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Synthesis and Structure−Property Relationships of Soluble Rigid−Flexible Copolyethers Containing Blue and Yellow Light Emitting Units

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A series of new rigid−flexible copolyethers containing blue- and yellow-emitting conjugated segments have been synthesized. The thermal, mechanical, and optical properties of the polymers are controlled by the type of the comonomers, their ratio at the preparation stage, and the length of the flexible spacer, as well as the structure of the blue monomer in the main chain. The polyethers were characterized by viscosimetry, thermal and mechanical analysis, NMR, and UV−vis and luminescence spectroscopy. The polymers obtained are soluble in common solvents, form free-standing films either from solution casting or after melt pressing, and show good mechanical properties. Regardless of the excitation wavelength, the polyethers show bright-yellow photoluminescence in solution, suggesting energy transfer from the blue to the yellow unit. In the solid state, the luminescence behavior is controlled by the monomer structure, the molar percentage of the comonomers, the length of the flexible spacer, and the excitation wavelength.

Introduction

The potential applications of conjugated polymers in device structures[1−8] are mainly due to the combination of their electrooptical properties with the advantage of the mechanical strength and ease of fabrication. The electroluminescence (EL) properties of a number of different conjugated polymers have been investigated, including poly(*p*-phenylenevinylene) and its ring-substituted derivatives,[9−13] poly(alkylthiophene)s,[14−15] poly(phenylene)s,[16−19] and others.[20]

Color tuning of the EL emission combined with improved solubility from polymer-based LEDs has been achieved mainly by “geometrical” control of the conjugation length via several different routes. These include, among others, substitution of side groups, which enhances the steric hindrance and leads also to the decrease of the planarity.[14,21−24] A different approach is the synthesis of polymers with conjugated fluorescent blocks of defined length into the polymeric main chain which are separated by flexible segments.[25−31] Chemical groups and molecular topology therefore control the

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(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

(3) Braun, D.; Heeger A. J. *J. Appl. Phys. Lett.* **1991**, *58*, 1982.

(4) Rothberg, L. J.; Lovinger A. J. *J. Mater. Res.* **1996**, *11*, 3174.

(5) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(6) Segura, J. L. *Acta Polym.* **1998**, *49*, 319.

(7) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(8) Sheats, J. R.; Chang, Y. L.; Roitman, D. B.; Stocking, A. *Acc. Chem. Res.* **1999**, *32*, 193.

(9) Gustafsson, G.; Gao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, C.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(10) Vestweber, H.; Greiner, A.; Lemmer, U.; Mahrt, R. F.; Richert, R.; Heitz, W.; Bässler, H. *Adv. Mater.* **1992**, *4*, 661.

(11) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.

(12) Xhang, C.; von Seggern, H.; Pakbaz, K.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35.

(13) Braun, D.; Staring, E. G. J.; Demandt, R. C. J. E.; Rikken, G. L. J.; Kessener, Y. A. R. R.; Venhuisen, A. H. J. *Synth. Met.* **1994**, *66*, 57.

(14) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1994**, *372*, 444.

(15) Herrema, J. K.; Van Hutten, P. F.; Gill, R. E.; Wildeman, J.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 8102.

(16) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(17) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190.

(18) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.

(19) Stamplf, J.; Tasch, S.; Leising, G.; Scherf, U. *Synth. Met.* **1995**, *71*, 2125.

(20) Klärner, G.; Lee J.; Davey, M.; Miller, R. *Adv. Mater.* **1999**, *11*, 115.

(21) Schlueter, A.-D.; Wegner, G. *Acta Polym.* **1993**, *44*, 59.

(22) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

(23) Connolly, M.; Karasz, F.; Trimmer, M. *Macromolecules* **1995**, *28*, 1872.

(24) Hilberer, A.; Brouwer, H. J.; Scheer, B. J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 4525.

(25) Hay, M.; Klavetter, F. L. *J. Am. Chem. Soc.* **1995**, *117*, 7112.

(26) Oberski, J.; Festag, R.; Schmidt, C.; Lüssem, G.; Wendorff, J. H.; Greiner, A.; Hopmeier, M.; Motamedi, F. *Macromolecules* **1995**, *28*, 8676.

(27) Kallitsis, J.; Gravalos, K.; Hilberer, A.; Hadziioannou, G. *Macromolecules* **1997**, *30*, 2989.

(28) Keegstra, M.; Cimrová, V.; Neher, D.; Scherf, U. *Macromol. Chem. Phys.* **1996**, *197*, 2511−2519.

(29) Gill, R. E.; Malliaras, G. G.; Wildeman, J.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132.

(30) Zyung, T.; Hwang, D.-H.; Kang, I.-N.; Shim, H.-K.; Hwang, W.-Y.; Kim, J.-J *Chem. Mater.* **1995**, *7*, 1499.

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performance of a material by modifying the electronic and optical properties of the polymers and by influencing their solid-state morphology. However, the mechanism leading to improved photoluminescence (PL) and EL efficiencies in copolymers is difficult to understand, because several effects have to be taken into account. For example, the incorporation of flexible nonconjugated segments into a rigid conjugated polymer will reduce the stiffness of the backbone and therefore affect the molecular order of the polymer. Because many electronic properties of conjugated polymers depend on the degree of order,[32−33] this concept can be an important tool to tailor their optical properties. The electronic structure of the copolymers dominates the emission features and phenomena such as the formation of excimers,[20] energy transfer, and exciton migration[34] are of great interest. So, the study of these materials allows the investigation of various structural parameters on the electronic and physical properties of the polymers.

