

Incorporation of Azobenzene Chromophore into Poly(amide-imide)

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ABSTRACT: Poly(amide-imide)s (PAI) bearing azobenzene chromophore groups were prepared by allowing a hydroxyl-containing azobenzene dye (Disperse Red 1) to react with and reactive-terminated PAI with weight-average molecular weights ranging from ~ 1.2 to 2.0×10^4 g/mol. Such PAI were prepared by the condensation of trimellitic anhydride (TMA) and 4,4'-methylene diphenyl diisocyanate (MDI). The final polymers presented a deep red color, with an absorption maxima in *N,N*-dimethylformamide (DMF) solution at 490 nm, close to the azobenzene reactant used

(Disperse Red 1) and molecular weights slightly higher than the pristine polymer, showing that the azo chromophore incorporation reaction does not lead to side reactions. The azofunctionalized polymer presented a high T_g value (170°C) that could be increased by a thermal curing process to 240°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 841–847, 2007

Key words: azo polymers; FT-IR; functionalization of polymers; poly(amide-imide)

INTRODUCTION

Poly(amide-imides)s (PAIs) are high-performance polymers noted for their thermal resistance. They are interesting substitutes for polyimides, being more economical and easily processed, since different from polyimides, PAI dissolves readily in organic solvents and can be processed as a thermoplastic material.¹ The polyimides are first obtained in the form of poly(amic acid), which is subjected thermal cyclodehydration to produce the polyimide. In the case of the PAIs, the imidization reaction occurs during polymer formation, but in many cases, the terminal groups are still reactive. These terminal groups can be reacted with blocking reagents, to prevent a self-curing process in the final product, or can be used to incorporate different moieties in the PAI structure. In the electro-electronic industry² PAIs are used in applications where high thermal and mechanical resistance are required, combined with easy processability in solution or as a thermoplastic, at lower costs than polyimides. PAIs have also been used in a number of other applications, such as surface alignment of liquid crystals,³ membranes for separation and purification,⁴ in integrated optics,⁵ and as an engineering plastic.⁶

The azobenzene chromophores are capable of undergoing *trans*–*cis*–*trans* isomerization reactions^{7,8} making

these structures potential active materials in applications such as optical data storage,⁹ optical switching,¹⁰ surface relief gratings,¹¹ and photoalignment of liquid crystals.¹² In all these applications, the use of the azo compound in polymers with a high glass-transition temperature is highly desirable, since the information “written” in the material can be easily erased by heating the material above its glass-transition temperature.

Many polyimides bearing azobenzene chromophores have been synthesized.^{13–17} In many cases, the incorporation of the chromophore in the polymeric chain is accomplished by the synthesis of a special monomer containing the chromophore and further copolymerized with commercial monomers to form the final polymer. Recently, PAIs having azobenzene moieties have also been prepared¹⁸ in this way. The synthesis of azobenzene-containing monomers is generally multi-step and time consuming. Here we present preliminary results of incorporation of azobenzene chromophores on PAI, using its reactive NCO and/or carboxylic acid terminal groups. These polymers have potential application in optical storage technology and will be studied in detail in the future.

EXPERIMENTAL

Synthesis of polyamide-imide

The PAI was synthesized by the reaction of equimolar quantities of trimellitic anhydride (TMA) and 4,4'-methylene diphenyl diisocyanate (MDI) in *N*-methyl-

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TABLE I
FTIR Relative Areas Calculated for PAI Samples

Sample	Time (h)	1776/1018 (imide/aromatic, before cure)	1776/1018 (imide/aromatic, after cure)
PAI2	5.5	2.5	1.9
PAI3	8	2.6	2.3
PAI4	10	2.5	2.2
PAI5	12	2.7	2.5
PAI6	14	3.0	2.1
PAI7	17	3.0	2.6

2-pyrrolidone (NMP). The reaction was performed in two steps. First, the reactants were mixed with the solvent at room temperature and stirred mechanically, gas being evolved by the reaction. The mixture was maintained at temperatures around 45–50°C until the gas evolution ceased (~ 10 h) and then heated at 120°C for a further 7 h. Samples were collected at different times (Table I). After the reaction, the samples were kept at –18°C and used in the dye incorporation reactions without purification. For characterization, the PAI powder was precipitated in methanol, followed by washing with methanol and drying to constant weight in a vacuum oven at 40°C.

