Polymer Bulletin 48, 261–269 (2002)

Polymer Bulletin

Imide-to-benzoxazole rearrangement in *ortho* substituted poly(4-4'-diphenylene pyromellitimide)s

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Received: 20 November 2001/Revised version: 19 March 2002/ Accepted: 19 March 2002

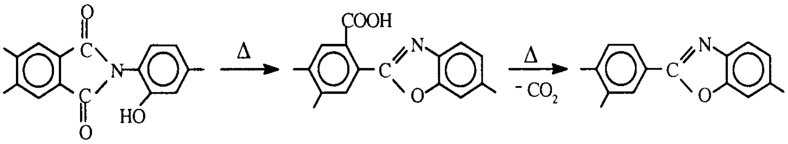
Summary

Ortho substituted poly(4,4'-diphenylene pyromellitimide)s were prepared from pyromellitic dianhydride and 3,3'-dihydroxybenzidine or 3,3'-dimethoxybenzidine. Thermal cyclodehydration of the corresponding poly(amic acid)s, PAA, led to the formation of *ortho*-hydroxy- or *o*-methoxy-polyimides, while catalytic imidization in the presence of aliphatic anhydrides was accompanied by acylation of the OH groups resulting in the formation of lateral acetoxy substituents. The direction of the latter reaction was controlled by the acidity of dehydration agents and the use of a catalyst. Imidization in the presence of acetic anhydride and pyridine led to poly[(3,3'-diacetoxy-4,4'-diphenylene)pyromellitimide] and the use of trifluoroacetic anhydride resulted in the formation of the corresponding polyisoimide with *ortho*-trifluoroacetoxy groups.This polyisoimide was completely soluble in amide solvents above 60ºC. The polymers were studied by FTIR spectroscopy, TGA, and WAXS. It was found that *ortho* substituents such as OH and methoxy groups could react with the imide cycle above 350ºC causing its rearrangement to benzoxazole. The formation of notable amounts of benzoxazole was also observed for *o*-acetoxy polyimides.

Introduction

Considerable efforts have been made in the field of aromatic polyimides to modify their structure and properties for specific applications in microelectronics, nonlinear optics, membrane separation, etc [1]. Among other approaches, this involves the synthesis of polymers with functional side groups such as hydroxy polyimides. Pendant OH groups can be further functionalized using specific substituents with a desirable property [2-5]. In a very early paper Kardash and Pravednikov [6] noted that hydroxy or methoxy groups in *ortho* position to the imide nitrogen in the diamine moiety could react with the heterocycle provoking its rearrangement to benzoxazole above 350°C. This observation was confirmed in recent studies of *ortho*-hydroxy polyimides based on 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane [7] or 3,3'-dihydroxybenzidine [8]. It has been found that the reaction of *o*-hydroxy groups with the imide cycle results in an imide-to-benzoxazole rearrangement shown in Scheme 1 [6-8].

Another important result of the study on polyimides based on 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane was the observation that substitution of the OH group with an *o*-acetoxy led to a decrease in the initial temperature of the imide-to-benzoxazole rearrangement by 50-80°C [7]. The esterification was easily attained during catalytic cyclodehydration of the corresponding PAA in the presence of acetic anhydride and pyridine. The resulting *o*-acetoxy polyimides demonstrated very good solubility in organic solvents. In the present study, the synthetic approach involving the catalytic dehydration of PAA with *o*-hydroxy groups in the diamine moiety has been extended toward rod-like poly(pyromellitimide)s based on 3,3'-dihydroxybenzidine. Poly(pyromellitimide)s with *o*-methoxy groups have also been studied. The ability of the polymers obtained to undergo imide-to-benzoxazole rearrangement was explored by FTIR spectroscopy, TGA, and WAXS.



