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Synthesis and efficient circularly polarized light emission of an optically active hyperbranched poly(fluorenevinylene) derivative

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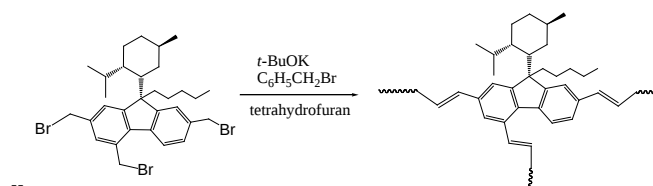
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An optically active, hyperbranched poly(fluorenevinylene) derivative was synthesized by polymerization of (-)-2,4,7-tris(bromomethyl)-9-neomenthyl-9-pentylfluorene. A spin-coated film sample of the polymer exhibited efficient circularly polarized light (CPL) emission in the visible range of 400–700 nm on photo excitation even without annealing processes leading to chain ordering.

Luminescent organic polymers are important as materials for organic light-emitting diodes (OLEDs) due to their tunable emission properties through molecular design and their inherent flexible nature and readiness in fabrication.¹ The most widely-studied luminescent polymers such as poly(*p*-phenylenevinylene),² polyfluorene,^{1b} and their derivatives³ have linear conjugated structures. However, for these polymers, interchain interactions are known to result in a low-energy emission and low emission efficiency due to excimer formation.⁴ In order to circumvent this drawback, three-dimensional, dendritic and hyperbranched conjugated polymers have been devised.^{5–7}

Herein, we present the synthesis and properties of a novel, chiral hyperbranched poly(fluorenevinylene) derivative. Chirality was readily introduced to the polymer chain by polymerizing optically active (-)-2,4,7-tris(bromomethyl)-9-neomenthyl-9-pentylfluorene (monomer) (a mixture of two diastereomers, $[\alpha]_D^{25} -58^\circ$ (CHCl₃, 1 g/dL, 0.1-dm cell)) having a chiral group attached to the 9-position of fluorene moiety (Scheme 1). The chiral polymer was designed after the achiral, parent polymer having two hexyl groups at the 9-position of fluorene ring.^{7a} The obtained polymer efficiently emitted circularly polarized light (CPL) without annealing processes. This observation is in sharp contrast to the fact



Scheme 1. Synthesis of an optically active, hyperbranched polymer.

that molecular ordering such as aggregate or liquid crystalline formation achieved by annealing has been the major trend of research toward efficient CPL emission.^{8,9}

The polymerization was carried out in tetrahydrofuran (THF) under conditions similar to those applied for the achiral, parent polymer.^{7a} The reaction of the monomer with *t*-BuOK and benzylbromide was conducted to afford a polymer soluble in THF and CHCl₃. The fact that the product was soluble indicates that no cross-linking took place and that the polymer has a hyperbranched structure.

Polymerization of (-)-2,4,7-tris(bromomethyl)-9-neomenthylfluorene has been also conducted. However, the product was mostly insoluble in THF and CHCl₃. The pentyl group at the 9-position of the fluorene ring seems to effectively prevent cross-linking in polymerization and also interchain interaction to result in high solubility of the hyperbranched polymer.

The product was purified by reprecipitation in methanol (Mn 29800, Mw/Mn 8.37 (vs. polystyrene)). Further, lower-molecular-weight fractions were removed from the product by fractionation using acetone. The acetone-insoluble part (58 wt%) had higher molecular weight (Mn 74300, Mw/Mn 4.77, $[\alpha]_D^{25} -64^\circ$ (CHCl₃, 1 g/dL, 0.1-dm cell)). Hereafter, structure and properties of the acetone-insoluble polymer are discussed.

The polymers is considered to consist of dendritic or branching (D), linear (L), and terminal (T) units.^{10,11} The ratio of these units was estimated from ¹H NMR spectrum of the polymer following the method of literature^{7a} and was used for the calculation of degree of branching (DB) which is defined as DB = ([D]+[T])/([D]+[L]+[T])^{10,11} (ESI). D/L/T was 0.23/0.23/0.54, and DB was 0.77. The DB of the chiral hyperbranched polymer was higher than that of the achiral, parent polymer^{7a} (DB 0.45~0.70). Bulkiness of neomenthyl group might reduce propagation giving linear units.

