Electronic Supplementary Material (ESI) for Polymer Chemistry.

RAFT Polymerization to form Stimuli-Responsive Polymers

Graeme Moad

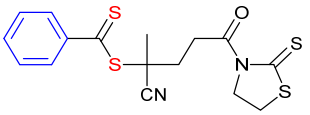
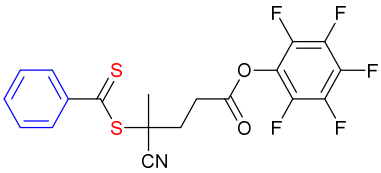
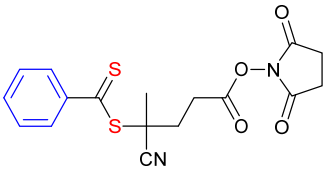
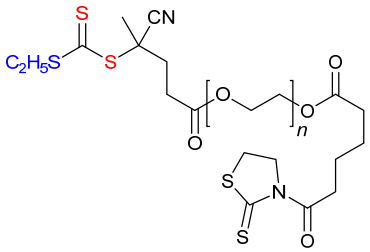
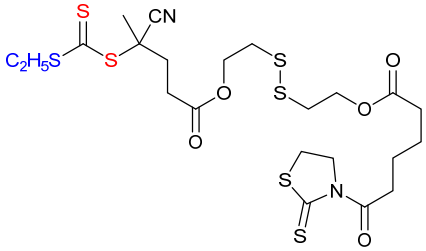
Supporting Information

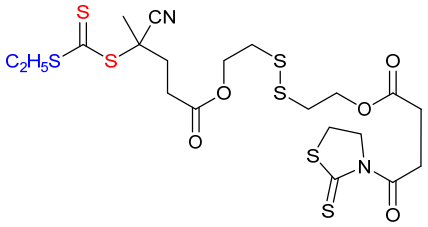
RAFT agents with active ester functionality

The major use of RAFT agents containing active ester functionality is in the preparation of other functional RAFT agents rather than mediating RAFT polymerization directly. Nonetheless these RAFT agents can and have been used. Care must be taken in exclude reactive nucleophiles in the polymerization medium. Examples of dithiobenzoate RAFT agents containing active ester functionality are shown in Table 29. Other examples are shown in Table S1.

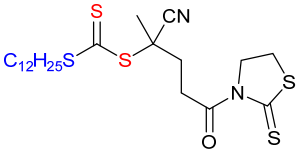
The active ester functionalities for the examples shown in **Error! Reference source not found.** are substantially more reactive that the thiocarbonylthio functionality towards, in particular, primary amines. Thus functionalization, conjugation and surface modification pre- or post-RAFT polymerization can be carried out without loss of the RAFT functionality.

Table S1 RAFT agents for active ester chemistry.

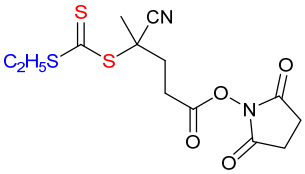
RAFT agent	Monomer(s)
 **1**	Precursor[1-5] methacrylamides: HPMAm[6]
 **2**	Methacrylates: tBMA[7] DEGMA[7,8] LMA[8,9] MMA[8] PEGMA[8,9] Methacrylamides: NIPMAm[a,8]
 **3**	Precursor[10-26] Styrenes: Error! Reference source not found.[27]
	*n*=2 Methacrylates: PEGMA[28] Methacrylamides: HPMAm[29] *n*=4 Methacrylates: PEGMA[30]
	Methacrylamides: HPMAm [31]



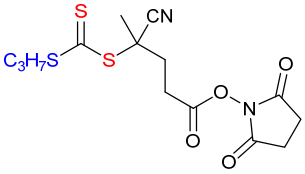
Acrylates: PEGA[32]



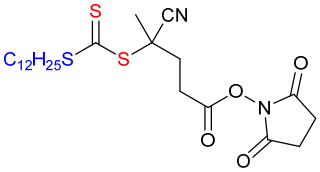
Methacrylates: HPMA copolymer[33]



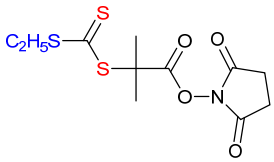
Precursor[34-38]
Methacrylates: DMAEMA[39] MMA[39]



