FTIR Studies of Structure Organization in Biphenyl Type Polyimides

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INTRODUCTION

Polybiphenyltetracarboxyimides (PBPIs) obtained by thermal imidization at temperatures even exceeding their Tg's possess relatively low degree of crystallinity, as measured by X-ray diffraction techniques and the problem of the type of morphological organization in such a systems remains not clear yet **[1-4]**. On the other hand the recent literature provides numerous examples evidencing an important role of the processing variables (*e.g.*, solvent and thermal histories) onto the macroscopic (optical, thermal, mechanical) properties **[2-8]** of the resulting PI materials. The above suggests the short-range order in the structure organization of aromatic PIs - to be a key factor in understanding the structure-property relationships. To obtain the molecular insight into the structure organization processes running along with the imidization as well as occurring during annealing of cured PIs - the advantage of infrared spectroscopy in probing the molecular (conformational state, molecular interactions accounted for packing) level of the structure was employed in this study. Some of our earlier IR-spectroscopic data on the features of the structure organization in the BPDA-PDA polyimide were recently reported **[4,7-9]**. In the present paper the spectroscopic approach elaborated was extended over a wider range of BPDA-derived polyimides. The common spectral features characteristic of crystal-like structure in these systems will be presented and discussed.

MATERIALS

The chemical structure of the investigated Biphenyl type polyimides is shown in **Fig. 1**. The polymers were prepared by thermal imidization according to the following procedure. Typically the precursor (PAA/PAE) films were cast from 10 wt% solutions (in DMAc/NMP) on a glass plate by doctor-blading. After drying at 60°C for 1h in an air convection oven, the films were removed and in a free-standing state imidized at T_i = const for 30 min. Samples obtained at 8 imidization temperatures (T_i = 130, 150, 170, 200, 250, 300, 350 and 400°C) were studied. Films of 6 different thicknesses ranging from 1 up to 100 μm were studied. The polymers obtained by imidization of the solvent-free films (of which the solvent was completely removed by washing out in distilled water) were studied as well. The syntheses of low molecular weight model compounds (**Fig. 2**) are described elsewhere **[6]**.

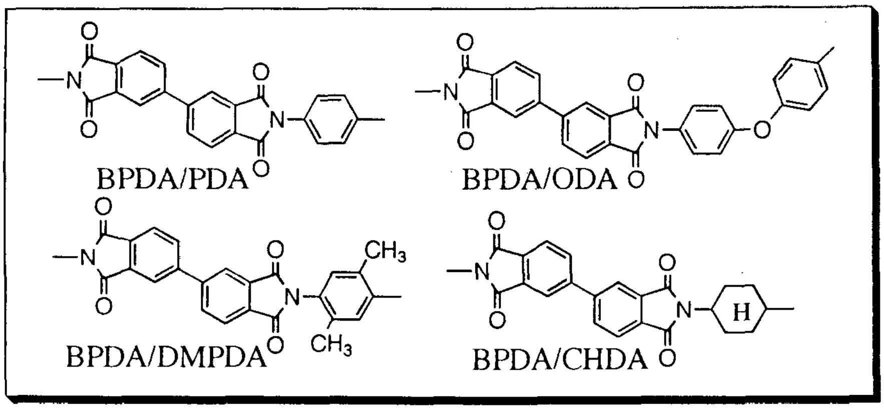

Figure 1 BPDA-derived polyimides studied.

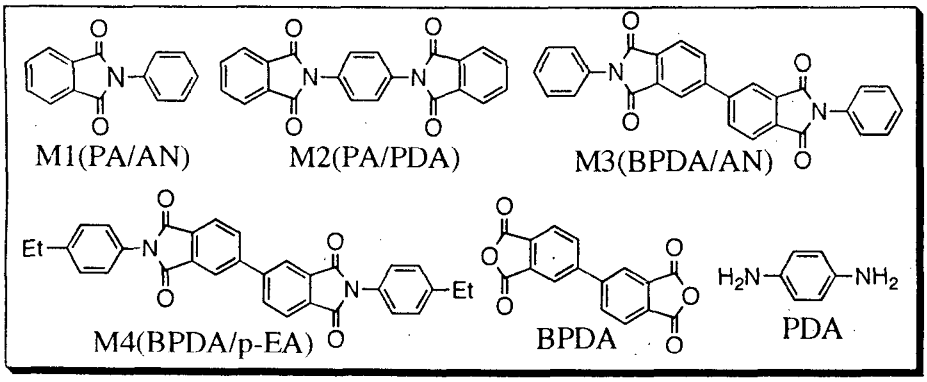

Figure 2 Model compounds used.

