

# Photoluminescence and Excimer Emission of Functional Groups in Light-Emitting Polymers

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**ABSTRACT:** Near-UV and blue-light-emitting polymers were synthesized with luminescent functional groups in the side chains or in the polymer main chain. The unsubstituted fluorophores, 2,5-diphenylfuran, 2-phenylbenzoxazole, and triphenylamine, do not form excimers in solution; however, in the case of polymers, excimer emission was negligible only with 2-phenylbenzoxazole derivatives. The monomers as well as the polymers, poly(2-(4-vinylphenyl)-benzoxazole), poly{*N*-(4-benzoxazol-2-yl-phenyl)-*N'*-[2-(methacryloyloxy)ethyl]urea}, and the polyurea of 2-(4-aminophenyl)-5-aminobenzoxazole with 1,5-diisocyanato-2-methylpentane, were strong blue emitters; photoluminescence shifted to longer wavelengths than that of 2-phenylbenzoxazole. Light-emitting polymers containing 2,5-diphenylfuran derivatives, including poly[2-(4-vinylphenyl)-5-phenylfuran], poly[2-(4-vinylphenyl)-5-(4-*tert*-butylphenyl)furan], and poly(*N*-[2-

(methacryloyloxy)ethyl]-*N'*-[4-[5-(4-*tert*-butylphenyl)-2-furyl]phenyl]urea), particularly in solid films, exhibited a strong blue excimer emission. The emission characteristics of polymers with triphenylamine side chains were influenced by the mode of attachment of the luminescent group. A longer spacer group between the lumophore and the polymer main chain successfully minimized excimer emission in poly{*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-(*N,N*-diphenylamino)phenyl]urea}, showing near UV/violet photoluminescence. Polymers with a shorter connecting group, such as poly[4-(*N,N*-diphenylamino)benzyl acrylate], displayed blue excimer emission. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1634–1645, 2003

**Key words:** functionalization of polymers; luminescence; monomers; synthesis

## INTRODUCTION

Light-emitting polymers exhibiting well-defined emission bands, good solubility, and film-forming properties are very desirable but often pose a synthetic challenge. Polymers carrying distinct luminescent functional groups in their side chains show good solubility in common organic solvents and excellent film-forming properties and are relatively easy to synthesize.<sup>1–5</sup> One frequent complication in solid films, however, is the increased tendency of the luminescent groups to form excimers, which causes a red shift and broadening of the emission band. Some of the factors influencing this process are the properties of the lumophores themselves. Other factors are related to the properties and configuration of the backbone polymer, the means by which the functional groups are attached to the backbone, and whether the lumophore is part of the backbone.

Photoluminescent compounds that show negligible excimer emission in solution and have medium or strong emission at short wavelengths, such as 2,5-

diphenylfuran, 2-phenylbenzoxazole, and triphenylamine,<sup>6,7</sup> were selected to serve as functional groups for this study of the influence of polymer architecture on photoluminescence and excimer emission. The type of polymer backbone and the mode of attachment were adjusted by synthesizing vinyl, acryloyl, and methacryloyloxyethylureido derivatives as monomers, by attaching the functional group to a preformed polymer by a polymer analog reaction, or by incorporating the functional group into a polyurea backbone. Photoluminescence of the parent lumophores could then be compared to the emission characteristics of monomers and of polymers in solution and solid films.

## EXPERIMENTAL

### Materials and synthesis

Chemicals were supplied by the Aldrich Chemical Co. (Milwaukee, WI) unless stated otherwise. Methylene chloride, methanol, ethyl acetate, and hexanes were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Tetrahydrofuran (THF) was dried by refluxing over and distilled from sodium/benzophenone, and DMF was distilled from CaH<sub>2</sub> and dried over 3 Å molecular sieves.

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### Synthesis of 2-(4-vinylphenyl)-5-phenylfuran (1)

Monomer **1** was prepared by the palladium-catalyzed cross-coupling reaction of 2-phenylfuran with 4-bromostyrene according to the procedure described previously.<sup>8</sup> The intermediate 2-phenylfuran was prepared according to the same procedure<sup>8</sup> by a cross-coupling reaction between furan and bromobenzene. The crude product was isolated and distilled *in vacuo* to yield 17.0 g pure 2-phenylfuran (89% yield on bromobenzene). The crude monomer **1** was purified by column chromatography with hexanes as an eluent to yield a bright yellow crystalline solid (90% yield on 4-bromostyrene).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 5.3 (d, 1H), 5.8 (d, 1H), 6.7 (dd, 1H), 6.7 (s, 2H), 7.3 (d, 1H), 7.4 (m, 4H), 7.7 (m, 4H).

### Preparation of poly[2-(4-vinylphenyl)-5-phenylfuran] poly(1)

Polymerization of 1.9 g (7.7 mmol) of 2-(4-vinylphenyl)-5-phenylfuran initiated by 0.072 g (0.44 mmol) of azobisisobutyronitrile (AIBN) was carried out under nitrogen in 40 mL of a dry THF solution at 60°C for 48 h. Conversion of the monomer was 88% by HPLC. The polymer was isolated by precipitation into methanol and dried in a vacuum oven to yield a 1.4 g light yellow powder at 74% yield.

### Preparation of 1/acrylonitrile (AN) copolymer

Copolymerization of 1.5 g (6.1 mmol) of 2-(4-vinylphenyl)-5-phenylfuran with 0.32 g (6.1 mmol) of AN initiated by 0.07 g (0.42 mmol) of AIBN was carried out under nitrogen in 25 mL of a dry THF solution at 60°C for 48 h. Conversion of AN was 33% by HPLC. The polymer was isolated by precipitation into methanol and dried in a vacuum oven to yield 1.3 g of a light yellow powder (71% yield). FTIR (polymer film/NaCl disk): —C≡N stretching at 2235 cm<sup>-1</sup>.

### Synthesis of 2-(4-vinylphenyl)-5-(4-*tert*-butylphenyl)furan (2)

The same procedures were used as for the synthesis of **1** for the cross-coupling reactions between furan and *tert*-butylbenzene and between 4-bromostyrene and 2-(4-*tert*-butyl)phenylfuran. The intermediate 2-(4-*tert*-butyl)phenylfuran was purified by column chromatography with hexanes as the eluent and isolated at 93% yield. The crude monomer was purified by column chromatography (hexanes/methylene chloride 1/1) to yield a yellow crystalline solid (83% yield on 2-(4-*tert*-butyl)phenylfuran).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 1.3(s, 9H), 5.3 (d, 1H), 5.8 (d, 1H), 6.7 (dd, 1H), 6.7 (s, 2H), 7.4 (m, 4H), 7.7(m, 4H).

### Preparation of poly[2-(4-vinylphenyl)-5-(4-*tert*-butylphenyl)furan] poly(2)

Polymerization of 2.5 g (8.3 mmol) of 2-(4-vinylphenyl)-5-(4-*tert*-butylphenyl)furan initiated by 0.070 g (0.42 mmol) of AIBN was carried out under nitrogen in 40 mL of a dry THF solution at 60°C for 57 h. Conversion of the monomer by HPLC was 52%. The polymer was isolated by precipitation into methanol and dried in a vacuum oven to produce 1.34 g of a light yellow powder at 52% yield.