In this article, we report on the synthesis and properties of a series of rigid−flexible copolyethers containing blue- and yellow-emitting segments. The changes in the molecular structure via the variation of the type of the chromophores, their ratios, and the length of the flexible spacer, as well as their different ways of attachment in the main chain, result in changes in the optical and processing properties of the polymers.[35−36] As blue chromophores, dihexyloxy-substituted quinquephenyl units,[37] styrylbiphenyl segments laterally attached to the main chain, or *m*-distyrylbenzene units[38] were selected. These structures represent different ways to increase solubility, such as the use of aliphatic substituents, the laterally asymmetric substitution, and the broken backbone. As a yellow chromophore, the acetoxy-functionalized 9,10-distyrylanthracene unit[39] was selected since anthracene is an attractive group due to the extension of the π system which causes a decrease of the electronic gap of the polymer.[40−42]

Experimental Section

Materials. Chemicals were purchased from Aldrich or Merck and were used as received unless otherwise specified. 1,10-Dibromodecane was recrystallized from methanol. Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone directly into the reaction flask. *N*,*N*-Dimethylformamide was purified by distillation over phosphorus pentoxide, and triethylamine was dried over potassium hydroxide.

Monomer Synthesis. The synthesis of 9,10-di(*p*-acetoxystyryl) anthracene **(1)** and 2′′,5′′-dihexyloxy-*p*-quinquephenyl-4,4′′′′-diol diacetate **(2)** has been described elsewhere.[37,39]

Synthesis of 2-(*p*-styrylbenzene)-1,4-phenyl Diol Diacetate (3). 2-(*p*-Bromobenzene)-1,4-phenyl diol diacetate (3.5 g, 10 mmol), styrene (4.66 g, 28 mmol), Pd(OAc)$_2$ (0.022 g, 0.1 mmol) and tri-*o*-tolylphosphine (0.18 g, 0.6 mmol) were added in a flask which was degassed and filled with argon. Triethylamine (4 mL) and DMF (25 mL) were added, and the mixture was heated to 100 °C under argon for 48 h. After being cooled, the precipitate was filtered off and washed with methanol. Recrystallization from 95% EtOH gave 2.3 g (60%) of the desired product, **3**; mp: 161−163 °C. ^{1}H NMR (CDCl$_3$): δ 2.10-(s, 3H), 2.30(s, 3H), 7.10(d, 1H), 7.12−7.14 (m, 3H), 7.18(d, 1H), 7.26(m, 1H), 7.36(m, 2H), 7.42(m, 2H), 7.50−7.55(m, 4H). ^{13}C NMR (CDCl$_3$): δ 21.31, 21.54, 121.90, 123.97, 124.21, 126.30, 126.93, 127.00, 128.22, 128.45, 129.16, 129.53, 129.67, 135.97, 136.36, 137.27, 137.60, 145.62, 148.83, 169.73, 169.78. FTIR (cm^{-1}): 3024, 1748, 1518, 1482, 1450, 1400, 1370, 1216, 1172, 1038, 1026, 968, 932, 910, 874, 842, 822, 780, 756, 728, 694, 622, 586, 546, 498.

Synthesis of 1,3-Di(*p*-acetoxystyryl) Benzene (4). 1,3-Dibromobenzene (2.36 g, 10 mmol), *p*-acetoxystyrene (4.66 g, 28 mmol), Pd(OAc)$_2$ (0.022 g, 0.1 mmol) and tri-*o*-tolylphosphine (0.18 g, 0.6 mmol) were added in a flask which was degassed and filled with argon. Triethylamine (4 mL) and DMF (25 mL) were added, and the mixture was heated to 100 °C under argon for 48 h. After being cooled, the precipitate was filtered off and washed with methanol. Recrystallization from CHCl$_3$/hexane gave 2.5 g (63%) of the desired product, **4**; mp: 210−212 °C. ^{1}H NMR (CDCl$_3$): δ 2.30(s, 3H), 7.05(d, 2H), 7.10(m, 4H), 7.15(d, 2H), 7.33(m, 1H), 7.40(m, 2H), 7.53-(m, 4H), 7.61(s, 1H). ^{13}C NMR (CDCl$_3$): δ 21.55, 119.44, 122.24, 125.16, 126.22, 127.97, 128.43, 129.13, 133.67, 135.51, 139.60, 150.52, 169.87. FTIR (cm^{-1}): 3034, 1756, 1572, 1504, 1428, 1380, 1240, 1106, 1046, 1018, 966, 916, 870, 856, 830, 802, 714, 692, 665, 596, 528.

Polymer Syntheses. A 0.75/0.25, 0.50/0.50, or 0.25/0.75 mmol ratio of monomer **A** (**1**) and **B** (**2**−**4**), 1 mmol of the respective dibromide, and 0.4 mmol of tetrabutylammonium hydrogen sulfate[43,44] were placed into a vessel equipped with a magnetic stirrer and an inlet/outlet and a vacuum inlet. The flask was evacuated and filled with argon several times, and then *o*-dichlorobenzene (5 mL) and 10 N NaOH (5 mL) were added. The reaction mixture was vigorously stirred at 80 °C for 24 h under argon. The mixture was diluted with chloroform. The polymer was separated by precipitation into a 10-fold excess of methanol, washed with methanol, and dried in vacuo for 24 h. Representative examples are given below.