Scheme 1. Imide-to-benzoxazole rearrangement [7]

Experimental

Material

Pyromellitic dianhydride (PMDA, 1,2,4,5-benzenetetracarboxylic dianhydride, Chriskev Co.) was crystallized from acetic anhydride and sublimed under vacuum at 180°C. 3,3'-dihydroxybenzidine, (Bz-*o*-OH, Chriskev Co) and 3,3'-dimethoxybenzidine (Bz-*o*-OCH_3, Sigma-Aldrich) were crystallized from ethanol/THF (70/30 vol.) and sublimed under vacuum at 180°C and 95°C, respectively. N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were dried and distilled over barium oxide under reduced pressure. All other reagents and solvents were used as received.

Polymer synthesis

Ortho substituted poly(pyromellitimide)s were prepared by a conventional two-step polycondensation with either thermal or catalytic dehydration of the precursor PAA [7]. The inherent viscosity ranged from 1.5 to 1.8 dL/g for all precursors studied. The precursor films were converted to the final polyimides either by heating at 300°C for 60 min under vacuum or by catalytic dehydration (chemical imidization) in the presence of an aliphatic anhydride and a catalyst at room temperature for 24 h. The imidization degree was followed by FTIR spectroscopy [9] and it was close to 100%

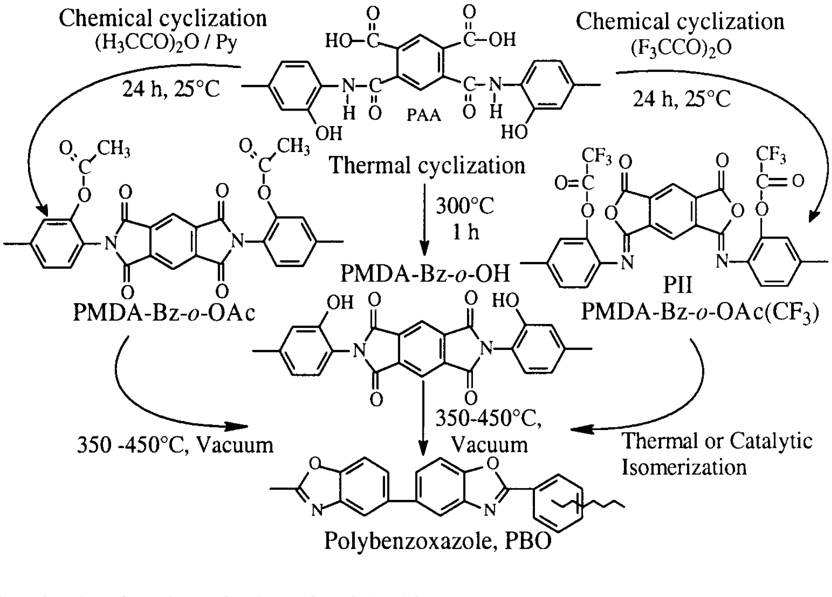
dichloride and Bz-*o*-OH as described elsewhere [7]. for all polymers studied. Polybenzoxazole, PBO, was prepared from isophthaloyl

Measurements

The chemical structure of the polymers obtained was studied by FTIR spectroscopy using a Bruker Equinox 55 spectrophotometer. A high resolution TA Instruments Thermogravimetric Analyzer, TGA 2950, was used for thermal analysis at a heating rate of 5°C/min in nitrogen. Inherent viscosity (η_{inh}) of the PAA (0.5 g/dL DMF solutions) was determined using an Ubbelohde viscometer at 25°C. Wide angle X-ray scattering (WAXS) measurements were performed on a Siemens D500 X-ray diffractometer (Ni-filtered Cu-Kα radiation, graphite monochromator).

Results and discussion

Poly(pyromellitimide)s with *ortho*-hydroxy or *o*-methoxy substituents (PMDA-Bz-*o*-OH and PMDA-Bz-*o*-OCH_3) were prepared via thermal imidization of the corresponding PAA at 300°C for 60 min (see Scheme 2). The catalytic cyclodehydration of the precursor with *ortho* OH groups in the benzidine moiety was accompanied by acylation of the hydroxyls leading to the formation of pendant *o*-acetoxy groups. The direction of the chemical imidization was controlled by the acidity of a dehydration agent and the use of catalysts. Treatment of PAA with acetic anhydride and pyridine (50/50 vol.) resulted in the formation of *o*-acetoxy polyimide, PMDA-Bz-*o*-OAc, while the use of trifluoroacetic dianhydride led to the corresponding polyisoimide, PMDA-BZ-*o*-OAc(CF_3), with *o*-trifluoroacetoxy substituents. The latter was completely soluble in DMF or NMP above 60°C.