Incorporation of the dye Disperse Red1 as terminal groups

About 2 g of the PAI synthesis reaction mixture (47% solids) was mixed with 6 mL of a solution of the dye Disperse Red 1 (DR1) in NMP (~ 0.05 g/mL). The mixture was heated at 130°C for 5 h under magnetic stirring. About 5 mL of *n*-butanol was added and the diluted mixture was heated at the same temperature for one additional hour. The addition of *n*-butanol was necessary to decrease the viscosity of the reaction mixture and to block the unreacted terminal groups. The deep red polymer obtained was precipitated in methanol, washed with methanol until the filtrate was completely colorless, and dried in vacuum at 40°C to constant weight. No spot of the dye was detected by thin layer chromatography of the precipitated polymer.

Polymer characterization

FTIR spectra were recorded in a Nicolet Nexus 470 spectrophotometer in transmission mode from KBr pellets, otherwise as stated. UV–vis spectra were recorded in a Hitachi U2001 spectrophotometer in *N,N*-dimethylformamide (DMF) solutions (0.04 mg/mL) and on films cast onto glass substrates from DMF solutions. HPSEC determinations were performed in an Agilent 1100 chromatographic system with a refractive index detector, in NMP containing LiBr at 60°C flowing at 0.7 mL/min, with two Waters H4ER columns and polystyrene standards. The concentra-

tion used was 3 mg/mL and the injection volume was 50 μ L. DSC measurements were performed in a TA 2960 differential calorimeter with a heating rate of 20°C/min. Cast films were cured by heating them at a rate of 10°C/min up to 250°C and keeping them at this temperature for 15 min in air.

RESULTS AND DISCUSSION

PAI characterization

The reaction scheme generally assumed^{19–21} for the formation of the PAI is shown in Figure 1. In the first step, the imidization reaction takes place, yielding mainly compound I, although formation of compound II cannot be ruled out. Upon heating, the amide group is formed, in this case, through reaction between the isocyanate groups and carboxylic acid of TMA residues. The terminal groups of the final polymer may be either carboxyl groups and/or isocyanate groups. As isocyanate terminal groups are highly reactive, any attempt to isolate the PAIs by precipitation could lead to an undesirable reaction, hindering the dye incorporation. Therefore, the dye incorporation step was performed with the crude PAI without isolating it from the synthetic mixture. But, for the PAI characterization, to remove the solvent and possible residual monomers and oligomers, the solid resins were isolated by precipitation in methanol, leading to fine yellow powders with final yields of about 85%.

The spectra of the precipitated PAIs powders were recorded and are shown in Figure 2. The main differences in the FTIR spectra are observed in the relative intensity of the bands in the 1800–1500 cm^{-1} region.

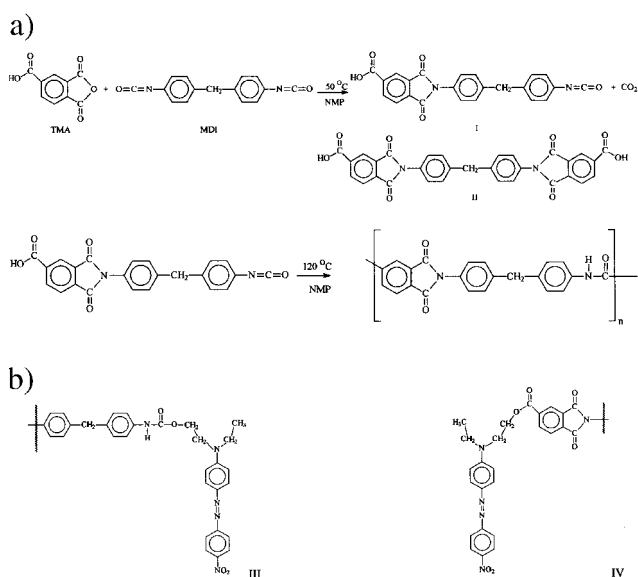


Figure 1 (a) Polyamide-imide formation, according to Refs. 19–21. (b) Examples of possible dye-incorporated structures formed by the reaction of DR1 with the isocyanate end group (III) and with the carboxylic end group (IV).

