Effects of Processing Conditions on Structure Organization of Aromatic Polyimide

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The aromatic polyimide (PI) investigated was poly(p-phenylene biphenyltetracarboxydiimide) (BPDA-PDA) prepared by thermal imidization of the corresponding polyamic acid (PAA) and/or polyamic acid methyl ester (PAE). The structure — local / conformational order, molecular interactions as well as the features of crystal-like morphology were studied by means of FTIR and WAXD methods as a function of : PAA/PAE drying conditions (extent of solvent removal); regime of thermal imidization (heating rate and imidization temperature, T_i = 130-400°C); film thickness, t = 1-100 μm); casting solvent (DMAc / NMP). The investigation revealed that the structure organization process run parallel to imidization. Conformational changes were detected in the polymers cured T_i at as low as 150°C, *i.e.*, at the early stage of imidization process, whereas the crystal-like order manifests itself in the polymers cured at T_i close to or above the T_g. For samples obtained at a given T_i, the yield of both the ordering processes dramatically depends on film thickness. Due to higher amount of volatiles retained, which provide the system higher molecular mobility, the thicker films always displayed an enhanced order.

EXPERIMENTAL SECTION

Materials. PAA films were cast from the 10 wt% solution 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 (= constant) 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 to 100 μm were studied.

Measurements. FTIR spectra were obtained on Digilab FTS-60 spectrometer at resolution 2 or 4 cm^{-1}; 128 to 256 scans were averaged for each spectrum collected. WAXD experiments were conducted on Mac Science MXP18A (CuKα, 40 kV, 300 mA). Detailed consideration of WAXD data will be reported elsewhere.[1]

RESULTS AND DISCUSSION

The main goal of this work was to reveal the features of structure organization in thick free-standing PI films as a function of processing conditions. FTIR and WAXD techniques were applied to characterize the structure. This paper presents mainly our FTIR results, hence, the information on the structure organization obtained is based on spectral behavior of some structure-sensitive IR bands.

FTIR spectroscopy due to its great potential in characterization of molecular level of the structure organization was widely used in evaluation of a variety of PI materials. These applications of FTIR were restricted, however, to films thinner than a few μm. To our knowledge, thicker PI films (t > 10 μm) were never studied by this method. The main reason for that is oversaturation of absorbance (D >> 1) in the spectral region 1800-1500 cm^{-1} — traditionally used for evaluation of the extent of imidization (α_i), crystallinity, molecular interactions.[**1-3**]

Thus in order to characterize the thick films, we had focussed on the spectral regions of the weaker bands 3600-2600 cm^{-1} and 1200-400 cm^{-1} (Figs.1-3), of which the first one was used mainly for estimation of α_i, whereas the second one — for analysis of the structure organization.

The spectral data used to select the structure-sensitive IR bands are presented in Figs.1 and 2. By comparison of "amorphous" spectrum of a chemically imidized film with "semi-crystalline" spectrum of a PI powder sample cured at 400°C, the following bands were attributed to the amorphous state: 1095, 1019, 763, 700, and 569 cm^{-1}.

The crystalline state manifests itself in appearance of 890, 550, 488 cm^{-1} single bands as well as doublets 1024 / 1013, 704 / 698, and 596 / 589 cm^{-1}. The spectral behavior of the structure-sensitive bands as a function of T_i is shown in Fig.2, which presents the spectra of 40 μm films prepared in one-step cure at different T_is. Concurrently with a decrease in the intensity of amorphous bands (*e.g.*, 1095 and 763 cm^{-1}), the bands 890 and 550 cm^{-1} related to the structure organization process are developing along with an increase in T_i.

