Synthesis of Functionalized RAFT Agents for Light Harvesting Macromolecules

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With the rapid development of nanotechnology, methodologies that will enable the cost-effective, controlled assembly of nanostructures in a routine manner are in high demand. Photoactive polymers are promising candidates to fulfill the materials requirements for energy storage and conversion devices, molecular sensors, and photonic materials.[1] Of particular interest is the utilization of efficient energy transfer processes in a polymer chain containing sequences of donor chromophores that absorb the incident light and the subsequent trapping of the energy in suitably placed acceptor species.[2] Such "antenna" polymers simulate the efficient light harvesting process of pigment arrays in the photosynthetic apparatus of green plants and can act to effectively increase the light absorption cross section of components in photomolecular devices.

The synthesis of photoactive polymers with well-defined architectures has long been of great interest to photochemists but is difficult to achieve by conventional free radical polymerization methods. Living radical polymerization has made great progress in recent years and emerged as one of the most effective synthetic routes to make well-defined polymers.[3] Among them, reversible addition−fragmentation chain transfer (RAFT) polymerization appears particularly useful and, in principle, could be applied to all classical radical polymerization systems.

The RAFT process involves performing a conventional free radical polymerization in the presence of certain thiocarbonylthio compounds S═C(Z)−SR that act as highly efficient reversible addition−fragmentation chain transfer agents and provide the polymerization with living characteristics. Following RAFT polymerization, nearly all polymer chains will have the thiocarbonylthio and R as end groups. RAFT polymerization thus provides a means of introducing specifically placed photoactive moieties into polymer chains using appropriately functionalized RAFT agents.

We have previously incorporated chromophores into RAFT agents by the coupling reaction of 4-cyano-4-((thiobenzoyl)sulfanyl)pentanoic acid (RAFT-acid) with the required hydroxy-functionalized chromophores.[4] However, the stability of the resulting ester linkage can limit the applications in a number of circumstances, such as in the presence of acid or base. Although the ester linkage could be replaced by a more stable amide linkage, this general method is limited by the low yield of the coupling reaction between RAFT-acid and amine-functionalized chromophores due to the competing aminolysis reaction of the thiocarbonylthio group by the amine.

We describe here a novel alternative method to introduce suitable chromophores into a RAFT agent. The overall process and mechanism are outlined in Scheme 1. This procedure involves performing a RAFT-like polymerization reaction, except the molar ratio of monomer to RAFT agent is kept at unity. A small amount (1−2% molar equivalent) of free radical initiator is used to initiate the reaction. In our work 2-cyanoprop-2-yl dithiobenzoate[5] and 2,2′-azobis(isobutyronitrile) (AIBN) were used as the RAFT agent and initiator, respectively. After reaction, the functionalized monomer unit (in this case with the required pendant chromophore) will be incorporated via a stable carbon−carbon linkage to form a new thiocarbonylthio compound. This new RAFT agent can be subsequently used for polymerizations when the chromophore will be inserted as a terminal to the polymer chains.

The mechanism of this reaction is similar to the mechanism of RAFT polymerization,[3d] except here the molar ratio between monomer and the RAFT agent is unity instead of a factor of 10^2−10^4. With an efficient RAFT agent and at the ratio of reactants employed, each monomer radical generated will be rapidly trapped by the RAFT agent (to form an intermediate radical) instead of propagating. Because of relative leaving abilities,[5] the intermediate radical species will prefer to fragment to form the product and a cyanopropyl radical, which will initiate another cycle.

We outline below the application of this procedure to synthesize light harvesting polymers of acenaphthylene containing a coumarin terminal energy trap. Acenaphthyl and coumarin chromophores were selected as the energy donor and acceptor, respectively, as they fulfill the spectral overlap requirements for radiationless energy transfer. (In dichloromethane, the Förster critical transfer distance for energy transfer from acenaphthene to coumarin is 33 Å.) Styrene-functionalized coumarin (St-coumarin)[4b] reacted with 2-cyanoprop-2-yl dithiobenzoate to give the required RAFT-coumarin with 85% yield at 70 °C after 24 h (Scheme 2).

The resulting coumarin-functionalized RAFT agent, RAFT-coumarin, can control the polymerization of acenaphthylene to produce the required polymer (Scheme 3).[5] The polydispersity of the polymer, P(AcN)-coumarin, is 1.1 measured by gel permission chromatography (GPC). The low polydispersity confirms that RAFT polymerization has occurred, and the poly(acenaphthylene) chains in P(AcN)-coumarin will have one dithiobenzoyl and one coumarin cyanopropyl group as chain ends. For comparative purposes, poly(acenaphthylene) without coumarin traps was synthesized by conventional AIBN-initiated free radical polymerization, yielding a polymer with polydispersity of 1.6 (P(AcN)-AIBN).