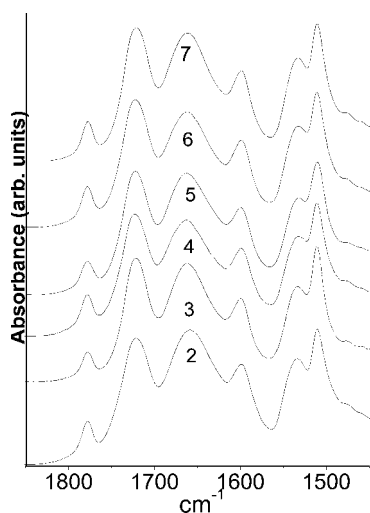


Figure 2 FTIR spectra of PAI at different reaction times.

The absorptions at 1776, 1720, and 1380 cm^{-1} are attributed to the imide group and those at 1660 and 1320 cm^{-1} to the amide group. The absorptions at 1600, 1510, 1410, 1080, and 1018 cm^{-1} are attributed to the aromatic group.²²

The degree of imidization can be followed by the ratio of the absorption area of the imide carbonyl stretching band at 1776 cm^{-1} to that of the aromatic vibration at 1018 cm^{-1} .²³ The aromatic absorption band at 1018 cm^{-1} is chosen in the case of PAIs spectra, since the more commonly used bands at 1600 or 1500 cm^{-1} are not always well resolved, owing to the presence of the imide and amide groups. The relative areas under the absorption bands were calculated by tracing the baseline between the peak valleys in the absorption mode and integrating the peak. The results are shown in Table I. These relative areas were almost constant in the first 10 h and then increased with the reaction time, showing that the imidization also occurred in the later stages of the polymerization, although 85% occurred in the first 5.5 h. Unfortunately, samples taken before 5 h of reaction were very unstable and the carbon dioxide evolution could not be controlled even at -18°C , thus preventing the samples from being analyzed. In this case, no calibration was performed and hence there was no way to calculate the extinction coefficients of the absorptions analyzed here. Therefore, the values shown in Table I should be analyzed only in a comparative way and not as absolute values.

The polymer growth can also be monitored by the ratio of imide/amide contents. For this, many FTIR band ratios can be used,^{20,24} in principle. But in our case, the solvent used in the PAI synthesis, NMP, presents bands very similar to the amide ones. The absorptions at ~ 1680 and 1300 cm^{-1} and the shoulder that appears on the 1500 cm^{-1} aromatic absorption peak were attributed to NMP.²⁴ If the ratio of imide to

amide band areas were due only to the PAI contribution, it would be expected that some clear relation could be detected with the reaction time, for example in the 1776/1660 cm^{-1} ratio. No such relation was observed with the reaction time indicating that, even after the precipitation and washing, some NMP remained in the sample powder and could not be removed by the vacuum-drying process used.

Dye incorporation

For the incorporation of the Disperse Red 1 (DR1) azo dye, only the end groups of PAI are available to react with the hydroxyl groups of the dye. These may be either isocyanate or carboxyl acid groups yielding, after the reaction with the dye, urethane [Fig. 1(b), III] or ester groups [Fig. 1(b), IV], respectively. Although the urethane formation is much more favored, owing to the higher reactivity of the isocyanate compared with the carboxyl group, some degree of the esterification cannot be completely ruled out at the temperature used (130°C). During this reaction an excess of the dye was used, in the ratio 1 : 3 (w/w) of dye : PAI. At a rough estimate, using the number-average molecular weight average of the polymer and assuming two terminal reactive groups, the molar ratio used was around 5 : 1 dye : PAI reactive group.

Since the dye incorporation reaction was performed with the crude PAI, prior to isolation by precipitation in methanol (pristine PAI), the differences between this sample and the PAI after precipitation (PAI ppt) was also explored by FTIR. The spectrum of the pristine PAI was recorded by placing a drop of the reaction mixture on a KBr pellet and drying it in a vacuum oven at 60°C for 24 h, to form a clear and transparent film. The spectrum of the PAI ppt was recorded in a KBr pellet. Both spectra for the sample PAI7 are shown in Figure 3. In the 4000–2000 cm^{-1} region (not shown), the main difference is the presence of a hydroxyl absorption band around 3500 cm^{-1} overlapping the N–H absorption band in the precipitated sample, probably due to moisture in the KBr.

