Controlled synthesis of luminescent polymers using a bis-dithiobenzoate RAFT agent

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A higher efficiency of excitation energy transfer occurs to a luminescent diphenylanthracenyl acceptor incorporated at the centre, rather than the end, of an acenaphthylene polymer chain.

Luminescent polymers are finding increasing applications in display devices, as sensors and probes of molecular environments and as light harvesting systems that mimic the light collection processes of natural photosynthetic pigment arrays.[1] The synthesis of luminescent polymers with well defined architectures is a requirement for the development of optimized structures for these, and new, applications. In particular the ability to place luminescent groups at particular locations along a polymer chain can potentially provide control of the process of excitation energy transfer.[2] We have previously described the application of controlled living radical polymerization using reversible-addition fragmentation chain transfer (RAFT) to produce linear and star-shaped light harvesting homopolymers and block copolymers of defined structure and low polydispersity.[3] We report here a further refinement of the RAFT method to place a highly luminescent group (diphenylanthracenyl, DPAn) at the centre position of a linear aromatic polymer chain (poly(acenaphthylene), PAcN) and describe the effects on energy transfer processes in the resulting polymer.

The RAFT method has proved one of the most versatile living free radical polymerisation techniques for synthesizing polymers and, in principle, can be applied to all classical radical polymerisation systems.[4] The RAFT process uses particular added chain transfer agents, often of the thiocarbonylthio type, to control reversible addition–fragmentation steps during the free radical polymerisation of a monomer. The overall process is given in Scheme 1.

It is apparent that RAFT polymerisation provides a means of introducing specifically placed luminescent groups into the polymer since a component of the functionalised RAFT agent (R) will be incorporated at the end of each polymer chain.[3] We have also described a method to readily synthesize appropriately functionalised RAFT agents *via* a reversible radical reaction between a vinyl monomer and 2-cyanoprop-2-yl dithiobenzoate (RAFT-IBN) (Scheme 2).[5]

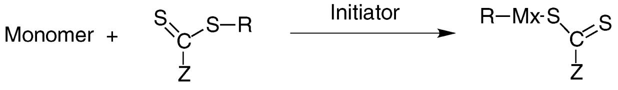
The resulting RAFT agent incorporates the required energy accepting luminescent group (A) *via* a stable carbon–carbon linkage and can be used to control the polymerisation of suitable vinyl monomers containing energy donor chromophores.

The method described in Scheme 2 can be extended to synthesize a bis-RAFT agent by using a divinyl monomer as the reactant and, for the application described here, we have used 9,10-(p,p'-divinyl)-diphenylanthracene.† The synthesis is summarized in Scheme 3. The resulting bis-RAFT agent has been used to control the polymerisation of the monomer acenaphthylene to produce poly(acenaphthylene) with a 9,10-diphenylanthracenyl chromophore centrally placed in the polymer chain. For comparative purposes, poly(acenaphthylene) with DPAn as an end group was also prepared by similar means but using the monofunctional RAFT agent prepared from 9-(p-vinylphenyl)-10-phenylanthracene (see Scheme 4).‡ The terminal dithiobenzoyl end groups, that have been shown by us previously to quench fluorescence in polymers,[3] were desulfurated by tributyltin hydride to obtain the required polymers P(AcN)–DPAn–P(AcN) and P(AcN)–DPAn.

The molecular weights of the final polymers determined by calculation, UV-vis spectroscopy and gel permeation chromatography (GPC) are provided in Table 1. The narrow molecular weight distribution (M_w/M_n <1.3) combined with the close agreement between M_n values determined by the spectrophotometric method and those calculated assuming a controlled RAFT mechanism, confirms that the polymer chains have the structure predicted. The M_n values determined by GPC are substantially lower reflecting the different elution behaviour of PAcN compared to the polystyrene GPC calibration standards.

Acenaphthyl and 9,10-diphenylanthracenyl were selected as the chromophores for the present work since they form an energy donor–acceptor pair that fulfils the spectral overlap requirements for radiationless electronic energy transfer (in dichloromethane, the Förster[6] critical transfer distance for this donor–acceptor pair is 28 Å). Furthermore, acenaphthyl can be preferentially excited between 290 nm and 320 nm with minimal direct excitation of DPAn.

A comparison of the fluorescence spectra observed from dilute ($<10^{-5}$ M) degassed dichloromethane (DCM) solutions



Scheme 1 Overall process for RAFT polymerization.

