

Synthesis and Fluorescence Properties of Aromatic-Aliphatic Copolyamides

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ABSTRACT: The aromatic-aliphatic copolyamides were synthesized by condensation polymerization of aromatic diamine PPD (or APS, where PPD is *p*-phenylene diamine and APS is aminophenyl sulfone), aliphatic diamine HDA (or EDA, where HDA is hexanediamine and EDA is ethylenediamine), and TPC (where TPC is terephthalyl chloride) with different molar ratios of aromatic diamine to aliphatic

diamine. The steady-state fluorescence of these condensed copolymers was investigated. These copolyamides exhibit strong blue-to-green fluorescence. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 315–321, 2005

Key words: aromatic-aliphatic copolymer; copolymerization; conjugated polymers; fluorescence

INTRODUCTION

π -conjugated polymers have received considerable attention because of their potential applications in nonlinear devices and in light-emitting diodes.^{1–21} For the light-emitting devices, the polymers must exhibit strong fluorescence and possess device efficiency, material stability, and excellent processing property. Short, rigid, conjugated polymers, or oligomers, generally emit strong fluorescence with higher fluorescence quantum yield, but they are brittle materials and lack needed fabrication properties. Polymers with a large scope of effective conjugation or high molecular weight may possess very good machining property but show poor solubility and low-luminescence quantum yield. Copolymers offer an attractive feature in the control of the chain structures, which allows polymers to possess suitable effective conjugated length, chain flexibility, and good solubility.

We reported here the preparation and fluorescence properties of aromatic-aliphatic copolyamides, which contain both blocks of rigid π -conjugated component and blocks of soft segment in the same polymer chain (Scheme 1). These copolyamides not only exhibit strong blue-to-green fluorescence but also possess excellent solubility in most of the organic solvent.

EXPERIMENTAL

Instrumentation

Fluorescence excitation and emission spectra were recorded at room temperature on a Shimadzu RF-540 fluorescence spectrophotometer (Kyoto, Japan). Elemental analysis was performed on a Carlo-Erba 1106 elemental analyzer (Milano, Italy). Molecular weight determination was carried out by using a capillary viscometer at 25°C; formic acid was used as solvent. Infrared spectra were obtained on a Shimadzu Alpha-Centauri FTIR infrared spectrophotometer (KBr disks Shimadzu, Kyoto, Japan). Ultraviolet absorption spectra were taken by using a Hitachi UV-3400 ultraviolet-visible spectrophotometer (Tokyo, Japan).

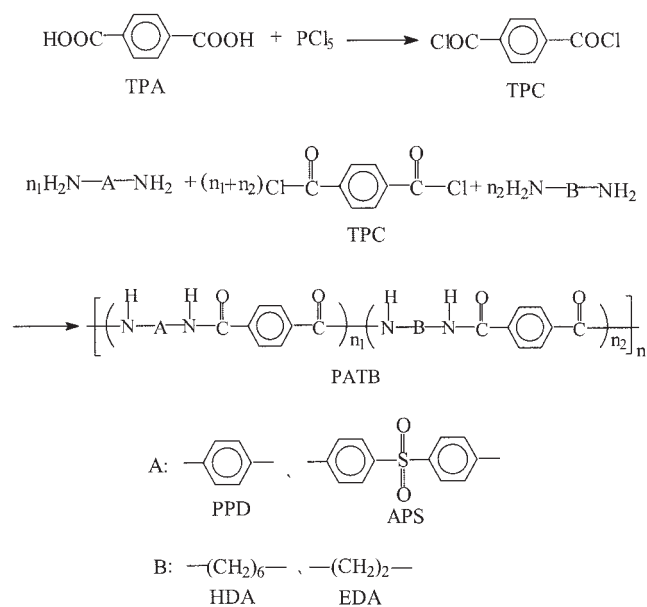
Materials

Ethylenediamine (EDA) was distilled before use. All other reagents and solvents were purchased from commercial sources and used as received unless noted otherwise.

