

One-Step Synthesis of Aromatic Polyimides Based on 4,4'-Diaminotriphenylmethane

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SYNOPSIS

The feasibility of using a one-step high-temperature polycondensation for the synthesis of aromatic polyimides, based on 4,4'-diaminotriphenylmethane (DA-TPM), was studied. It was found that the reaction of DA-TPM with various aromatic dianhydrides in nitrobenzene at 180–200°C resulted in the formation of the high molecular weight soluble polyimides, PI-TPM. The reaction solutions cooled to ambient temperature were used for casting films. These PI-TPM films significantly exceeded their prototypes obtained by the thermal imidization of poly(amic acids) in terms of solubility and tensile properties. All studied polyimides demonstrated well-distinguished glass transition at 260–320°C. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Synthesis of aromatic polyimides based on 4,4'-diaminotriphenylmethane (DA-TPM) was described for the first time by Koton et al. in 1980.¹ In that work the polyimides resulting from the thermal imidization of poly(amic acids), PAA, were found to be brittle and insoluble in any organic solvent.

In a recent article,² it has been shown that flexible self-supporting films with good tensile properties could be produced from DA-TPM and aromatic dianhydrides if thermal imidization is replaced by a chemically induced process occurring at room temperature. The obtained polyimides, PI-TPM, demonstrated good solubility in amide solvents and pyridine.

This could make them suitable for a one-step high-temperature polycondensation. This method is obviously more convenient than the conventional two-step synthesis via PAA or other precursors. However, its application has been restricted, because

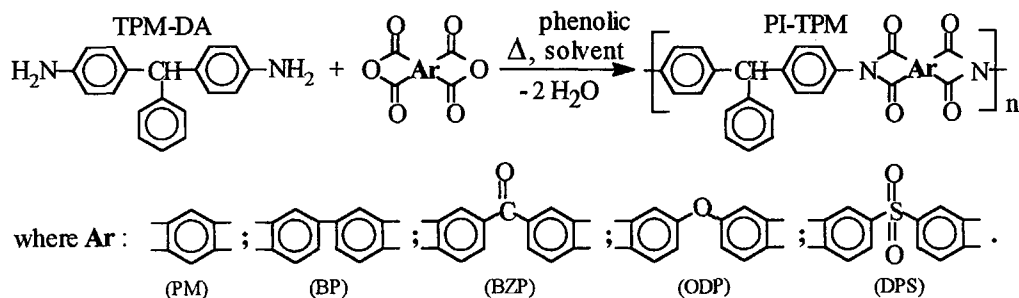
there are very few inexpensive monomers that could result in formation of soluble high-performance polyimide films.³

The aim of the present work was to investigate the feasibility of the one-step high-temperature polycondensation for producing high molecular weight soluble polyimides from DA-TPM and various aromatic dianhydrides. The thermal and mechanical properties of the resulting PI-TPM films have also been studied.

EXPERIMENTAL

The synthesis of the diamine, DA-TPM, is described elsewhere.^{2,4,5} Polymer grade DA-TPM (mp 124–125°C) was obtained by repeated recrystallization from benzene followed by a continuous heating at 100°C and 10⁻⁶ mmHg. Dianhydrides were used as received from Chriskev Co. Solvents nitrobenzene, *m*-cresol, and *p*-chlorophenol were obtained from Aldrich. The polyimides, PI-TPM, were produced by the one-step high-temperature polycondensation in a phenolic solvent.⁶

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The obtained polyimides are named according to the type of the above-shown dianhydride moieties as PM-TPM, BP-TPM, BZP-TPM, ODP-TPM, and DPS-TPM, respectively. Films were cast from the reaction solutions at 50–60°C onto glass plates and dried at 200°C and 10⁻⁶ mmHg for 48 h. Then they were stripped from the plates, placed in metal frames, and heated under 10⁻⁶ mmHg for 24 h at 230°C, and then for 1 h at 275°C.

The chemical structure of the obtained polymers was studied by ¹³C CP-MAS NMR and FTIR spectroscopy. Solid-state NMR spectra were recorded with proton decoupling on a Varian Unity plus 300 NMR spectrometer operating at 75.47 MHz for ¹³C. Approximately 300 mg of each sample, as a film, was packed into a 7-mm diameter silicon nitride rotor with Kel-F packs. The spectra were obtained under Hartmann–Hann matching conditions with a contact time of 1000 μs, repetition time of 4 s, and a spinning rate of 4.2 kHz. The measurements were made using a spinlock radiofrequency of 60 kHz, and typically 1028 transients per spectrum were recorded. Elimination of spinning side bands was accomplished by the TOSS sequence.⁷ Chemical shifts were referenced to the right peak of hexamethylbenzene at 17.36 ppm (with respect to TMS) determined on a separate sample.⁸

