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Tailored Polymers by Free Radical Processes

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SUMMARY: This paper describes a versatile and effective method for the control of free radical polymerization and its use in the preparation of narrow polydispersity polymers of various architectures. Living character is conferred to conventional free radical polymerization by the addition of a thiocarbonylthio compound of general structure S=C(Z)SR, for example, $S{=}C(Ph)SC(CH_3)_2Ph$. The mechanism involves Reversible Addition-Fragmentation chain Transfer and, for convenience of referral, we have designated it the RAFT polymerization. The process is compatible with a very wide range of monomers including functional monomers such as acrylic acid, hydroxyethyl methacrylate, and dimethylaminoethyl methacrylate. Examples of narrow polydispersity (≤ 1.2) homopolymers, copolymers, gradient copolymers, end-functional polymers, star polymers, A-B diblock and A-B-A triblock copolymers are presented.

Introduction

Conventional free radical polymerization is currently used to manufacture a vast range of commercial polymer products. This is largely due to its many attractive characteristics. These include (a) its applicability to the polymerization of a wide range of monomer types (e.g. acrylates, acrylamides, styrenes and vinyls), (b) its compatibility with a wide range of solvents and functional groups (e.g. OH, COOH, NR_2 and NCO), (c) its ability to provide an unlimited number of copolymers, when one considers the variety of compositions and molecular size, and (d) the convenient reaction conditions under which it can be performed. This last point includes the possibility of conducting polymerizations in bulk, solution, suspension or emulsion over a wide range of temperatures (typically 0 to 150 °C).

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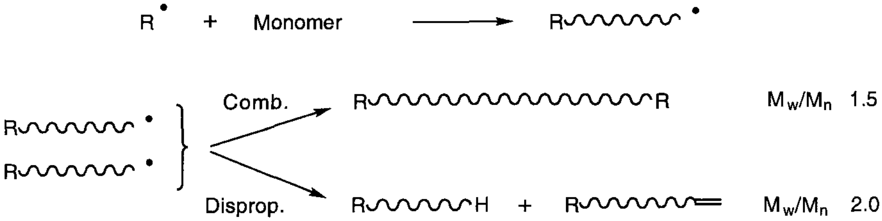
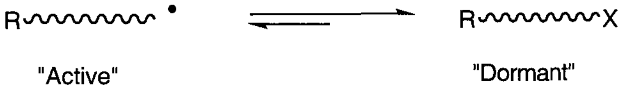
The major limitation of conventional free radical polymerization is poor control over polymer structure, in particular, molecular weight distributions, end-group functionalities, and chain architecture. This limitation is inherent in the mechanism (Scheme 1). Propagating radicals, produced by the addition of initiator - derived radicals to monomer react with each other (termination) at near diffusion controlled rates giving rise to "dead" polymer chains with polydispersities, as measured by M_w/M_n, of no better than 1.5.



Scheme 1. Mechanism of conventional free radical polymerization

Over recent years a great deal of research effort has been devoted to find ways of minimizing the statistical self destruction of chain propagating radicals. The techniques devised for this purpose have been labelled "living" or "controlled" free radical polymerization processes$^{1)}$. The common feature of these techniques is the use of reagents which convert chain propagating radicals into a "dormant" form in equilibrium with the "active" form (Scheme 2).



Scheme 2. Living free radical polymerization

Under the appropriate conditions, the concentration of the "active" propagating radicals is kept very low to reduce the rate of their termination by self reaction. In addition, the conditions are such that all the propagating radicals have an equal probability of growth and this gives rise to polymers of low polydispersities ($M_w/M_n < 1.5$). Furthermore, the concentration of the reagents used dictates the number of chains formed enabling the prediction of the number average molecular weight of the polymer at a given conversion of monomer. When the polymerization is stopped, the vast majority of the polymer chains are in the dormant form, i.e., they possess an end group that can be reactivated. Reactivation of these chains in the presence of a second monomer will give rise to A-B diblock copolymers, again with low polydispersities.

The living radical polymerization techniques that have received the greatest attention are nitroxide-mediated polymerization and atom transfer radical polymerization (ATRP). The first technique was devised in our laboratories2) in the early 1980's and exploited more recently by a number of groups for the synthesis of narrow polydispersity homopolymers and block copolymers of styrene and styrene derivatives3-7). In its present state of development, however, nitroxide-mediated polymerization appears to have less utility for the living polymerization of other monomer systems8-10).

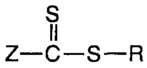
ATRP is a more versatile technique11,12). However, it requires unconventional initiating systems (e.g. organic halide/copper halide/2,2'-bipyridine), which can have poor solubility in certain polymerization media, is not applicable to acidic monomers (e.g. acrylic acid) and produces products that are contaminated with metal ions.

Some time ago, we introduced chain transfer by addition-fragmentation for the control of molecular weight of polymers and for the synthesis of mono- and di-end functional polymers including macromonomers13-15). Methacrylate based macromonomers are one example of addition-fragmentation chain transfer agents. When these are used in the polymerization of methacrylates the chain transfer process is reversible and we have shown that this confers living characteristics to the polymerization by applying the methodology to the preparation of narrow polydispersity homo and block copolymers16,17).