Preparation of the terephthalyl chloride (TPC)

TPC was prepared according to the procedure described in the literature.²² A mixture of terephthalic acid and phosphorus chloride, PCl_5 (molar ratio = 1 : 2), was heated to 110°C and refluxed for 1 min to give yellow crystal. The resulting mixture was then cooled down and petroleum ether (60–90°C fraction) was added and heated until the yellow crystal was completely dissolved. The mixture was filtered, and the filtrate was then cooled to room temperature to give a yellow crystal product, melting point (m.p.) 83–84°C.

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Scheme 1 Synthetic pathway.

Preparation of the copolymers²³

A mixture of lithium chloride, LiCl (0.2 g, 4.72 mmol), and *N,N'*-dimethylacetamide, DMAC (10 mL), was stirred at room temperature under nitrogen until all LiCl was dissolved. A solution of hexanediamine, HDA (0.12 g, 1.03 mmol), in DMAC (3 mL) was added. The reaction mixture was heated to 100°C and stirred for 0.5 h. Then the mixture was cooled to -10°C and a solution of TPC (0.4 g, 1.96 mmol) in DMAC (3 mL) was added and stirred for 0.5 h at room temperature, *p*-phenylene diamine, PPD (0.1 g, 0.93 mmol), in DMAC (5 mL) was then added and stirred at room temperature for 1 h, at 40°C for 1 h, at 60°C for 2 h, at

80°C for 1 h, respectively, and finally stirred at room temperature overnight. The color of the reaction mixture was different because of the variation of the molar ratio of the reactant. Different precipitant was used to get copolyamides HDA-*co*-TPC-*co*-PPD (abbreviated as PHTP) with a different molar ratio of HDA to PPD (e.g., water was used as the precipitant when the molar ratio of HDA to PPD was 1 : 9–4 : 6; methanol was used as the precipitant when the molar ratio of HDA to PPD was 1 : 1, respectively).

Other copolyamides, EDA-*co*-TPC-*co*-APS (PETA), HDA-*co*-TPC-*co*-APS (PHTA), and EDA-*co*-TPC-*co*-PPD (PETP), were prepared using the same procedure described above.

DISCUSSION

IR analysis

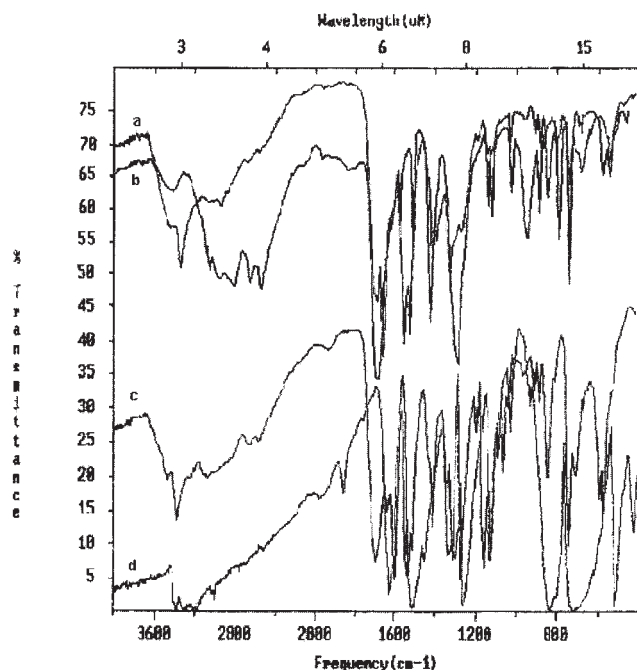
The IR data for monomers PPD, TPC, copolyamides TPC-PPD, HDA-TPC, EDA-TPC, APS-TPC, PETP, PETA, and PHTP are listed in Table I. The appearance of new bands at 1526–1575 cm⁻¹, which is the characteristic of $\nu_{\text{C-N}}$ absorption in the IR spectra of the copolyamides, indicates the formation of the C–N bonds. IR spectra of some compounds are shown in Figure 1.