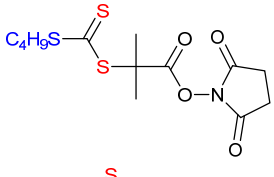
Precursor[40]



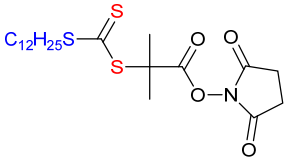
Precursor[23,41,42]
Methacrylates: HPMA copolymer[33]



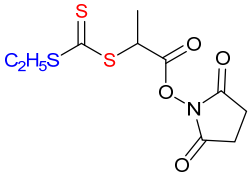
Precursor[43,44]



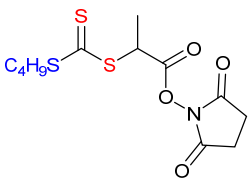
Precursor[45-48]
Pcrylamides: NIPAm[49,50] NAM[51]



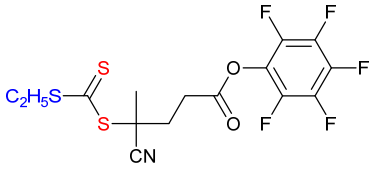
Precursor[41,52-58]
acrylates: DMAEA[59]



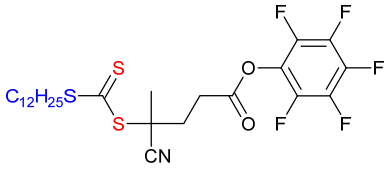
Precursor[60]
Methacrylates: PDFMA[b]-*co*-PEGMA[60]
Acrylates: BA[39] HEA[39] PEGA[39]
Acrylamides: NAM[39] NIPAM[39]



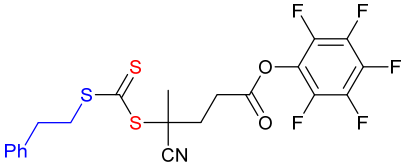
Acrylates: HEA[61]



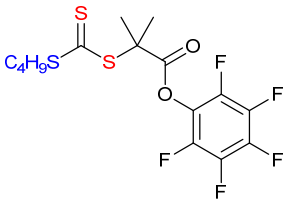
Precursor[39]
Methacrylamides: HPMAm[61]
Acrylamides: DMDOMA[c62]



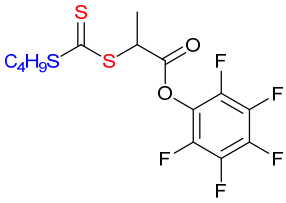
Precursor[63]



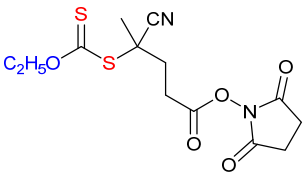
Precursor[64]
Copolymer[65]



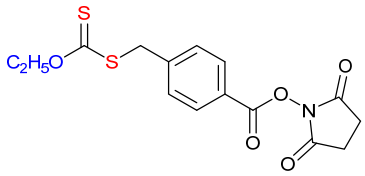
Acrylates: OPA[d 66]
Acrylamides: DMAm[67 68] HEAm[e, 69-71] NAM[68]
HIPAM[68]
Styrenes: VTPA[f, 72]
Other: MVK [g 73]



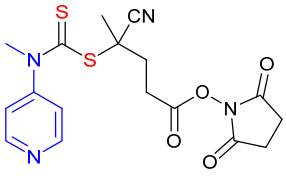
Acrylates: HEA[61]



Precursor[74]



Vinyls: NVP[75]



Vinyls: NVP[76]

[a] NIPAMm – N-isopropylmethacrylamide. [b] PDFMA – perfluorodecyl methacrylate. [c] DMDOMA – [(2,2-dimethyl-1,3-dioxolane)methyl]acrylamide. [d] OPA – 2-oxopropyl acrylate, [e] HEAm – hydroxyethylacrylamide. [f] VTPA – 4,4′-Dimethyl-4′′-vinyltriphenylamine. [g]MVK – methyl vinyl ketone.

References

1. C. Li, J. Han, C. Y. Ryu and B. C. Benicewicz, *Macromolecules*, 2006, **39**, 3175-3183.
2. J. Liu, W. Yang, H. M. Zareie, J. J. Gooding and T. P. Davis, *Macromolecules*, 2009, **42**, 2931-2939.
3. J. Xu, L. Tao, J. Liu, V. Bulmus and T. P. Davis, *Macromolecules*, 2009, **42**, 6893-6901.
4. J. Xu, L. Tao, C. Boyer, A. B. Lowe and T. P. Davis, *Macromolecules*, 2010, **43**, 20-24.