The main differences between the pristine and precipitated PAI spectra were observed in the 1800–1500 cm^{-1} region. The imide band at 1776 cm^{-1} was more intense than in the precipitated sample, indicating that low-molecular-weight fragments that were lost in the precipitation process were richer in imide groups. The higher intensity of the absorption band at 1660 cm^{-1} (Fig. 3) may indicate that the solvent NMP could not be completely removed by simple vacuum drying at the low temperatures used to prepare the sample for the FTIR measurements. The same was true for the all the PAI samples, prepared with the various reaction times. Thus, based on the reaction scheme shown in Figure 1 and the results above, it is possible that compounds I and II were still present in the reaction

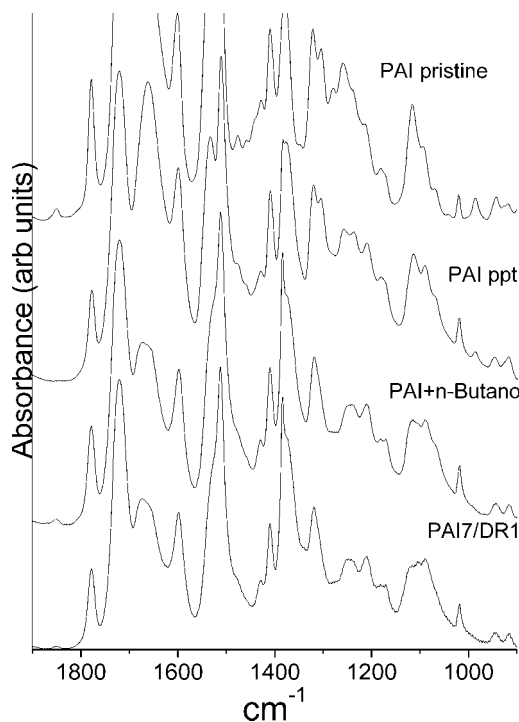


Figure 3 FTIR spectra of the PAI7 samples: before (pristine) and after (ppt) precipitation, after the reaction with *n*-butanol and after the dye-incorporation reaction.

mixture used in the dye incorporation, although we could not detect the isocyanate groups by FTIR, probably due to their low concentration.

Preliminary tests of the dye incorporation reaction, using only NMP as solvent, yielded extremely fine and heterogeneous powders after precipitation with methanol. The addition of *n*-butanol to this reaction mixture was necessary to reduce the viscosity of the reaction mixture, facilitating the precipitation in methanol. The red precipitate obtained in all PAI samples with the aid of *n*-butanol was highly homogenous, easy to filter, and formed brilliant deep red films from NMP or dimethylsulfoxide (DMSO) solutions.

To investigate the influence of the addition of *n*-butanol on the properties of PAI, an aliquot of the PAI7 reaction mixture was heated with *n*-butanol under the same conditions as in the dye incorporation reaction, but without the dye. FTIR results for the reactions of PAI with *n*-butanol are also shown in Figure 3. Comparing the precipitated PAI powders obtained without (PAI ppt) and with the use of *n*-butanol (PAI + *n*-butanol), the main differences are in the range of 1800–1200 cm^{-1} , but most of the changes can be attributed to the more efficient removal of the NMP in the precipitation process when using *n*-butanol. The imide band at 1776 cm^{-1} is more intense for the sample obtained with the use of *n*-butanol, suggesting that the use of *n*-butanol permitted the recovery of fractions richer in imide groups that, otherwise, were lost in the precipitation/filtration processes.

The deep red polymers obtained after the dye incorporation reaction were completely soluble in NMP, DMF, and DMSO, partially soluble in methyl-ethylketone (MEK), tetrahydrofuran (THF), and dioxane and insoluble in alcohols, including *n*-butanol. It is important to note that the pristine PAI samples were soluble in NMP, only slightly soluble in DMF and DMSO, and completely insoluble in the other solvents cited above. This change in the solubility profile is an indication of the successful incorporation of the dye.

The FTIR spectra for all PAI/DR1 samples have the same features, so that only the results for PAI7/DR1 are shown in Figure 3. The spectra of the azobenzene derivative of PAI are similar to that of pristine one. There is no clear change in the region 4000–2000 cm^{-1} (not shown), comparing the pristine PAI with the derivatized PAI. The reduced intensity of the 1660 and 1300 cm^{-1} bands and the shoulder at 1530 cm^{-1} can be attributed to the more effective removal of NMP during the precipitation process.