Chirality of the monomer and the polymer was examined by circular dichroism (CD) spectra (Fig. 1). The monomer indicated a Cotton effect with a negative signal corresponding to UV absorptions in a THF solution in the range of

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wavelength shorter than 350 nm, indicating that the π -electrons in fluorene unit of the monomer are in a chiral environment under the effect of the neomenthyl group (Fig. 1A). Kuhn's dissymmetry factor ($g = \Delta\epsilon/\epsilon$) was -0.63×10^{-4} at 300 nm. The polymer also showed an intense CD spectrum in a THF solution (Fig. 1B). The UV spectrum of the polymer indicated a strong band peaked around 375 nm that was not seen in the monomer spectrum. This band may be based on the fluorenevinylene conjugation system. That the polymer indicated CD absorptions in the entire wavelength range where the polymer absorbs suggests that the entire conjugation system is under the chiral effect of the neomenthyl group. The g factor at 300 nm was -0.99×10^{-4} .

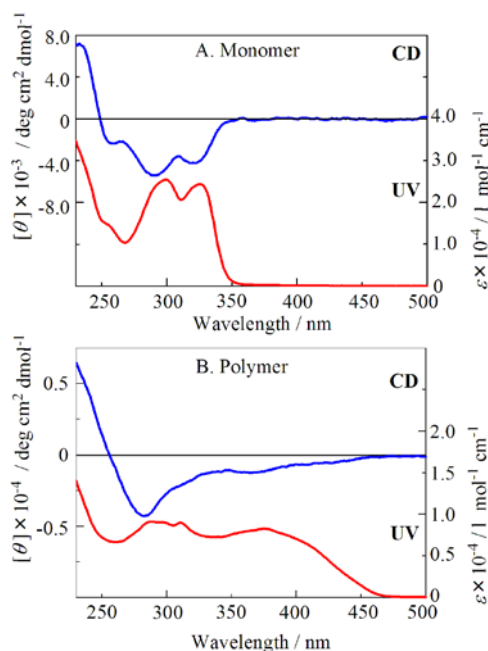


Fig. 1 CD and UV spectra of (-)-2,4,7-tris(bromomethyl)-9-neomenthyl-9-pentylfluorene (monomer) (A) and the hyperbranched polymer (B). [in THF, room temperature, conc. 1.00×10^{-3} M]

The polymer also indicated a CD spectrum in a spin-coated film form. The spectral shape was similar to that in solution with g factor at 300 nm of -1.44×10^{-4} , suggesting that the chiral structure of the polymer does not largely change by film fabrication.

Fig. 2 shows the fluorescence spectra of the polymer in solution and in film on irradiation at 378 nm. Both in solution and in film, the polymer exhibited a broad emission band in the range of 400–700 nm. The film emission was as intense as the solution emission and was slightly red shifted.

CPL emission of the polymer was measured by irradiating the film at 375-nm pulsed laser light.^{8a} The CPL-fluorescent spectra are shown in Fig. 3A. A significant difference in intensity between right-handed (R-) and left-handed (L-) CPL emission was confirmed. The photo luminescent dissymmetry factor (g_{PL}) was calculated according to $g_{PL} = 2(IL - IR)/(IL + IR)$, where IL and IR are the intensities of L- and R-CPL emission, respectively, and its dependence on

wavelength is shown in Fig. 3B. g_{PL} value was highest (-0.45) at 430 nm and was -0.16 at 490 nm (emission peak maximum). These g_{PL} values are ca. 10^3 times greater than the g values for CD absorption of the polymer and the monomer.