5. J. Xu, L. Tao, C. Boyer, A. B. Lowe and T. P. Davis, *Macromolecules*, 2011, **44**, 299-312.
6. L. Tao, J. Liu, J. Xu and T. P. Davis, *Org. Biomolecular Chem.*, 2009, **7**, 3481-3485.
7. K. T. Wiss and P. Theato, *J. Polym. Sci., Part A, Polym. Chem.*, 2010, **48**, 4758-4767.
8. P. J. Roth, K. T. Wiss, R. Zentel and P. Theato, *Macromolecules*, 2008, **41**, 8513-8519.
9. P. J. Roth, D. Kessler, R. Zentel and P. Theato, *J. Polym. Sci., Part A, Polym. Chem.*, 2009, **47**, 3118-3130.
10. Q. Zheng and C. Y. Pan, *Macromolecules*, 2005, **38**, 6841-6848.
11. Q. Zheng and C. Y. Pan, *Eur. Polym. J.*, 2006, **42**, 807-814.
12. M. Bathfield, F. D'Agosto, R. Spitz, M. T. Charreyre and T. Delair, *J. Am. Chem. Soc.*, 2006, **128**, 2546-2547.
13. A. M. dos Santos, J. Pohn, M. Lansalot and F. D'Agosto, *Macromol. Rapid. Commun.*, 2007, **28**, 1325-1332.
14. K. Yuan, Z. F. Li, L. L. Lu and X. N. Shi, *Mater. Lett.*, 2007, **61**, 2033-2036.
15. K. Yuan, L.-L. Lu, Z.-F. Li and X.-N. Shi, *Chin. J. Chem.*, 2008, **26**, 1929-1934.
16. R. Briquel, J. Mazzolini, T. L. Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson and R. Spitz, *Angew. Chem., Int. Ed. Engl.*, 2008, **47**, 9311-9313.
17. P. Sun, Y. Zhang, L. Shi and Z. Gan, *Macromol. Biosci.*, 2010, **10**, 621-631.
18. X. Jiang, A. Housni, G. Gody, P. Boullanger, M.-T. Charreyre, T. Delair and R. Narain, *Bioconjugate Chem.*, 2010, **21**, 521-530.
19. N. Gurbuz, S. Demirci, S. Yavuz and T. Caykara, *J. Polym. Sci., Part A, Polym. Chem.*, 2011, **49**, 423-431.
20. S. Demirci, S. Kinali-Demirci and T. Caykara, *J. Polym. Sci., Part A, Polym. Chem.*, 2013, **51**, 1612-1619.
21. H. Yang, F. Liang, X. Wang, Y. Chen, C. Zhang, Q. Wang, X. Qu, J. Li, D. Wu and Z. Yang, *Macromolecules*, 2013, **46**, 2754-2759.
22. Q. Li, K. Yang, Y. Liang, B. Jiang, J. Liu, L. Zhang, Z. Liang and Y. Zhang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21954-21960.
23. D. Togashi, I. Otsuka, R. Borsali, K. Takeda, K. Enomoto, S. Kawaguchi and A. Narumi, *Biomacromolecules*, 2014, **15**, 4509-4519.
24. N. J. Warren, O. O. Mykhaylyk, D. Mahmood, A. J. Ryan and S. P. Armes, *J. Am. Chem. Soc.*, 2014, **136**, 1023-1033.
25. N. J. Warren, J. Rosselgong, J. Madsen and S. P. Armes, *Biomacromolecules*, 2015, **16**, 2514-2521.
26. T. Koga, E. Aso and N. Higashi, *Langmuir*, 2016, doi: 10.1021/acs.langmuir.1026b01617.
27. K. A. Aamer and G. N. Tew, *J. Polym. Sci., Part A, Polym. Chem.*, 2007, **45**, 5618-5625.
28. Y. Liu, M. Li, D. Wang, J. Yao, J. Shen, W. Liu, S. Feng, L. Tao and T. P. Davis, *Aust. J. Chem.*, 2011, **64**, 1602-1610.
29. L. Tao, J. Xu, D. Gell and T. P. Davis, *Macromolecules*, 2010, **43**, 3721-3727.
30. L. Tao, J. Liu, J. Xu and T. P. Davis, *Chem. Commun.*, 2009, 6560-6562.
31. L. Tao, G. Chen, L. Zhao, J. Xu, E. Huang, A. Liu, C. P. Marquis and T. P. Davis, *Chem. Asian J.*, 2011, **6**, 1398-1404.
32. H. Liu, J. Zhang, X. Luo, N. Kong, L. Cui and J. Liu, *Eur. Polym. J.*, 2013, **49**, 2949-2960.
33. A. A. A. Smith, K. Zuwala, O. Pilgram, K. S. Johansen, M. Tolstrup, F. Dagnæs-Hansen and A. N. Zelikin, *ACS Macro Lett.*, 2016, **5**, 1089-1094.
34. S. Catrouillet, J. C. Brendel, S. Larnaudie, T. Barlow, K. A. Jolliffe and S. Perrier, *ACS Macro Lett.*, 2016, **5**, 1119-1123.
35. H. Li, M. Miteva, K. C. Kirkbride, M. J. Cheng, C. E. Nelson, E. M. Simpson, M. K. Gupta, C. L. Duvall and T. D. Giorgio, *Biomacromolecules*, 2015, **16**, 192-201.
36. H. Li, S. S. Yu, M. Miteva, C. E. Nelson, T. Werfel, T. D. Giorgio and C. L. Duvall, *Adv. Funct. Mater.*, 2013, **23**, 3040-3052.

