Influence of polymer conformations on the aggregation behaviour of alternating dialkylsilylene-[4,4′-divinyl(cyanostilbene)] copolymers†

Chih-Hsien Chen,*a Shern-Long Lee,*a Tsong-Shin Lim,b Chun-hsien Chen*a and Tien-Yau Luh*a

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The influence of the substituents at silicon on the aggregation enhanced emission (AEE) of alternating dialkylsilylene-[4,4′-divinyl(cyanostilbene)] copolymers 3 and 4 is examined. The presence of the bulky isopropyl group in 3b significantly enhances the quantum yield upon aggregation. On the other hand, the emission intensity of the methyl-substituted polymer 3a is only slightly enhanced under the same conditions. The bulky isopropyl substituents on silicon may exert the Thorpe–Ingold effect on these copolymers resulting in conformation difference, which may dictate the nature of the aggregation between polymers, and hence, the photophysical behaviour of these polymers.

Introduction

The conformation of a polymer chain and the feature of its interchain interactions should be closely related, and an ensemble of these factors, *inter alia*, will determine the macroscopic properties of polymers and nanomaterials.† Direct correlation of the polymer conformation with the aggregation properties, in general, is a nontrivial problem. Interrelationship between the conformation of poly(p-phenylene-ethynylene)s, substituted with well-designed hydrophobic and hydrophilic moieties, and interchain interactions has been explored. Substituents on poly(p-phenylene-vinylene)s have been shown to control the interchain interactions, hence the mode of aggregation can be adjusted. It is known that a change of medium, ionic strength, temperature, irradiation, and other relevant factors may affect the polymer conformation and the aggregation nature of polymers. Circular dichroic (CD) properties of certain silicon-containing polymers are enhanced upon aggregation. In this regard, the nature of the substituents on silicon may play an important role in the conformation of the polymers and hence the aggregated form.

We recently found that the photophysical properties of alternating dialkylsilylene-divinylarene copolymers 1 depend on the size of the substituent R on silicon, which may exert the Thorpe–Ingold effect on the conformation of these copolymers. The advantage of using polymer 1 is that the chromophores Ar1 and Ar2 as well as the alkyl substituent R can readily be modified. The conformational equilibrium of the distyrylsilane subunit in 1 may...
dictate the overall morphology of the polymer, and hence, the
distance between the two adjacent chromophores in these
polymers can be tuned (eqn (1)). Indeed, the STM images of 1 (Ar\textsuperscript{1} =
Ar\textsuperscript{2} = 1,4-C\textsubscript{6}H\textsubscript{4}, R = Me) exhibit a fluffy morphology, whereas those of 1 with same chromophores and R = Ph show a coil-like
structure.\textsuperscript{16} The emission wavelength of methyl substituted 2a
appears at much shorter wavelengths than that of isopropyl-
substituted 2b, presumably due to the different folding nature of
these two polymers. In addition, 2a is CD inactive in dilute
solution (10 mg L\textsuperscript{-1}) and becomes active only in the aggregated
state at a high concentration (1 g L\textsuperscript{-1}), whereas 2b shows CD
response at dilute conditions.

It is known that the emission of small molecules such as
substituted cyano-substituted stilbenes can be enhanced upon
aggregation.\textsuperscript{12,13} Planarisation of chromophore and restriction of
excimer formation in the presence of the cyano substituent may
account for this unusual photophysical behaviour.\textsuperscript{12,13} Siloles and
other related systems behave similarly. The aggregation
enhanced emission (AEE) has also been found in polymers such as
polysiloles,\textsuperscript{14} poly(p-phenylene-ethynylene),\textsuperscript{15} poly(1,4-bis(β-
cyano-4-methylstyryl)benzene),\textsuperscript{16} polycatenylenes,\textsuperscript{17} and poly
quinolines.\textsuperscript{18} It is therefore envisaged that a variation of the
substituent R on silicon in 1 may offer a useful probe to elucidate
the relationship between the conformation of the individual
polymer and the aggregation nature of these polymers. 4,4’-
Divinyl-cyano-stilbene chromophore was chosen because similar
monomers with related chromophores are known to exhibit
aggregation induced emission (AIE).\textsuperscript{12} We now wish to report
the synthesis and photophysics of alternating dialkylsilylene-
(divinyl(cyano-stilbene)) copolymers 3 and 4.

Results and discussion

Synthesis

The synthesis of monomer 5 and copolymers 3 and 4 are sum-
marised in Scheme 1. The Heck reaction of aryl halides with
vinylsilanes is the key protocol for the synthesis of 3–5 and the
details are described in the Experimental section. It is noteworthy
that the orientations of the cyano substituents in 3b are random,
while those in 4 are unidirectional.