As reported by us previously,[4] the dithiobenzoyl end group is able to quench the excited donors and thus can lower the overall excitation energy transfer efficiency from acenaphthyl to coumarin chromophores. To reduce this competitive quenching process, a water-soluble photoinactive "spacer" was inserted between dithiobenzoyl and acenaphthyl sequences by block copolymerization with acrylic acid (Scheme 3). The hydrophilic

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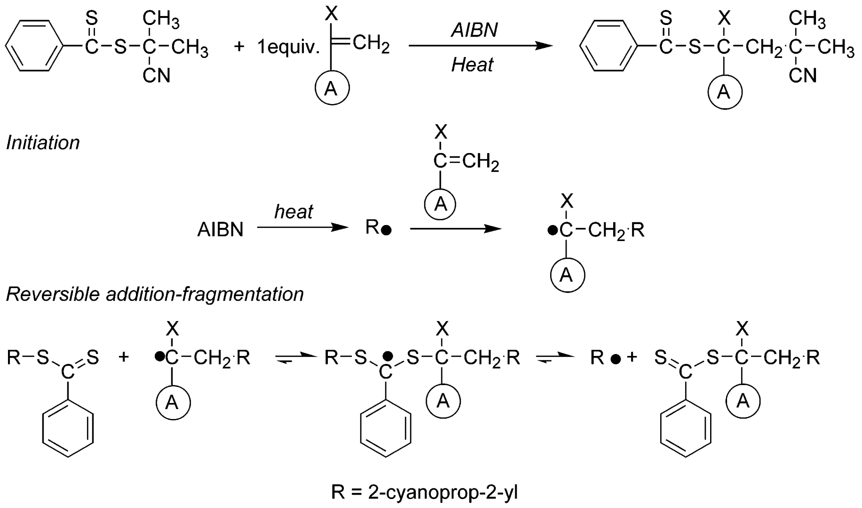
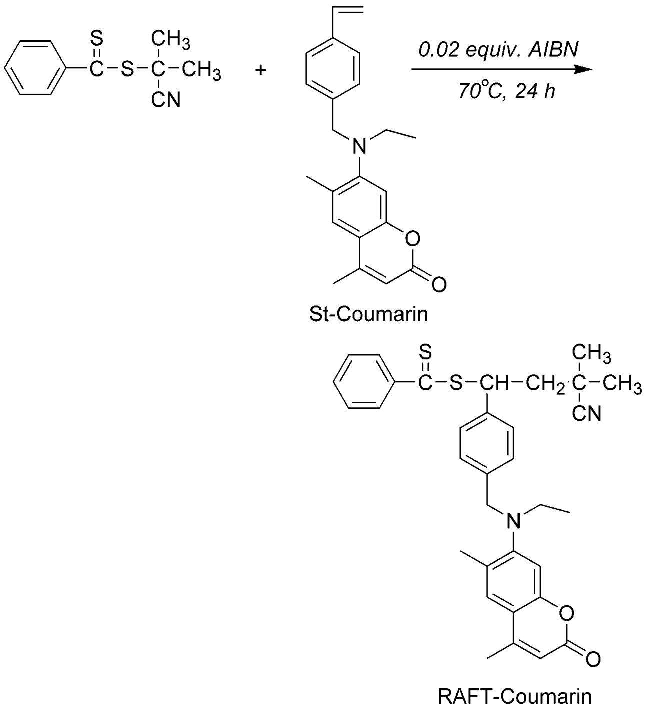
Scheme 1



acrylic acid block in this amphiphilic polymer, P(AA)-*b*-P(AcN)-coumarin, confers water solubility.

Scheme 2



Comparison of the molar extinction coefficients of acenaphthene and RAFT-coumarin confirms that the absorbance at an excitation wavelength of 295 nm is almost exclusively (>95%) due to the acenaphthyl chromophores in P(AcN)-coumarin and P(AA)-*b*-P(AcN)-coumarin.

The fluorescence spectra of P(AcN)-AIBN, P(AcN)-coumarin, and P(AA)-*b*-P(AcN)-coumarin are presented in Figure 1. Comparison of the fluorescence spectra of the polymers using 295 nm excitation shows that incorporation of the coumarin terminal effectively quenches the emission from acenaphthyl groups (maximum at 330 nm), leading to emission from the coumarin chromophores (450 nm). Furthermore, the fluorescence excitation spectrum of the coumarin emission contains a major contribution attributable to acenaphthyl absorption. These observations confirm that energy trans-