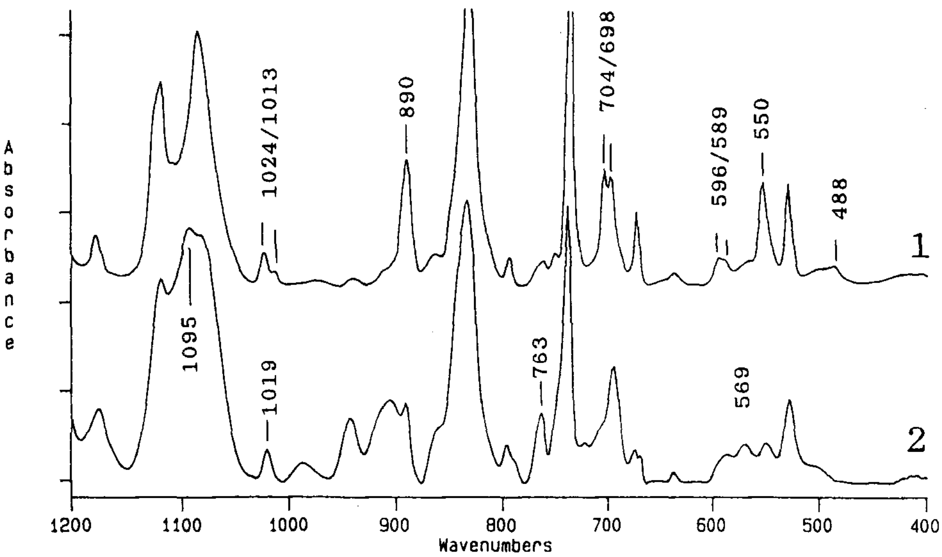

Fig.1 Structure-sensitive bands in FTIR spectra (1200-400 cm^{-1}) of BPDA-PDA polyimide: (1) 40 μm film cured at 400°C and (2) 15 μm film chemically imidized in acetic anhydride / pyridine (7/3) binary solution at 50°C for 24 h.

It follows from the plots of the relative intensities of the bands 890 and 550 cm^{-1} as a function of T_i (Fig.4A) that the structure organization process responsible for these spectral changes starts already at T_i = 150°C where the actual α_i does not exceed 20-25 % and practically levels off at T_i = 250°C. These FTIR results are in keeping with WAXD data[**1,4**], according to the fact that the macromolecules of PAA in the course of imidization (and at higher T_is) assume a more extended chain conformation. This led us to conclude that the described behavior of the 890 and 550 cm^{-1} bands should be attributed to local (conformational ordering — the process which for rigid and semi-rigid polymers typically runs ahead of crystallization.

According to the WAXD results, the periodicity along the chain direction further improves upon annealing at temperatures above the Tg (> 330°C). The corresponding changes in the FTIR spectra (see below) indicate that the differences in local ordering between the samples cured at different T_i (< Tg) are partly erased upon annealing at higher temperatures. The latter process also leads to formation of a crystal-like morphology.[**1,4**] In the FTIR spectra, this process reveals in narrowing of bands, band shifts, and band splittings.[**5**] These effects result in appearance of well-defined doublets 1024 / 1013, 706 / 694, and 596 / 589 cm^{-1} as well as of some additional bands (*e.g.*, 488 cm^{-1}) (Fig.2), which are observed for the samples cured or annealed at temperatures close to or above the T_g. These IR bands are indicative of a lateral crystal-like order and together with other above-listed structure-sensitive bands were used as criteria for evaluation of molecular organization in BPDA-PDA polyimide as a function of processing variables. In particular, there were compared in terms of molecular order the pairs of

