

# Synthesis and Properties of Aromatic Poly(amine-amide)s Based on 4,4'-Dicarboxy-4''-(N-indolyl)triphenylamine

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## ABSTRACT

A series of novel aromatic poly(amine-amide)s with pendent *N*-phenylindole units having inherent viscosities of 0.75–1.28 dL/g were prepared via the direct phosphorylation polycondensation reaction of an indole-derived triphenylamine-containing dicarboxylic acid, 4,4'-dicarboxy-4''-(*N*-indolyl)triphenylamine, with various aromatic diamines. The poly(amine-amide)s were readily soluble in various organic solvents and could be cast into flexible and strong films. The polymer films have good thermal stability with glass-transition temperatures of 254–316 °C and 10% weight loss temperature in excess of 500 °C. These polymers showed ultraviolet visible absorption maxima at 337–353 nm and blue fluorescence emission maxima at 449–465 nm in *N*-methyl-2-pyrrolidinone solution with fluorescence quantum yields ranging from 1.0% to 15.0%. Cyclic voltammograms of the poly(amine-amide) films prepared by casting polymer solutions onto the indium tin oxide coated glass substrate exhibited one oxidative redox couple around 1.10–1.21 V (oxidation half-wave potential) versus Ag/AgCl in an acetonitrile solution.

## INTRODUCTION

Triaryl amines have attracted considerable interest as hole transport materials for use in multilayer organic electroluminescence (EL) devices due to their relatively high mobilities and their low ionization potentials.<sup>1,2</sup> The feasibility of utilizing spin-coating and ink-jet printing process for large-area EL devices and possibilities of various chemical modifications (to improve emission efficiencies and allow patterning) make polymeric materials containing triarylamine units very attractive.<sup>3–4</sup> To enhance the hole injection ability of polymeric emissive materials such as poly(1,4-phenylenevinylene)s (PPV) and polyfluorenes (PF), there have been several reports on PPV and PF derivatives involving hole-transporting units such as triarylamine or carbazole groups in the emissive  $\pi$ -conjugated core/main chains<sup>5,6</sup> or grafting them as side chains in a polymer<sup>7</sup> or attaching them onto the polymer chain-ends or the outer surface of dendritic wedges.

Indole is an aromatic heterocyclic organic compound. It has a bicyclic structure, consisting of a six-membered benzene ring fused to a five-membered nitrogen-containing pyrrole ring. The indole structure can be found in many organic compounds like the amino acid tryptophan and in tryptophan-containing protein, in alkaloids, and in pigments. Certain indole derivatives were important dyestuffs until the end of the 19th century. In the 1930s, interest in indole intensified when it became known that the indole nucleus is present in many important alkaloids, as well as in tryptophan and auxins, and it remains an active area research today.<sup>8</sup> To the best of our knowledge, there have never been attempts to incorporate the indole structure into high-performance polymers. Herein we describe the preparation of the novel indole-based diamine monomers, 4,4'-dicarboxy-4''-(*N*-indolyl)triphenylamine, and its derived poly(amine-amide)s containing the electro-rich triphenylamine core with indolyl *para*-substituted on the pendent phenyl ring. The general properties of the resulting polymers such as inherent viscosities, solubility, film-forming ability, crystallinity, thermal properties, electrochemical behavior, and photoluminescence are also reported. The incorporation of bulky, three-dimensional *N*-indolyltriphenylamino moiety was expected to hinder close chain packing and provided enhanced solubility in organic solvents. In addition, the indole group in each repeat unit allows chemical modification for specific application; for example, through electrophilic substitution or electrochemical coupling.

## MONOMER SYNTHESIS

### Synthesis of 4,4'-Dicarboxy-4''-(*N*-indolyl)triphenylamine (4)

The new bulky indole-substituted triphenylamine-containing dicarboxylic acid monomer 4 was successfully synthesized by the alkaline hydrolysis reaction of the dinitrile compound, 4,4'-dicyano-4''-(*N*-indolyl)triphenylamine (3), which was resulted from the condensation reaction of *N*-(4-aminophenyl)indole (2) with 4-fluorobenzonitrile in dried DMSO using sodium hydride as the strong base (Scheme 1). IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic techniques were used to identify the structures of the dinitrile intermediate and the dicarboxylic acid monomer. The IR spectra (Figure 1) of dinitrile compound 3 gave a characteristic sharp peak at 2225 cm<sup>-1</sup> peculiar to the cyano group. After hydrolysis, the characteristic absorption of the cyano group disappeared, and the carboxylic acid group showed a typical carbonyl absorption band at 1680 cm<sup>-1</sup> (C=O stretching) together with the appearance of broad bands in the region of 2700–3400 cm<sup>-1</sup> (OH stretching) (Figure 1). Figure 2 illustrates the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the targeted dicarboxylic acid monomer. Assignments of each carbon and proton are assisted by the two-dimensional NMR spectra, and these spectra agree well with the proposed molecular structure of diacid monomer 4.

