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Synthesis of light harvesting polymers by RAFT methods

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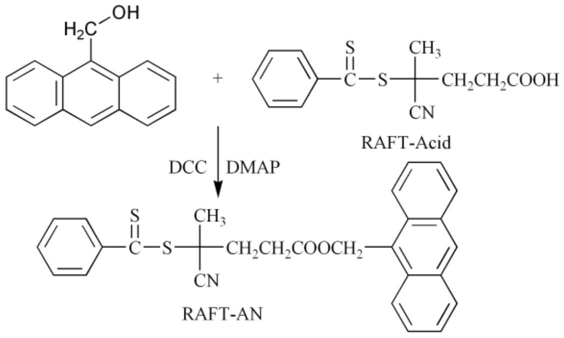
Polymers prepared by RAFT polymerisation containing acenaphthyl energy donors and a terminal anthryl energy acceptor have a narrow molecular weight distribution and exhibit excitation energy transfer efficiencies up to 70%.

The development of molecules capable of mimicking the light harvesting process of natural photosynthesis has been a long-standing goal of synthetic chemists.[1] The use of polymeric structures for the assembly of arrays of chromophores within a single macromolecule containing relatively few energy-acceptor units was pioneered by Fox *et al*.[2] and Guillet *et al*.[3] and was further explored by other researchers.[4] These polymers are known as 'light-harvesting' or 'antenna' polymers. Many of the light harvesting polymers reported to date are synthesized by conventional free radical polymerisation. Unfortunately, due to the inevitable, near diffusion-controlled bimolecular radical coupling and disproportionation reactions, the polymers made by conventional radical polymerisation usually have a broad molecular weight distribution and lack molecular weight and architecture control.

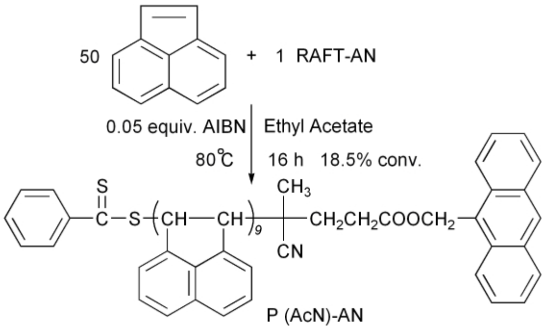
Living radical polymerisation has recently emerged as one of the most effective synthetic routes to well-defined polymers. Several approaches have been reported: nitroxide mediated polymerisation[5] (NMP), atom transfer radical polymerisation[6] (ATRP) and reversible addition fragmentation chain transfer polymerisation[7] (RAFT). However, the use of NMP and ATRP in the synthesis of block copolymers and other structures of complex architecture has been limited by the fact that the processes are not compatible with certain monomers or reaction conditions, or both. For example, although NMP can be successfully used for making block copolymers based on styrene and its derivatives, it appears to have less utility for other systems. ATRP has limitations with monomers or initiators containing acid functionality and generates products contaminated with metal ions. However, in principle, all classic radical systems can be converted to the RAFT process in the presence of efficient transfer reagents.

Energy acceptors can be incorporated into the RAFT agents by reaction of appropriate species with functional dithiobenzoates such as 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (RAFT-Acid).[8] These RAFT agents can be used to control the free radical polymerisation of the monomer containing energy donor chromophores. Acenaphthyl and 9-anthryl chromophores were selected as the energy donor and acceptor respectively as they fulfil the spectral overlap requirements for radiationless energy transfer and acenaphthyl can be preferentially excited with minimal direct excitation of the anthracene from 290 to 320 nm.[4]

The anthryl acceptor was introduced into the RAFT agent to produce RAFT-AN by the coupling of RAFT-Acid and 9-anthracenemethanol in the presence of dicyclohexylcarbodiimide (DCC) as coupling agent and 4-dimethylaminopyridine (DMAP) as catalyst in dichloromethane (Scheme 1).