### Synthesis of 2-(4-vinylphenyl)-benzoxazole (3)

Monomer **3** was prepared by the palladium-catalyzed cross-coupling reaction of benzoxazol-2-ylzinc chloride with 4-bromostyrene according to a previously described procedure.<sup>8,9</sup> The monomer was purified by column chromatography (hexanes/ethyl acetate 8/1) and recrystallized from isopropanol/water to yield a beige crystalline solid in 27 % yield.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 5.3 (d, 1H), 5.8 (d, 1H), 6.7 (dd, 1H), 7.3 (m, 2H), 7.5 (m, 3H), 7.7 (m, 1H), 8.19 (d, 2H).

### Preparation of poly[2-(4-vinylphenyl)-benzoxazole] poly(3)

In a dry nitrogen-flushed round-bottom flask equipped with a mechanical stirrer and reflux condenser, monomer **3** (0.9 g, 4.1 mmol) was dissolved in dry degassed THF (20 mL). The polymerization was carried out at 60°C for 48 h using AIBN (7 mg, 0.041 mmol) as the initiator. The polymer was isolated as a white powder in 14% yield by precipitation in methanol, filtration, and drying under vacuum for 24 h.

### Synthesis of 4-(*N,N*-diphenylamino)benzyl acrylate (4)

The precursor 4-(*N,N*-diphenylamino)benzyl alcohol was obtained by reduction of 4-(*N,N*-diphenylamino)benzyl aldehyde, supplied by H.W. Sands Co. (Jupiter, FL), with sodium borohydride. Sodium borohydride, 1.34 g (35.4 mmol), was added to a suspension of 12.0 g (44 mmol) 4-(*N,N*-diphenylamino)benzyl aldehyde in 200 mL ethanol and agitated at 30°C for 30 min, then poured into 700 mL ice water. The slurry was acidified with 12.8% aqueous sulfuric acid to pH 2, then adjusted to pH 9 with an ammonium hydroxide solution and extracted with methylene chloride. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the alcohol was obtained in 72% yield (8.7 g) by crystallization from methylene chloride/hexanes. Esterification of 4-(*N,N*-diphenylamino)benzyl alcohol (3.8 g, 13.7 mmol) with excess acryloyl chloride (7.5 g, 82.7 mmol) was carried out in methylene chloride with triethylamine (23 mL, 165 mmol) under nitrogen at ambient temperature. After isolation and purification

of the crude product by column chromatography with THF as the eluent, monomer **4** was obtained at close to quantitative yield.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 5.1 (s, 2H), 5.8(d, 1H), 6.1 (dd, 1H), 6.4 (d, 1H), 6.9–7.3 (aromatic, 14H).

#### Preparation of poly[4-(*N,N*-diphenylamino)benzyl acrylate] poly(**4**)

Polymerization of 1.0 g (3.0 mmol) of 4-(*N,N*-diphenylamino)benzyl acrylate initiated by 0.028 g (0.17 mmol) of AIBN was carried out under nitrogen in 20 mL of dry THF solution at 60°C for 48 h. The product, predominantly oligomers of **4**, was isolated by precipitation into methanol and dried in a vacuum oven to produce 0.83 g of light yellow powder (83% yield).

#### Synthesis of {*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-(*N,N*-diphenylamino)phenyl]urea} (**5**)

The monomer was prepared by a three-step reaction as follows: 4-(*N,N*-Diphenylamino)-1-nitrobenzene was synthesized following the procedure of Gauthier and Fréchet.<sup>10</sup> The product was purified by column chromatography using hexanes/ethyl acetate and recrystallized from isopropanol to obtain a yellow crystalline solid.

Yield 3.31 g (24%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 6.8 (d, 2H), 7.15 (m, 6H), 7.3 (t, 4H), 8.0 (d, 2H).

The corresponding (*N,N*-diphenyl)-1,4-diaminobenzene was obtained by room-temperature catalytic hydrogenation of 4-(*N,N*-diphenylamino)-1-nitrobenzene (2.84 g, 9.78 mmol) in 30 mL THF, using 0.54 g of a palladium catalyst (10 wt % on activated carbon) in a hydrogen atmosphere. After 24 h, the reaction mixture was filtered through a pad of Celite to remove the catalyst. Evaporation of the solvent yielded the (*N,N*-diphenyl)-1,4-diaminobenzene. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): 6.75–7.2 (14 H, aromatic protons). The crude amine was dissolved in 20 mL dry THF and reacted with isocyanatoethyl methacrylate (1.1 g, 11.7 mmol). After 12 h at room temperature, monomer **5** was isolated by evaporation of the solvent and purified by column chromatography (methylene chloride/ethyl acetate) and recrystallized from acetonitrile to yield 1.036 g (26%) of a white crystalline solid.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): 1.8 (s, 3H), 3.3 (m, 2H), 4.1 (t, 2H), 5.64 (s, 1H), 6.02 (s, 1H), 6.20 (NH, 1H), 6.8–7.3 (aromatic, 14H), 8.5 (NH, 1H).

#### Preparation of poly{*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-(*N,N*-diphenylamino)phenyl]urea} poly(**5**)

Monomer **5** (0.86 g, 2.10 mmol) was dissolved in 20 mL THF in a dry nitrogen-flushed reaction vessel equipped with a magnetic stirrer, reflux condenser, and a rubber septum cap. The AIBN initiator (0.022 g, 0.13 mmol) was added to run the polymerization at

60°C for 48 h. The polymer was precipitated into methanol, filtered, and dried under a vacuum at room temperature and isolated as a white solid at 76% yield.

#### Synthesis of *N*-(4-benzoxazol-2-yl-phenyl)-*N'*-[2-(methacryloyloxy)ethyl]urea (**6**)

Monomer **6** was prepared by the reaction of isocyanatoethyl methacrylate (IEM) with 2-(4-aminophenyl)benzoxazole. The amine was synthesized by the reaction of equimolar amounts of 4-aminobenzoic acid and 2-aminophenol in polyphosphoric acid (PPA).<sup>11</sup> The mixture was slowly heated to 200°C. After 3 h, the mixture was cooled to 100°C and poured into ice water with rapid stirring. The yellow precipitate was filtered and washed several times with water and then with a 10% aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. The final product was obtained by recrystallization in methanol/water to yield 6.0 g (57%) of a beige crystalline solid.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): 5.9 (NH, 2H), 6.6(d, 2H), 7.2(m, 2H), 7.6(m, 2H), 7.8(d, 2H).

IEM (3.9 mL, 0.025 mol) was slowly added to a solution of 2-(4-aminophenyl)benzoxazole (4.9 g, 0.023 mol) in 100 mL dry THF (100 mL) and allowed to react at room temperature for 24 h. Monomer **6** was isolated by evaporation of the solvent and purified by recrystallization from isopropanol/water to yield 6.0 g (73%) of a white crystalline solid.

<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, ppm): 1.84 (s, 3H), 3.37 (m, 2H), 4.10 (t, 2H), 5.64 (s, 1H), 6.03 (s, 1H), 6.42 (NH, 1H), 7.3–8.02 (aromatic, 8H), 8.9 (NH, 1H).

#### Preparation of poly{*N*-(4-benzoxazol-2-yl-phenyl)-*N'*-[2-(methacryloyloxy)ethyl]urea} poly(**6**)

In a dry nitrogen-flushed reaction vessel equipped with a magnetic stirrer, reflux condenser, and rubber septum cap, monomer **6** (2.5 g, 6.8 mmol) was dissolved in 40 mL degassed and dry THF. The AIBN initiator (0.0117 g, 0.068 mmol) was added and the polymerization run at 60°C for 48 h. The polymer was isolated by precipitation in methanol, filtration, and drying under a vacuum to yield 2.09 g (84%) of a white solid.