RESULTS AND DISCUSSION

Spectral Features of Crystal-like Order in BPDA-PDA

The spectral effects accompanying the structure organization processes in BPDA-PDA can be roughly subdivided into three groups:

(1) Those related to the conformational behavior. The most prominent features of the crystalline preferred conformations - are the bands at 890 and 550 cm^{-1}; those characteristic of amorphous state are - 1095, 763 and 569 cm^{-1} bands[**4-6**]. The development of the bands attributed to the crystalline conformation (and concurrent decrease of amorphous bands) as a function of T_i levels off however at about T_i = 250°C[**4**]. These features were revealed from the spectral comparisons of the "crystalline rich" (obtained by fast cure at T_i = 400°C[**3,4**] with completely amorphous[**4**] chemically imidized PI.

(2) The occurrence in the spectra of samples cured at T_i > 250°C of a series of doublets (e.g., 1024/1013; 706/694; 596/589 cm^{-1}) as well as additional peaks (e.g., 488 cm^{-1}) was considered as a result of crystal field band-splittings or that of increase of molecular interactions between the phenylene rings - indicative of appearance of the crystal-like order. **Fig. 3** illustrates some of these changes. Closer examination revealed that the C-H stretching modes (3100-3000 cm^{-1}) are also very sensitive to structure organization in BPPIs [**9**]. "Nucleation" of the "fine structure" of C-H stretching bands (**Fig.4**) suggests a higher local order in packing

of phenylene rings for the films cured at T_i above 350°C.

(3) Effects related to further development of crystal-like order: better defined structure of the above listed doublets (**Fig.3**); better resolution of the peaks of the C-H stretching envelope, caused by narrowing of peaks (**Fig.4**). These changes are specially marked for polymers obtained by the fast curing regime (at $T_i > 350°C$) , *i.e.*, when the T_i throughout all the process exceeds the effective glass transition temperature of the curing system and/or for thicker films, providing, thus, a higher molecular mobility through both the high temperature and the lag in the volatiles release. These spectral changes proceed concurrently with the band-shifts of the C=O and C-N stretching bands described in the literature, as those attributed to the crystalline preferred conformation of PI chain[10].

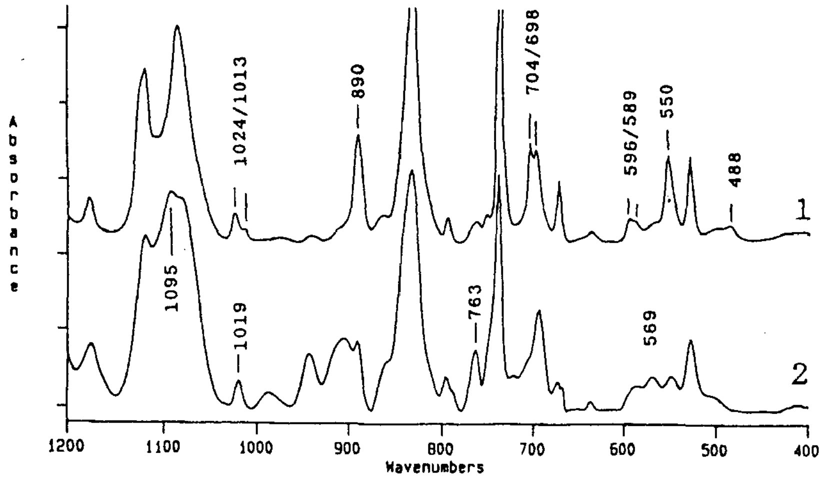

Figure 3 Structure-sensitive bands in FTIR spectra (1200-400 cm^{-1}) of BPDA-PDA polyimide: 1 —40 μm film cured at 400°C for 0.5h ; 2 — 15 μm chemically imidized film.