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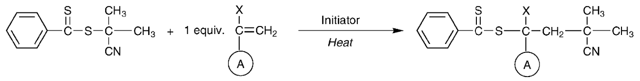
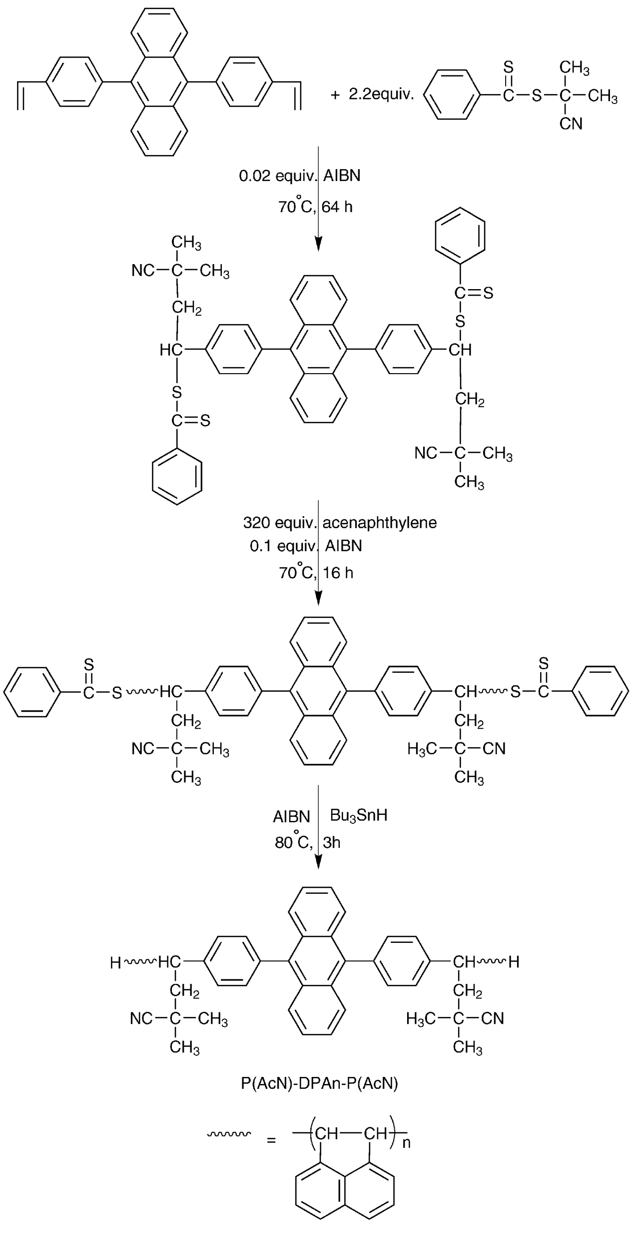


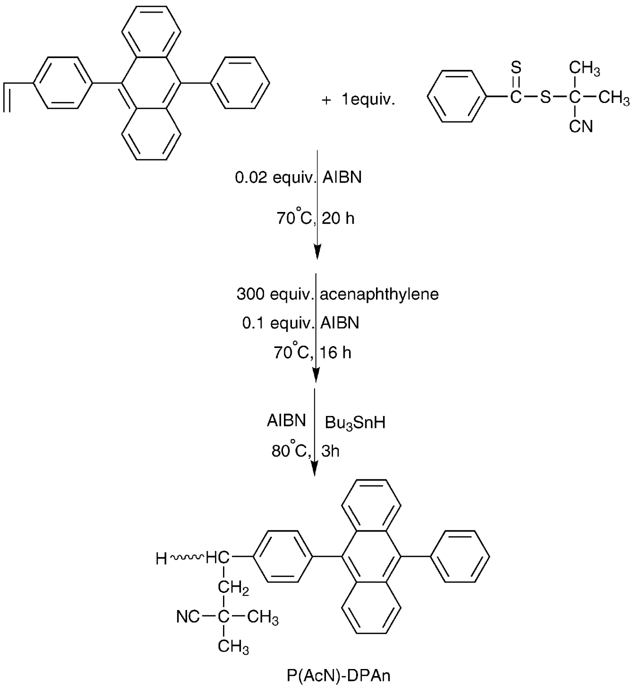
Scheme 2 General procedure for the synthesis of functionalized RAFT agents.

of the two polymers is presented in Fig. 1. The fluorescence quantum yield of the DPAn fluorophore in the polymers in deoxygenated DCM solutions using an excitation wavelength of 355 nm (where only DPAn asborbs) was determined to be 0.70 and 0.76 for P(AcN)–DPAn–P(AcN) and P(AcN)–DPAn, respectively by comparison with the fluorescence of anthracene in ethanol (fluorescence quantum yield of 0.27)[7] as a reference compound.

Photoexcitation of both polymers at 295 nm (see Fig. 1), where absorption is almost exclusively due to acenaphthyl groups, results in fluorescence being predominantly emitted from DPAn (emission maximum at 420 nm). Furthermore, the fluorescence excitation spectrum of the DPAn emission contained a major contribution attributable to acenaphthyl absorption demonstrating that energy transfer to the DPAn moiety from acenaphthyl groups in the polymer is occurring. The efficiencies of energy transfer from acenaphthyl to DPAn in the polymers were determined by the method described previously[3] and are reported in Table 2.



Scheme 3 Synthesis of P(AcN)–DPAn–P(AcN).



Scheme 4 Synthesis of P(AcN)–DPAn.

The luminescence spectrum in Fig. 1 for P(AcN)–DPAn–P(AcN) exhibits a more strongly quenched emission from acenaphthyl (at 328 nm) and enhanced emission from DPAn (at 420 nm) compared to P(AcN)–DPAn. The calculated excitation energy transfer (EET) efficiencies confirm that energy transfer in the polymer with the centrally located DPAn trap is significantly higher (80%) than that for the end-located trap (61%), even though both polymers have almost identical donor : acceptor ratios.