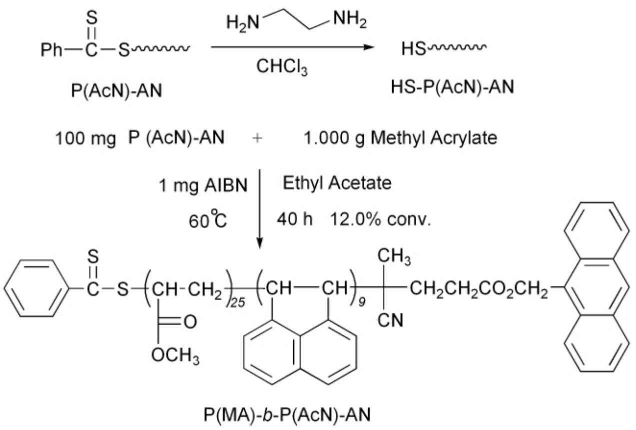


Scheme 1



Scheme 2

Polymers were synthesized according to RAFT methods as described previously[7] using the RAFT-AN (see Scheme 2) and were precipitated twice into MeOH to remove the unreacted monomers. As the absorption spectrum of dithiobenzoyl groups overlaps with the fluorescence emission of acenaphthyl chromophores, dithiobenzoyl groups can also acts as traps of the energy in photoexcited poly(acenaphthylene). To avoid this effect of dithiobenzoyl groups on the energy transfer efficiency from acenaphthyl to anthryl groups, two strategies were used (Scheme 3): (i) treating the polymers with amine to convert the dithiobenzoyl group to a thiol (SH-P(AcN)-AN), and (ii) inserting a photoinactive 'spacer' between the dithiobenzoyl



Scheme 3

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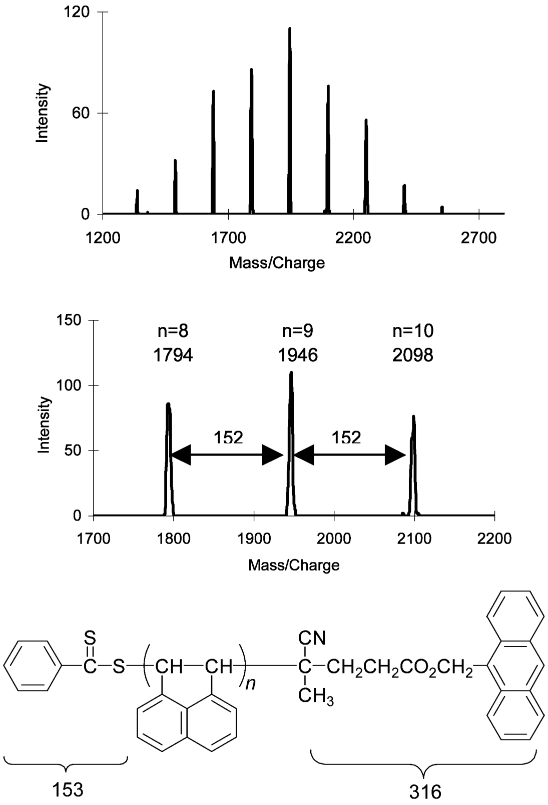
group and acenaphthyl sequences by block copolymerisation with methyl acrylate (P(MA)-*b*-P(AcN)-AN).

The polydispersity of the P(AcN)-AN sample before precipitation was determined to be 1.08 by gel permeation chromatography (GPC). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS) was used to determine the actual molecular weights of the polymers (see Fig. 1). The polymer mass peaks observed are consistent with the predicted structure. This also serves to confirm the mechanism of RAFT polymerisation.



1946 = 9 ×152 (acenaphthylene) + 153 + 316 + 108 (Ag+)

Fig. 1 Top: MALDI-TOF mass spectrum of poly(AcN)-AN. Matrix: dithranol, cationizing agent: silver trifluoroacetate, solvent: chloroform. Middle: Expanded region of top spectrum. The peaks are labelled with their measured mass and the corresponding number of repeat units. The interpeak distances reflect the mass of the constituent repeating units. Bottom: Demonstration of end group analysis by calculation of a representative peak of the polymer distribution.

The molecular weight of the polymer can also be determined by comparing the UV absorption spectrum of a polymer solution to solutions of known concentration of RAFT-AN and acenaphthene. The molecular weights of the polymer obtained by the different techniques are shown in Table 1. The M_n values determined by UV and MALDI-TOF mass spectrometry are quite close to the calculated M_n, which indicates that most poly(acenaphthylene) chains have one dithiobenzoyl and one anthryl group as chain ends.