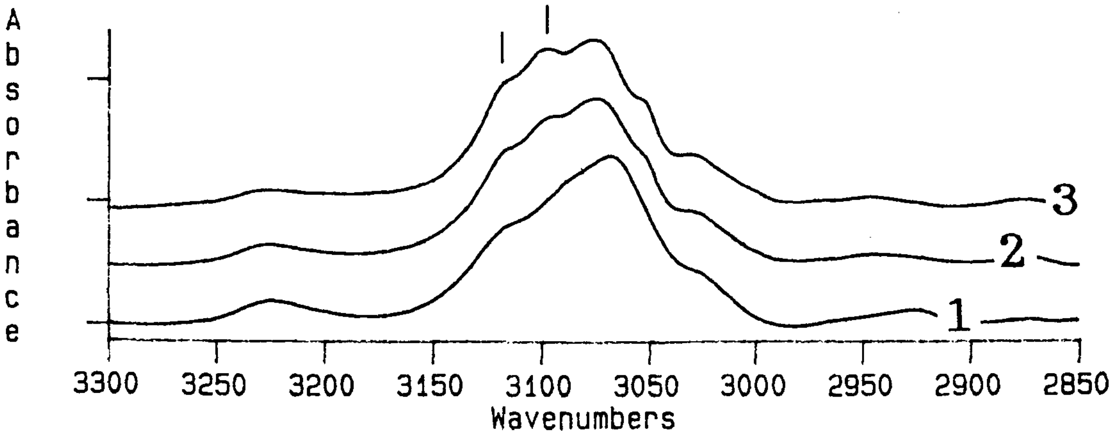

Figure 4 C-H stretching region for 40 μm BPDA-PDA films thermally imidized at different conditions: 1 - cured at 250°C for 0.5h; 2 - (1) subsequently annealed at 400°C for 0.5h; 3 - cured at 400°C for 0.5h.

Infrared Spectral Assignments

In order to interpret the observed spectral features related to the structure organization in BPPIs a careful assignments of IR-bands are required. A series of FTIR spectra of individual low molecular weight model compounds (**Fig.2**) were employed for this reason. It gave us a possibility to justify the tentative assignments for the bands arisen from the imide group as well as in many cases to distinguish between the vibrational modes of the 1,4-disubstituted (PDA; ODA) and 1,2,4-trisubstituted (BPDA) benzene rings. Another approach of spectro-chemical modeling is illustrated in **Fig.5**, where the fragments (700-400 cm^{-1}) of the BPDA-PDA and BPDA-CHDA spectra are compared. As follows from this figure, the replacement of the 1,4-disubstituted phenylene ring by 1,4-trans-CHDA moiety discloses the assignments of the bands in this spectral region arising from trisubstitution, disubstitution as well as 660 cm^{-1} band attributed to the CH deformation of the CHDA. The assignments of the bands of the IR-spectra of the BPPIs and related model compounds will be reported elsewhere [**12**].