37. D. S. W. Benoit, S. Srinivasan, A. D. Shubin and P. S. Stayton, *Biomacromolecules*, 2011, **12**, 2708-2714.
38. C. L. Duvall, A. J. Convertine, D. S. W. Benoit, A. S. Hoffman and P. S. Stayton, *Molecular Pharmaceutics*, 2010, **7**, 468-476.
39. S. C. Larnaudie, J. C. Brendel, K. A. Jolliffe and S. Perrier, *J. Polym. Sci., Part A, Polym. Chem.*, 2016, **54**, 1003-1011.
40. X. Huang, D. Appelhans, P. Formanek, F. Simon and B. Voit, *ACS Nano*, 2012, **6**, 9718-9726.
41. O. O. Oyeneye, W. Z. Xu and P. A. Charpentier, *RSC Advances*, 2015, **5**, 76919-76926.
42. N. Zammarelli, M. Luksin, H. Raschke, R. Hergenröder and R. Weberskirch, *Langmuir*, 2013, **29**, 12834-12843.
43. J.-Y. Wang, K. Wang, X. Gu and Y. Luo, *ACS Biomaterials Science & Engineering*, 2016, **2**, 887-892.
44. K. Yang, X. Huang, L. Xie, C. Wu, P. Jiang and T. Tanaka, *Macromol. Rapid. Commun.*, 2012, **33**, 1921-1926.
45. H. Li, M. Li, X. Yu, A. P. Bapat and B. S. Sumerlin, *Polym. Chem.*, 2011, **2**, 1531-1535.
46. J. Tian, F. Zheng and H. Zhao, *J. Phys. Chem. C*, 2011, **115**, 3304-3312.
47. G. Feng, H. Chen, J. Li, Q. Huang, M. J. Gupte, H. Liu, Y. Song and Z. Ge, *Biomaterials*, 2015, **52**, 1-13.
48. Z. Jia, V. A. Bobrin, N. P. Truong, M. Gillard and M. J. Monteiro, *J. Am. Chem. Soc.*, 2014, **136**, 5824-5827.
49. H. Li, A. P. Bapat, M. Li and B. S. Sumerlin, *Polym. Chem.*, 2011, **2**, 323-327.
50. P. Wilke, W. L. A. Brooks, R. Kühnle, B. Sumerlin and H. G. Börner, in *Progress in Controlled Radical Polymerization: Materials and Applications*, American Chemical Society, 2012, pp. 271-285.
51. G. Gody, D. A. Roberts, T. Maschmeyer and S. Perrier, *J. Am. Chem. Soc.*, 2016, **138**, 4061-4068.
52. Y. Oz, M. Arslan, T. N. Gevrek, R. Sanyal and A. Sanyal, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19813-19826.
53. S. Wang, X. Huang, G. Wang, Y. Wang, J. He and P. Jiang, *J. Phys. Chem. C*, 2015, **119**, 25307-25318.
54. D. Montarnal, N. Delbosc, C. Chamignon, M.-A. Virolleaud, Y. Luo, C. J. Hawker, E. Drockenmuller and J. Bernard, *Angew. Chem., Int. Ed. Engl.*, 2015, **54**, 11117-11121.
55. X. Huang, S. Wang, M. Zhu, K. Yang, P. Jiang, Y. Bando, D. Golberg and C. Zhi, *Nanotechnology*, 2015, **26**, 15705.
56. D. J. Phillips, I. Prokes, G.-L. Davies and M. I. Gibson, *ACS Macro Lett.*, 2014, **3**, 1225-1229.
57. D. J. Phillips, G.-L. Davies and M. I. Gibson, *Journal of Materials Chemistry B*, 2015, **3**, 270-275.
58. T. Xing and L. Yan, *RSC Advances*, 2014, **4**, 28186-28194.
59. F. Fan, W. Wang, A. P. Holt, H. Feng, D. Uhrig, X. Lu, T. Hong, Y. Wang, N.-G. Kang, J. Mays and A. P. Sokolov, *Macromolecules*, 2016, **49**, 4557-4570.
60. K. Ma and Z. An, *Macromol. Rapid. Commun.*, 2016, **37**, 1593-1597.
61. N. Vanparijs, S. Maji, B. Louage, L. Voorhaar, D. Laplace, Q. Zhang, Y. Shi, W. E. Hennink, R. Hoogenboom and B. G. De Geest, *Polym. Chem.*, 2015, **6**, 5602-5614.
62. N. Vanparijs, R. De Coen, D. Laplace, B. Louage, S. Maji, L. Lybaert, R. Hoogenboom and B. G. De Geest, *Chem. Commun.*, 2015, **51**, 13972-13975.
63. R. Potzsch, S. Fleischmann, C. Tock, H. Komber and B. I. Voit, *Macromolecules*, 2011, **44**, 3260-3269.
64. A. K. Pearce, B. E. Rolfe, P. J. Russell, B. W. C. Tse, A. K. Whittaker, A. V. Fuchs and K. J. Thurecht, *Polym. Chem.*, 2014, **5**, 6932-6942.
65. A. V. Fuchs, B. W. C. Tse, A. K. Pearce, M.-C. Yeh, N. L. Fletcher, S. S. Huang, W. D. Heston, A. K. Whittaker, P. J. Russell and K. J. Thurecht, *Biomacromolecules*, 2015, **16**, 3235-3247.

