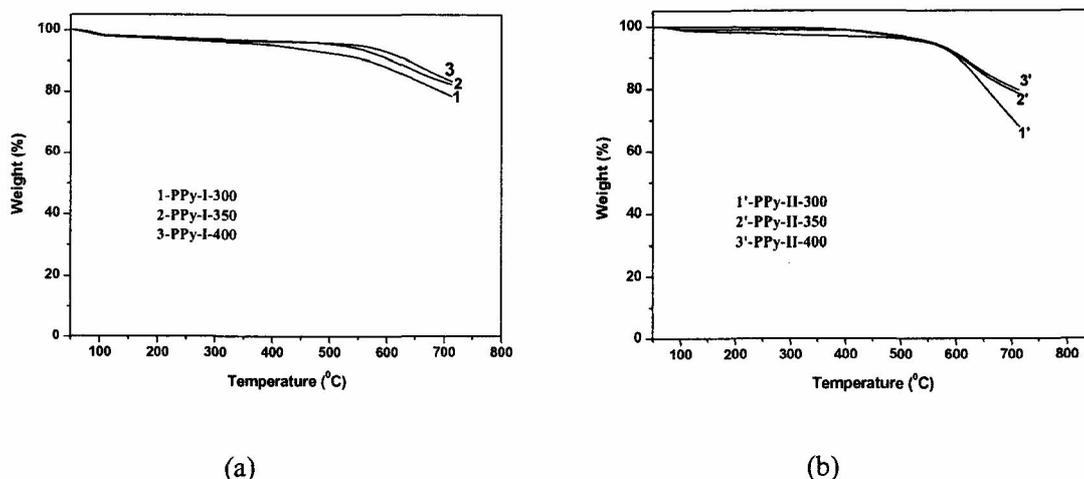

(a)   (b)

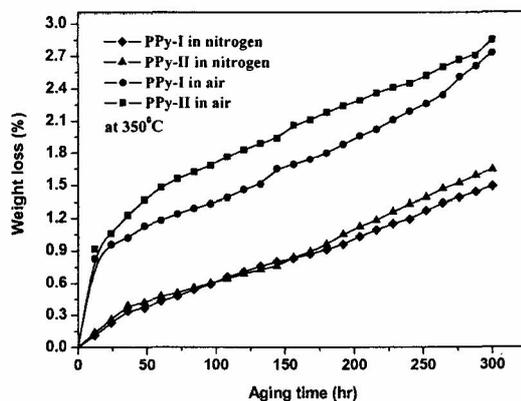Figure 5. TGA curves of PPy films (in nitrogen, heating ratio: 20°C/min)

Figure 6. Isothermal aging of PPy films in nitrogen and air

Table 3. Thermal properties of PPy films [a]

PPy		T_g (^{0}C)	T_d (^{0}C)	$T_{5\%}$ (^{0}C)	$T_{10\%}$ (^{0}C)	R_w (%)
PPy-I	300	_[b]	534.5	402.2	568.6	80.0
	350		565.4	519.7	610.3	83.0
	400		567.2	551.4	637.3	84.4
PPy-II	300		545.3	544.8	601.7	70.6
	350	368.6	559.4	540.1	607.8	80.1
	400		562.7	552.5	610.8	80.6

[a] T_g: glass transition temperatures; T_d: initial thermal decomposition temperature; $T_{5\%}$, $T_{10\%}$: temperatures at 5% and 10% weight loss, respectively; R_w: residual weight at 700℃.

[b] No glass transition was observed in DSC measurement.

Mechanical and dielectric properties

Mechanical properties of PPy films, including tensile strengths, elongations at break, and tensile moduli were measured and the results were summarized in **Table 4**. Generally speaking, heteroaromatic polymers, especially those with ladder or semi-ladder structures, showed poor mechanical properties due to the rigid molecular chains and strong inter- or intra-molecular interactions. Conventional PPys, typical semi-ladder polymers, also exhibited poor mechanical properties. However, the present PPy films had tensile strengths of 72.2-84.3MPa, elongations at break of 6.4-8.2%, and tensile moduli of 2.2-2.5GPa. Although not as high as polyimides, they were acceptable to be coatings or membranes. No doubt, the improved mechanical properties came from the asymmetric molecular structures.

Dielectric properties of PPy films were investigated and the results were listed in Table 4. In summary, the polymers exhibited good dielectric properties, and PPy-II showed the better ones. The volume resistances of the polymers were at the level of 10^{15} Ω·cm and the dielectric breakdown strengths were higher than 100V/μm. The dielectric constants of the films were 3.64 for PPy-I and 3.53 for PPy-II, which were a bit higher than that of typical aromatic polyimide (Kapton®: 3.5). The higher dielectric constants of the present PPy were mainly attributed to the more large polarity of the conjugation structures.