Steady state photophysical properties of 3–5

The absorption spectra of monomer 5 are compared with those
of polymers 3 and 4 in Fig. 1 and the relevant photophysical
properties are summarised in Table 1. The absorption maximum
(\(\lambda_{\text{max}}\)) of 5 in THF appeared at 360 nm, whereas the absorption
of the thin film of 5, prepared by thermal evaporation on a quartz
substrate, exhibited broader full width at half maximum (fwhm)
at the similar wavelength than that in solution. The \(\lambda_{\text{max}}\) for 3a,
with methyl substituents on silicon, was observed at the similar
wavelength. On the other hand, the \(\lambda_{\text{max}}\) for 3b and 4, having
isopropyl groups on silicon, exhibited bathochromic shifts rela-
tive to those of 3a and 5. It is worth noting that the fwhm for
polymers 3 and 4 was also broader than that for 5.

The emission profiles of 3–5 in dilute THF solution (1 \times 10\textsuperscript{-5} M)
are shown in Fig. 2 and the quantum yields of these substrates
are outlined in Table 1. Like the related monomer 13,\textsuperscript{12b} the
quantum yield of 5 was extremely low (<0.001). The emission

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Absorption spectra of (a) 5 in THF (1.0 \times 10\textsuperscript{-1} M, black), (b) thin
film of 5 (green, arbitrary unit), (c) 3a in THF (3.2 mg L\textsuperscript{-1}, red), (d) 3b
THF (3.7 mg L\textsuperscript{-1}, blue), and (e) 4 in THF (3.7 mg L\textsuperscript{-1}, brown).}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Material & Absorbance
\hline
5 & 0.12
3a & 0.02
3b & 0.03
4 & 0.11
\hline
\end{tabular}
\caption{Absorption data for 5, 3a, 3b, and 4.}
\end{table}

References:
Solvent-induced aggregation of polymers

The aggregation behaviour of polymers was studied in a mixed solvent of \textit{n}-hexane and THF. Polymers 3 and 4 are highly soluble in THF but sparingly soluble in \textit{n}-hexane. It is interesting to note that these polymers gave clear solutions in 80\% \textit{n}-hexane and 20\% THF without precipitation. Dynamic light scattering investigations revealed that the average particle sizes of 3a and 3b were 90 and 100 nm, respectively, under these conditions (Fig. 4). These results indicate that 3 may exist in an aggregated state in mixed \textit{n}-hexane–THF co-solvents. The photophysical properties of 3 and 4 in these mixed solvents at different ratios are tabulated in Table 1 and the spectra are shown in Fig. 5–7. The quantum yields for 3a were only slightly increased in these mixed solvent systems. It is particularly noteworthy that the quantum yields of 3b and 4 were significantly enhanced as the ratio of \textit{n}-hexane increased under the same conditions. The orientations of chromophores in 3b are random, while those in 4 are unidirectional. However, there was little discrepancy in photophysical properties between these two isomeric polymers in aggregated states.

As shown in Fig. 5, little changes in Stokes shifts for 3a were observed for the solvent dependent photophysical behaviour. On the other hand, the Stokes shifts for 3b and 4 decreased with increasing \textit{n}-hexane content in these mixed solvents. A decrease in Stokes shifts implies that the chromophore may become more rigid as the polarity of the mixed solvent decreased. As shown in Table 1, quantum yields of 3b and 4 were only slightly increased in these mixed solvent systems. It is noteworthy that the quantum yields of 3b and 4 were significantly enhanced as the ratio of \textit{n}-hexane increased under the same conditions. The orientations of chromophores in 3b are random, while those in 4 are unidirectional. However, there was little discrepancy in photophysical properties between these two isomeric polymers in aggregated states.

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likely that the isopropyl substituents on silicon as in 3b and 4 would exert the Thorpe–Ingold effect on the local conformation of the divinylsilane moiety, and hence the overall conformation of the polymer.9,10 On the other hand, the methyl-substituted polymers such as in 3a would be more fluxional.9,10 Such conformational difference may affect the nature of the aggregation of these dialkylsilylene-divinylarene copolymers 3 and 4.

Solid state properties

The glass transition temperature ($T_g$) of 3b ($150 \degree C$) is higher than that of 3a ($118 \degree C$).† Powder X-ray diffraction (XRD) of both 3a and 3b showed three characteristic peaks at $2\theta = 40, 46,$ and 68°.† However, the half widths of these peaks for 3a were slightly broader than those of 3b. The crystal sizes of 3a and 3b, calculated by Scherrer’s formula,24 were 9.9 and 11.5 nm, respectively.† These results suggest that 3a and 3b might exhibit a similar packing structure, but the range of the ordered orientation seems to be more extended in 3b than in 3a. The scanning tunneling microscopic (STM) images of 3a and 3b are shown in Fig. 8. It is interesting to note that the morphology for each of the polymeric molecules 3a in aggregated form appears to be an elongated rod, whereas 3b shows a coil-like molecular structure. This observation was similar to those reported earlier on related polymers.11,22c The discrepancy in solid state properties between 3a and 3b might correlate to the photophysical behaviour of the aggregation properties of these polymers in solution, although the actual mode of interactions remains to be solved.

