

Synthesis and Properties of Polybenzimidazobenzophenanthrolines

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SYNOPSIS

Polycondensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) with 3,3'-diaminobenzidine (DAB) and 3,3',4,4'-tetraaminodiphenyl ether (TADPE), respectively, in *N,N'*-dimethylacetamide (DMAc) at room temperature was found to produce high-viscosity polybenzimidazobenzophenanthroline (PBIPA) precursors. The PBIPA films, exhibiting excellent thermal and mechanical properties, were conveniently prepared by the heat cure of precursors. UV-vis spectra and IR spectra of PBIPA were measured. The permeability to H₂, O₂, and N₂ of these two polymer membranes was determined at 30°C and 1 atm.

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INTRODUCTION

Ladder polymers of the polybenzimidazobenzophenanthrolines (PBIPA) have been known for more than 20 years.¹ These polymers possess thermal stability at temperatures above 500°C and excellent mechanical properties and, therefore, have been investigated as high-performance polymers for use in advanced aerospace applications. The π conjugation and especially the significant π -orbital overlap expected for these highly packed polymers may lead to enhancement in optical nonlinearities.²⁻⁴ High conductivity in polymers is achieved by doping or pyrolysis methods,⁵⁻⁷ making use of their conjugated structure.

Customarily, PBIPAs were synthesized according to the literature procedure,⁸ namely, by condensation of 1,4,5,8-naphthalenetetracarboxylic acid (NTCA) with tetraamines in poly(phosphoric acid) (PPA) under an inert atmosphere at high temperature followed by the troublesome procedure of the isolation of the polymer from PPA.

In this article, we report a synthetic procedure commonly used for the preparation of polyimide, i.e., the condensation of 1,4,5,8-naphthalenetetra-

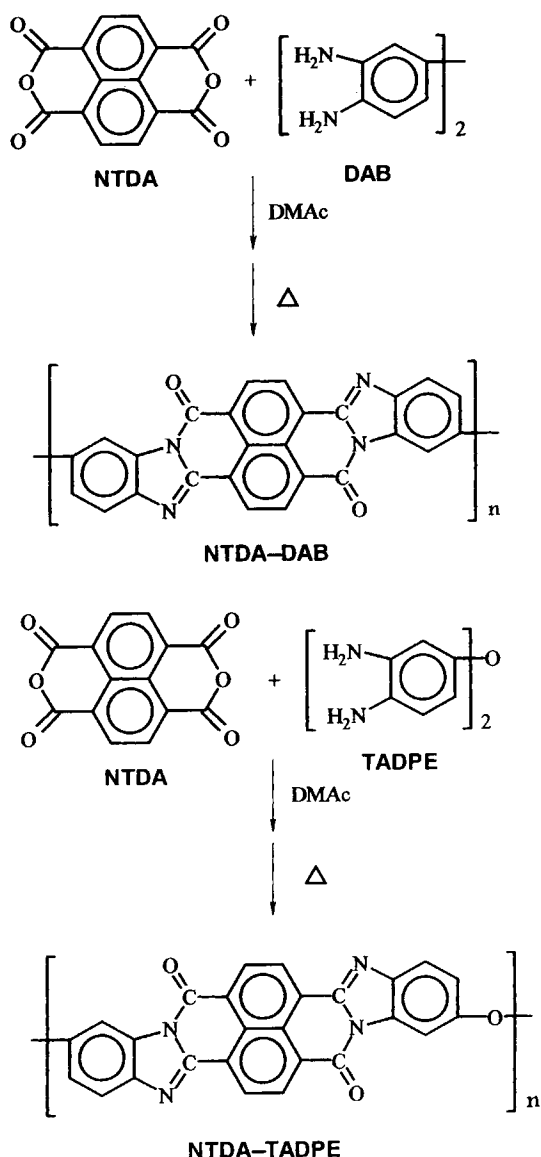
carboxylic dianhydride (NTDA) with aromatic tetraamines in *N,N'*-dimethylacetamide (DMAc) at room temperature to produce the precursor of PBIPA. These films could be obtained by casting the solution of the precursor on a glass plate followed by cyclopolymerization through heat treatment. Two types of polymers, NTDA-3,3'-diaminobenzidine (DAB) and NTDA-3,3',4,4'-tetraaminodiphenyl ether (TADPE) were synthesized by this method. Using this method, the synthesis of PBIPAs appeared to be convenient. The gas-separation property of these two polymer membranes was determined.