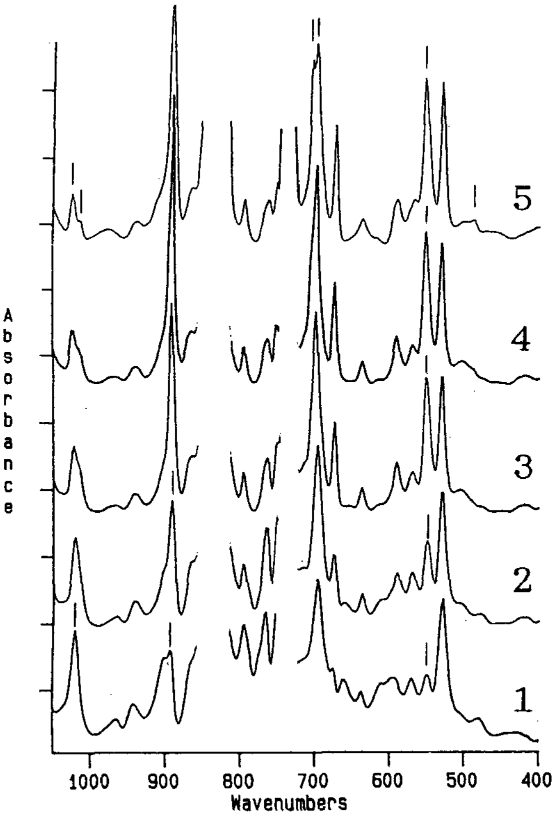

Fig.2 FTIR spectra (1050-400 cm^{-1}) of 40 μm PI films as a function of imidization temperature:(1) 150, (2) 170, (3) 200, (4) 250, and (5) 400°C.

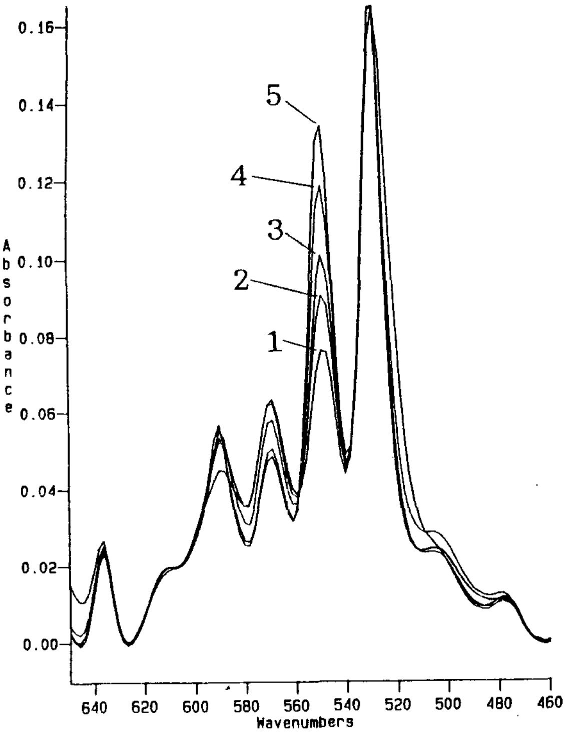

Fig.3 Intensity of the 550 cm^{-1} band for PI films cured at 170°C as a function of film thickness: (1) 8, (2) 35, (3) 45, (4) 60, and (5) 80 μm

samples, differing in only one of the following parameters of their histories : casting solvent (DMAc / NMP); heating rate (fast / slow); temperature profile of cure regime (one-step / stepwise); supported / free-standing; air and substrate sides of films cured in supported state.

But the most striking result of this study was an extremely strong dependence of the yields of the structure organization processes on the film thickness. Indeed, as follows from Figs.3 and 4, the dependence of the relative intensity of the conformation-sensitive bands 890 and 550 cm^{-1} on film thickness (t = variable) at given T_i (= constant) is almost as strong as that shown in Fig.2 which illustrates the spectral behavior of the same bands as a function of T_i (= variable) at given thickness (t = constant). According to these data, the thicker films always possess appreciably higher local conformational order. The film thickness also dramatically influences the yield of the crystal-like order. For example, the films (t > 60 μm) cured at 250°C are more crystalline that the 5-10 μm films cured at 350°C; 0.5-2 μm films cured at 400°C display rather weak features of the crystal-like order.

Strong dependence of the structure organization on film thickness suggests that the volatiles, *i.e.*, residual solvent and/or by-product of cyclization (H_2O for PAA, CH_3OH for PAE) act as plasticizers to be responsible for the observed structure differences. Film thickness in this context is expected to influence the structure through (diffusional) control of the volatiles release.