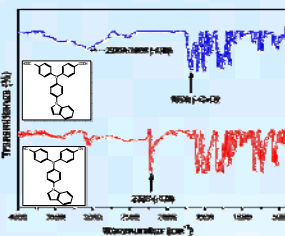
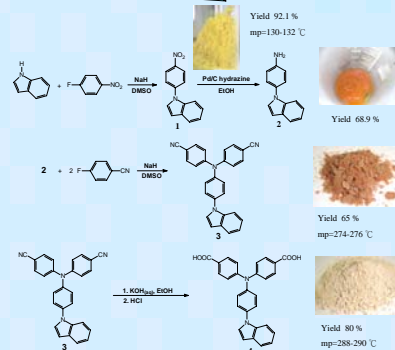


Figure 1. IR spectra of compound 3 and 4.

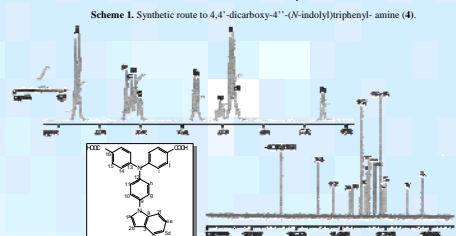
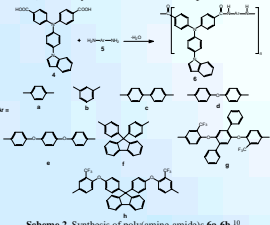


Figure 2. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of target dicarboxylic acid monomer 4 in DMSO-*d*<sub>6</sub>.

## POLYMER SYNTHESIS AND SOLUBILITY

A typical example for polymerization is as follows. A mixture of equimolar amounts (1.0 mmol) of the dicarboxylic acid monomer 4 (0.4485 g) and 9,9-bis(4-aminophenyl)fluorene (5) (0.3485 g), 1.5 mL of NMP, 0.2 g of CaCl<sub>2</sub>, 1.2 mL of TPP, and 0.3 mL of pyridine was heated with stirring at 120 °C for 3 h. The resulting viscous solution was poured slowly with stirring into 150 mL of methanol, giving rise to a fibrous precipitate. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried to give a quantitative yield of poly(amine-amide) 6f. The inherent viscosity of the polymer was 0.76 dL/g, measured in DMAc (containing 5 wt % LiCl) at a concentration of 0.5 g/dL at 30 °C. The other poly(amine-amide)s were synthesized in a similar procedure.



Scheme 2. Synthesis of poly(amine-amide)s 6a-6h.<sup>10</sup>

Polymer	$\eta_{inh}$ (dL/g)	Solubility <sup>a</sup>						
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	
6a	0.79	(+) <sup>b</sup>	(+)	(+)	(+)	(+)	(-)	
6b	0.75	(+)	(+)	(+)	(+)	(+)	(-)	
6c	0.95	(+)	(+)	(+)	(+)	(+)	(-)	
6d	1.80	(+)	(+)	(+)	(+)	(+)	(-)	
6e	0.79	(+)	(+)	(+)	(+)	(+)	(-)	
6f	0.76	(+)	(+)	(+)	(+)	(+)	(-)	
6g	0.86	(+)	(+)	(+)	(+)	(+)	(+)	
6h	0.85	(+)	(+)	(+)	(+)	(+)	(+)	

<sup>a</sup> Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc/5 wt % LiCl at 30°C.  
<sup>b</sup> Solubility: (+) soluble at room temperature; (-) insoluble even on heating.  
<sup>c</sup> Solvent: NMP; *N*-methyl-2-pyrrolidinone; DMAc; *N,N*-dimethylacetamide; DMF; *N,N*-dimethylformamide; DMSO; dimethyl sulfoxide; THF; tetrahydrofuran.  
<sup>d</sup> Data in parentheses are those of analogous poly(amine-amide)s 6<sup>c</sup> having the corresponding diamine residue as in the 6 series.

## THERMAL STABILITY

Table 2. Thermal properties of poly(amine-amide)s

Polymer	$T_g$ at 5% weight loss / $T_g$ at 10% weight loss / °C		$T_d$ at 5% weight loss / $T_d$ at 10% weight loss / °C		Char yield (wt%) <sup>c</sup>		
	In N <sub>2</sub>	In air	In N <sub>2</sub>	In air			
6a	285 (294) <sup>a</sup>	280	514	509	602	556	73
6b	258 (269)	245	424	435	505	521	80
6c	274 (292)	264	441	452	540	532	78
6d	254 (264)	250	426	463	516	540	74
6e	255 (251)	255	456	507	541	562	70
6f	305 (316)	303	477	522	536	594	73
6g	266 (250)	250	470	515	556	577	70
6h	277 (250)	265	487	493	564	549	70

<sup>a</sup> Midpoint temperature of baseline shift on the second DSC heating scan (rate 20 °C/min) of the sample after quenching from 400 °C.  
<sup>b</sup> Softening temperature measured by TMA using a penetration method.  
<sup>c</sup> Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.  
<sup>d</sup> Residual weight percentages at 800 °C under nitrogen flow.  
<sup>e</sup> Values in parentheses are data of analogous poly(amine-amide)s 6<sup>c</sup> having the corresponding diamine residue as in the 6 series.