UV analysis

UV absorption spectra from the solution of copolymers in dimethyl sulfoxide (DMSO) were recorded and shown in Table II and Figure 2. Compared to those of the corresponding monomers, the absorption wavelengths from the copolymers were different. Shifts appeared in the spectra of the copolymers. This

TABLE I
IR Analysis Data of the Copolyamides

Compound	δ	δ_{NH_2}	ν_{NH_2}	$\nu_{\text{C=O}}$	δ	$\nu_{\text{C-N}}$	ν_{CH_2}	ν
PPD	835	1513	3307		1042			1630
TPC	854			1725	1016			1573
TPD-PPD	820	1545	3320	1650	1015	1265		1611
		1265				1545		
HDA-TPC	829	1502	3306	1638	1018	1557	2862	1587
EDA-TPC	791	1501	3306	1702	1016	1549	2806	1633
APS-TPC	833	1526	3368	1688	1016	1526	$\nu_{\text{S=O}}$ 1108 1146	1629
PETP	827	1502	3305	1734	1017	1584	2932	1637
PETA	826	1501	3417	1685	1018	1585	2890	1572
							$\nu_{\text{S=O}}$ 1153	
PHTP (1 : 9)	881	1509	3065	1688	1018	1574	2814	1609
PHTP (3 : 7)	881	1510	3488	1688	1019	1510	2824	1575
PHTP (1 : 1)	830	1518	3331	1696	1017	1546	2936	1610



a: PTPH(1:1) b: PHTP (3:7) c: APS-TPC d: PPD

Figure 1 IR spectra of compounds.

suggested that there exist some changes of effective conjugated range in the copolyamide chain. The variation of the molar ratio of aromatic to aliphatic diamine in the copolymers also led to changes in their UV absorption spectra. The result indicates that the molar ratio of aromatic to aliphatic diamine in the copolymers may influence the range of effective π -conjugation in the copolymer chain. This result also suggests that we can improve the fluorescence, solubility, or

TABLE II
UV Analysis Data of Monomers
and Several Copolyamides^a

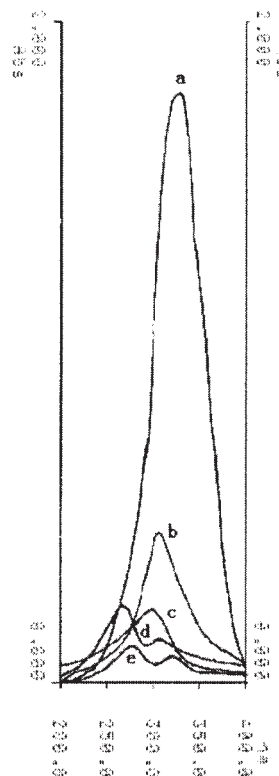
Compound	PPD	TPC	PHTP (1:9)	PHTP (1:1)	PHTP (9:1)
λ_{\max_1}	332	302	280	269	281
λ_{\max_2}			320	310	325

^a UV spectra were recorded at room temperature in DMSO.

TABLE III
Element Analysis Data and Molecular Weight of the Copolyamides^a

Polymer	C%	H%	N%	\bar{M}_p
PHTP	68.75 (69.42)	6.07 (5.79)	11.06 (11.57)	3.79×10^4
PHTA	64.55 (65.38)	5.86 (5.13)	8.66 (8.97)	2.53×10^3
PETA	63.20 (63.38)	4.61 (4.32)	10.57 (9.86)	3.03×10^3
PETP	67.09 (67.29)	4.05 (4.67)	13.19 (13.08)	2.52×10^4

^a Calculated values are shown in parentheses.



a: PPD b: PHTA c: HDA d: PHTP(1:1) e: PHTP(1:9)

Figure 2 UV spectra of monomers and several copolyamides.

processing properties of the copolyamides by employing different molar ratios of aromatic to aliphatic diamine. Consequently, we can get copolymers that contain both blocks of rigid π -conjugated component and blocks of soft segment in the same polymer chain and which not only exhibit strong blue-to-green fluorescence but also possess excellent solubility in most of the organic solvents.