In order to obtain a better understanding of the effects of casting solvents on imidization process as well as on the structure organization of the resulting PIs, a special investigation of the complexes between DMAc / NMP and PAA / PAE (formed at the initial precursor stage as well

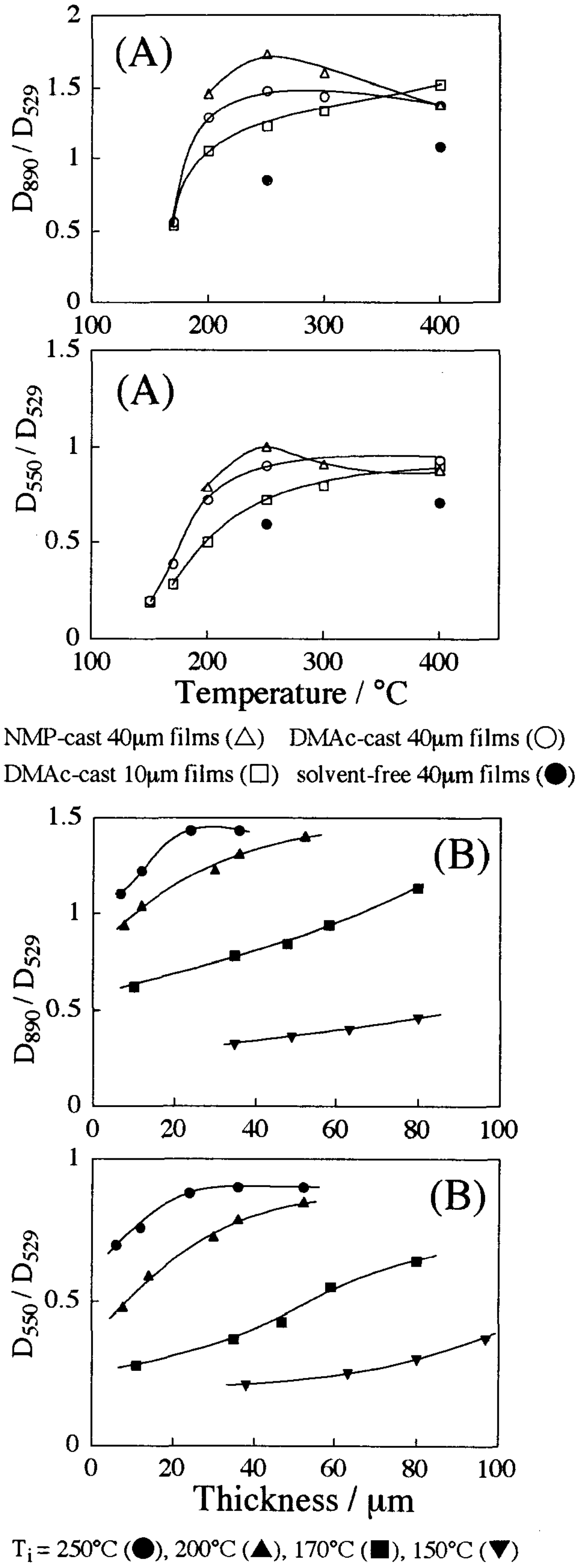

Fig.4 Relative intensity of the 890 and 550 cm^{-1} bands as a function of (A) imidization temperature and (B) film thickness.