The ester and/or urethane groups that are probably responsible for the incorporation of the dye in the PAI chains should both appear in the range 1740–1680 cm^{-1} .²⁵ As no clear changes were observed in this region, they may be overlapped by the imide and amide carbonyl absorption bands or their contents were too low to be detected by FTIR. Also, the absorption bands of the dye all coincide with the PAI ones. Thus, from this result alone, the possibility of dye molecules being adsorbed on the polymer cannot be completely ruled out. The occurrence of only an adsorption process was discarded, however, because in the thin layer chromatography experiments the PAI/DR1 samples did not yield a separated spot of the dye. Another indication of the dye incorporation is the fact that the Disperse Red 1 dye is highly soluble in alcohols and readily sublimates at 80°C, and no decrease in the dye content could be observed after heating the polymer powder at this temperature for several hours or by the reprecipitation of the polymer in alcohols.

The PAI and the PAI/DR1 powders were analyzed by HPSEC and the molecular weight averages calculated are plotted in Figure 4 against the reaction time of PAI formation. Regarding the PAI formation, the weight-average molecular weight (M_w) of the pristine PAI increased slightly in the first 14 h, and then more rapidly until 17 h, which was the longest time interval studied, owing to the high viscosity of the reaction medium. As the M_n values showed almost constant values over the whole range, the polydispersity (M_w/M_n) increased with the M_w values.

The molecular weight averages determined for the samples before and after the incorporation of the dye followed the same trend, indicating that there was no degradation or other side reaction that could alter the molecular weight in a significant manner. The values of the molecular weight averages were 10–30% higher

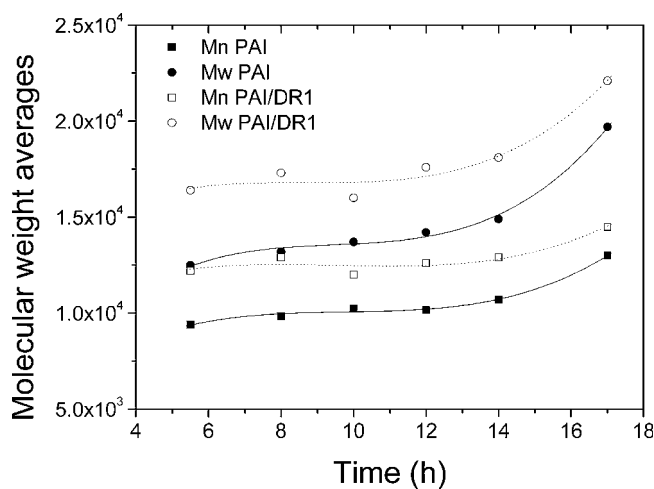


Figure 4 Molecular weight averages of the PAIs and PAIn/DR1 plotted against the reaction time of PAI formation. The lines are only to guide the eye.

for the dye-incorporated samples, but the polydispersity values were almost the same. This increase in the molecular weights cannot be due only to the incorporation of the dye into the PAI chains. As the molecular weight determination by HPSEC is not an absolute method, changes in the polymer structure after the dye incorporation may affect the hydrodynamic behavior of the polymer, leading to higher rises in the apparent molecular weight than expected. Therefore we can only compare the trends in the values of the molecular weight.

To clarify these observed changes in the molecular weights, the molecular weight distribution for two PAI, (collected after 8 and 17 h of reaction time and precipitated in methanol) and the same samples after the dye-incorporation reaction are shown in Figure 5. It seems that the higher the reaction time of PAI formation, the lower is the molecular weight change as well as the dye incorporation. However, the shape of

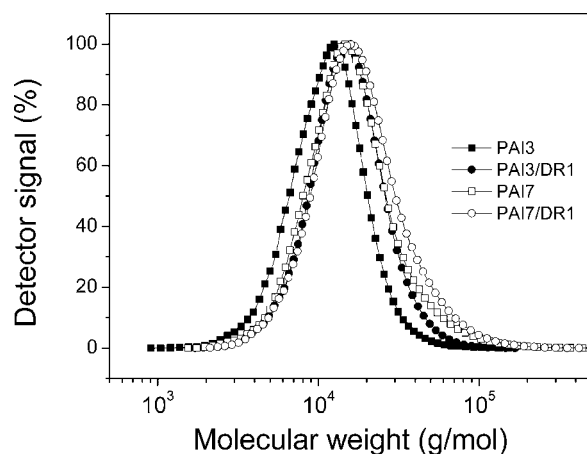


Figure 5 Molecular weight distributions of PAI and PAI/DR1 samples.