Element analysis and molecular weight determination²⁴

The elemental and molecular weight analytical results are shown in Table III. The experiment results are in accordance with the calculated values. This suggests

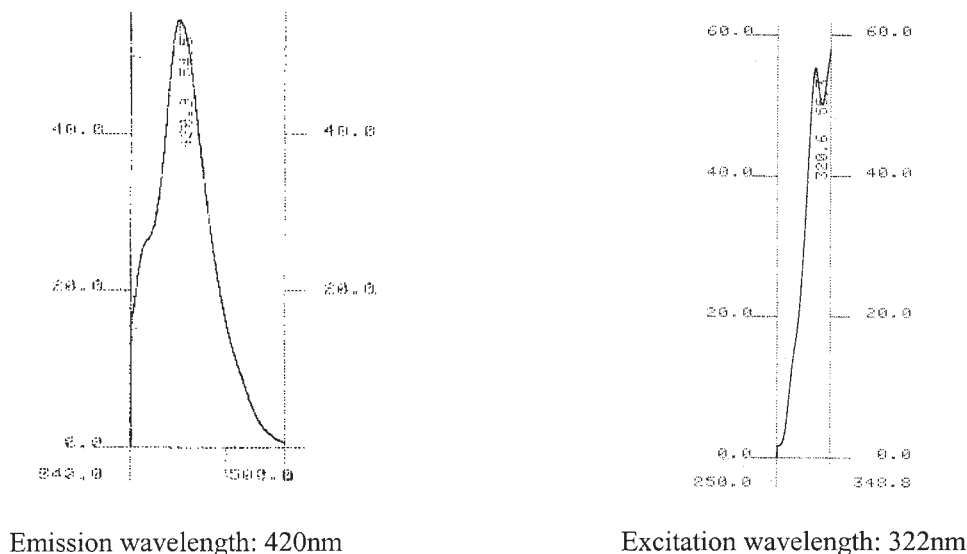


Figure 3 Fluorescence spectra of DMSO.

that the copolyamides contain expected rigid moiety and soft component in their main-chain construction.

Solubility of the copolyamides

All reported copolyamides, PHTP, PHTA, PETA, and PETP, possess good solubility in polar organic solvents such as DMAC, dimethylformamides (DMF), DMSO, and tetrahydrofuran (THF). The solubility of these copolyamides could be improved or modified by using different molar ratios of diamine of aromatic to aliphatic. The solubility would be generally enhanced by using more aliphatic diamine in the reactions. Solubility is a very important factor to be considered in patterning thin films or devices for photo/electroluminescence.

Fluorescence properties

The steady-state fluorescence both in solution and in solid was investigated. The excitation and emission spectra were taken at room temperature. The results are shown in Figures 3–11.

Fluorescence in solution

DMSO itself emits fluorescence, but the intensity is much lower than that of monomers PPD and TPC, as is shown in Figure 3 and 4. Both in intensity and in emission wavelengths, the fluorescence spectra of copolyamides are distinguished from those of the corresponding monomers PPD and TPC from which the copolymers were formed.

Effect of the molar ratio of aromatic to aliphatic diamine

Because the reaction of terephthalyl chloride with diamine belongs to the category of the Schotten–Baumann reaction, which generally need very low activation energy,²⁵ the component molar ratio of aromatic to aliphatic in the copolyamide chain is basically consistent with that in the corresponding reaction. As shown in Figure 5, the fluorescence intensity was changed with the variation of the molar ratio of aromatic to aliphatic in the reaction; this can also be described as the fluorescence intensity changing with the variation