***I**-11-75/25.* ^{1}H NMR (CDCl$_3$): δ 0.87(m, B, 6H), 1.13−1.85-(m, AB, 52H), 4.05(m, AB, 12H), 6.89(d, A, 2H $J = 16.4$ Hz), 7.01−7.05(m, AB, 8H), 7.07(s, B, 2H), 7.47(m, A, 4H), 7.62−7.68(m, AB, 16H), 7.77(d, A, 2H, $J = 16.0$ Hz), 8.41(m, A, 4H). ^{13}C NMR (CDCl$_3$): δ 22.99, 23.01, 26.18, 26.48, 29.65, 29.70, 29.82, 29.98, 30.12, 30.15, 68.56, 69.10, 115.22, 115.27, 125.47, 126.59, 126.91, 128.19, 128.43, 128.60, 130.06, 130.30, 137.32, 159.58. FTIR (KBr, cm^{-1}): 3032, 2924, 2854, 1606, 1508, 1488, 1470, 1386, 1248, 1206, 1174, 1110, 1028, 967, 822, 758, 524.

***II**-11-75/25.* ^{1}H NMR (CDCl$_3$): δ 1.29−1.86(m, AB, 36H), 4.05(m, AB, 8H), 6.89(2d, AB, 3H, $J = 16.4$ Hz), 6.97−7.02(m, AB, 7H), 7.15(d, B, 1H), 7.22(m, B, 1H), 7.36(m, B, 2H), 7.46-(m, AB, 6H), 7.54−7.63(m, AB, 8H), 7.80(d, A, 2H, $J = 16.4$ Hz), 8.41(m, A, 4H). ^{13}C NMR (CDCl$_3$): δ 26.48, 29.69, 29.75, 29.83, 29.94, 29.98, 30.02, 68.58, 68.61, 69.06, 115.18, 115.23, 115.26, 125.42, 125.48, 126.43, 126.51, 126.89, 126.95, 128.11, 128.18, 128.26, 128.98, 129.09, 129.13, 129.96, 130.03, 130.10, 130.15, 137.28, 159.53, 159.62. FTIR (KBr, cm^{-1}): 3033, 2934, 2843, 1604, 1508, 1472, 1383, 1298, 1246, 1214, 1172, 1109, 1035, 961, 824, 792, 754, 692, 529.

***III**-11-75/25.* ^{1}H NMR (CDCl$_3$): δ 1.28−1.86(m, AB, 36H), 4.05(m, AB, 8H), 6.90(2d, AB, 4H, $J = 16.6$ Hz), 7.01(m, AB,

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(31) Malliaras, G. G.; Herrema, J. K.; Wildeman, J.; Wieringa, R. H.; Gill, R. E.; Lampoura, S. S.; Hadziioannou, G. *Adv. Mater.* **1993**, *5*, 721.

(32) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T., Elsenbaumer, R., Reynolds, J., Eds.; Marcel Dekker: New York, 1998.

(33) *Semiconducting Polymers;* Hadziioannou, G.; van Hutten, P. F., Eds.; Wiley-VCH: Weinheim, 1999.

(34) Swager, T. M.; Gil, C. J.; Wrighton, M. C. *J. Phys. Chem.* **1995**, *99*, 4886.

(35) Greiner, A.; Bolle, B.; Hesemann, P.; Oberski, J. M.; Sander, R. *Macromol. Chem. Phys.* **1996**, *197*, 113.

(36) Chung, S.; Kim, K.; Jin, J. *Polymer* **1999**, *40*, 1943.

(37) Konstandakopoulou, F.; Gravalos, K.; Kallitsis, J. *Macromolecules* **1998**, *31*, 5264.

(38) Suzuki, M.; Lim, J.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574.

(39) Konstandakopoulou, F.; Kallitsis, J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3826.

(40) Garay, R. O., Naarmann H.; Müllen, K. *Macromolecules* **1994**, *27*, 1922.

(41) Moroni, M.; Le Moigne J.; Luzzati, S. *Macromolecules* **1994**, *27*, 562.

(42) Kobayashi, E.; Jiang J.; Furukawa, J. *Polym. J.* **1990**, *22*, 266.

(43) Percec, V.; Kawasumi, M. *Macromolecules* **1993**, *26*, 3917.

(44) Percec, V.; Kawasumi, M. *Macromolecules* **1993**, *26*, 3663.

8H), 7.12(d, B, 2H, $J = 16.4$ Hz), 7.33(m, B, 1H), 7.40(m, B, 2H), 7.47(m, AB, 8H), 7.62(m, AB, 5H), 7.80(d, A, 2H, $J = 16.0$ Hz), 8.41(m, A, 4H). ^{13}C NMR (CDCl$_3$): δ 26.47, 29.70, 29.82, 29.97, 31.37, 68.52, 68.58, 115.13, 115.23, 123.15, 125.48, 126.73, 126.94, 128.13, 128.18, 130.03, 130.29, 130.40, 133.20, 137.29, 159.58. FTIR (KBr, cm^{-1}): 3033, 2924, 2843, 1604, 1510, 1468, 1384, 1302, 1248, 1172, 1114, 1020, 968, 798, 758, 529.