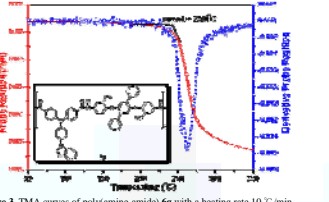


Figure 3. TMA curves of poly(amine-amide) 6g with a heating rate 10 °C/min.

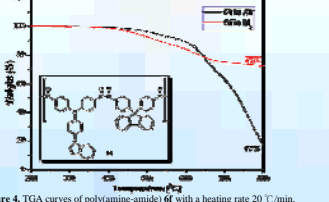


Figure 4. TGA curves of poly(amine-amide) 6f with a heating rate 20 °C/min.

## OPTICAL AND ELECTROCHEMICAL PROPERTIES

Table 3. Optical and Electrochemical properties of Polyamide

Index	Solution <sup>a</sup>		$\eta_{inh}$ (dL/g)	Film		$E_{ox}(V)^b$		$E_{red}(V)^c$	Band Gap (eV)	HOMO / LUMO (eV) <sup>d</sup>
	$\lambda_{max}$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )		$\lambda_{max}$ (nm)	$\epsilon$ (L mol <sup>-1</sup> cm <sup>-1</sup> )	(vs. Ag/AgCl)	(vs. Ag/AgCl)			
6a	349	449	1.0	399	464	1.17	1.18, 1.52	2.67	5.53 / 2.86	
6b	339	455	9.0	387	432	1.21	1.23, 1.55	3.00	5.57 / 2.57	
6c	353	454	3.0	404	459	1.21	1.29, 1.66	2.91	5.57 / 2.98	
6d	341	458	4.0	389	426	1.20	1.24, 1.53	2.91	5.56 / 2.65	
6e	338	455	6.0	396	440	1.18	1.19, 1.62	2.82	5.54 / 2.76	
6f	339	457	14.0	406	461	1.10	1.15, 1.39	2.59	5.46 / 2.90	
6g	337	464	15.0	410	459	1.10	1.17, 1.35	2.70	5.46 / 2.76	
6h	340	465	12.0	412	456	1.11	1.20, 1.37	2.60	5.47 / 2.87	

<sup>a</sup> Polymer concentration of 1.0 × 10<sup>-3</sup> mol/L in NMP.  
<sup>b</sup> UV-vis absorption measured in NMP (1 × 10<sup>-3</sup> mol/L) at room temperature.  
<sup>c</sup> CV spectra measurements in NMP (1 × 10<sup>-3</sup> mol/L) at room temperature.  
<sup>d</sup> Oxidation half-wave potentials ( $E_{ox}$ ) from cyclic voltammograms.  
<sup>e</sup> Oxidation peak potential ( $E_p$ ).  
<sup>f</sup> The data were calculated with the following equation:  $Gap = |E_{ox} - E_{red}|$  (eV).  
<sup>g</sup> The HOMO energy levels were calculated from CV and were referenced to ferrocene (4.8 eV). LUMO = HOMO-Gap.

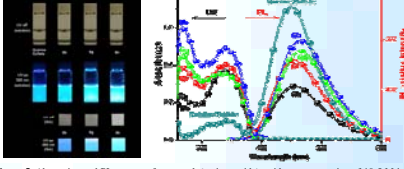


Figure 5. Absorption and PL spectra of some poly(amine-amide)s with a concentration of 10<sup>-5</sup> M in NMP. The photograph shows the physical appearance of polymer solution (10<sup>-5</sup>M) and thin films (thickness: 5–10 μm) before and after exposure on UV irradiation (excited at about 365 nm). Quinine sulfate dissolved in 1N H<sub>2</sub>SO<sub>4</sub> (aq) (10<sup>-5</sup> M) was used as the standard ( $\Phi_F = 0.546$ ).

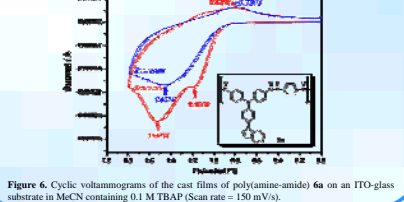


Figure 6. Cyclic voltammograms of the cast films of poly(amine-amide) 6a on an ITO-glass substrate in MeCN containing 0.1 M TBAP (Scan rate = 150 mV/s).

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