Scheme 2. Synthesis of *ortho*-substituted polyimides

The chemical structure of the resulting polymers was studied by FTIR spectroscopy (see Fig 1 and Table 1). Strong peak of ν(Ph-O-CO) at 1185 cm^{-1} and complete disappearance of ν(OH) band around 3400 cm^{-1} in the spectrum of PMDA-Bz-*o*-OAc confirmed the formation of *o*-acetoxy groups. Strong multiple vibration peaks ν(C-F) at 1113-1218 cm^{-1} can also be seen for the polyisoimide with *o*-trifluoroacetoxy substituents (Fig 1 D).

Thermal analysis of PMDA-Bz-*o*-OH, PMDA-*o*-Bz-OCH$_3$, and PMDA-Bz-*o*-OAc revealed that all these polymers lost weight in nitrogen in two well-defined stages (Fig 2 and Table 2). Similar TGA curves were previously observed for various *o*-hydroxy polyimides [6-8,10] as well as for the rod-like poly(pyromellitimide)s with lateral methoxy groups in the diamine moiety [6,11,12]. It was shown that the initial 20% weight loss in *o*-hydroxy polyimides originates from the imide-to-benzoxazole rearrangement followed by the decarboxylation of resulting carboxy-benzoxazole fragments [7,8,10]. The unusual thermal behavior of methoxy polyimides has still to be explained.

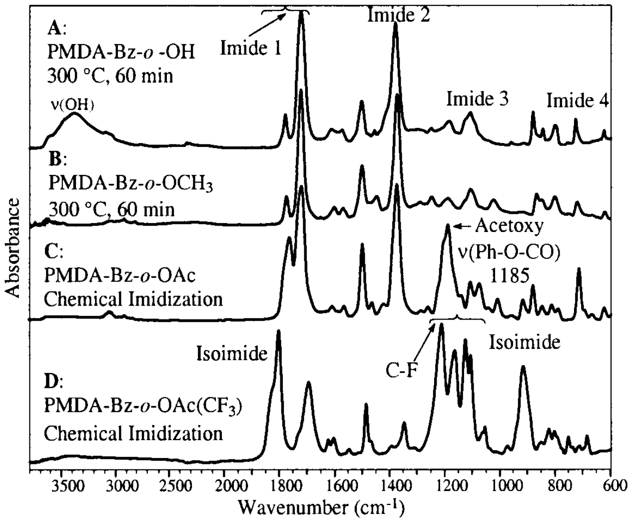


Figure 1. FTIR spectra of polyimides PMDA-Bz-*o*-O**R**

The comparison of the TGA curves in Fig 2 shows good agreement between PMDA-Bz-*o*-OH and PMDA-Bz-*o*-OCH$_3$ in terms of the starting temperature, temperature at peak, and weight loss at the first stage of the slope (see Table 2).

The initial differences in the FTIR spectra of PMDA-Bz-*o*-OH and PMDA-Bz-*o*-OCH$_3$ resulting from the thermal imidization at 300°C (Table 1) almost disappeared after these films were heated at 450°C for 60 min under vacuum. The resulting spectra were very similar, both showing strong peaks at 1610, 1544, 1461, 1267, 1060, and 813 cm^{-1} (see Fig 3A), which coincide well with the characteristic absorption maxima of the model polybenzoxazole, PBO [13-17]. Both methods, TGA and FTIR indicated that the conversion above 90% was reached in the imide-to-benzoxazole rearrangement of