Except for peak intensities, the series **I**-*n-x*/*y*, **II**-*n-x*/*y*, and **III**-*n-x*/*y* present similar IR and NMR spectral characteristics.

Polymer and Monomer Characterization. Intrinsic viscosities of the polymers were measured in CHCl$_3$ at 30 °C with an Ubbelohde-type viscometer in a Scott Gerate AVS 310.

Molecular weight estimations were determined by size exclusion chromatography (SEC) with a Marathon II HPLC pump using a Fasma 500 UV/vis detector at 254 nm and calibrated with monodisperse polystyrene standards through 500 and 10^4 Å “styragel” columns at 25 °C with tetrahydrofuran as solvent.

The ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian VXR 300 spectrometer, with deuterated chloroform and DMSO as solvents and TMS as internal standard.

FTIR spectra were obtained using a Perkin-Elmer 1600 spectrometer.

Tensile tests were performed using a J. J. tensile tester type 5001 according to ASTM D882-67.

Dynamic mechanical properties were determined at 10 Hz by a RSA II mechanical spectrometer from Rheometric Scientific, Ltd.

Thermal properties of the polymers were determined by DSC SP equipped with an AutoCool accessory from Rheometric Scientific, Ltd.

UV spectra were recorded on a U-2001 Hitachi spectrometer. Fluorescence was measured on a Perkin-Elmer luminescence spectrometer LS 50B.

Results and Discussion

Polymerizations of varying proportions of monomer **A** (**1**) and monomer **B** (**2**−**4**) with aliphatic α,ω-dibromides were carried out using the phase-transfer catalyst tetrabutylammonium hydrogen sulfate.[43−44] The polyethers obtained, **I**-*n-x*/*y* to **III**-*n-x*/*y* (see Scheme 1) are differentiated by the molar percentage of the comonomers **A** and **B** (*x*/*y*) as well as by the number of methylene units in the flexible spacer (*n*). For each type of copolymer, we have studied samples with **A/B** monomer ratios of 75/25, 50/50, and 25/75. The composition of the statistically random copolymers was estimated from the monomer feed ratio at the preparation stage. Polyethers **I**-*n-x*/*y* and **II**-*n-x*/*y* are soluble in common solvents, whereas polyethers **III**-*n-x*/*y* are soluble in 1,1,2,2-tetrachloroethane. The improved solubilities of polyethers **II**-*n-x*/*y* and **III**-*n-x*/*y* compared to those of the parent polyethers allowed the preparation of free-standing films in all cases (**I**-*n-x*/*y* to **III**-*n-x*/*y*) by casting from solution or by melt pressing.

The characterization of the synthesized polyethers using viscosimetry and size exclusion chromatography is shown in Table 1. The intrinsic viscosity values of the polymers measured at 30 °C in CHCl$_3$ solutions ranged from 24 to 49 mL/g. The molecular weights have been estimated by GPC based on calibration with polystyrene standards and $\overline{M}_n$ values in the range 16 000−47 000, and polydispersity indexes $\overline{M}_w/\overline{M}_n$ of 1.5−2.3 were obtained. In the case of polyether **III**-*n-x*/*y*, GPC measurements were not performed due to its limited solubility in THF at room temperature. Structural characterization of the polyethers synthesized was performed using FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopies. In all cases, the configuration of the vinylene unit is in the trans form. ^{1}H NMR integration indicates that the copolymer composition reflects the comonomer ratio used during preparation.

The thermal properties of the polymers were examined using differential scanning calorimetry. Glass transitions were detected between 40 and 92 °C for the different copolymers and spacer length. Since these transitions are quite broad, dynamic mechanical analysis has been used in order to elucidate the influence of the various structural characteristics of the polyethers synthesized on the glass-transition temperature.

Polyethers **I**-*n-x*/*y* are amorphous except for **I**-*11-25*/*75* and **I**-*10-x*/*y* which show one or more endotherms in the range 156−226 °C during the first heating scan. Polyethers **II**-*n-x*/*y* are amorphous except for polyether **II**-*10-75*/*25* where two endotherms at 213 and 226 °C are observed during the first heating scan. Polyethers **III**-*n-x*/*y* exhibit one or more endotherms in the range 153−222 °C during the first heating scan except for **III**-*11-75*/*25* which is amorphous. Comparison of their thermal behavior with polyethers **III**-*n-100*/*0* and **III**-*n-0*/*100* shows that the copolymerization results to a decrease of the temperatures as well as the enthalpy values of the endothermic transitions. As shown by the thermal analysis, characteristics such as rigidity, linearity, and flexible spacer length determine the thermal behavior of the polymers.[45] The hexyloxy side groups of the substituted quinquephenyl segment of **I**-*n-x*/*y* discourage polymer chains from packing tightly and forming crystalline domains. The asymmetric structure of **II**-*n-x*/*y*, due to the laterally attached styrylbiphenyl conjugated segment, is thought to be the major reason of the inability of polyether **II**-*n-x*/*y* to crystallize. In contrast, the replacement of the anthracene unit with the *m*-benzene ring, in the case of **III**-*n-x*/*y*, allows a more ordered packing. This shows that the structure of the blue chromophore controls the thermal properties of the synthesized copolymers.