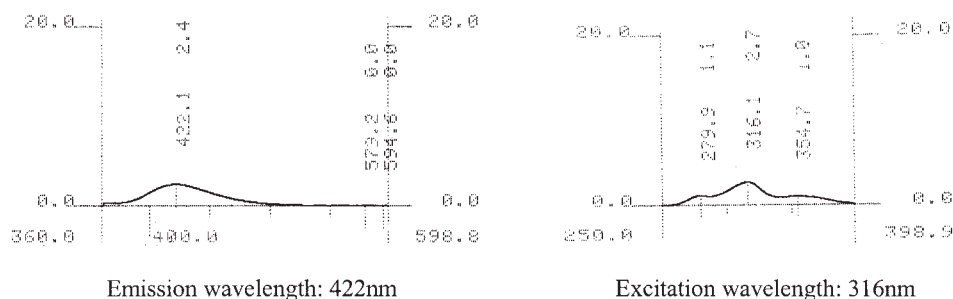


Figure 4 Fluorescence spectra of TPC in DMSO.

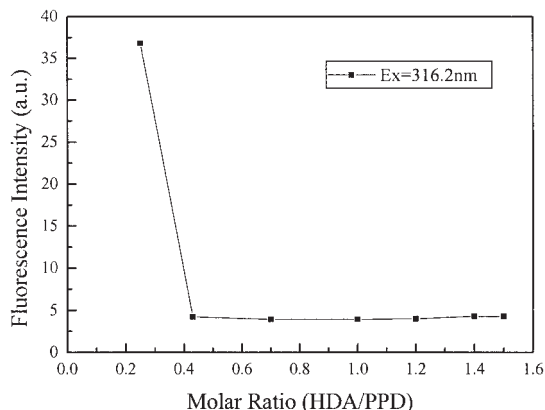


Figure 5 The relationship between molar ratio and fluorescence intensity in solution.

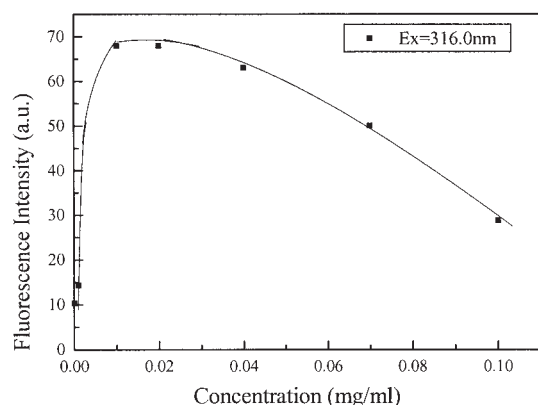


Figure 6 The relationship between concentration and fluorescence intensity of PHTP(HDA/PPD = 3 : 7).

of component molar ratio of aromatic to aliphatic in the copolymer chain. There are two kinds of segments in the copolyamide chain, one is soft component (consists of aliphatic diamine such as hexanediamine or ethylenediamine) and the other is rigid moiety (consists of aromatic diamine such as *p*-phenylene diamine or aminophenyl sulfone). The fluorescence intensity and wavelength or color of the copolymers is closely related to their rigid segments, whereas the solubility of the copolymers is determined by their soft component.

Also as shown in Figure 5, the fluorescence intensity first decreased with the increase of the molar ratio of HDA to PPD (from 0.25 to 0.43); then the fluorescence intensity slowly increased with the increase of the molar ratio (from 0.43 to 1.5). The molar ratio of aromatic to aliphatic segment in the copolymer chain may influence the effective range of conjugation or the degree or electron delocalization, consequently influencing fluorescence intensity and wavelength.