#### Synthesis of *N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-[5-(4-*tert*-butylphenyl)-2-furyl]phenyl]urea (**7**)

2-(4-Aminophenyl)-5-(4-*tert*-butylphenyl)furan was first synthesized by a procedure similar to those used in the synthesis of monomers **1** and **2** for the cross-coupling reactions between furan and *tert*-butylbenzene (purification and yield given above under **2**) and between 4-bromo-*N,N*-bis(trimethylsilyl)aniline and 2-(4-*tert*-butyl)phenylfuran. After the cross-coupling reaction, the reaction mixture was acidified with a dilute HCl solution, then neutralized with NaHCO<sub>3</sub>.

The crude product was extracted with ether and the solution was washed and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After isolation and purification by column chromatography with methylene chloride/hexanes 8/2 and methylene chloride as eluents, 3.7 g of the product was obtained (38.5% yield). Monomer 7 was obtained by the reaction of 3.7 g (12.7 mmol) of 2-(4-aminophenyl)-5-(4-*tert*-butylphenyl)furan with 2.4 g (15 mmol) of 2-(isocyanato)ethyl methacrylate in dry THF at room temperature. The crude product was purified by column chromatography (methylene chloride/ethyl acetate 9/1, methylene chloride) and crystallization from acetonitrile to yield a yellow, crystalline solid (2.4 g, 5.5 mmol, 43% yield).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 1.3(s, 9H), 1.88 (s, 3H), 3.5 (m, 2H), 4.22 (t, 2H), 5.55 (s, 1H), 6.05 (s, 1H), 6.6 (s, 2H), 7.3–7.6 (aromatic, 8H).

#### Preparation of poly(*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-[5-(4-*tert*-butylphenyl)-2-furyl]phenyl]urea) poly(7)

Polymerization of 1.3 g (2.9 mmol) of *N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-[5-(4-*tert*-butyl)phenyl]-2-furyl]phenyl]urea initiated by 0.034 g (0.21 mmol) of AIBN was carried out under nitrogen in 25 mL of a dry THF solution for 48 h. The polymer was isolated by repeated precipitation into methanol and dried in a vacuum oven to produce 1.1 g of a light yellow solid at 82% yield.

#### Synthesis of polymer 8

Polymer 8 was obtained by esterification of the copolymer maleic anhydride/methyl vinyl ether (Gantrez<sup>®</sup> AN119). First, 3.0 g of Gantrez<sup>®</sup> (20 mmol maleic anhydride) and 2.75 g (10 mmol) of 4-(*N,N*-diphenylamino)benzyl alcohol were dissolved in methyl ethyl ketone and refluxed for 48 h to yield 5.48 g of a partially esterified anhydride copolymer. The alcohol was fully converted in 24 h (determined by NMR spectroscopy and HPLC analysis). Subsequently, the polymer was dispersed in 1-propanol and refluxed for 48 h to open the remaining anhydride rings with 1-propanol.

#### Synthesis of 2-(4-aminophenyl)-5-aminobenzoxazole (9) (ref. 12)

PPA was added to equimolar amounts of 4-aminobenzoic acid (6.852 g, 0.05 mol) and 2,4-diaminophenoldihydrochloride (9.850 g, 0.05 mol) in a round-bottom flask equipped with a mechanical stirrer and condenser. The mixture was slowly heated to 110°C. After the foaming subsided, the mixture was heated to 200°C. After 3 h, the reaction was cooled to 100°C and poured into rapidly stirred ice water. The precipitate was filtered, washed several times with water, and

then with a 10%  $\text{Na}_2\text{CO}_3$  solution. The final product was obtained by recrystallization (several times with charcoal treatment) from methanol/water to yield 1.8 g (16%) of a white crystalline solid.

$^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , ppm): 4.9 (NH, 2H), 5.8 (NH, 2H), 6.5(d, 1H), 6.6 (d, 1H), 6.7(s, 1H), 7.2(d, 2H), 7.7(d, 2H).

#### Preparation of the polyurea of 9 with 1,5-diisocyanato-2-methylpentane

A solution of 1,5-diisocyanato-2-methylpentane (0.75 g, 4.44 mmol) in 3 mL DMF was added dropwise to 2-(4-aminophenyl)-5-aminobenzoxazole (1.00 g, 4.44 mmol) dissolved in 20 mL dry DMF (with 5% w/v LiCl) at 0°C. The mixture was allowed to react at RT for 2 h, then heated to 100°C for 3 h. The polymer, 1.68 g of a white solid (96% yield), was obtained by precipitation into methanol, filtration, and drying under a vacuum at 40°C.

#### Characterization

##### Spectroscopy

$^1\text{H-NMR}$  spectra were obtained on a Varian 400 instrument. UV/visible absorption spectra were obtained using a Hewlett–Packard 8452A diode array spectrophotometer and quartz cuvetts of 10-mm path length. The sample concentration was adjusted to keep the absorbance under 2.0.

Photoluminescence spectra (uncorrected photoluminescent intensities) were recorded on a SPEX FLUOROLOG instrument using front-face excitation with a nonpolarized source. A quartz cuvet of a 1-mm path length was used for the solutions. IR spectroscopy was performed using a Perkin–Elmer 1600 Series FTIR spectrophotometer on a polymer film coated on a NaCl disk.

##### Chromatography

The monomer purity and residual monomer content in polymerization mixtures was determined using a Hewlett–Packard 1090 HPLC instrument equipped with a diode array detector and a YMC ODS-AQ 5- $\mu\text{m}$  column (150–46 mm). Variants of a gradient elution method was utilized with methanol and an aqueous 75 mmol/L triethylammoniumphosphate buffer (pH 3.5); the detection wavelength was adjusted according to the absorption maximum of the individual monomers. Monomers were purified until eluted as a single peak in the chromatogram and purity was also confirmed by spectral analysis of the peak.

Molar mass of the polymers was determined using a Hewlett–Packard 1090 HPLC instrument equipped with a diode array detector, an RI detector (Model HP 1047A), and a PL-gel 10- $\mu\text{m}$  mixed-bed column (600–

7.5 mm). The eluent was either THF using a 1 mL/min elution rate or DMF with 0.01 mol LiBr using a 0.7 mL/min elution rate, depending on the polymer type. PL Caliber GPC software and calibration with polystyrene standards of a narrow molar mass distribution were used to calculate the molar mass.