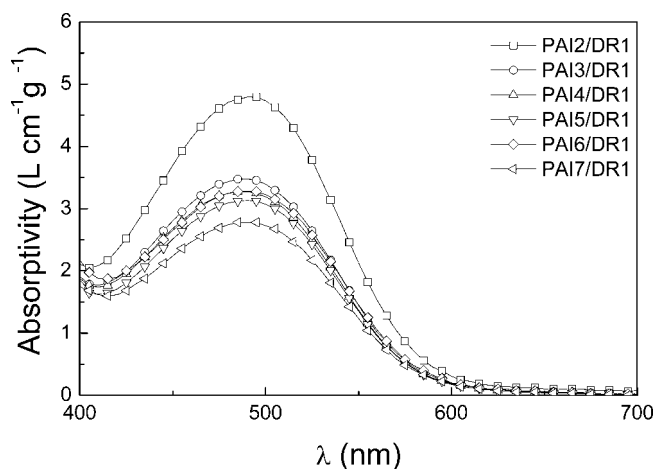


Figure 6 UV-vis spectra of PAI/DR1 in DMF solutions.

the molecular weight distribution profile is similar for the pristine and dye-incorporated samples. It is important to add that no peaks were obtained at molecular weights lower than 2000 g/mol, denoting the absence of free dye in the sample.

The UV-vis spectra of the PAIn-DR1 in DMF solution are shown in Figure 6. All PAI/DR1 showed the wavelength of maximum absorbance (λ_{\max}) at 490 nm. The peak absorbance (λ_{\max}) for the pure dye was at 500 nm in DMF and 490 nm in ethanol. Although the λ_{\max} showed that DR1 has some degree of solvatochromism, the values of molar absorptivity were equal within the experimental error, for both solvents, viz. $34,070 \pm 370$ and $33,860 \pm 390$ L mol⁻¹ cm⁻¹, respectively, for ethanol and DMF. Assuming that the absorptivity of the dye molecule is not greatly affected by the incorporation of the dye as a terminal group on the PAI backbone, the dye content incorporated can be estimated from the values of absorbance of PAI-DR1 using a calibration curve obtained with the pure dye. The results from this estimate, in % weight, are shown in Table II. The dye content incorporated in the PAI backbone should be inversely proportional to its molecular weight, since the number of terminal groups decrease proportionately as the polymer chains grow. As can be seen from the results presented in Table II, the dye contents decreased with the use of PAI of higher molecular weight, as expected.

TABLE II
Dye Contents of PAI/DR1 in wt %

Sample	Incorporated dye (wt %)
PAI 2/DR1	4.4
PAI 3/DR1	3.2
PAI 4/DR1	3.0
PAI 5/DR1	2.9
PAI 6/DR1	3.0
PAI 7/DR1	2.6

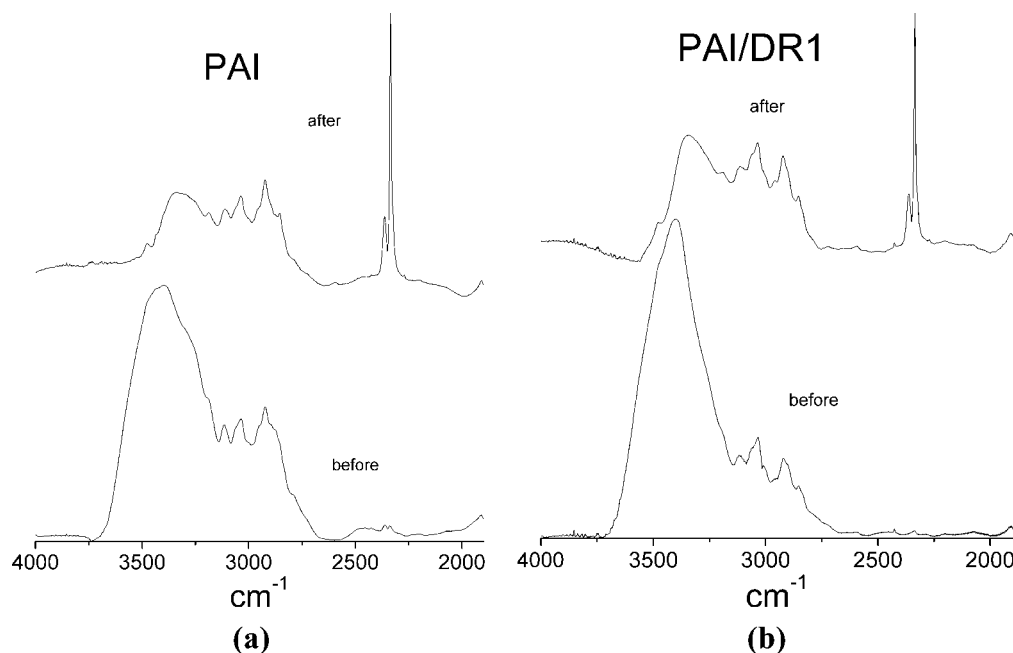


Figure 7 FTIR spectra of (a) PAI and (b) PAI-DR1 before and after thermal curing: 4000–2000 cm^{-1} region.