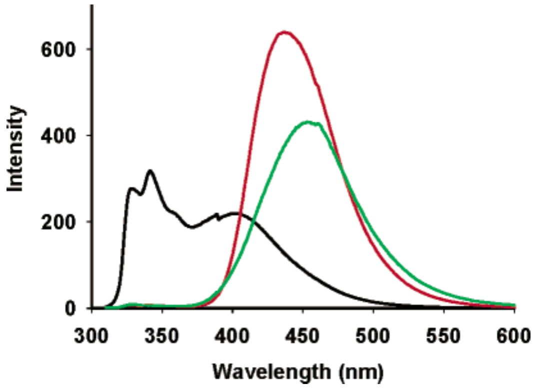
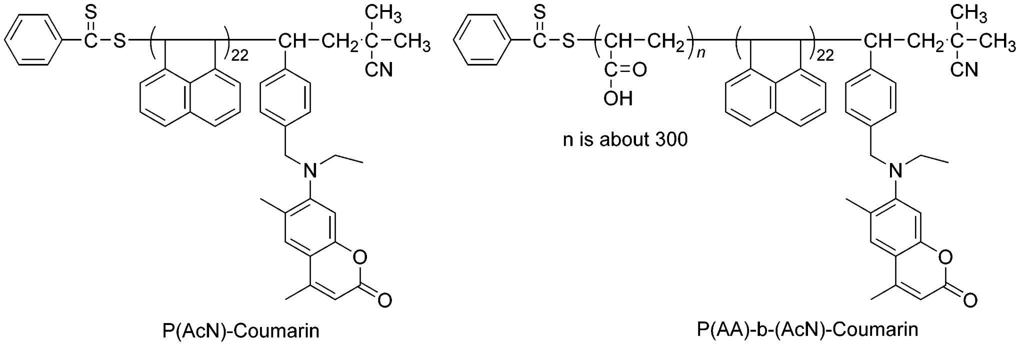


Figure 1. Fluorescence spectra of P(AcN)-AIBN (black —), P(AcN)-coumarin (red —) in dichloromethane, and P(AA)-*b*-P(AcN)-coumarin (green —) in aqueous NaOH (pH 11); excitation at 295 nm.

Scheme 3



fer to the coumarin moiety from acenaphthyl groups in the polymer is occurring.

Because of the presence of a competing quenching process involving the dithiobenzoyl group, the energy transfer efficiency of acenaphthyl groups to coumarin in P(AcN)-coumarin is only 35% although nearly all (>95%) acenaphthyl emission is quenched. The energy transfer efficiency increased to 100% for P(AA)-*b*-P(AcN)-coumarin in an aqueous pH 11 solution. There are two possible processes leading to this increase. The disappearance of the orange color of the polymer solution during dialysis indicated that the dithiobenzoyl group had been hydrolyzed, thus removing the competing quenching process. In an aqueous solution it is also likely the hydrophobic poly(acenaphthylene) block will collapse, further reducing interchromophore separations and thus enhancing the energy transfer efficiency.[6] The maximum of the coumarin emission in the pH 11 aqueous solution is red-shifted to 455 nm compared to 435 nm in dichloromethane, indicating a change in environment for the chromophore.

In conclusion, the modified RAFT procedure described provides an efficient and simple way to prepare functionalized RAFT agents. These RAFT agents can be applied to incorporate end group functionality in polymers and have been used here to make linear and diblock light harvesting polymers that exhibit high energy transfer efficiencies.

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Supporting Information Available: Experimental details for synthesis of the RAFT-coumarin reagent and the polymers; absorption and fluorescence spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−91. (b) Adronov, A.; Frechet, J. M. J. *Chem. Commun.* **2000**, 1701−10. (c) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.

(2) (a) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469−82. (b) Fleming, C. N.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* **2001**, 123, 10336−10347. (c) Pei, J.; Liu, X. L.; Yu, W. L.; Lai, Y. H.; Niu, Y. H.; Cao, Y. *Macromolecules* **2002**, *35*, 7274−80.

(3) (a) Matyjaszewski, K., Ed. *ACS Symp. Ser.* **2000**, *768*. (b) Matyjaszewski, K., Ed. *ACS Symp. Ser.* **2003**, *854*. (c) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Appl. WO 98/01478 (*Chem. Abstr.* **1998**, *128*, 115390). (d) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−62.

(4) (a) Chen, M.; Ghiggino, K. P.; Mau, A. W. H.; Rizzardo, E.; Thang, S. H.; Wilson, G. J. *Chem. Commun.* **2002**, 2276−77. (b) Chen, M.; Ghiggino, K. P.; Launikonis, A.; Mau, A. W. H.; Rizzardo, E.; Sasse, W. H. F.; Thang, S. H.; Wilson, G. J. *J. Mater. Chem.* **2003**, *13*, 2696−2700.

(5) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−72.

(6) Guillet, J. E.; Rendall, W. A. *Macromolecules* **1986**, *19*, 224−30.

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