## RESULTS AND DISCUSSION

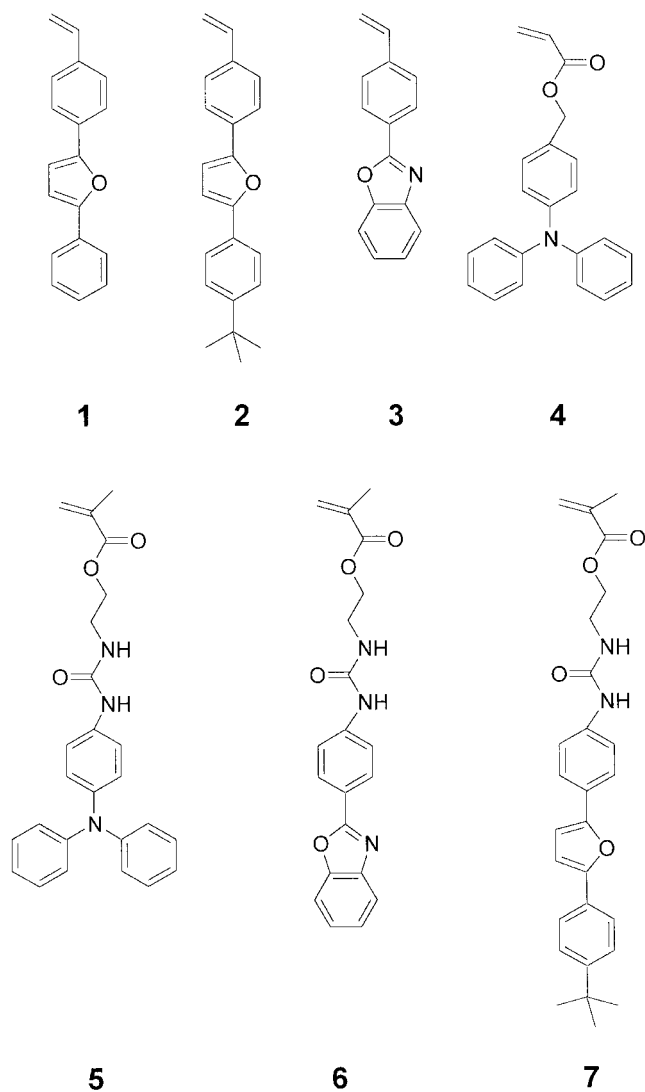
### Monomer and polymer synthesis

The luminescent monomers are shown in Scheme 1. The vinyl group is directly attached to the fluorophore in monomers 1–3. Four chemical bonds separate the polymerizable group from the fluorophore in the acrylate 4, and in the methacryloyloxyureido derivatives, the length of the spacer group is eight chemical bonds. With the exception of monomer 4, these monomers or their polymers have not been reported in the literature. Vinyl derivatives of 2,5-diphenylfuran 1 and 2 and 2-phenylbenzoxazole 3 were synthesized by

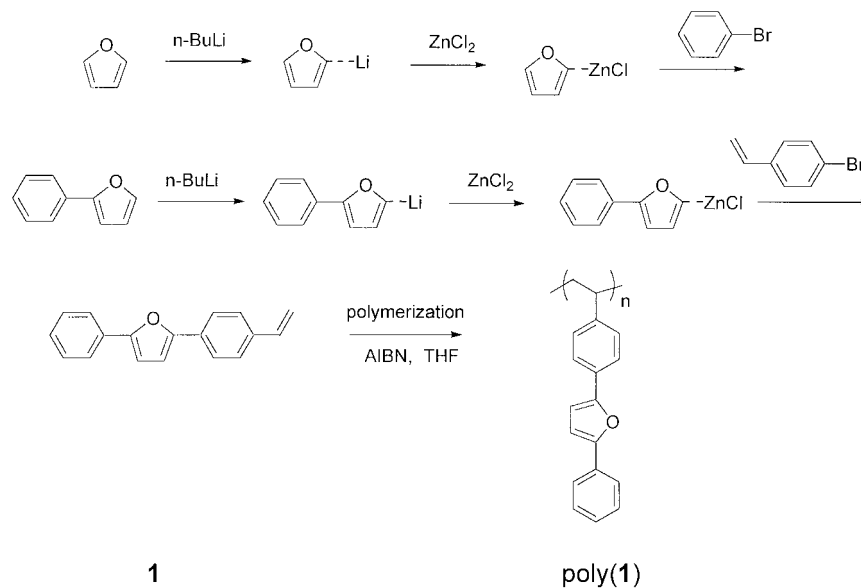
cross-coupling reactions of the corresponding furan or benzoxazole and 4-bromostyrene, following the procedure described for the synthesis of furan derivatives<sup>8</sup>; one example is shown in Scheme 2. The acryloyl derivative of triphenylamine 4 was prepared by the reduction of 4-(*N,N*-diphenylamino)benzaldehyde to 4-(*N,N*-diphenylamino)benzyl alcohol with sodium borohydride and subsequent esterification with acryloyl chloride, summarized in Scheme 3. The polymer of 4 was used for hole transport.<sup>13–15</sup> The methacryloyloxyethylureido derivative of triphenylamine 5 was obtained by the reduction of 4-nitrophenyldiphenylamine by hydrogenation to 4-diphenylaminoaniline and reacting it with IEM, similar to the synthetic procedure used in ref. 3 to prepare the monomeric triarylamine, shown in Scheme 4. The methacryloyloxyethylureido derivative of the 2-phenylbenzoxazole 6 was obtained by first synthesizing 2-(4-aminophenyl)benzoxazole<sup>11</sup> and then reacting the amine with IEM. The methacryloyloxyethylureido derivative of the 2,5-diphenylfuran 7 was prepared by reacting 2-(4-aminophenyl)-5-(4-*tert*-butylphenyl)furan with IEM. The amine 2-(4-aminophenyl)-5-(4-*tert*-butylphenyl)furan was obtained by a coupling reaction similar to that described in ref. 8, except that the amino group was protected by bis(trimethylsilyl) substitution. In a postpolymerization reaction, the fluorophore 4-(*N,N*-diphenylamino)benzyl alcohol was incorporated by a ring-opening reaction with the anhydride ring of the alternating copolymer maleic anhydride/methyl vinyl ether (Gantrez<sup>®</sup> AN 119) 8, shown in Scheme 5.

Free-radical solution polymerizations were conducted in THF or toluene using AIBN as an initiator in a batch process with agitation under nitrogen at 60°C. Conversion was determined periodically (HPLC, NMR, and/or gravimetric measurement). Polymerization times were extended to 48 h to achieve 70–80% conversions. The substituted styrene monomers 1, 2, and 3 were found to homopolymerize much more slowly than did styrene, reaching under 50% conversion in 24 h. Polymerization of 2-(4-vinylphenyl)benzoxazole 3 was the slowest, reaching only 14% conversion in 48 h. This may be due to the high degree of delocalization over the conjugated  $\pi$ -electron structure in the luminescent monomers, decreasing the reactivity of the growing radicals. It also resulted in a lower molar mass, further discussed in the following section. When no delocalization could take place between the growing radical and the 2-phenylbenzoxazole functional group, as in monomer 6, conversion and molar mass were both significantly higher under comparable reaction conditions.

The reduced reactivity of conjugated radicals was further evidenced in copolymerizations. For example, an attempt to copolymerize 1 with styrene (in 1/1.27 molar ratio) produced only the homopolymer of 1, and 100% of the styrene remained unreacted even after 48 h (determined by HPLC analysis). This result