In regards to the mechanical properties and since flexible luminescent polymers which can sustain mechanical stresses are needed for devices, the mechanical behavior of these materials is of great interest.[46] Moreover, the high mechanical stability is necessary in order to lower the film thickness and so minimize the ohmic drop while avoiding the risks of short-circuiting. In that respect, dynamic mechanical analysis and stress−strain measurements of the synthesized copolymers were performed for the film-forming samples. The results were identical for melt-pressed and solution-cast films except for polyethers **III**-*11-50*/*50* and **III**-*7-50*/*50* which after melt pressing became dark and insoluble due to thermal cross-linking reactions.

The copolymers studied show high storage modulus (E') values at room temperature and a broad relaxation in the range 40−92 °C. In all cases, as the percentage of the di(styryl)anthracene unit increases, the T_g is shifted to higher temperatures. Comparison of the glass transitions of the copolymers **I**-*n-x*/*y* to **III**-*n-x*/*y* with

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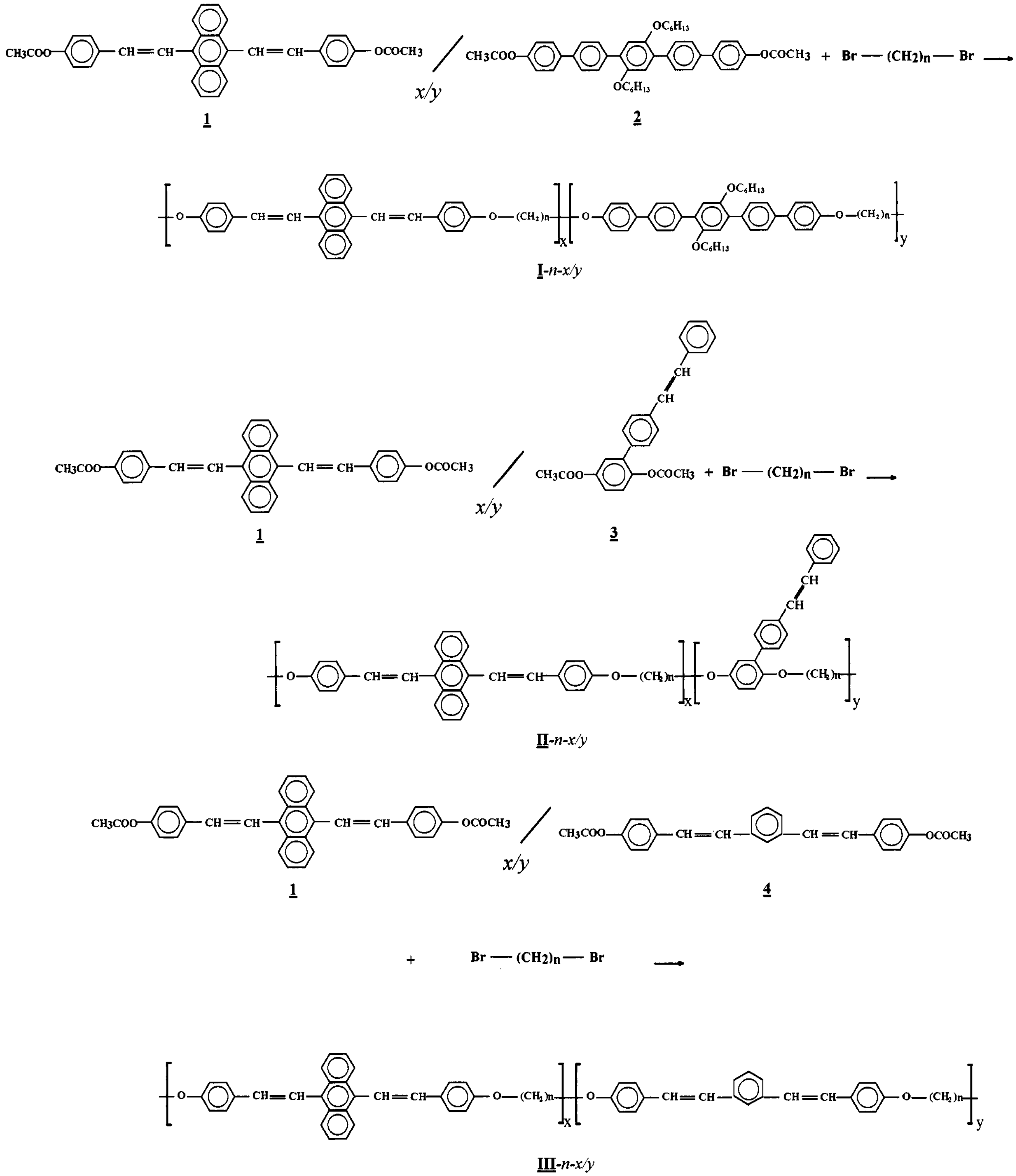
(45) Meurisse, P.; Noel, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1981**, *13*, 55.

(46) Okuzaki, H.; Ikeda, N.; Kubota, I.; Kunugi, T. *Macromolecules* **1999**, *32*, 5606.

Scheme 1



the same ratio of *x*/*y* and the same flexible spacer segment shows that the T_g values of polyethers **I**-*n*-*x*/*y* and **II**-*n*-*x*/*y* are lower than those of polyether **III**-*n*-*x*/*y*, as seen in Figure 1. This is due to the resulting looser packing of the polymeric main chains in the case of the dihexyloxy-substituted quinquephenyl segment (**I**-*n*-*x*/*y*) and the laterally attached styrylbiphenyl-conjugated segment (**II**-*n*-*x*/*y*). The stress–strain properties of the synthesized polyethers were measured to get an estimate of the mechanical properties at large deformation, in relation to their dynamic mechanical properties, see Figure 2. The tensile strength σ_b for polyethers **I**-*11-25/75* and **II**-*11-75/25* and especially the elongation at break (ϵ_b) with values of 270% and 360%, respectively, show that materials with good mechanical properties which combine light-emission are obtained.