EXPERIMENTAL

Polymer Synthesis

The polymer synthesis is shown in Scheme 1. Stoichiometric amounts of NTDA and DAB or TADPE at a concentration of 10% solids in DMAc were magnetically stirred in a round-bottom flask with a stopcock at room temperature. The reaction solution turned homogeneous as the reaction proceeded. After 1-2 days, the viscosity of the polymer precursor increased. The solution of the precursor was filtered at once and cured at high temperature before gelation. Inherent viscosities of 0.89 and 0.77 dL/g, respectively, for precursors of NTDA-TADPE and

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Scheme 1 Synthesis of NTDA-DAB and NTDA-TADPE.

NTDA-DAB were measured at a concentration of 0.5 g/dL in DMAc at 30°C.

Film Preparation

Polymer films were prepared by casting the appropriate volume of the polymer precursor solution on a clean glass plate, followed by heating on a hot plate at 85°C for 1 h to evaporate most of the solvent. Then, the glass plate was put into an oven while the temperature was gradually increased to 300°C and kept at that point for 3 h by a slow flow of argon

into the oven. After cooling, the films were removed from the glass plate by soaking in water and dried.

POLYMER CHARACTERIZATION

IR spectroscopy was used to determine the degree of cure of PBIPA. Spectra were obtained on films prepared on KBr tablets with a Perkin-Elmer 683 infrared spectrophotometer. The polymer films for UV-vis spectra on a Hitachi 340 recording spectrophotometer were prepared on silica glass. Thermogravimetric analyses were performed on a Perkin-Elmer TGA 7 thermogravimetric analyzer at 10°C/min in air or nitrogen. Mechanical property measurements were performed on an Instron 1122 tester at a strain rate of 10 mm/min using polymer films at room temperature. The gas permeability property was measured with an RSK Model K-315N-01 gas transmission rate measurement apparatus produced by RSK Rikaseiki Kogyo Co.

RESULTS AND DISCUSSION

Polymer Properties

The thermal stability of NTDA-DAB and NTDA-TADPE polymers appeared excellent. Thermogravimetric analyses (TGA) curves for two types of polymers in air and nitrogen are shown in Figure 1. From this, it can be seen that the presence of an ether bond in the NTDA-TADPE polymer appears to have little detrimental effect on the thermal stability, especially in air. The decomposition temperature of both types of polymers are all above 600°C either in air or nitrogen.

Mechanical properties of polymer films are given in Table I. As we can see, both types of polymer films exhibited excellent tensile strength, and NTDA-TADPE polymer film possessed a higher elongation at break than that of the NTDA-DAB film due to the ether linkage in its polymer repeat unit.

Polymer Characterization

PBIPA films appeared black and silvery with low light transmittance. It can reflect images as does a mirror. The appearance suggested that a high degree of conjugation existed in these two polymers.

An elemental analysis for NTDA-TADPE and NTDA-DAB was done.

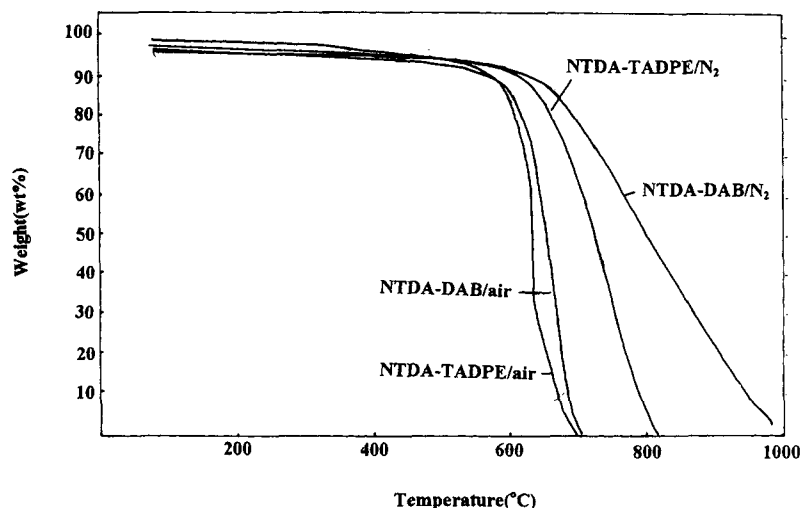


Figure 1 TGA of NTDA-DAB and NTDA-TADPE polymers. The rate of heating is 10°C/min in N₂ and air.