**Scheme 1** Photoluminescent monomers.

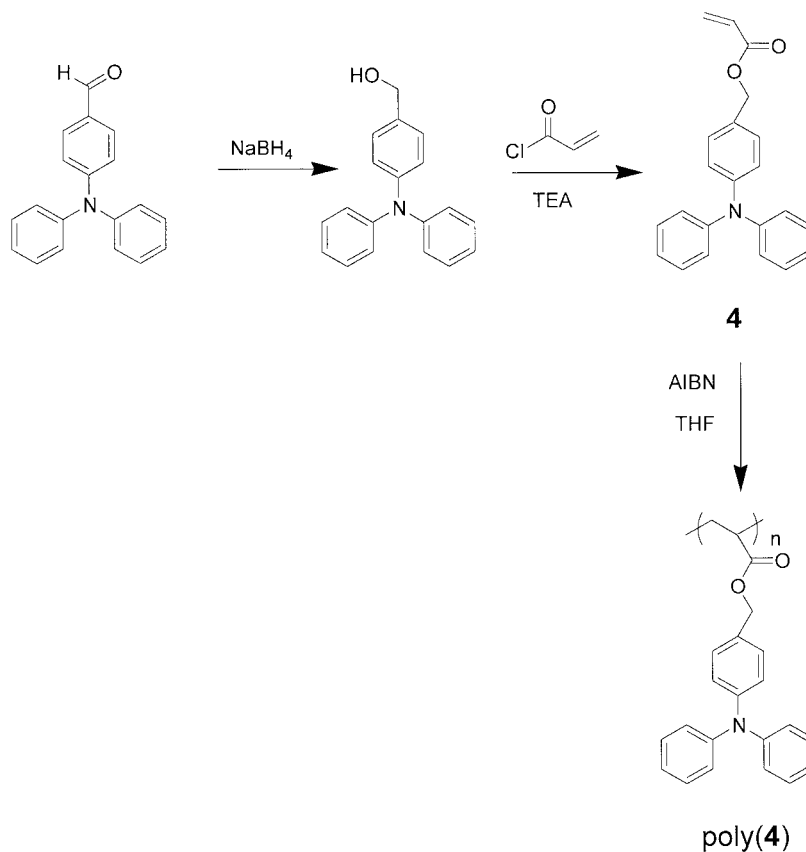


**Scheme 2** Synthesis of poly[2-(4-vinylphenyl)-5-phenylfuran].

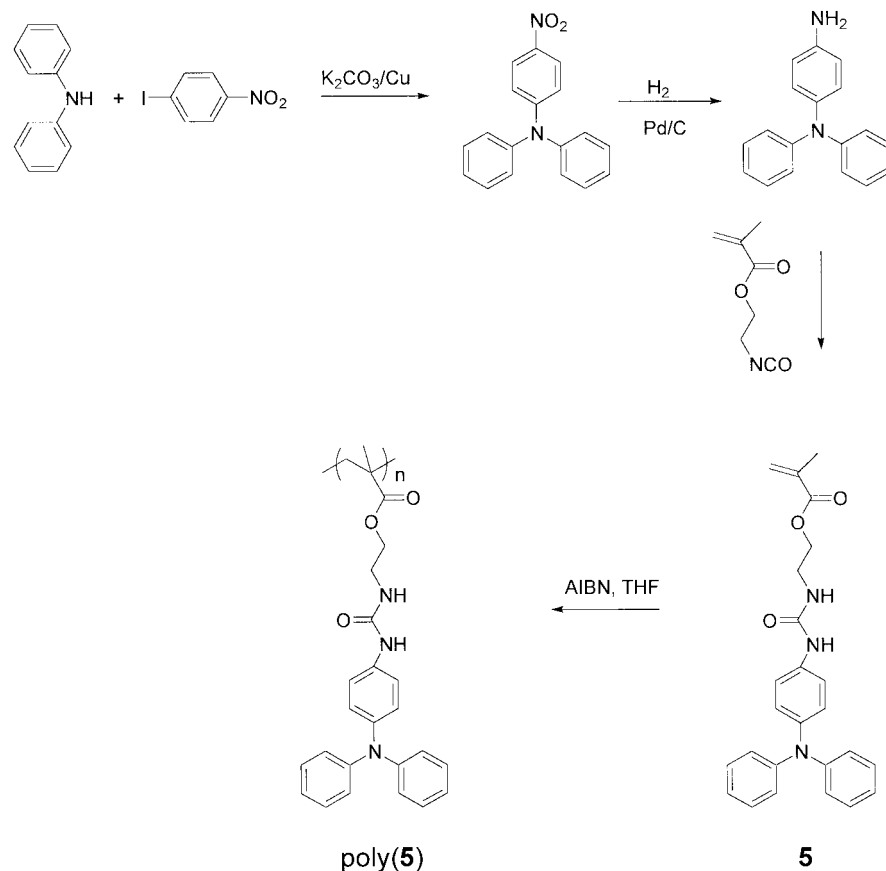
is somewhat unexpected, since copolymerization of 9-(4-vinylphenyl)-10-phenylanthracene with styrene has been reported using ATRP.<sup>16</sup> The 2,5-diphenylfuran fluorophore could be incorporated into copolymers by a polymer analog coupling reaction between 2-phenylfuran and copolymers of 4-bromostyrene,

similar to that used for the synthesis of compound **1**.<sup>8</sup> This alternative synthetic route (not presented here) with copolymers of 4-bromostyrene would yield copolymers with 2,5-diphenylfuran side groups.

Copolymerization with AN (in a 1/1 molar ratio), which was expected to form an electron donor/acceptor



**Scheme 3** Synthesis of poly[4-(*N,N*-diphenylamino)benzyl acrylate].

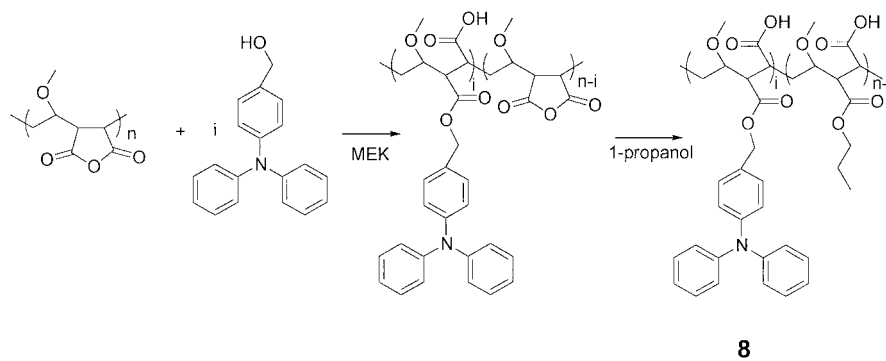


**Scheme 4** Synthesis of poly{N-[2-(methacryloyloxy)ethyl]-N'-[4-(N,N-diphenylamino)phenyl]urea}.

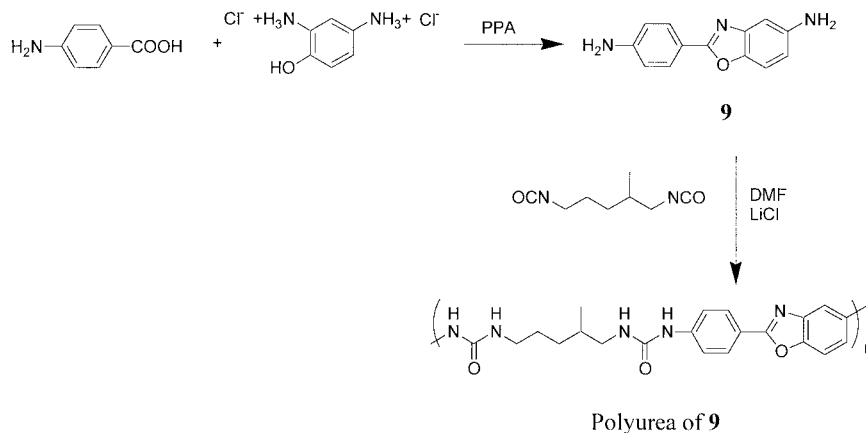
tor charge-transfer complex with **1**, produced a polymer yield of 70% (by weight) after isolation. Only 33% of the AN was incorporated in 48 h, determined by HPLC analysis of the polymerization sample. The presence of AN in the polymer was also confirmed by IR spectroscopy (a strong  $\text{—C}\equiv\text{N}$  resonance at  $2235\text{ cm}^{-1}$  observed in the spectrum of the isolated polymer).