Infrared spectra were recorded by using a FTIR spectrophotometer Nicolet 510P. Inherent viscosity (η_{inh}) was determined in 0.5 g/dL *N,N*-dimethylformamide (DMF) solutions in a Ubbelohde viscometer at 25°C. For BP-TPM, η_{inh} was determined in 0.5 g/dL nitrobenzene solution at 50°C, because this polyimide is insoluble in DMF at room temperature. A Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis at a heating rate of 5°C/min. The glass transition temperatures, T_g , were determined by a film-elongation technique using a Du Pont Thermomechanical Analyzer, Model 2940 (samples of 13 × 4 × 0.0025 mm; tension 0.1N; a nitrogen atmosphere; heating rate 5°C/min). Mechanical testing of the polymer films was performed by using an Instron Tester, Model 111, at a drawing rate of 50 mm/min, on samples of 20 × 5 × 0.0025 mm.

RESULTS AND DISCUSSION

The one-step high-temperature polycondensation of the aromatic diamines and tetracarboxylic acid dianhydrides in phenolic solvents might be especially effective for processing monomers of moderate reactivity.³ The method is also known to be less sensitive to the stoichiometry of reagents than the conventional two step synthesis.^{9,10} For these reasons, in contrast to our previous article devoted to the synthesis of PM-TPM and BZP-TPM films via chemical imidization of PAA,² in this study no extensive purification technique, such as high vacuum sublimation, was used either for the DA-TPM, or the dianhydrides.

After optimization of the synthesis conditions, the high molecular weight PI-TPM were prepared by the one-step polycondensation in nitrobenzene at 180–200°C. The reaction solutions with a concentration of solids of 10–15 wt % were intensively stirred for 4 h under a nitrogen flow. The inherent viscosity of PI-TPM is shown in Table I. It is important to note that all monomers used in this study dissolved completely in the reaction solutions under these conditions, and the resulting polymers did not precipitate even being cooled to room temperature. The films were cast directly from the reaction solutions. Better films were obtained if the solution was preheated to 50–60°C.

The molecular weight of the polyimides, in particular, PM-TPM and BZP-TPM, prepared under the above-described conditions, was practically the same or even slightly higher than for their prototypes resulting from the chemical imidization of PAA.² Catalysis of the polycondensation reaction by small amounts of benzoic acid or isoquinolin (1–3 wt %) ^{9,10} did not increase the inherent viscosity significantly.

The chemical structure of the PI-TPM prepared by the one-step high-temperature polycondensation was confirmed by both high-resolution ¹³C CP-MAS NMR and FTIR spectroscopy. The ¹³C-NMR spectrum of BZP-TPM is shown in Figure 1. It presents the general characteristic pattern of all studied PI-TPM. The imide carbonyl carbon resonance occurred at around 165 ppm, methine carbon of the triphenylmethane moiety

appeared at 56 ppm, and the aromatic carbons showed two broad peaks in the range of 120 and 150 ppm. In some spectra (as in the case of PM-TPM), three broad peaks could be distinguished in the aromatic region. Beside these peaks, the signal of the carbonyl of the benzophenone moiety at 193 ppm can also be seen in Figure 1. The results are in good agreement with solid state NMR studies of polyimides and their model compounds reported by other authors.^{11,12} The infrared spectra of the obtained PI-TPM showed intensive characteristic imide bands around 1780 and 1720, 1380, 1110, and 720 cm^{-1} .

It was found by means of TMA that all PI-TPM demonstrated well-distinguished second-order phase transition in the range from 260 to 320°C. The exact values of T_g within this interval depended on the chain rigidity determined by the structure of the dianhydride moiety (see Fig. 2).

The weight loss temperatures in both nitrogen or air, as well as the mechanical properties—Young's modulus, E_o , tensile strength, σ_b , and elongation at break, ϵ_b , are presented in Table I. In regard to all these characteristics, there is no big difference between PI-TPM films freshly prepared by the one-step synthesis or by the chemical imidization.² An important advantage of the former is the higher stability under prolonged exposure to air and humidity.

These films showed no change of the initial properties after 6 months of storing in the air atmosphere, while the chemically imidized PI-TPM could rapidly lose their elasticity after several weeks under the same conditions. Higher stability of the polyimides resulting from the one-step polycondensation may be attributed to the more regular chemical structure. The infrared spectra of these polymers did not indicate even slight traces of isoimide or residual amic acid units, which are known to be very common for the polyimides prepared by the conventional two-step synthesis.^{3,13} These units should be considered as defect sites because of their susceptibility to hydrolysis.