The optical properties of the polyethers synthesized were investigated in solution and in solid state. The polyethers consist of two different conjugated segments which show blue and yellow photoluminescence, respec-

Table 1. Viscosimetric and GPC Characterization of the Synthesized Polymers

copolymer	[η] ^{a} (mL/g)	$\bar{M}_n$ ^{b}	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
I−*11−75/25*	32	35 000	55 000	1.6
I−*11−50/50*	27	23 000	41 000	1.8
I−*11−25/75*	48	47 000	69 000	1.5
I−*10−50/50*	27	24 000	35 000	1.5
I−*10−25/75*	24	20 000	36 000	1.8
II−*11−75/25*	49	32 000	46 000	1.5
II−*11−50/50*	31	21 000	35 000	1.7
II−*11−25/75*	29	21 000	35 000	1.7
II−*10−50/50*	24	16 000	26 000	1.7
II−*10−25/75*	26	18 000	31 000	1.7
II−*8−50/50*	30	22 000	12 000	1.8
II−*7−50/50*	29	27 000	15 000	1.8

^{a} In $CHCl_3$ at 30 °C. ^{b} In THF based on PS standards.

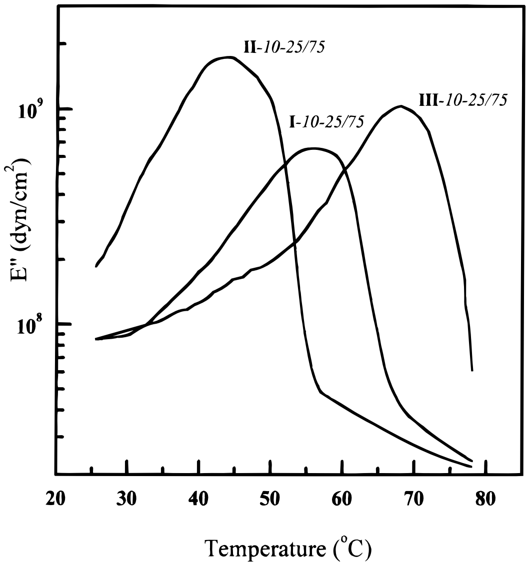


Figure 1. Temperature dependence of loss *E*″ modulus at 10 Hz of polyethers **I**-*10-25/75*, **II**-*10-25/75*, and **III**-*10-25/75*.

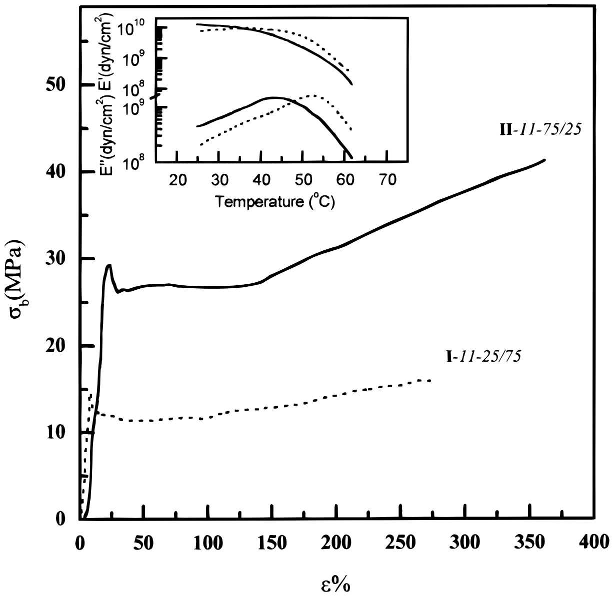


Figure 2. Stress−strain curves of polyethers **I**-*11-25/75* and **II**-*11-75/25*. Inset: Temperature dependence of storage *E*′ and loss *E*″ moduli at 10 Hz of the polyethers.

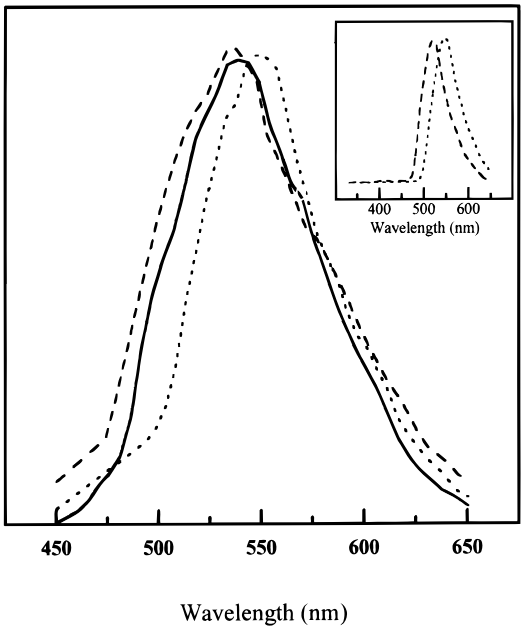


Figure 3. Emission spectra of polyether **I**-*11-75/25* (—), **II**-*11-75/25* (— — —) and **III**-*11-75/25* (- - -) in $CHCl_3$ solutions excited at 420 nm. Inset: Emission spectra of **II**-*11-75/25* (— — —) and **III**-*11-75/25* (- - -) after excitation at 320 and 310 nm, respectively.