The UV–vis spectra of the cast films of PAI/DR1 cast on to glass were also recorded. The spectra were similar for all PAI/DR1 samples. In all cases, spectra recorded in solution and in cast films had the same maxima, the cast film showing only an enlargement of the absorption, typical of the absorption of solid samples, with no indications of aggregation.

Curing process

FTIR spectra of PAI and PAI/DR1 were recorded from KBr pellets before and after the thermal curing process. The pellets were heated at $10^\circ\text{C}/\text{min}$ to 250°C and kept at this temperature for 15 min. The FTIR spectra were recorded before and after thermal curing, from the same pellet. The same thermal treatment was used to cure pure PAI films, yielding very stable and flexible self-supporting films.

FTIR spectra in the $1900\text{--}500\text{ cm}^{-1}$ region (not presented) showed no significant changes due to thermal treatment in the PAI/DR1 samples. In pure PAI films, the absorptions at 1300 and 980 cm^{-1} disappeared and the band at 1660 cm^{-1} decreased substantially after the thermal treatment. These bands are associated with the solvent NMP that could be present in the sample, even after its precipitation in methanol. In all cases, for all PAI samples as well PAI/DR1 samples, the relative areas of imide/aromatic ring band (Table I) decreased after thermal treatment, indicating that imide groups participate, in some way, in the crosslinking process.

In the $4000\text{--}1900\text{ cm}^{-1}$ region shown in Figure 7(a) and 7(b), the absorption band in $\sim 3400\text{ cm}^{-1}$ decreased substantially with the thermal treatment for

both samples, probably due to the elimination of water from the KBr by the thermal treatment. The peaks at 2360 and 2330 cm^{-1} appear only in the samples after thermal treatment and are characteristic of CO_2 molecules. They were not present in the sample before thermal treatment and did not decrease even after 30 min of dry nitrogen purging of the equipment. It can be attributed to the CO_2 generated in the curing process of the PAI and PAI/DR1 that was partially trapped in the KBr pellet.

Figure 8 shows the DSC trace for the PAI/DR1, before thermal treatment. A glass transition can be seen clearly at about 170°C and an exothermic peak associated to the CO_2 release in the curing process, at about 250°C , confirming that thermal treatment at

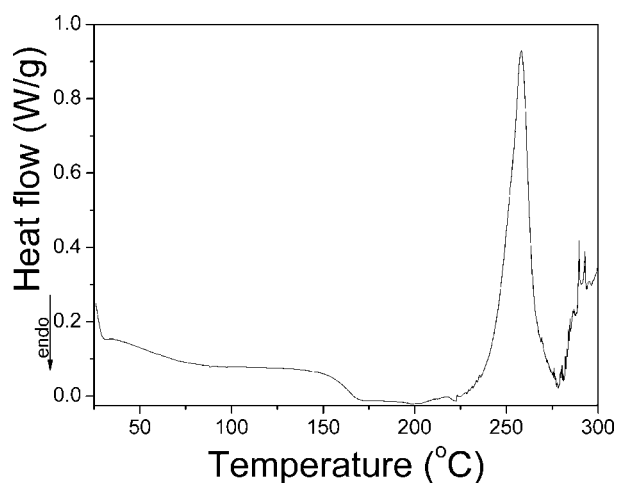


Figure 8 DSC trace of PAI before thermal curing.

250°C can lead to cured samples. Very similar traces were obtained for all PAI/DR1 samples that showed similar T_g values. The T_g values after thermal treatment increased to about 240°C in all samples.

CONCLUSIONS

PAIs having azobenzene chromophores as terminal groups were successfully obtained. The polymers have a deep red color and an absorption band around 500 nm. The glass-transition temperature, around 170°C, can be increased by curing to value of 240°C. It has been shown that the curing process of both PAI and PAI-DR occurs more intensely at 250°C, with the release of carbon dioxide molecules.

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