NTDA-TADPE:

ANAL: Calcd for C₂₆H₁₀N₄O₃: C, 73.24%; H, 2.35%; N, 13.15%.

Found: C, 69.29%; H, 3.03%; N, 12.47%.

NTDA-DAB:

ANAL: Calcd for C₂₆H₁₀N₄O₂: C, 76.09%; H, 2.46%; N, 13.65%.

Found: C, 70.76%; H, 3.15%; N, 12.19%.

The samples were heated again for 2 h at 400°C under argon.

Found for NTDA-TADPE: C, 70.14%; H, 2.72%; N, 12.30%.

Found for NTDA-DAB: C, 72.31%; H, 2.76%; N, 12.65%.

It should be pointed out that the elemental analyses were not in complete agreement with calculated values for a fully cyclized structure. This is not uncommon for highly fused aromatic heterocyclic

polymers. The elemental analyses for the elements carbon and nitrogen of NTDA-DAB is comparable with that of the literature.⁸

Figure 2 shows the IR spectra of NTDA-TADPE and NTDA-DAB polymers. The spectra of these two polymers were similar except that ether absorption was observed in the IR spectrum of the NTDA-TADPE polymer. The IR spectrum of NTDA-DAB (called BBB in the literature) is almost the same as that in the literature.⁸ Absorption in the 3500 and 1780 cm⁻¹ regions, which were also shown in the literature,⁸ are believed to be due to incomplete cyclization, nonlinear branching, or anhydride end groups.

Figure 3 shows the UV-vis spectra of the thin films of NTDA-TADPE and NTDA-DAB on silica substrates. By comparison, the UV-vis spectrum of PMDA-TADPE (derived from pyromellitic dianhydride PMDA and TADPE) is also shown in Figure 3. It can be seen that the spectra of NTDA-derived polymers were greatly red-shifted from that of

Table I Properties of Polymers

Polymers	Decomposition Temperature (°C)		Tensile Strength (kg/cm ²)	Elongation at Break (%)
	Air	N ₂		
NTDA-TADPE	614	619	1550	6.0
NTDA-DAB	626	636	1410	4.0

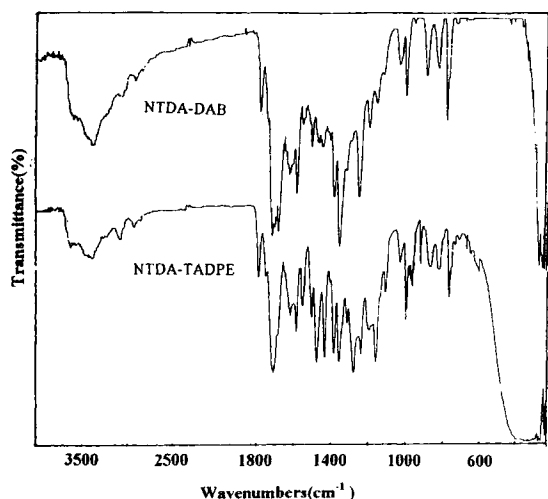


Figure 2 IR spectra of NTDA-DAB and NTDA-TADPE polymers.

PMDA-TADPE except for the absorption band at the 220 nm region. It would suggest that the π -electron delocalation of NTDA-derived polymers is greater than that of the PMDA-derived polymer.

The UV spectra of both types of NTDA-derived polymers are almost the same except that the UV spectrum of NTDA-DAB showed a slight red shift compared with that of NTDA-TADPE, which can be explained by the difference in structure of both types of polymers.