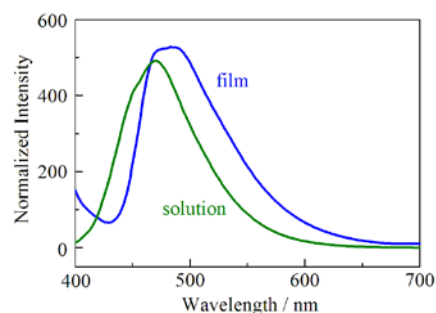


Fig. 2 Fluorescence spectra of hyperbranched polymers in THF solution and in film obtained by excitation at 378 nm. Intensity was normalized to a constant absorbance at 378 nm. [solution samples, conc. 1.00×10^{-5} M, 1-cm cell]

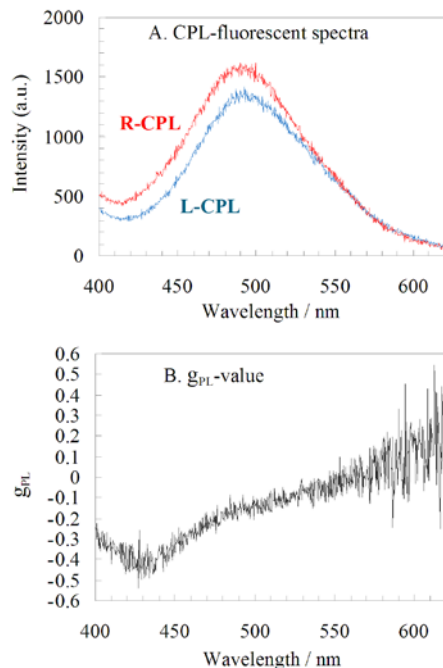


Fig. 3 CPL-fluorescent spectra (A) and g_{PL} -vs.-wavelength plot (B) of the hyperbranched polymer film. The spectra were obtained on excitation at 375 nm.

The g_{PL} values observed here of the order of 10^{-1} are comparable to those reported for polymers with highly-ordered intra- and intermolecular structures⁹ and those for crystalline or liquid crystalline low-molecular-weight compound systems.⁸ This is noteworthy because the hyperbranched polymer studied in this work was not annealed to attain ordered structures. In addition, hyperbranched polymers generally do not have close chain packing.¹¹ Lack of highly-ordered structures in the polymer was supported by the following examinations. Differential

scanning calorimetric (DSC) analyses of the polymer indicated no clear exo- or endothermic transitions from room temperature to 195°C at which the polymer starts to decompose (ESI). In addition, polarized microscopic observations of the film sample used for the CPL experiments did not show any textures suggesting ordered structures.

Furthermore, difference in light transmittance between L- and R-CPL in the wavelength range of 400-700 nm, where the polymer emits light and does not absorb light, was too small to explain the g_{PL} values; g values for transmission were of the order of 10^{-2} (ESI). In addition, L-CPL was found to more readily transmit the film than R-CPL while R-CPL was more intense than L-CPL in emission. These results most conclusively indicate that the observed, effective CPL emission is not due to ordering in the film.

In order to obtain information on the reason why the chiral hyperbranched polymer shows large g_{PL} values, the CPL emission spectrum of 9-neomenthyl-9-pentylfluorene, as a model monomeric unit, was measured in a THF solution (ESI). This unit has never been used as a part of repeating units in polymers to the best of our knowledge. In contrast to the hyperbranched polymer, this compound showed only moderate CPL emission with a g value of 10^{-4} order. This result clearly indicates that the observed intense CPL emission from the hyperbranched polymer is not due to this particular and unprecedented chiral moiety in the polymer structure. Based on this conclusion, we propose that a rather amorphous state in the solid state may enhance CPL emission for the hyperbranched polymer while ordered intra- and interchain structures play an important role in CPL emission for linear polymers.⁹

Furthermore, the hyperbranched polymer showed only weak CPL emission in a THF solution (ESI). This means that solid-state, amorphous polymer structure is important to enhance CPL emission.

In addition, the acetone-soluble, lower-molecular-weight fraction (M_n 7300, M_w/M_n 3.71, $[\alpha]_D^{25}$ -67° (CHCl₃, 1 g/dL, 0.1-dm cell), DB 0.73) obtained from the original polymerization product indicated CPL emission with much less efficiency compared with the acetone-insoluble, higher-molecular-weight polymer discussed so far (ESI). This suggests that an extended hyperbranched structure enhances CPL emission. The extended hyperbranched structure may result in a more amorphous material.

In conclusion, we have synthesized a novel, chiral, hyperbranched poly(fluorenevinylene) derivative and found its effective CPL emission. This work has shown for the first time that effective CPL emission can be attained without the aid of molecular ordering and that an amorphous state may even enhance CPL emission ability.

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