tively. The absorption spectra obtained in dilute $CHCl_3$ solutions for polyethers **I**-*n-x/y* to **III**-*n-x/y* exhibit absorption bands at 350 and 420 nm (**I**-*n-x/y*), 320 and 420 nm (**II**-*n-x/y*), and 310 and 420 nm (**III**-*n-x/y*). The PL spectra are obtained after excitation at the maxima of the absorption bands of the blue- and yellow-emitting monomer, respectively. Each series, **I**-*n-x/y*, **II**-*n-x/y*, and **III**-*n-x/y*, presents identical electronic properties in solution which are independent of the structure of the nonconjugated segment. Representative examples are shown in Figure 3. The spectra of **I**-*n-x/y* (538 nm), **II**-*n-x/y* (536 nm), and **III**-*n-x/y* (550 nm) show an emission centered around a single maximum, regardless of the excitation wavelength. Excitation at the absorption maximum of the blue monomer gives rise to a PL emission which is identical with that observed when the copolymer is excited at 420 nm, i.e., where the di(styryl)-anthracene comonomer absorbs. Since the emission maxima of the blue-emitting segment at 420 (**I**-*n-0/100*), 418 (**II**-*n-0/100*), and 408 nm (**III**-*n-0/100*) overlap with the absorption maxima of the yellow-emitting, antracene-containing segment, energy transfer is possible, resulting in emission only from the latter unit.

The photoluminescence behavior of the copolymers was also studied in the solid state. The peak maxima of the PL spectra of self-standing thin films (70 μm) of the copolymers after excitation at 350 (**I**-*n-x/y*), 320 (**II**-*n-x/y*), and 310 nm (**III**-*n-x/y*) appear at about 540 nm which is the same maximum as that observed in solution. Although the same behavior was expected for the excitation at 420 nm, in some cases, results are obtained that were more complicated than the emission in solution or after excitation at the absorption maximum of the blue chromophore in solid state. So, polyethers **I**-*11-50/50* and **I**-*10-50/50* show a second peak at 570 nm compared to their emission in solution. A more complicated behavior was obtained for the copolymers **II**-*n-50/50*, as shown in Figure 4. The copolymer **II**-*7-50/50* has almost the same optical behavior in solution and in solid state, whereas **II**-*10-50/50* and **II**-

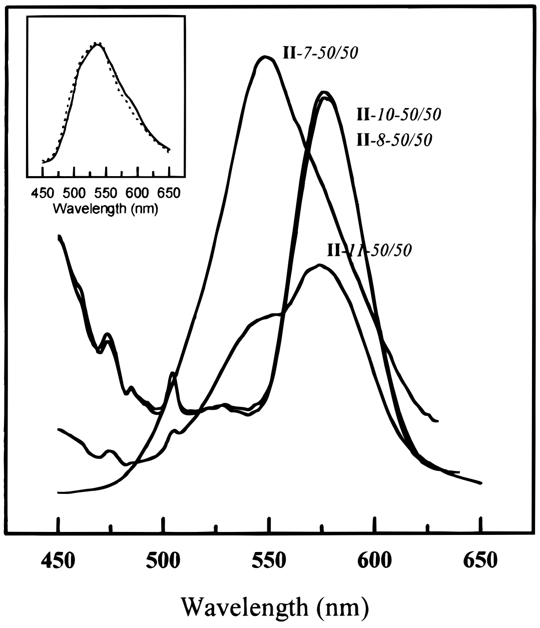


Figure 4. Emission spectra of polyether **II**-*7-50/50*, **II**-*8-50/50*, **II**-*10-50/50*, and **II**-*11-50/50* in solid state after excitation at 420 nm. Inset: Emission spectra of **II**-*7-50/50* (- - -) and **II**-*10-50/50* (—) in $CHCl_3$ solutions excited at 420 nm.

8-50/50 (with even number of methylene units) show a redshift in the emission spectra in solid state while their spectra show vibronic structure. Moreover, a clear spectral narrowing compared with their solution spectra as well as with their odd number homologues, is observed. Such redshift in going from solution to the solid state has been also observed in other systems and has been attributed to the existence of ordered structures which enable of interactions of the chromophores.[47−49] As seen in Figure 5, the emission behavior of the copolymer **II**-*11-50/50* is dependent on the excitation wavelength. Excitation at 320 nm shows vibronic structure with peaks at 545 and 570 nm. The latter peak is much more pronounced after excitation at 420 nm. To gain some more insight on the mechanism of the observed energy transfer,[50] a blend of the homopolymers **II**-*11-100/0* and **II**-*11-0/100* in 50/50 composition was also examined. In blend (film or solution), excitation at 320 nm resulted in an emission at 540 nm without the vibronic structure observed for the copolymers. The absence of an emission at 420 nm strongly supports that energy transfer from the blue to the yellow light emitting unit occurs in solution as well as in the solid state. In the solid state, since the blends are phase-separated the main mechanism of energy transfer is probably the one which is related to self-reabsorption, because of the distance between the blue and yellow chromophores which are located on the different domains of the immiscible blends. Of course, a different mechanism followed by the blends and copolymers cannot be excluded based on the present measurements.

