Tailored Polymer Architectures by Reversible Addition-Fragmentation Chain Transfer

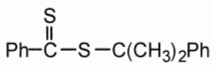
Ezio Rizzardo, John Chiefari, Roshan Mayadunne, Graeme Moad and San Thang*

CSIRO Molecular Science, Bag10, Clayton South, Victoria 3169, Australia
ezio.rizzardo@molsci.csiro.au

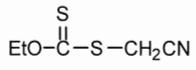
Living radical polymerization methods that allow the preparation of polymers with predetermined molecular weight, narrow molecular weight distribution and tailored architecture (e.g. block, graft, stars) are offering a vast range of new and advanced materials. With applications ranging from surfactants, dispersants, coatings and adhesives, to microelectronics, membranes, drug delivery, and biomaterials they have the potential of revolutionizing a large part of the polymer industry.

Recently, we reported an effective and versatile living radical polymerization process which functions by reversible addition-fragmentation chain transfer (RAFT process). The process is performed simply by adding a suitable thiocarbonylthio compound (**1**) to an otherwise conventional free radical polymerization. The degree of polymerisation is given by the ratio of monomer consumed to the amount of RAFT agent employed.

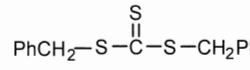
Examples of useful thiocarbonylthio compounds (RAFT agents) are shown below in **1a**, **1b** and **1c**



1a



1b



1c

The versatility and effectiveness of RAFT polymerization is demonstrated by the experimental results shown in Table 1.

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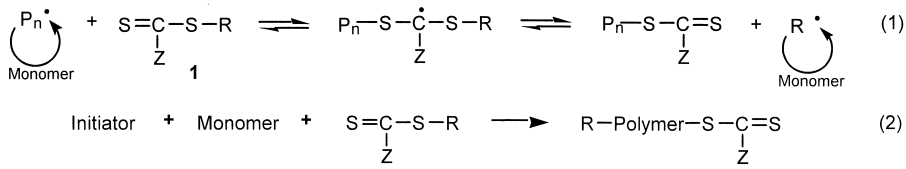
Table 1. Molecular masses and molecular mass distributions for polymers synthesized by RAFT polymerization.

Polymer	M_n	M_w/M_n	%Conv
Poly(methyl methacrylate)	56 200	1.12	95
Polystyrene	88 200	1.16	57
Poly(methyl acrylate)	108 200	1.18	97
Poly(vinyl acetate)	7 030	1.18	66
Poly(acrylic acid)	66 900	1.13	53
Poly(dimethyl acrylamide)	88 700	1.08	76

A simplified mechanism is outlined in equation (1) and the overall process in equation (2).



The living nature of RAFT polymerization is indicated by a linear increase in molecular weights with conversion, a correspondence between calculated molecular weights and those measured by GPC, and the narrow polydispersity of the polymers produced. These characteristics are shown in Figure 1 for the thermal polymerization of styrene in the presence of thiocarbonylthio compound **1a**.

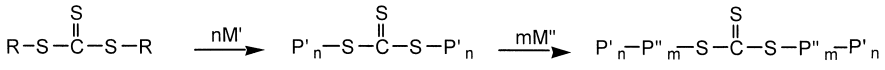
As RAFT polymerization is a living process it can also be used to synthesize polymers of more complex architecture.

Table 2,Examples of AB diblock, ABA triblock, star, star-block, and gradient copolymers.

Polymer	M_n(gpc) x10^{-3}	M_w/M_n
PBA-*block*-PAA	34+19	1.19
PS-*block*-PDMA	20+23	1.24
PMMA-*block*-PMAA	3+2	1.18
PEO-*block*-PS	1+7	1.07
PS-*block*-PBMA-*block*-PS	26+36+26	1.08
PS-*block*-PMA-*block*-PS	20+13+20	1.22
star-$(PS)_4$	92	1.07
star-$(PMA\text{-}block\text{-}PS)_4$	104+26	1.18
PMMA-*gradient*-PBA	42	1.13

BA = butyl acrylate, AA = acrylic acid, S = styrene, DMA = N,N-dimethyl acrylamide, MMA = methyl methacrylate, MAA = methacrylic acid, EO = ethylene oxide, BMA = butyl methacrylate, MA = methyl acrylate

An interesting example is provided by the use of the symmetrical trithiocarbonate **1c** to prepare ABA block copolymers in two steps, as shown below.



1c (3)

This approach was used to synthesize poly(styrene-*block*-methyl acrylate-*block*-styrene) by first polymerizing styrene (M') to M_n 13 200 and following with methyl acrylate (M") to M_n 53 300. The GPC traces of the polymers from this experiment are shown in Figure 2.

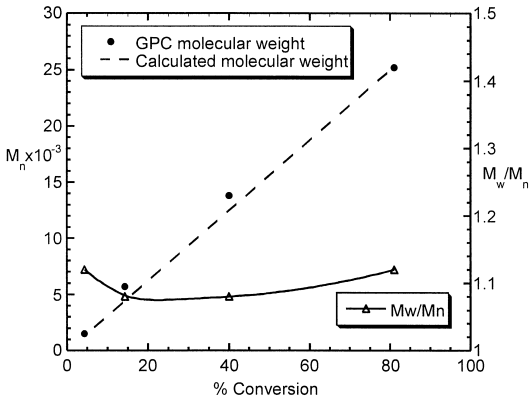


Figure 1: $\overline{M}_n$ and $\overline{M}_w / \overline{M}_n$ as function of monomer conversion for thermal polymerization of styrene in the presence of compound **1a**.

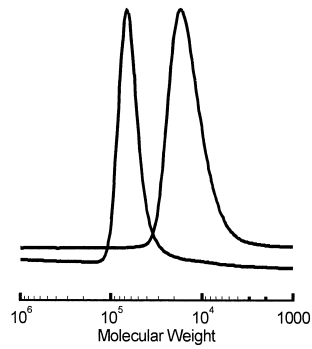


Figure 2: GPC traces of polymers obtained by sequential polymerization of styrene and methyl acrylate according to scheme (3).

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