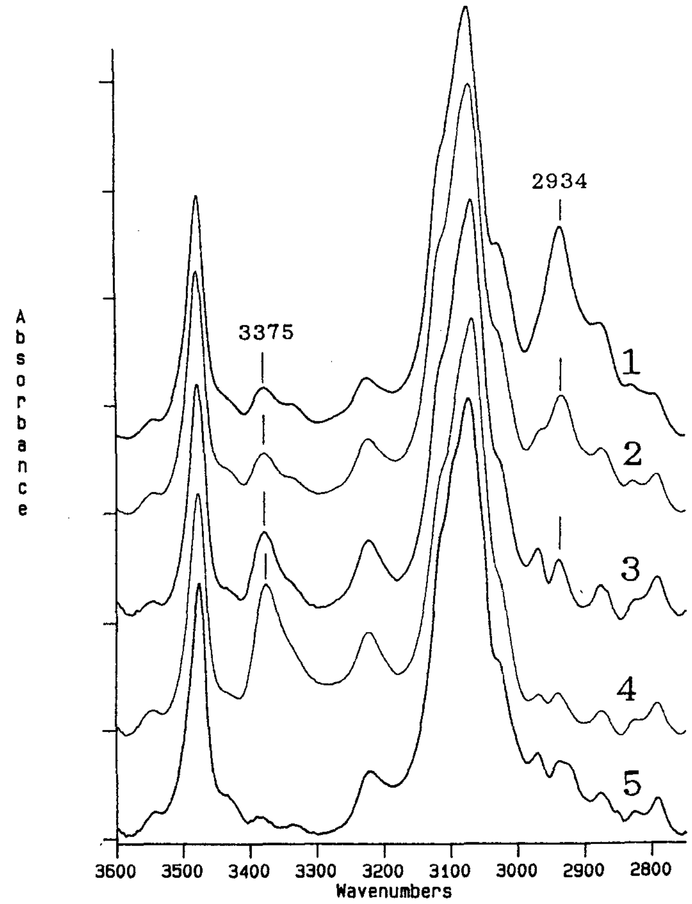

Fig.5 FTIR spectra of PI films cured at 250°C (t = variable):
(1) 95 μm, (2) 40 μm, (3) 15 μm, (4) 4-6 μm, (5) 5-6 μm film cured at 400°C.

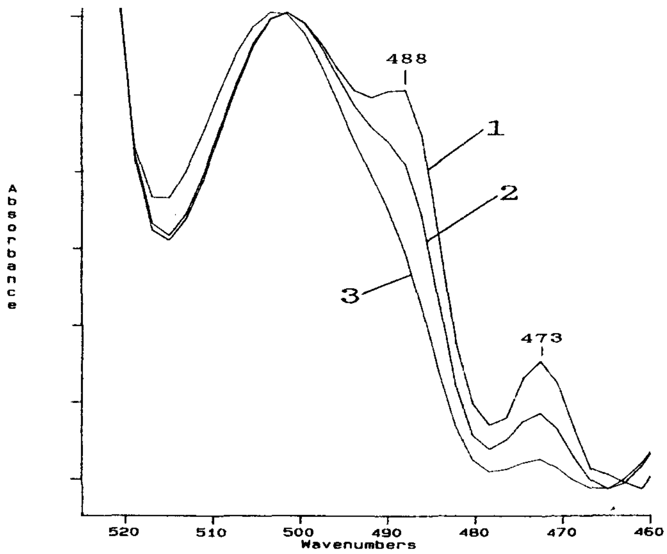

Fig.6 Effect of film thickness on crystal-like order in PI films cured at 250°C (t = variable): (1) 20, (2) 50, (3) 95 μm.

as in the course of imidization) was conducted.[**1**]

Also it was found that in films of the polymers with α_i exceeding 90 %, the solvent is retained predominantly in free / non-bonded state (see Table 1). This fact provides a possibility to quantitatively control the concentration of residual solvent.

The effects of film thickness on the concentration of the retained solvent (band 2934 cm^{-1} for DMAc) and α_i (band 3375 cm^{-1} for the unreacted NH groups) for the films cured at 250°C is illustrated in Fig.5. The amount of residual solvent varies from 0 (for 5-10 µm films) to 2.5 wt% (for the films thicker than 80 µm). The corresponding α_i for thin films (freed of solvent under cure conditions) does not exceed 94 ± 1 %, whereas imidization in thick films (due to solvent-enhanced molecular mobility) is completed. As was mentioned above, higher molecular mobility drives the polymer chains in thick films to higher conformational order, whereas a very low progress in the crystal-like ordering is achieved at 250°C (Fig.2). Thinner films (5-20 µm) cured at the same temperature possess considerably lower local order with no signs of the crystal-like order (Fig.6).