Kinetic measurements

Time-resolved fluorescence spectroscopy using femto-second Ti-sapphire laser equipped with a streak camera was employed to give the fluorescence decay lifetimes by single exponential fitting. The decay profiles for 3a, 3b and 4 are shown in Fig. 9 and the results are also outlined in Table 1. The lifetimes for 3a in

![Fig. 4](image1.png) Particle size distribution of 3a (red) and 3b (blue) in n-hexane/THF (80/20).

![Fig. 5](image2.png) Absorption (solid lines) and emission spectra (dashed lines) of 3a in different ratios of n-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

![Fig. 6](image3.png) Absorption (solid lines) and emission spectra (dashed lines) of 3b in different ratios of n-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

![Fig. 7](image4.png) Absorption (solid lines) and emission spectra (dashed lines) of 4 in different ratios of n-hexane/THF: 0/100 (black), 50/50 (red), 67/33 (green), 75/25 (blue), and 80/20 (brown).

![Fig. 8](image5.png) STM images of (a) 3a and (b) 3b on highly ordered pyrolytic graphite (HOPG). Imaging conditions: $E_{bias}$, $I_{tunneling}$ and image sizes were 0.95 V, 90 pA, and 50 × 50 nm.
different mixed n-hexane–THF solvents were around 190 ps, whereas those for 3b and 4 were gradually increased from 180 to 350 ps under the same conditions. An increase of fluorescence lifetimes may be attributed to the lower contribution from other radiationless decay processes, and hence, a higher quantum yield would be expected. These kinetic results were consistent with the steady state measurement discussed above.

Conclusions
In summary, we have demonstrated an interesting feature on the influence of the substituents at silicon on the AEE of alternating dialkylsilylene[divinyl(cyanostilbene)] copolymers 3 and 4. The presence of the bulky isopropyl group in 3b significantly enhances the quantum yield upon aggregation. On the other hand, the emission intensity of the methyl-substituted polymer 3a is only slightly enhanced under the same conditions. It is known that the substituents on silicon may exert the Thorpe–Ingold effect on silylene-spaced divinylarene copolymers. Consequently, the conformation of 3b may be very different from that of 3a due to the steric effect. It seems likely that this conformation difference may dictate the nature of the aggregation between polymers, and hence, the photophysical behaviour of these polymers. The present study offers a preliminary platform to correlate the conformation of this silicon-containing polymer and the mode of interchain aggregation.

Experimental section

General
High-resolution mass spectrometric measurements were obtained from a Jeol-JMS-700 mass spectrometer using the FAB method in 3-nitrobenzyl alcohol matrix and the EI method was collected with a resolution of 8000(3000) (5% valley definition). Gel permeation chromatography (GPC) was performed on a Waters GPC machine using an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1 mL min⁻¹). Waters Styragel HR2, HR3, HR3, and HR4 (7.8 × 300 mm) columns were employed for molecular weight determination, and polystyrenes were used as the standard (Mn values ranging from 375 to 3.5 × 10⁶). Absorption spectra were recorded on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield was obtained using coumarin-I in EtOAc as reference (Φ = 0.99). Particle sizes of polymers in mixed co-solvent were measured on a Malvern Zetasizer Nano S90 using dynamic light scattering. X-Ray powder diffraction patterns were recorded on a PANalytical X’Pert PRO. The glass transition temperature was measured on a LT-Modulate DSC 2920 calorimeter.

(Z)-2,3-Bis(4-iodophenyl)acrylonitrile (8)
A solution of NaOH (50 mg) in ethanol (30 mL) was added dropwise to the mixture of 6 (2.43 g, 10.0 mmol) and 4-iodobenzaldehyde (2.32 g, 10.0 mmol) in ethanol (50 mL). The reaction mixture was stirred at rt for 1 h. The precipitate was collected as a white solid (4.11 g, 90%); mp 157–158 °C; ¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, J = 8.8 Hz, 2H), 7.44 (s, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 95.4, 97.3, 111.4, 117.1, 127.4, 130.5, 132.6, 133.5, 138.08, 138.09, 141.0; IR (KBr) ν 3046, 2221, 1581, 1486, 1405, 1345, 1010, 992, 926, 832, 817 cm⁻¹; HRMS (EI⁺) (M⁺) calcd for C₁₅H₉I₂N: 456.8825. Found: 456.8826.