Copolymerization was included in our study to determine the influence of a possible alternating tendency on the reactivity of the monomers and on excimer emission of the lumophore. Attraction between an electron-rich growing radical and an electron-poor

monomer (or vice versa) would favor alternation. We found that neither was the reactivity enhanced nor was the excimer emission diminished by copolymerizing the luminescent monomers with a common, non-emitting monomer. All the other luminescent monomers, **4–7**, were homopolymerized only. Polymerization of **4** produced predominantly oligomeric species under the conditions used in our studies (see molar mass in the next section); however, for practical reasons, these oligomers will be discussed with the polymers and designated as poly(**4**). The 2-phenylbenzoxazole fluorophore was incorporated into a polymer main chain by first synthesizing the diamino deriva-



**Scheme 5** Polymer analog reaction with Gantrez AN 119.



**Scheme 6** Polyurea synthesis from 2-(4-aminophenyl)-5-aminobenzoxazole (**9**) and 1,5-diisocyanato-2-methylpentane.

tive 2-(4-aminophenyl)-5-aminobenzoxazole **9** (ref. 12) and subsequently reacting with 1,5-diisocyanato-2-methylpentane to form a polyurea, summarized in Scheme 6.

#### Molar mass of polymers

The molar mass was determined by size-exclusion chromatography; the results are compiled in Table I. Polymers with ureido linkage between the methacrylate ester backbone and the lumophore showed a very broad molar mass distribution with THF as the eluent. A concentration series of samples displayed a shift in the curve shape, indicative of an interaction between the column and the polymer. When DMF with 0.01M LiBr salt was used as the eluent, the curve shape was close to Gaussian with polydispersity index (PDI) between 1.5 and 2; these results are reported in Table I. The molar mass of the polyurea of **9**, insoluble in THF but soluble in DMF/0.01M LiBr, was also determined with this eluent. Two other polymers, poly[2-(4-vinylphenyl)benzoxazole], poly(**3**), and poly[4-(*N,N*-diphenylamino)benzyl acrylate], poly(**4**), were analyzed using both eluents with very similar results, showed in Table I. Polymerization of 4-(*N,N*-diphenylamino)benzyl acrylate **4** produced only oligomers, the average of

eight monomer units per chain, which was close to the resolution limit of the GPC column. This may account for its apparently low PDI. The styrene-analog polymers, polymers of **1**, **2**, and **3**, are also in the relatively low molar mass range, which may be due to stabilization of the growing radical by the extended  $\pi$ -conjugated structure, that was also manifested by the low polymerization rate, discussed before. Remarkably, when the  $\pi$ -conjugated system is well isolated from the growing radical, as in the methacryloyloxyethylureido derivatives of triphenylamine **5**, of 2-phenylbenzoxazole **6**, and of 2-phenyl-5-(4-*tert*-butylphenyl)furan **7**, the molar mass is significantly higher. This indicates that the limiting event is not chain transfer or retardation by the functional groups, and lower molar mass can be attributed to slower propagation.

#### Photoluminescence

UV-visible absorption and fluorescence spectra of the monomers and polymers were obtained in a dilute THF solution and in thin films of polymers spin-cast on glass, summarized in Table II. (The diamine **9** and its polyurea, which were insoluble in THF, were analyzed in and spin-cast from DMF solutions.) Emission maxima as well as excimer emission were compared to

**TABLE I**  
Molar Mass of Fluorescent Polymers by Size-exclusion Chromatography

Sample	$M_n$	$M_w$	PDI	Eluent
Poly( <b>1</b> )	7700	13,700	1.78	THF
1/AN copolymer	8500	18,200	2.14	THF
Poly( <b>2</b> )	7000	14,600	2.08	THF
Poly( <b>3</b> )	16,900	30,500	1.81	THF
Poly( <b>3</b> )	20,000	35,600	1.78	DMF/0.01M LiBr
Poly( <b>4</b> )	2600	3200	1.23	THF
Poly( <b>4</b> )	2700	3300	1.22	DMF/0.01M LiBr
Poly( <b>5</b> )	64,900	108,000	1.67	DMF/0.01M LiBr
Poly( <b>6</b> )	89,000	165,000	1.84	DMF/0.01M LiBr
Poly( <b>7</b> )	78,700	147,000	1.87	DMF/0.01M LiBr
Polyurea of <b>9</b>	2750	8900	3.24	DMF/0.01M LiBr



**TABLE II**  
**Absorption and Fluorescence of Fluorophores, Fluorescent Monomers and Polymers**

Sample	Type <sup>a</sup>	Absorption maxima <sup>b</sup> (nm)	Photoluminescence maxima <sup>b</sup> (nm)	Excitation (nm)
2,5-Diphenylfuran	0.2 g/L in benzene	<b>328</b>	355, <b>372</b> , 390	313
2,5-diphenylfuran	20 g/L in benzene		355, <b>372</b> , 390	313
<b>1</b>	0.005% in THF	<b>346</b> , (362)	(370), <b>400</b> , (430)	320
Poly( <b>1</b> )	0.007% in THF	(328), <b>332</b> , (348)	(386), 402, <b>423</b> , (443)	320
Poly( <b>1</b> ), 2nd synthesis	0.01% in THF	(324), <b>332</b> , (350)	385, 408, <b>426</b> , (450)	320
<b>1/AN</b> copolymer	0.01% in THF	(326), <b>332</b> , (350)	(362), 379, 403, <b>426</b> , (446)	320
<b>1/AN</b> copolymer	2.53% in THF		(382), (406), <b>430</b> , 454	320
<b>1/AN</b> copolymer	Film		<b>438</b> , <b>460</b> (broad)	300
<b>2</b>	0.007% in THF	(336), <b>348</b> , (364)	(390), <b>405</b>	300
<b>2</b>	2.174% in THF		(401), <b>425</b> , (448)	300
Poly( <b>2</b> )	0.001% in THF	(319), (325), <b>333</b> , (350)		
Poly( <b>2</b> )	0.0073% in THF		365, 383, <b>405</b> , <b>427</b>	300
Poly( <b>2</b> )	2.49% in THF		(366), (386), 406, <b>428</b> , (445)	300
Poly( <b>2</b> )	Film		<b>433</b> , <b>450</b> (broad)	300
<b>7</b>	0.0151% in THF	<b>338</b> , (360)	(380), <b>395</b> , (413)	300
<b>7</b>	2.32% in THF		(381), <b>395</b> , (440), <b>460</b> , (490) broad, bimodal	300
Poly( <b>7</b> )	0.0054% in THF	<b>342</b> , (366)	(380), <b>396</b> , <b>431</b> , (456) broad, bimodal	300
Poly( <b>7</b> )	2.00% in THF		(380), <b>397</b> , <b>433</b> , 459 broad, multimodal	300
2-Phenylbenzoxazole	In cyclohexane	<b>300</b>	(316), <b>330</b> , (348)	
<b>3</b>	0.0016% in THF	(308), <b>320</b> , 334	(367), <b>382</b>	300
<b>3</b>	0.0054% in THF		(368), <b>381</b>	300
<b>3</b>	1.96% in THF		(368), <b>382</b>	300
Poly( <b>3</b> )	0.0015% in THF	295, <b>303</b> , 317		
Poly( <b>3</b> )	0.0199% in THF		(398), <b>414</b>	300
Poly( <b>3</b> )	2.123% in THF		(398), <b>415</b>	300
<b>6</b>	0.001% in THF	<b>316</b>		
<b>6</b>	0.0366% in THF		<b>368</b> , (381)	300
<b>6</b>	1.984% in THF		<b>369</b> , (381)	300
Poly( <b>6</b> )	0.0223% in THF	<b>312</b> , (316)	<b>383</b> (tail from 450–520 nm)	300
Poly( <b>6</b> )	1.993% in THF		<b>384</b> (tail from 450–520 nm)	300
Poly( <b>6</b> )	Film		<b>408</b> (some tailing)	300
<b>9</b>	0.002% in DMF	<b>336</b> , (312)	<b>454</b> broad	300
<b>9</b>	1.00% in DMF		<b>454</b> broad	300
Polyurea of <b>9</b>	0.002% in DMF	<b>340</b> , (302)	<b>411</b> somewhat broad	300
Polyurea of <b>9</b>	2.008% in DMF		<b>414</b> somewhat broad	300
Polyurea of <b>9</b>	Film		<b>430</b> somewhat broad	300
Triphenylamine	In cyclohexane	<b>300</b>	<b>355</b>	313
<b>4</b>	0.00634% in THF	<b>302</b>		300
<b>4</b>	0.0064% in THF		<b>375</b> long tail (400–600 nm)	300
<b>4</b>	2.122% in THF		(368), <b>372</b> , 376 long tail (400–600 nm)	300
Poly( <b>4</b> )	0.00085% in THF		<b>367</b> , <b>463</b> (twin peaks)	300
Poly( <b>4</b> )	0.0085% in THF	<b>302</b>	<b>373</b> , <b>464</b> (twin peaks)	300
Poly( <b>4</b> )	2.54% in THF		<b>373</b> , <b>465</b> (twin peaks)	300
<b>5</b>	In THF	<b>304</b>	<b>380</b>	300
Poly( <b>5</b> )	0.0035% in THF	235, <b>304</b>	<b>380</b> , (390)	300
Poly( <b>5</b> )	0.01% in THF	(234), <b>304</b>	<b>390</b>	300
Poly( <b>5</b> )	1.95% in THF		<b>382</b>	300
Poly( <b>5</b> )	2.49% in THF		<b>386</b>	300
Poly( <b>5</b> )	Film		<b>392</b> (low intensity tail from 450–550 nm)	300
<b>8</b>	In THF	<b>308</b>	<b>377</b> , (400), (420) broad, tailing to 600 nm	320