It seems to be of interest to note that in respect to the polymers under study FTIR method provides an unique possibility to probe the three levels of molecular mobility: the first starting from that of very short-range required for the reacting groups to meet in the cyclization act (through α_i); the second, related to the local conformational order (following the intensities of the conformation-sensitive bands); and the third, of larger scale cooperative molecular motions required for the crystal-like ordering (band splittings).

Fig.7 shows the results on structure changes upon annealing at 400°C for the films cured at 250°C. It follows from these comparisons that in the solvent-free thin films the conformational ordering somewhat improves but still is lower than that observed for the thick films cured at 250°C; also some witnesses of the crystal-like order appear. The annealed thick films display a considerable increase in the crystal-like order (Fig.7), surpassing the thin films cured at 400°C in one-step regime.

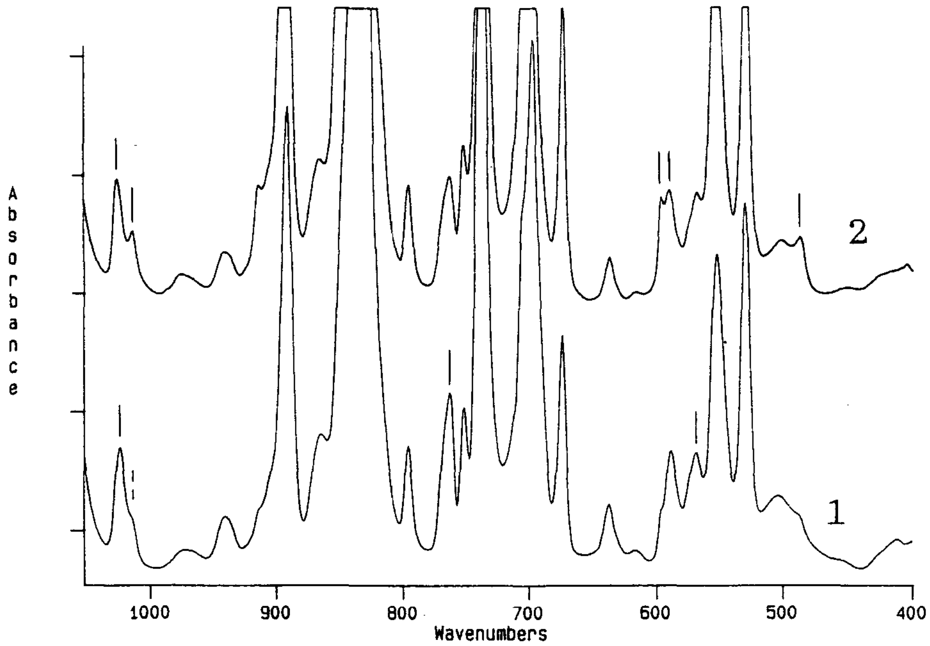

Fig.7 Effects of annealing (400°C; 0.5 h) on structure organization in PI films cured at 250°C (t = variable): (1) 20 and (2) 95 µm.

The yield of imidization and of the structure organization processes in PI films obtained from the solvent-free PAA films are considerably lower as compared to those from the common solvent-bearing counterparts. It is important to note that the films in which after the drying stage the rest of solvent was completely washed out by water also demonstrate dependence of α_i and ordering on film thickness, clearly indicating that the low molecular weight by-products of cyclization (H_2O for PAA, CH_3OH for PAE) do influence the molecular mobility in the curing system, though to much lower extent than the residual casting solvents do.

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Table 1 Peak wavenumbers and extinction coefficients of specific IR bands of solvent.

	neat liquid		in PAA film	in PI film
solvent	peak / cm^{-1}	ε / M^{-1} cm^{-1}	peak / cm^{-1}	peak / cm^{-1}
DMAc	2935	51	2935	2934
	1648	326	1605	1647
	473	21	479	474
NMP	2881	40	2881	2881
	1688	219	1651	> 1685
	471	43	476	471