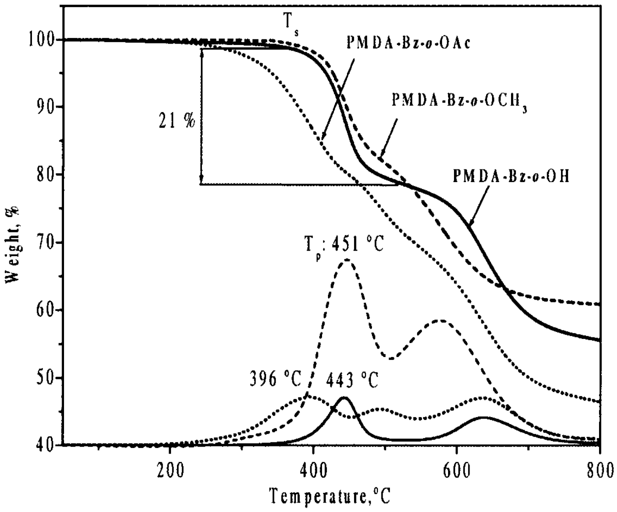


Figure 2. TGA curves of the *ortho*-substituted polyimides PMDA-Bz-*o*-**OR** (5°C/min, nitrogen)

Table 1. Infrared spectral changes upon treatment of PMDA-Bz-*o*-OR films at 450°C under vacuum [a]

Initial Polymers, cm^{-1}			After Heating at 450 °C, cm^{-1}			Probable assignment of the Band, cm^{-1}
-H	-Ac	-CH$_3$	-H	-Ac	-CH$_3$	
3401 m, br	--	--	--	3467	3434	ν(O-H)
1778 m	1781 m	1779 m	1779 w	1780 m	1774 w	ν(C=O) in phase, imide 1
1722 vs	1730 vs	1726 vs	1725 m	1726 s	1720 m	ν(C=O) out-of-phase, imide 1
--	--	--	1618 s	1616 s	1617 s	C=N Stretching of benzoxazoles (oxazole 1) [13-16]
--	--	--	1559 m	1564 w	1560 w	Typical band of benzoxazole (oxazole 2) [13-14,17]
1502 m	1500 m	1505 m	--	--	--	Substituted phenyl ring
--	--	--	1462 vs	1464 s	1462 s	Typical band of benzoxazole [13-14]
1381 vs	1373 vs	1378 vs	1376 sh	1375 s	1375 sh	ν(CNC) axial imide 2
1110 m	1106 m	1110 m	--	--	--	ν(CNC) transversal imide 3
--	--	--	1061 vs	1062 m	1062 m	Ar-O-C stretching of benzoxazoles [13-17]
--	--	--	813 vs	813 s	813 vs	Benzoxazole ring deformation [13-16]

[a] - vs-very strong; s-strong; m-medium; w-weak; br-broad; sh-shoulder

polyimides with either *o*-hydroxy or *o*- methoxy substituents. Thus, it can be concluded that the *ortho*-methoxy substituents can also react with the imide cycle provoking the rearrangement to benzoxazole above 350°C, and the reactivity of *o*-OCH3 is comparable with that of *o*-hydroxy group.

Table 2. Weight loss temperatures by TGA for polyimides PMDA-Bz-*o*-**OR** in nitrogen

R	T_s^a, °C	T_p^a, °C	Weight Loss, %
-H	371	443	21
$-CH_3$	368	451	20
-Ac	233	396	29

[a] - Ts - Starting temperature of weight loss, T_p - Temperature at the derivative pick (see Fig 2)

The results of TGA and FTIR spectroscopy were supported by WAXS analysis, which was found to be quite sensitive in following the chemical rearrangement in *ortho*-substituted polyimides. Previous studies on the supramolecular structure of non-substituted poly(4,4'-diphenylene pyromellitimide), PMDA-Bz, demonstrated that the intensity and sharpness of the multiple (*00l*) reflections corresponding to the fiber repeat always increased as a result of post-imidization annealing at temperatures up to 450°C due to the continuous improvement in the intermolecular packing [18].