Table 1 Comparison of molecular weights obtained by various methods

	M_n by UV	M_n by MALDI-TOF/MS	M_n by calculation[a]
Poly(AcN)-AN	1975	1791	1875

[a] Theoretical molecular weights were calculated using the expression M_n(calc) = ([monomer]/[RAFT agent]) × conversion × M.W. of monomer + M.W. of RAFT agent. The above expression does not include the small number of chains formed from the initiator. It also assumes complete consumption of RAFT agent.

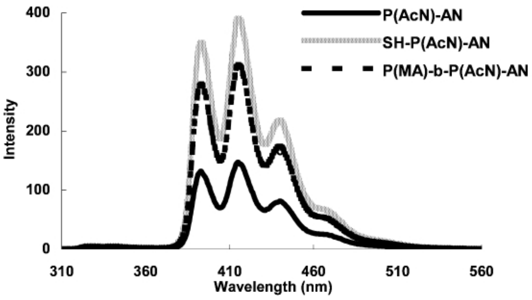


Fig. 2 Fluorescence spectra of acenaphthylene polymers in dilute, degassed dichloromethane solution excited at 295 nm. All solutions have the same absorbance at 295 nm.

A comparison of the fluorescence spectra of the different polymers is presented in Fig. 2. Photoexcitation of P(AcN)-AN, SH-P(AcN)-AN and P(MA)-*b*-P(AcN)-AN at 295 nm, where absorption is almost exclusively due to acenaphthyl groups, results in fluorescence being predominantly emitted from the anthryl end (Fig. 2). Furthermore, the fluorescence excitation spectrum of the 9-anthryl emission contained a contribution attributable to acenaphthyl absorption. These observations confirm that energy transfer to the anthryl end group is occurring. At the solution concentrations used (polymer concentrations $< 10^{-5}$ M) only intrachain energy transfer processes are possible during the excited state lifetime.

The efficiency of excitation energy transfer in the polymers can be determined by comparison of the fluorescence excitation spectrum and the absorption spectrum as described previously.[9,10] The efficiency of acenaphthyl to anthryl energy transfer in poly(AcN)-AN is 15%. This low value can be attributed to the presence of a competing non-fluorescent energy trap (*i.e.* the dithiobenzoyl group). After removing the dithiobenzoyl group, the energy transfer efficiency increased to 70% in SH-P(AcN)-AN confirming this hypothesis. Introducing 'spacer' monomer units between the dithiobenzoyl group and the acenaphthyl donors as in P(MA)-*b*-P(AcN)-AN also increased the energy transfer efficiency to 56%. The smaller effect on energy transfer efficiency by synthesising the block copolymer is most likely due to the ability of the dithiobenzoyl group to fold back and quench the excited acenaphthyl groups due to the flexibility of the poly(methyl acrylate) chain.

In summary, we have shown that well defined light harvesting polymers can be synthesised using RAFT methods. The mechanisms of excitation energy transfer operating in such polymers are currently under investigation.

Notes and references

1 A. Adronov and J. M. J. Fréchet, *Chem. Commun.*, 2000, 1701.
2 R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, 1969, **50**, 1532; R. B. Fox and R. F. Cozzens, *Macromolecules*, 1969, **2**, 181.
3 D. Ng and J. E. Guillet, *Macromolecules*, 1982, **15**, 724.
4 S. E. Webber, *Chem. Rev.*, 1990, **90**, 1469; M. A. Fox, *Acc. Chem. Res.*, 1992, **25**, 569; K. P. Ghiggino and T. A. Smith, *Prog. React. Kinet.*, 1993, **18**, 375.
5 D. H. Solomon, E. Rizzardo and P. Cacioli, *US Patent* 4581429; *Chem. Abstr.*, 1985, **102**, 221335.
6 J. S. Wang and K. Matyjaszewski, *Macromolecules*, 1995, **28**, 7901; M. Sawamoto and M. Kamigaito, *Trends Polym. Sci.*, 1996, **4**, 371.
7 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559; Y. K. Chong, P. T. Le, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1999, **32**, 2071.
8 S. H. Thang, Y. K. Chong, R. T. A. Mayadunne, G. Moad and E. Rizzardo, *Tetrahedron Lett.*, 1999, **40**, 2435.
9 F. Bai, C. H. Chang and S. E. Webber, *Macromolecules*, 1986, **19**, 2484.
10 K. P. Ghiggino, D. J. Haines, T. A. Smith and G. J. Wilson, *Can. J. Chem.*, 1995, **73**, 2015.

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