66. K. Godula, D. Rabuka, K. T. Nam and C. R. Bertozzi, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 4973-4976.
67. W.-D. Quan, A. Pitto-Barry, L. A. Baker, E. Stulz, R. Napier, R. K. O'Reilly and V. G. Stavros, *Chem. Commun.*, 2016, **52**, 1938-1941.
68. T. R. Wilks, J. Bath, J. W. de Vries, J. E. Raymond, A. Herrmann, A. J. Turberfield and R. K. O'Reilly, *ACS Nano*, 2013, **7**, 8561-8572.
69. S.-J. Richards, L. Otten and M. I. Gibson, *Journal of Materials Chemistry B*, 2016, **4**, 3046-3053.
70. L. Otten, D. Vlachou, S.-J. Richards and M. I. Gibson, *Analyst*, 2016, **141**, 4305-4312.
71. S.-J. Richards and M. I. Gibson, *ACS Macro Lett.*, 2014, **3**, 1004-1008.
72. F. Mathias, M. N. Tahir, W. Tremel and R. Zentel, *Macromol. Chem. Phys.*, 2014, **215**, 604-613.
73. K. Godula, M. L. Umbel, D. Rabuka, Z. Botyanszki, C. R. Bertozzi and R. Parthasarathy, *J. Am. Chem. Soc.*, 2009, **131**, 10263-10268.
74. S. Aroua, E. G. V. Tiu, M. Ayer, T. Ishikawa and Y. Yamakoshi, *Polym. Chem.*, 2015, **6**, 2616-2619.
75. L. McDowall, G. Chen and M. H. Stenzel, *Macromol. Rapid. Commun.*, 2008, **29**, 1666-1671.
76. J. Zheng, L. Wang, X. Zeng, X. Zheng, Y. Zhang, S. Liu, X. Shi, Y. Wang, X. Huang and L. Ren, *ACS Appl. Mater. Interfaces*, 2016, **8**, 18684-18692.