(Z)-2-(4-Bromophenyl)-3-(4-iodophenyl)acrylonitrile (9)
A solution of NaOH (50 mg) in ethanol (30 mL) was added dropwise to the mixture of 7 (1.96 g, 10.0 mmol) and
4-iodobenzaldehyde (2.32 g, 10.0 mmol) in ethanol (50 mL). The reaction mixture was stirred at rt for 1 h. The precipitate was collected as a white solid (3.73 g, 91%); mp 135–136°C; 1H NMR (CDCl3, 400 MHz): δ 4.74 (s, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl3, 100 MHz): δ 97.3, 111.3, 117.2, 123.6, 127.3, 130.5, 132.1, 132.6, 132.9, 138.1, 141.0; IR (KBr) ν 3047, 2220, 1645, 1490, 1403, 1073, 1002, 919, 833, 820 cm⁻¹; HRMS (FAB+) (M⁺) calcd for C15H9BrIN: 401.1989. Found: 401.1989.

(Z)-2,3-Bis[(E)-2-(trimethylsilyl)vinyl]phenyl]acrylonitrile (5)

A mixture of 8 (0.91 g, 2.0 mmol), Pd(OAc)2 (45.0 mg, 0.2 mmol), and Bu4NOAc (1.82 g, 6.0 mmol) in dry DMF (30 mL) was stirred at 80 °C for 24 h. After filtration over celite, the crude product was chromatographed on silica gel (10% CH2Cl2/hexane) to give 8 as a yellow solid (0.16 g, 20%); mp 128–129°C; 1H NMR (CDCl3, 400 MHz): δ 7.42 (s, 1H), 7.52 (d, J = 19.2 Hz, 1H), 7.61 (d, J = 19.2 Hz, 1H), 6.89 (d, J = 19.2 Hz, 1H), 6.90 (d, J = 19.2 Hz, 1H), 7.45–7.55 (m, 5H), 7.64 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl3, 100 MHz): δ −1.12, −1.11, 110.5, 118.0, 125.9, 126.7, 126.8, 129.5, 131.3, 132.30, 133.0, 133.7, 139.0, 140.2, 140.9, 142.2, 142.3; IR (KBr) ν 3056, 2993, 2955, 2894, 2217, 1600, 1511, 1416, 1251, 982, 868, 836 cm⁻¹; HRMS (FAB+) (M⁺) calcd for C25H31NSi2: 408.8995. Found: 408.8994.

(Z)-2-(4-Bromophenyl)-3-((E)-2-(dimethyl(vinyl)silyl)vinyl)phenyl]acrylonitrile (12)

A mixture of 9 (0.82 g, 2.0 mmol), 11b (0.34, 2.0 mmol), Pd(OAc)2 (22.0 mg, 0.1 mmol), and Bu4NOAc (1.21g, 4.0 mmol) in dry DMF (30 mL) was stirred at 80 °C for 24 h. After filtration over celite, the crude product was chromatographed on silica gel (10% CH2Cl2/hexane) to give 12 as a pale yellow solid (90.0 mg, 20%); mp 88–89°C; 1H NMR (CDCl3, 400 MHz): δ 1.00–1.20 (m, 14H), 5.85 (dd, J = 7.8, 17.0 Hz, 1H), 6.15 (d, J = 17.0 Hz, 1H), 6.18 (d, J = 7.8 Hz, 2H), 6.56 (d, J = 19.2 Hz, 1H), 7.00 (d, J = 19.2 Hz, 1H), 7.50 (s, 1H), 7.53–7.59 (m, 6H), 7.88 (d, J = 8.4 Hz, 2H); 13C NMR (CDCl3, 100 MHz): δ 11.5, 18.3, 18.4, 109.7, 117.4, 123.0, 125.6, 126.5, 127.0, 129.3, 131.8, 132.48, 132.50, 133.1, 134.5, 140.1, 141.5, 145.0; IR (KBr) ν 3120, 3047, 2983, 2222, 1640, 1491, 1403, 1390, 1070, 998, 910, 818 cm⁻¹; HRMS (FAB+) (M⁺) calcd for C25H28BrNSi: 449.1176. Found: 449.1176.

General procedure for the preparation of 3

A mixture of dialkyldivinylsilane (0.2 mmol), 8 (82.0 mg, 0.2 mmol), Pd(OAc)2 (3.0 mg), and Bu4NOAc (60.0 mg, 0.2 mmol) in dry DMF (3.0 mL) was refluxed under N2 for 24 h. After cooling to rt, the mixture was poured into EtOAc. The precipitate was collected and dissolved in THF, and then reprecipitated with MeOH. The product was collected by filtration and washed with MeOH.
irradiation to form the aggregates of polymers for photophysical measurements.

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Notes and references