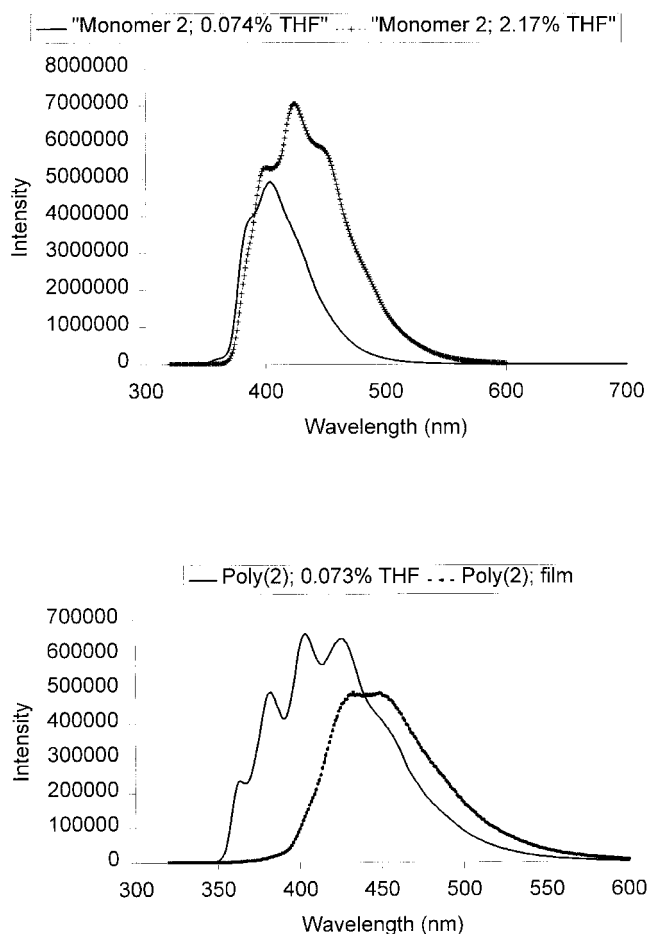
<sup>a</sup> Concentration of solutions in weight percent, unless otherwise noted.

<sup>b</sup> Main maximum bold; shoulder wavelength in parentheses.

those of the unsubstituted aromatic compounds 2,5-diphenylfuran, 2-phenylbenzoxazole, and triphenylamine, also listed in Table II as reported in the literature.<sup>6,7</sup> All monomers and polymers had absorption and emission maxima of a longer wavelength than that of the unfunctionalized, parent lumophore.

The unsubstituted 2,5-diphenylfuran and the monomers and polymers containing this fluorophore have

broad, even multimodal fluorescence spectra. Unexpectedly, while diphenylfuran showed no shift in the emission maximum with increasing concentration (the emission maxima are practically the same at 0.2 and 20 g/L concentration), monomer **2** emits at a longer wavelength and has a broader emission spectrum at the higher concentration (405 and 425 nm, respectively). Poly(**2**) displays both of these maxima, and the emis-

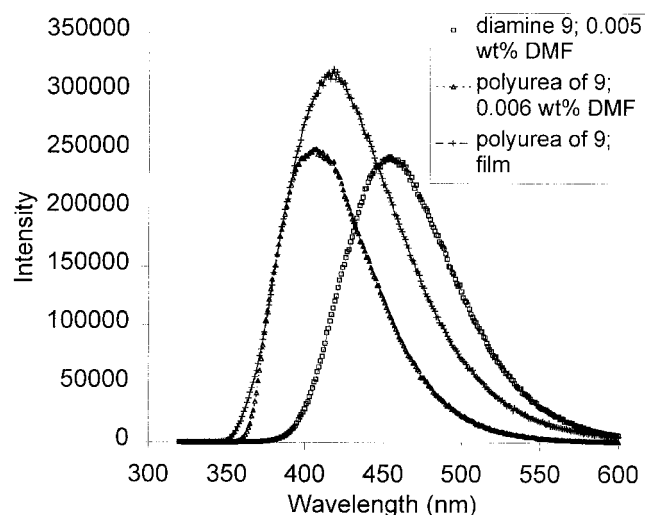


**Figure 1** Photoluminescence of poly[2-(4-vinylphenyl)-5-(4-*tert*-butylphenyl)furan]. Emission spectra of monomer and polymer solution in THF and polymer film.