Conclusion

In summary, two novel asymmetric polypyrrolones were synthesized from a-BPDA and aromatic tetraamines by a standard condensation polymerization method. Asymmetric moiety endowed the PPy films with acceptable mechanical properties

Table 4. Mechanical and dielectric properties of PPy films [a]

Polymer	T_s (MPa)	E_b (%)	T_m (GPa)	R_v ($\Omega\cdot cm$)	B_s (V/μm)	ε (1MHz)
PPy-I	72.2	6.4	2.5	2.7×10^{15}	104	3.64
PPy-II	84.3	8.2	2.2	4.5×10^{15}	118	3.53

[a] E_b: elongation at break; T_s: tensile strength; T_m: tensile moduli; R_v: volume resistance; B_s: breakdown strength; ε: dielectric constant

and good dielectric properties, while sustaining the intrinsic thermal stability. Flexible and tough PPy films with good combined properties, including T_ds of higher than 500^{0}C, tensile strengths of higher than 70MPa, and dielectric breakdown strengths of higher than 100V/μm were achieved. Otherwise, the PPy films showed good light-absorbing characteristics. The good combined properties made the present PPy films good potential candidates for high-tech applications.

Acknowledgment

[1] F. C. Lu, J.M.S.-Rev. Macromol. Chem. Phys. 1998, C38, 143.

[2] V. L. Bell, J. Appl. Polym. Sci. 1970, 14, 2385.

[3] L. W. Frost, G. M. Bower, J. Polym. Sci. Part A-1, 1971, 9, 1045.

[4] M. J. Piao, M. X. Wan, F. C. Lu, J. Polym. Sci. Part A: Polym. Chem. 1996, 34, 1567.

[5] D. Sek, E. S. Balcerzak, E. Grabiec, Polymer 1999, 40, 2419.

[6] X. S. Gao, F. C. Lu, J. Appl. Polym. Sci. 1996, 59: 1315.

[7] M. Z. Catherine, J. K. William, J. Polym. Sci. Part B: Polym. Phys. 1999, 37, 1235.

[8] M. Z. Catherine, J. K. William, J. Polym. Sc.i Part B: Polym. Phys. 1999,37,1251.

[9] D. Sek, E. Schab-Balcerzak, E. Grabiec, A. Volozhin, T. Chamenko, Polymer 2000, 41, 49.

[10] S. H. Hsiao, K. H. Lin, J. Polym. Sci, Part A: Polym. Chem. 2005, 43, 331.

[11] M. Hasegawa, Z. M. Shi, R. Yokata, F. F. He, H. Ozawa, High Perform. Polym. 2001, 13, 355.

[12] R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, R. Sato, High Perform. Polym. 2001, 13, S61.

[13] J. G. Smith Jr., J. W. Connell, P. M. Hergenrother, L. A. Ford, J. M. Criss, *Macromol. Symp.* **2003**, 199, 401.

[14] P. M. Hergenrother, K. A Watson, J. G. Smith Jr, J. W. Connell, R. Yokota, *Polymer* **2002**, 43, 5077.

[15] I. Rozhanskii, K. Okuyama, K. Goto, *Polymer,* **2000**, 41, 7057.

[16] R. T. Foster, C. S. Marvel, *J. Poly. Sci., Part A: Polym. Chem.* **1965**, 3, 417.

[17] C. P. Yang, Y. Y. Su, *Polymer,* **2005**, 46, 5791.

[18] J. G. Liu, L. F. Wang, H. X. Yang, H. S. Li, Y. F. Li, L. Fan, S. Y. Yang, *J. Poly. Sci., Part A: Polym. Chem.* **2004**, 42, 1845.

[19] H. X. Yang, J. G. Liu, X. J. Zhao, Y. F. Li, L. Fan, S. Y. Yang, *Chin. J. Poly. Sci.* **2005**, 23, 521.

[20] W. R. Dunnavant, *Polym. Lett.* **1968**, 6, 49.

[21] M. Hasegawa, K. Horie, *Prog. Poly. Sci.* **2001**, 26, 259.

主链含有不对称联苯基团的新型耐高温聚吡咙

刘金刚 赵晓娟 杨海霞 李洪深 范 琳 杨士勇

（中国科学院化学研究所高技术材料实验室，北京 100080）

摘 要：采用不对称联苯二酐单体，2,3,3',4'-联苯四甲酸二酐（a-BPDA）分别与两种芳香族四胺单体，3,3',4,4'-四胺基联苯（TABP）和 3,3',4,4'-四胺基二苯醚（TADPE）通过两步热环化工艺制备了两种新型不对称聚吡咙（Polypyrrolone，PPys）。通过红外光谱（FT-IR）技术追踪了吡咙化反应历程，结果发现，在吡咙化的过程中主要发生两次脱水反应。同时，还考察了固化温度对 PPy 材料综合性能的影响。结果表明，350℃固化的 PPy 薄膜具有优良的耐热稳定性，氮气中 10%失重温度超过 600℃，700℃时的残余重量百分数超过 80%。此外，该材料还具有良好的力学性能以及介电性能。

关键词：聚吡咙；聚酰亚胺；耐高温涂层；2,3,3',4'-联苯四甲酸二酐