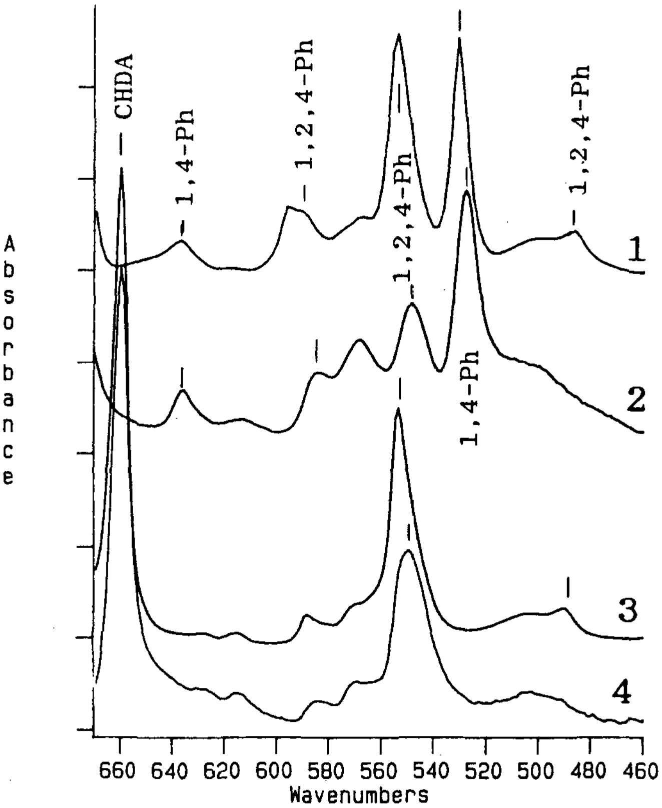

Figure 5 FTIR spectra of BPDA-PDA (curves 1 and 2) and BPDA-CHDA (curves 3 and 4) polyimides: 1 and 3 - crystalline rich samples; 2 and 4 - amorphous samples.

Spectral Comparisons of BPDA-derived PIs

Basing on the spectral comparisons of BPDA-PDA, BPDA-ODA and BPDA-CHDA polymers it will be demonstrated that the most prominent spectral changes arising from development of crystal-like order in these systems have much in common and are immediately related to the structure sensitive bands of the BPDA moiety, suggesting the conformational behavior in BPDA moieties and the molecular interactions between these fragments are the driving force to the crystal-like ordering. For BPDA-ODA some bands attributed to ODA vibrational modes are also affected by annealings indicating that by analogy with Kapton the intramolecular rotations of phenylenes about the C-O-C linkage of ODA moiety are involved in conformational changes [**10,11**], whereas no features of crystal-like order were observed in the PIs comprised of BPDA and DMPDA or TMPDA moieties (**Fig.6**).

More examples of the applicability of the common spectral criteria chosen for evaluation of the molecular order in BPDA-derived PIs as a function of the following processing variables: precursor (PAA/PAE); casting solvent (DMAc/ NMP); drying procedure (amount of residual solvent in PAA films); regime of curing (fast/slow/stepwise) as well as of the film thickness - will be presented and discussed.

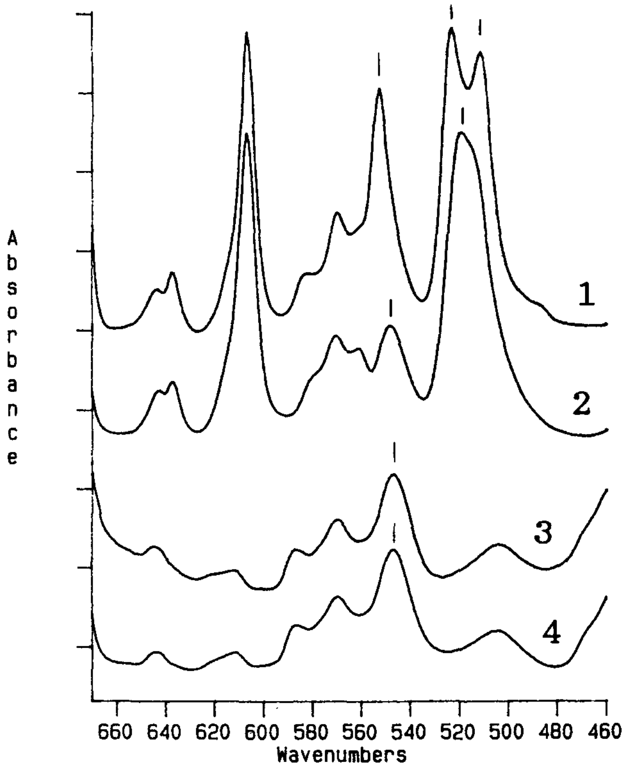

Figure 6 FTIR spectra of BPDA-ODA (curves 1 and 2) and BPDA-DMPDA (curves 3 and 4) polyimides: 1 and 3 - samples cured at 400°C for 0.5h; 2 and 4 - samples cured at 250°C for 0.5h.

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