Effect of the concentration

Figures 6 and 7 show the dependence of the fluorescence intensity on the concentration of copolyamide PHTP(HDA/PPD = 3 : 7) in DMSO. The fluorescence intensity from the solution of PHTP in DMSO first increased with the increase of the concentration (from 0.0005 to 0.01 mg/mL) and then decreased with the increase of the concentration (from 0.01 to 0.1 mg/mL). This is attributed to the concentration quenching effect, which is related to the interaction between molecules in solution. In lower concentration, the distance is larger and the interactions between molecules are weaker. In this case, the fluorescent intensity is depen-

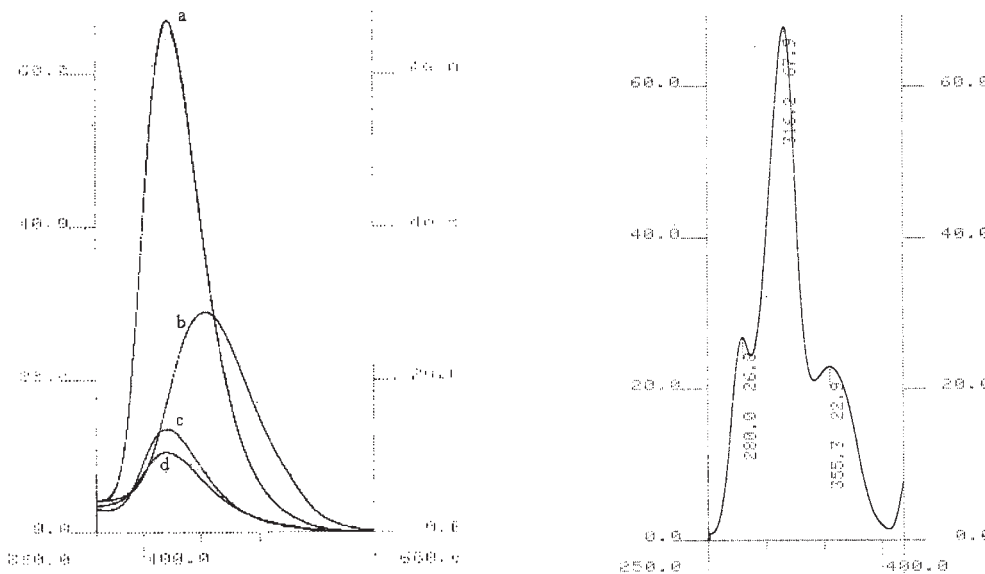


Figure 7 Fluorescence spectra of PHTP(HDA/PPD = 3 : 7) in DMSO.

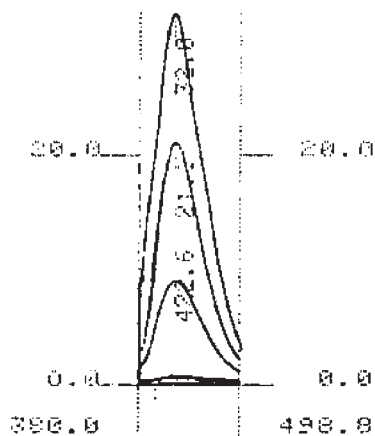


Figure 8 The relationship between concentration and fluorescence intensity of PHTA.

dent mainly on the single polymer molecular emission, and the strength of the emission will increase with the increase of the concentration (from 0.0005 to 0.01 mg/mL). In contrast in the higher concentration, the distance is smaller and the interactions are stronger between molecules. The relaxation from the excited states through nonradiative processes is enhanced with the increased interactions between the molecules; therefore, the emission intensity is decreased with the increase of the concentration (from 0.01 to 0.1 mg/mL).

When its concentration was 0.01 mg/ml, the copolymer PHTP(HDA/PPD = 3 : 7) exhibits strongest fluorescence excited at the same conditions. This indicates that the emitting center and the interactions between molecules are in their optimum conditions. In this concentration, the structure of the copolymer is also stable. Similarly, Figures 8 and 9 show the emission intensity is decreased with the increase of the concentration of PHTA.

Fluorescence in solid

The solid sample emission spectra were obtained at room temperature excited at 238 nm. The results are shown in Figure 10.