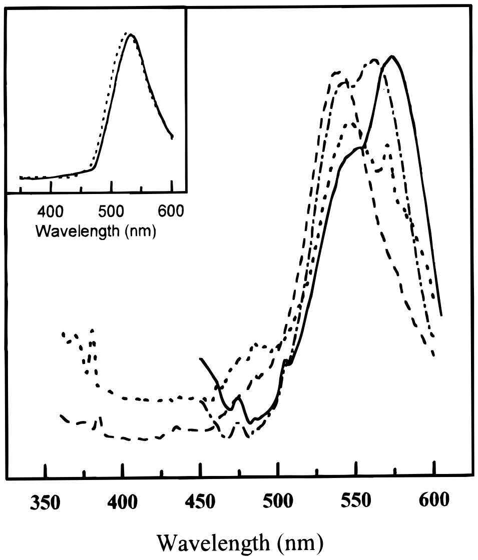


Figure 5. Emission spectra in solid state of **II**-*11-50/50* (excited at 320 (- - -) and 420 nm (—)) and a 50/50 composition blend of **II**-*11-100/0* and **II**-*11-0/100* (excited at 320 (— — —) and 420 nm (— - — -). Inset: Emission spectra of **II**-*11-50/50* (—) and blend (- - -) in $CHCl_3$ solutions excited at 320 nm.

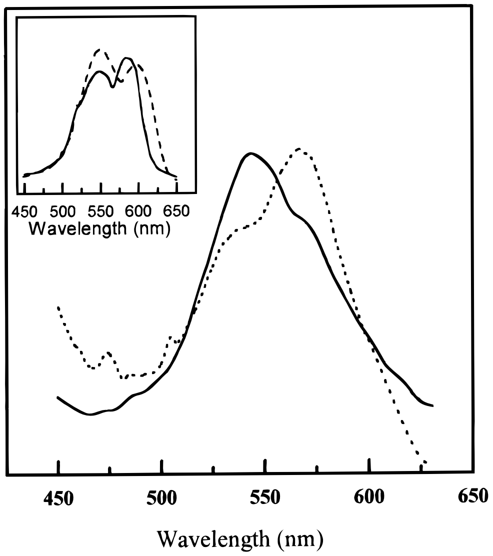


Figure 6. Emission spectra of polyether **II**-*10-75/25* in solid state before (—) and after annealing at 170 °C for 15 h (- - -), excited at 420 nm. Inset: Emission spectra of polyether **III**-*11-25/75* (—) and **III**-*10-25/75* (- - -) in solid state after excitation at 420 nm.

The hypothesis that a more ordered structure is responsible for the redshift in the emission of the copolymers is supported by the results presented in Figure 6 where the quenched film of **II**-*10-75/25* shows only a shoulder at 570 nm and the main peak is at 540 nm, whereas after annealing, the shoulder at 570 nm becomes the main emission peak with a significant reduction of the peak at 540 nm.

Photoluminescence spectra of solid-state polyethers **III**-*n-50/50* and **III**-*n-25/75* after excitation at 420 nm also show peaks at 550 and 600 nm. Figure 6 reveals that there is a dependence of the optical behavior of **III**-*n-x/y* in the solid state on the spacer segment length. So, polyether **III**-*11-25/75* shows a peak at 550 nm and a second much more intense peak at 580 nm, whereas in the case of polyether **III**-*10-25/75*, the higher inten-

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(47) Sarker, A.; Strehmel, B.; Neckers, D. *Macromolecules* **1999**, *32*, 7409.

(48) Song, X.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 7816.

(49) Song, X.; Geiger, C.; Leinhos, U.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 10340.

(50) Stampfl, J.; Tasch, S.; Leising, G.; Scherf, U. *Synth. Met.* **1995**, *71*, 2125.

sity emission is centered at 550 nm followed by a second peak at 600 nm. The emission peaks at 550 nm are due to the excited state of the isolated chains of the copolymers, whereas the emission peaks at 580 and 600 nm probably correspond to the excimer emission. Since the emission maxima of polyethers **I**-*n*-*x*/*y* to **III**-*n*-*x*/*y* in solution are similar, the observed differences in solid state (polyether **III**-*n*-*x*/*y* shows a second peak at 580−600 nm even at 25/75 composition) may be due to the manner of attachment of the blue light-emitting segments in the polymer backbone and the resulting arrangement of the chromophores in solid state.

In conclusion, the synthesis of soluble, easily processable rigid−flexible copolymers containing blue and yellow segments has been accomplished. These luminescent polymers show good mechanical properties. Depending on the structure of blue monomer, the molar percentage of comonomers, and the length of the aliphatic spacer, materials with controlled thermal properties are obtained. The photophysical properties of the polymers synthesized are identical in solution regardless of the excitation wavelength, suggesting energy transfer from the blue to the yellow segment. This, in combination with the photophysical behavior of immiscible blends composed of the two homopolymers, suggests that this behavior is possibly due to self-absorption after photon emission. In the solid state, the optical properties are strongly dependent on the copolymer structure and composition. The observed bathochromic shift in some cases supports the view that $\pi-\pi$ interactions of the chromophores are responsible for the observed complex behavior.

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Supporting Information Available: ^{1}H NMR integration of polyethers and DSC data obtained from the first heating scan and after annealing at various temperatures. This material is available free of charge via the Internet at http://pubs.acs. org.

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