The diffraction pattern of PMDA-Bz-*o*-OH film resulting from the thermal imidization at 300°C for 60 min presents similar *00l* peaks (Fig 4A) alone with a broad and intense amorphous halo at 17.5 degrees (5.1 Å). Heating at 350°C resulted in an increase in the intensity and sharpness of all reflections observed indicating the improvement in the intermolecular packing. However, further heating at 400°C under vacuum led to almost complete disappearance of the fiber repeat *00l* accompanied by a diminution and broadening of the intermolecular peak around 5.1 Å (Fig 4C). Similar disordering was also observed for the *o*-methoxy and *o*-acetoxy poly(pyromellitimide)s heated at 400°C under

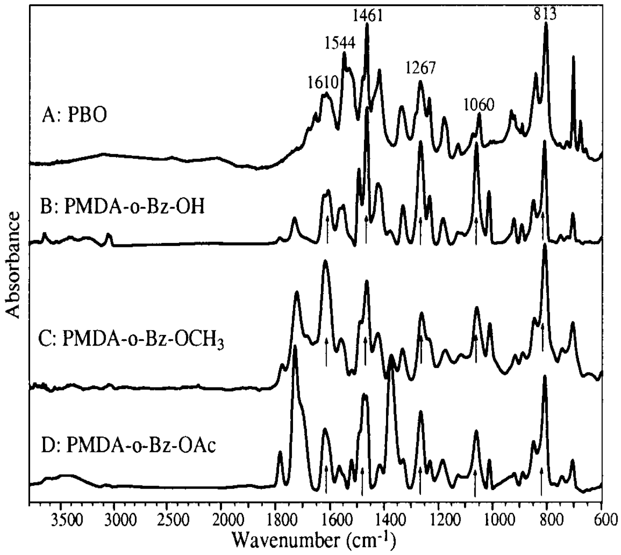


Figure 3. FTIR spectra of PMDA-Bz-*o*-**OR** polyimides after heating at 450 °C for 1 h under vacuum

PMDA-Bz [18]. vacuum and this presents an important difference with respect to non-substituted

Amorphization of the *ortho* substituted polyimides took place at notably lower temperatures than the temperature of their thermal decomposition in nitrogen, by TGA, and coincided well with the beginning of the imide-to-benzoxazole rearrangement. It would be logical to propose that this disordering was caused by the formation of the intrinsically irregular macrochains constituted by both imide and benzoxazole unites of different contour lengths. Intramolecular packing could not be improved even at the conversion to benzoxazole above 90% because of indefinite type of substitution of the phenylene rings resulting from the non-selective rearrangement and further decarboxylation of pyromellitic units (see Scheme 2).

The imide-to-benzoxazole rearrangement of the *o*-acetoxy polyimides based on 2,2'-bis(3-amino-4-hydroxiphenyl)hexafluoropropane was previously reported by Likhatchev et. al. [7]. The rearrangement in that case started at lower temperature and proceeded to a deeper conversion than for the corresponding *o*-hydroxy polyimides, as indicated by both TGA and FTIR. This was explained by higher reactivity of the *o*-acetoxy group in the imide-to-benzoxazole rearrangement due to the “leaving group” effect [7,8]. The results of the thermo gravimetric analysis of PMDA-Bz-*o*-OAc looked similar. This polymer started to lose weight at temperatures lower by 100-130°C than the *o*-hydroxy poly(pyromellitimide) PMDA-Bz-*o*-OH (see Fig 2 and Table 2). However, the FTIR measurements indicated that the conversion to benzoxazole attained for the *o*-acetoxy polyimide was significantly lower. It can also be seen that the TGA curve for PMDA-Bz-*o*-OAc shown in Fig 2 is more complicated, presenting three derivative peaks instead of only two typical for PMDA-Bz-*o*-OH and PMDA-Bz-*o*-OCH_3.