Table 1 Comparison of polymer molecular weights determined by various methods

	M_n by GPC[a]			
	M_n	M_w/M_n	M_n by UV[b]	Calculated M_n[c]
P(AcN)–DPAn–P(AcN)	5000	1.26	10 200	9900
P(AcN)–DPAn	3500	1.21	9500	9200

[a] GPC was performed in THF using a refractive index detector, and molecular weights are reported as linear polystyrene equivalents. [b] In the UV method, the absorbance of the polymer solution is compared to the absorbance of solutions of known concentrations of acenaphthylene homopolymer and the incorporated RAFT agents at 297 and 347 nm, respectively. [c] Theoretical molecular weights were calculated using the expression M_n(calc) = ([monomer]/[RAFT agent]) × fractional conversion × M_W of monomer + M_W of RAFT agent.

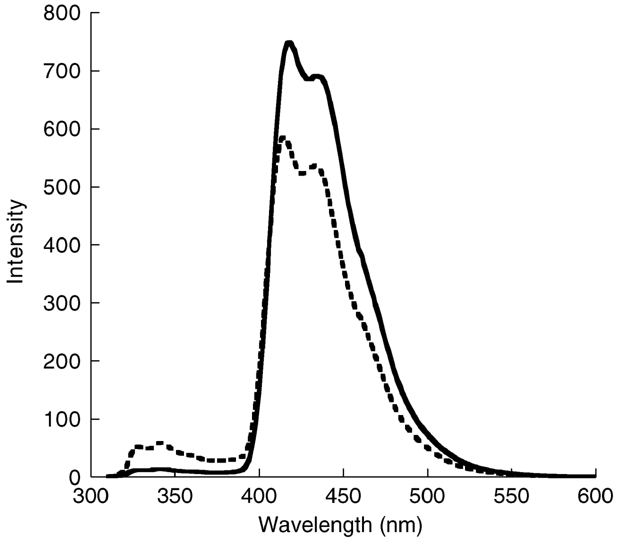


Fig. 1 The fluorescence spectra of P(AcN)–DPAn–P(AcN) (—) and P(AcN)–DPAn (- - -) in degassed DCM solutions excited at 295 nm. The polymer solutions have the same absorbance at the excitation wavelength.

Table 2 Donor/acceptor ratios and excitation energy transfer (EET) efficiencies for the polymers

	Donor/acceptor	EET efficiency (%)
P(AcN)–DPAn–P(AcN)	60	80
P(AcN)–DPAN	57	61

It has been shown that in acenaphthylene polymers, energy migration among adjacent acenaphthyl chromophores occurs with high efficiency but can be interrupted by trapping at sites of polymer heterogeneity including excimer (excited dimer) sites.[8] While both polymers have similar molecular weights and donor : acceptor ratios, it might be expected that a migrating exciton resulting from photoexcitation of acenaphthyl chromophores will have, on average, a shorter distance to travel and successfully reach the centrally located, rather than an end-located, DPAn trap. The energy migration process can thus explain the higher energy transfer efficiency observed in P(AcN)–DPAn–P(AcN).

In conclusion, a difunctional RAFT agent has been synthesised using a radical addition–fragmentation reaction. These RAFT agents can be used to incorporate luminescent energy traps as a centrally located component of polymer chains. For the polymers studied in this work locating a DPAn chromophore at the centre, rather than the end, of a PAcN chain leads to significantly higher energy transfer efficiencies.

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† A mixture of 2-cyanoprop-2-yl dithiobenzoate (2.0 molar equiv.), AIBN, 9,10-(p,p'-divinyl)-diphenylanthracene,[9] and chlorobenzene was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and heated in a 70 °C oil bath for 64 h. After purification by column chromatography, an orange solid product was obtained (47% yield). 1H NMR (500 MHz, $DCCl_3$-d3, ppm): δ 1.33 (t, 6H, 2 × –CH3), 1.53 (s, 6H, 2 × –CH3), 2.30–2.45 (m, 4H, 2 × –CH2–), 5.32 (q, 2H, 2 × –S–CH(Ar)–), 6.88–7.94 ppm (m, 13H, ar.).

‡ A mixture of 2-cyanoprop-2-yl dithiobenzoate (1.0 molar equiv.), AIBN, 9-(p-vinylphenyl)-10-phenylanthracene,[9] and chlorobenzene was degassed through three freeze–pump–thaw cycles, sealed under vacuum, and heated in a 70 °C oil bath for 20 h. After purification by column chromatography, an orange solid was obtained (75% yield). 1H NMR (400 MHz, $DCCl_3$-d3, ppm): δ 1.33 (t, 3H, –CH3), 1.53 (s, 3H, –CH3), 2.30–2.45 (m, 2H, –CH2–), 5.32 (q, 1H, –S–CH(Ar)–), 6.88–7.94 ppm (m, 21H, ar.).

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