Permeation Property

Gases permeate through a nonporous polymer membrane by a solution-diffusion process. The permeability, P , can be written as the product of an effective solubility of the penetrant in the polymer matrix, S , and the diffusivity coefficient of the penetrant in the polymer matrix, D , as shown in eq. (1)^{9,10}:

$$P = DS \quad (1)$$

The ideal separation factor α , which is an index of the overall selectivity of a polymer, can be expressed in terms of eq. (2):

$$\alpha = \frac{P(A)}{P(B)} \quad (2)$$

where $P(A)$ and $P(B)$ are the permeability for gases A and B.

The mean intersegmental distance was taken to be represented by the d -spacing obtained from the maxima in wide-angle X-ray diffraction spectra, as suggested by O'Brien et al.¹¹ This distance was measured to be 3.5 and 3.4 Å, respectively, for NTDA-TADPE and NTDA-DAB.

The permeability, diffusivity, and solubility coefficient data measured at 30°C and 1 atm for H₂, O₂, and N₂ for these two types of polymers are summarized in Tables II-IV. The apparatus and experimental procedure used to measure permeability were described elsewhere.^{12,13}

The films for the gas permeability measurement were prepared at a cure temperature of 300°C for 3 h. The gas permeability of NTDA-DAB is substantially higher than that of NTDA-TADPE, whereas the selectivity of the former polymer is slightly lower than that of the latter. The higher permeability of NTDA-DAB relative to that of NTDA-TADPE depends on both solubility and diffusivity contributions, and the former tends to be the dominant factor. The solubility of all gases in NTDA-DAB is about twice of that in NTDA-TADPE, whereas the increase of diffusivity of NTDA-DAB over that of NTDA-TADPE ranges from 20 to 60%. The wide-angle X-ray diffraction measurement also shows that these two types of polymers contained similar packing densities.

CONCLUSIONS

The present method for the synthesis of polybenzimidazobenzophenanthrolines exhibited ad-

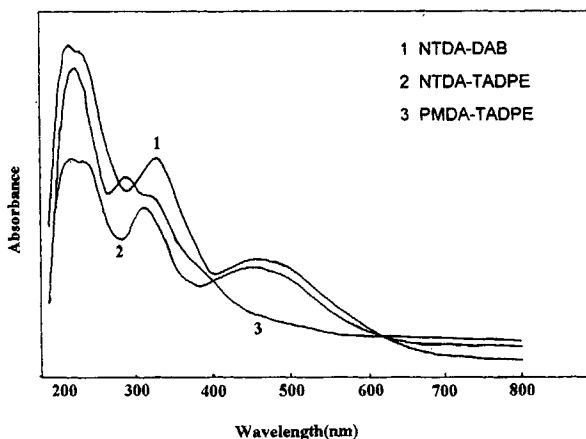


Figure 3 UV-vis spectra of NTDA-DAB and NTDA-TADPE polymers.

Table II Permeability Coefficient and Perselectivity of Polymers

Polymer	P_{H_2}	P_{O_2}	P_{N_2}	α_{H_2/N_2}	α_{O_2/N_2}
NTDA-TADPE	6.00	0.314	0.041	146	7.7
NTDA-DAB	14.9	0.862	0.121	123	7.1

Unit: 10^{-10} cm³ (STP) cm/cm² s cmHg.**Table III Diffusivity Coefficient and Diffusivity Selectivity of Polymers**

Polymer	D_{H_2}	D_{O_2}	D_{N_2}	D_{H_2}/D_{N_2}	D_{O_2}/D_{N_2}
NTDA-TADPE	4680	26.2	2.83	1654	9.26
NTDA-DAB	5610	33.0	4.50	1247	7.33

Unit: 10^{-10} cm²/s.**Table IV Solubility Coefficient and Solubility Selectivity of Polymers**

Polymer	S_{H_2}	S_{O_2}	S_{N_2}	S_{H_2}/S_{N_2}	S_{O_2}/S_{N_2}
NTDA-TADPE	1.28	12.0	14.4	0.089	0.83
NTDA-DAB	2.66	26.1	27.0	0.099	0.97

Unit: 10^{-3} cm³ (STP)/cm³ cmHg.

vantages in a mild reaction condition and convenient separation of polymers from the solvent, especially in the preparation of films. The permeability of H₂, O₂, and N₂ in NTDA-DAB is substantially higher than that in NTDA-TADPE. The difference in permeability depends on both solubility and diffusivity contributions.

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