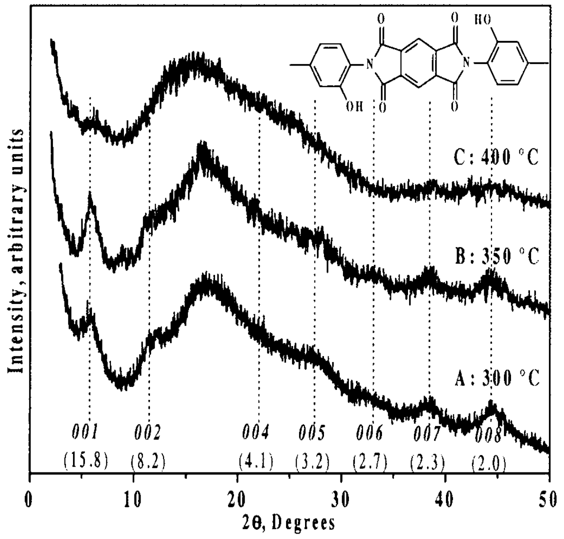


Figure 4. WAXS patterns of PMDA-Bz-*o*-OH films heated for 1 h under vacuum at 300°C (A), 350°C (B), and 400°C (C)

TGA of the polyisoimide PMDA-BZ-*o*-OAc(CF_3) resembled general features of the thermogravimetric curves shown in Fig 2 for the *o*-acetoxy polyimide but the latter polyisoimide started to loose weight at notably lower temperatures. FTIR spectra recorded on the films heated to 300-400ºC showed a high degree of isomerization to the imide structure and a very low conversion to benzoxazole.

The lower conversion to benzoxazole of the rod-like poly[(3,3'-diacetoxy-4,4'-diphenylene) pyromellitimide], as compared to those previously reported for the flexible chain polyimides derived from 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane [7], may be due to the different type of substitution of the diamines in these polymers. Phenolic esters are known to undergo *Fries rearrangement* yielding *para*- and/or *ortho*-acylphenoles [19]. The particular direction and conversion of this reaction is strongly affected by the presence of any other substituent in the phenyl ring especially in the *meta* position. In 3,3'-diacetoxy-4,4'-diphenylene fragments of PMDA-BZ-*o*-OAc, *meta* position is occupied by a C-C bond bridging two phenyl rings of the benzidine moiety. The *para* and *ortho* positions with respect to the acetoxy groups remain vacant, and thus, might be active in the *Fries rearrangement*. This suggestion was supported by the appearance of the characteristic OH band around 3400 cm^{-1} in the spectra of PMDA-Bz-*o*-OAc heated at 350°C.

In the *o*-acetoxy moieties derived from 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, the *para* position with respect to the acetoxy groups is occupied by a hexafluoropropane bridging group and there is no *meta* substitiuent. This might enhance the reactivity of the *o*-acetoxy substituent in the imide-to-benzoxazole rearrangement. The chemistry of *ortho*-acetoxy-imides is presently being explored using model compounds, the results will be reported.

Conclusions

Poly(4,4'-diphenylene pyromellitimide)s with *ortho* OH, OCH_3, or OAc groups in the diamine moiety were prepared by either thermal or chemical imidization of the corresponding PAA. It was found that cyclodehydration of the *ortho*-hydroxy poly(amic acid) was accompanied by the acylation of OH group leading to the formation of *ortho*-acetoxy substituents. The polyisoimide PMDA-BZ-*o*-OAc(CF_3) with *o*-trifluoroacetoxy groups in the benzidine moiety was completely soluble in DMF and NMP above 60º. All *ortho*-substituted polyimides studied underwent imide-to-benzoxazole rearrangement when heated above 350ºC that led to the disordering in their intermolecular packing as registered by WAXS. The reactivity of *o*-OCH_3 substituents in this reaction was comparable with those previously reported for the *ortho* hydroxy groups [7-8,10]. The conversion of *ortho*-acetoxy polyimide PMDA-BZ-*o*-OAc was notably lower. The pathway of this reaction will be further studied using low molecular weight model compounds.

Acknowledgements. The authors are grateful to Miguel Canseco, Leticia Baños and Carmen Vázquez-Ramos for their valuable contribution to this work. This work was carried out under the financial support from CONACYT, grant No. 27163-U.

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