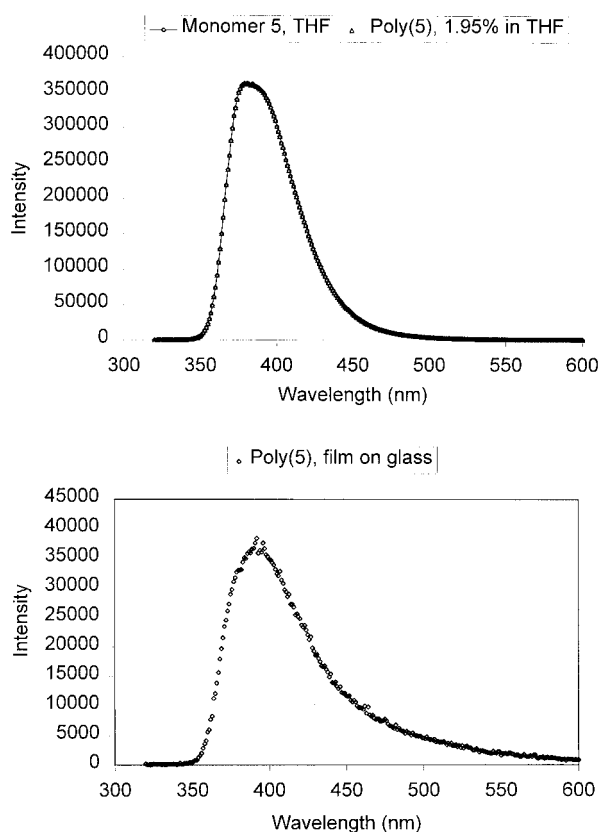
sion spectrum is broad at low and high polymer concentrations. In the coated film form, both maxima shift to longer wavelengths; the corresponding emission spectra are shown in Figure 1. Similar trends were observed with poly(1) and also with the copolymer of 1 and AN. Copolymerization of 1 with a nonemitting, electron-withdrawing monomer did not reduce excimer emission at a higher concentration or in the dry film form. Monomer 7 also displayed a second emission maximum at the higher concentration, and both maxima appeared in the emission spectrum of poly(7). Excimer emission was equally pronounced at higher concentrations in solution and in the solid film, whether the 2,5-diphenylfuran was directly attached to the polymer chain, as in poly(1), poly(2), and the copolymer of 1 with AN, or separated from the main polymer chain by eight bonds, as in poly(7). All polymers in this study containing a substituted diphenylfuran lumophore displayed broad, or even multimodal emission spectra, with a negligible influence by the mode of attachment of the fluorescent group to the polymer main chain.

The emission of polymers containing a substituted 2-phenylbenzoxazole fluorophore, poly(3) and poly(6),

on the other hand, shows little evidence of excimer formation. Both monomers 3 and 6 display emission spectra that are red-shifted in comparison with the parent lumophore, but neither shows significant broadening or additional maxima at higher concentration. The emission spectra of the corresponding polymers poly(3) and poly(6) show a further minor red shift [slightly larger for poly(3), in which the lumophore is immediately attached to the polymer main chain], but no additional maxima, not even in the solid film form of poly(6). Incorporating the 2-phenylbenzoxazole functional group into the main chain of a polyurea, poly(9), allowed us to compare the emission characteristics of this lumophore as part of the polymer main chain with the side-chain lumophores, poly(3) and poly(6). The emission spectrum of the diamine 2-(4-aminophenyl)-5-aminobenzoxazole 9 showed a strong red shift (over 120 nm) in comparison with 2-phenylbenzoxazole, which may be attributed to the electron-donor amino substituents. No additional maxima appeared and the shift did not increase, however, with increasing concentration. The emission spectrum of the corresponding polyurea, which was formed by reacting the diamine with 1,5-diisocyanato-2-methylpentane (Scheme 6), in turn, was actually blue-shifted, displaying a monomodal, although somewhat broad blue emission around 415 nm in solution and at 430 nm in the coated film. The emission spectra of the polyurea as well as that of the precursor diamine are shown in Figure 2. There is a minor influence by the mode of attachment of the substituted 2-phenylbenzoxazole fluorophore on its emission characteristics, when incorporated as part of the polymer main chain or a side-chain functional group. There is a significant difference in the solubility of these polymers, however, with implications for coating. [The solubility of the main chain polymer



**Figure 2** Photoluminescence of polyurea of 2-(4-aminophenyl)-5-aminobenzoxazole 9. Emission spectra of diamine 9, polymer solution in DMF and polymer film.



**Figure 3** Photoluminescence of poly{*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-(*N,N*-diphenylamino)phenyl]urea}. Emission spectra of monomer and polymer solution in THF and polymer film.

poly(9) is limited to DMF and DMSO, while the polymers with side chain lumophores poly(3) and poly(6) are soluble in common organic solvents.]

The mode of attachment of the triphenylamine fluorophore to a polymer backbone had a strong influence on the emission characteristics of these polymers. The absorption and emission spectrum of triphenylamine shows a single maximum at 300 and 355 nm, respectively.<sup>6</sup> The emission maxima of the monomers containing this lumophore 4 and 5 exhibit only a moderate red shift, 375 and 380 nm, respectively; however, the emission spectrum of 4 is multimodal at the highest concentration. The oligomeric material containing this lumophore, poly[4-(*N,N*-diphenylamino)benzyl acrylate], poly(4), shows a bimodal emission spectrum at all concentrations, and 8, prepared by a polymer analog reaction with Gantrez, shows a broad emission spectrum with long tailing. In both cases, the lumophore is separated from the polymer backbone by only four chemical bonds (a carboxylate group), which may predispose the lumophores to excimer emission. The emission spectrum of poly{*N*-[2-(methacryloyloxy)ethyl]-*N'*-[4-(*N,N*-diphenylamino)phenyl]urea}, poly(5), on the other hand, remains relatively narrow at all concentrations, as well as in the solid film. The emission maximum of the poly-

mer is between 380 and 390 nm at all concentrations and 392 nm in the film (only a minor red shift from the monomer at 380 nm), shown in Figure 3. Excimer formation was suppressed in this polymer with a longer spacer group (eight bonds) separating the fluorophore from the main chain.

## CONCLUSIONS

Photoluminescence studies on a series of polymers containing one of three violet-to-blue-emitting lumophores in their side chain and on a polyurea with the lumophore incorporated into the main chain explored how the mode of attachment of the functional group to the polymer chain influence their emission characteristics. The fluorophores, 2,5-diphenylfuran, 2-phenylbenzoxazole, and triphenylamine, show negligible excimer emission in their unsubstituted form. Therefore, it was intriguing that excimer emission was insignificant only with polymers containing the 2-phenylbenzoxazole functional groups. The mode of incorporation of 2-phenylbenzoxazole into the polymer, however, still influenced the wavelength of the emission maximum, but it was independent of polymer concentration. It shifted the emission spectrum of these photoluminescent polymers into the visible region; they were all strong blue emitters.

Polymers containing substituted diphenylfuran in their side chain showed broad, multimodal emission spectrum at a higher concentration or in the coated film form, interpreted as excimer emission. This was evident whether the luminescent group was separated from the polymer main chain by only one (vinyl derivatives) or eight chemical bonds (methacryloyloxyethylureido derivative). Neither separating the functional group from the polymer main chain nor adding a bulky *tert*-butyl substituent to the fluorophore was sufficient to minimize the excimer emission. All the polymers containing a diphenylfuran lumophore were strong blue emitters with a broad, multimodal emission spectrum.

In contrast, the emission characteristics of the triphenylamine lumophore were strongly dependent on the mode of attachment to the polymer. The emission spectrum was broad or bimodal, attributed to excimer emission, when it was connected through a carboxylate group to the polymer main chain (separated only by four chemical bonds). Excimer emission of this fluorophore was successfully eliminated by further separation (eight bonds) from the polymer chain in the methacryloyloxyethylureido derivative. This polymer emitted in the near UV/violet region (390–400); the other polymers were blue emitters. The polymers described in this study are interesting potential candidates for application in electroluminescent devices.

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