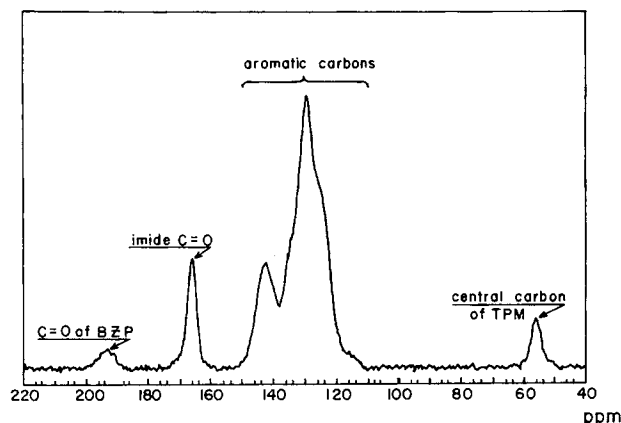


Figure 1 High-resolution solid-state ^{13}C -NMR spectrum of BZP-TPM.

The most rigid PI-TPM films obtained in this study—PM-TPM and BP-TPM—could bear comparison in terms of their thermal and mechanical properties with the industrial high-performance polyimide film UPILEX R³ produced by the one-step high-temperature polycondensation from 4,4-oxidianiline (ODA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride. The advantage of DA-TPM is that it can be used in combination with pyromellitic dianhydride, PMDA, while the pair ODA-PMDA results in formation of insoluble polyimides, which cannot be processed via the one-step process.

CONCLUSIONS

It can be concluded that the initially reported insolubility of PI-TPM polyimides¹ should not be considered as an inherent property. It should be attributed to the drawbacks of the specific synthesis method: thermal imidization of PAA.

It was found that one-step high-temperature polycondensation is well suitable for producing high

Table I Properties of PI-TPM Obtained by One-Step High-Temperature Polycondensation

Polymer	Inherent Viscosity, η_{inh} (dL/g)	Mechanical Properties			Weight Loss by TGA, °C			
					Air		Nitrogen	
		E_o (Gpa)	σ_b (Mpa)	ϵ_b (%)	5%	10%	5%	10%
PM-TPM	1.5	2.0	164	38	502	524	530	556
BP-TPM	0.6 ^a	1.8	150	42	498	516	525	541
BZP-TPM	1.2	1.5	138	70	463	488	509	536
ODP-TPM	1.1	1.4	134	58	459	476	502	538
DPS-TPM	0.5	1.6	107	20	431	457	492	519

^a 0.5 g/dL nitrobenzene solution at 50°C; for the rest of PI-TPM η_{inh} was determined in 0.5 g/dL DMF solutions at 25°C.

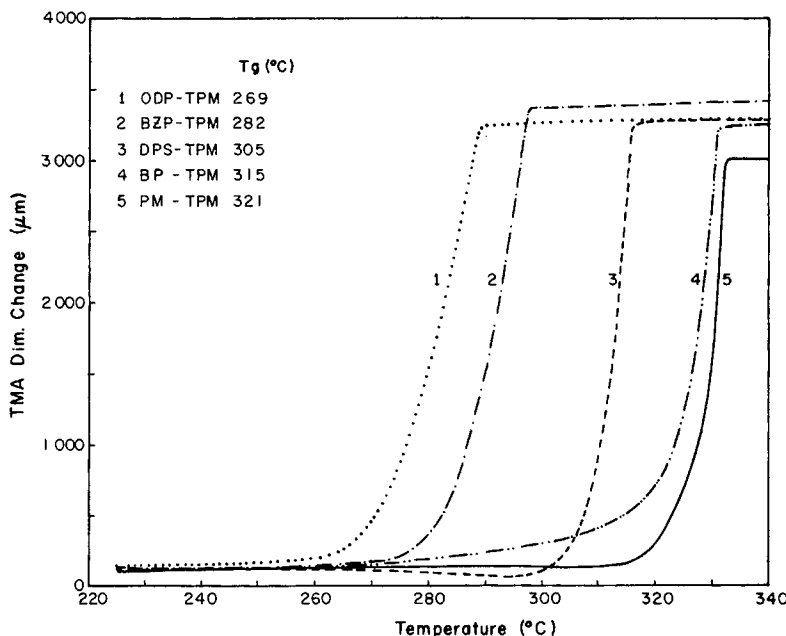


Figure 2 Thermomechanical curves of PI-TPM.

molecular weight polyimides from DA-TPM and various aromatic dianhydrides, including the most rigid PMDA. The resulting PI-TPM films are well soluble in phenolic solvents. Most of them, except BP-TPM, are also soluble in amide solvents, as it was recently reported for PM-TPM and BZP-TPM obtained by chemical imidization.² The polyimide films prepared by the one-step polycondensation demonstrated higher stability in mechanical properties under prolonged exposure to air and humidity.

Taking into consideration the availability of the monomer DA-TPM, the PI-TPM films resulting from the one-step polycondensation can be considered as promising candidates for several practical applications. It also can be very interesting for studying the effect of the different synthetic routes to the fine chemical structure, supramolecular packing, and physico-chemical properties of aromatic polyimides.

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