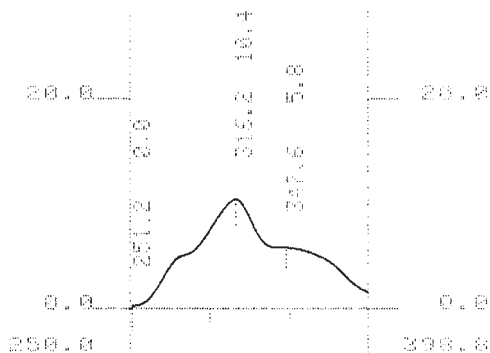


Figure 9 Fluorescence spectra of PHTA.

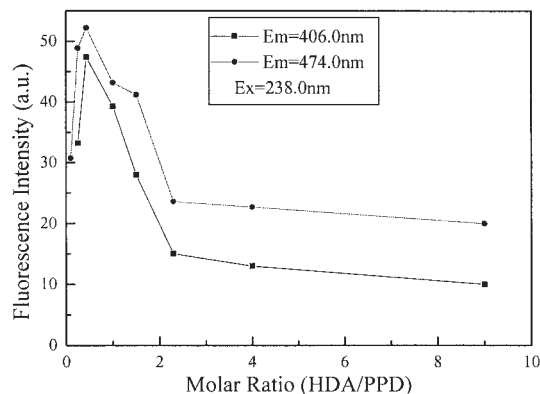


Figure 10 The relationship between molar ratio and fluorescence intensity of PHTP.

Effect of molar ratio

Figure 10 shows the relationship between molar ratio and fluorescence intensity of PHTP. The two curves indicate the emission intensities with varied molar ratios. It shows the fluorescence intensity of PHTP enhanced with increasing molar ratio when the molar ratio (HDA/PPD) ranged from 0.1 to 0.3. In copolyamides, the increase of the parasubstituted phenyl intensifies the fluorescence. One reason is that the paraphenyl effect can intensify the fluorescence; another reason is that band gap energy decreases, the rate of nonradiation increases, and thus, the fluorescence will be weak. So the common effect is the combination of two factors. The rate of soft and rigid fragment in the structure of copolyamides synthesized by a different molar ratio is different. The conjugation of appropriate range can intensify the fluorescence.

Comparison of four kinds of compounds

All synthesized copolyamides exhibit fluorescence at room temperature in the range of 402–469 nm that belongs to the blue–green fluorescence. As shown in Figure 11, the fluorescence intensity of copolyamides decreased from a to d; what is more, the maximum excitation wavelength of a, b is 233.5 nm and that of c, d is 238 nm, respectively. As seen by comparing a, b, c, and d, the fluorescence is enhanced with the addition of 1,4-phenylene in the copolyamide chain. Generally in a small range of effective π -conjugated system, the fluorescence intensity may increase following the addition of a paraposition phenyl ring to that system, but more phenyl ring led to the expansion of the π -conjugated system, which will result in the nonradiative decay, thus decreasing the fluorescence. The result we observed is the summation of the two effects.

CONCLUSION

Copolyamides that contain both blocks of rigid π -conjugated component and blocks of soft segment in the

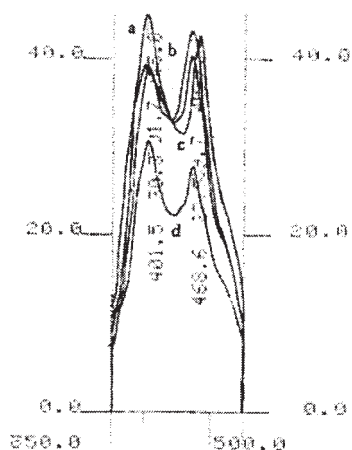


Figure 11 Fluorescence spectra of four kinds of compounds.

same polymer chain were synthesized in low temperature by using solution-condensed polymerization. The copolyamides were characterized by UV, IR, and elemental and molecular weight analysis. These copolymers not only exhibit strong blue-to-green fluorescence but also possess excellent solubility in most of the organic solvent.

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