In this paper we report on our recent development of a new and versatile living radical polymerization process which also operates by a mechanism of Reversible Addition-Fragmentation chain Transfer and have designated it the RAFT polymerization18-20).

RAFT Polymerization

RAFT polymerization is performed by simply adding a chosen quantity of a thiocarbonylthio compound (**1**) (examples are shown in Fig. 1) to a conventional free radical polymerization mixture (same monomers, initiators, solvents, temperatures, etc). It thus offers similar versatility and convenience to conventional free radical polymerization but provides polymers of narrow polydispersities and of predetermined chain length. The degree of polymerization of the polymer formed is given by the ratio of the number of monomer units consumed to the number of dithio compound molecules employed.



$$Z-\overset{\overset{\displaystyle S}{\|}}{C}-S-R$$

1

2 Z=Ph, R=$C(CH_3)_2Ph$

3 Z=Ph, R=$CH(CH_3)Ph$

4 Z=Ph, R=CH_2Ph

5 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CO_2Na$

6 Z=Ph, R=$C(CH_3)_2CN$

7 Z=CH_3, R=CH_2Ph

8 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CH_2OH$

9 Z=Ph, R=$C(CH_3)(CN)CH_2CH_2CO_2H$

Fig. 1. Examples of dithio chain transfer agents

The effect on molecular weight and polydispersity of addition of a dithio compound to an otherwise conventional free radical polymerization is shown by the GPC traces in Fig. 2. Thus, thermal polymerization of styrene at 110 °C for 16 hrs resulted in a 72% conversion to polystyrene of M_n = 323,700 and M_w/M_n = 1.74, whereas in the presence of $1.47x10^{-2}$ M cumyl dithiobenzoate (**2**), polystyrene of M_n = 30,900 and M_w/M_n = 1.05 was obtained in 53% yield. The lower conversion in the presence of the dithio compound is most likely due to a reduction in the gel effect brought about by the formation of lower molecular weight polymer.

Thiocarbonythio reagents (**1**) are a well-known class of organic compounds and are generally easy to prepare[21)]. For example, cumyl dithiobenzoate (**2**) can be obtained in good yield by the addition of dithiobenzoic acid to α- methylstyrene[18,22)].

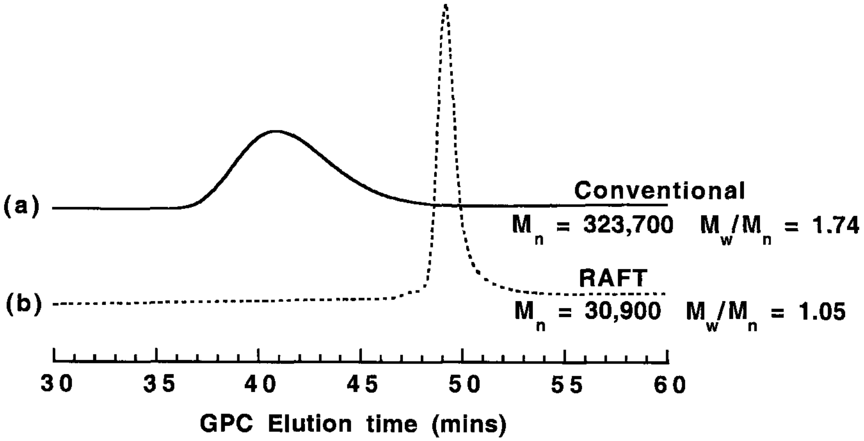
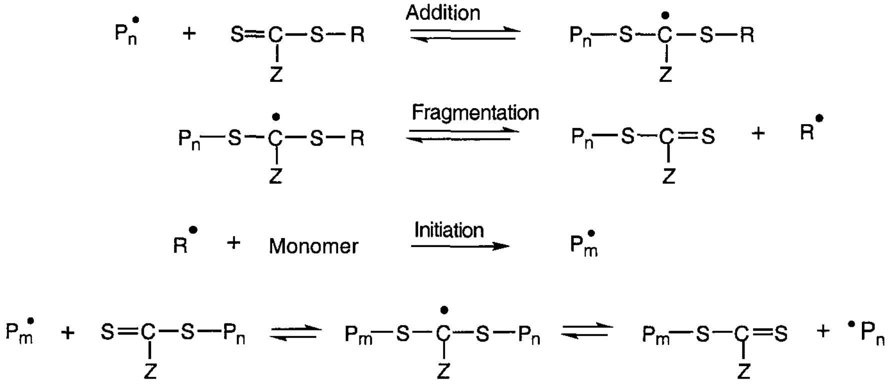


Fig. 2. Comparison of conventional and RAFT polymerization. (a) Thermal polymerization of styrene at 110 °C. (b) Thermal polymerization of styrene at 110 °C in the presence of $1.47x10^{-2}$ M cumyl dithiobenzoate(2)

Mechanism

The mechanism of RAFT polymerization is envisaged to involve a series of addition-fragmentation sequences as shown in Scheme 3. In the early stages of the polymerization, addition of a propagating radical ($P_n^\bullet$) to the dithio compound [S=C(Z)SR] followed by fragmentation of the intermediate radical gives rise to a polymeric dithio compound [P_nS(Z)C=S] and a new radical ($R^\bullet$). Reaction of the radical ($R^\bullet$) with monomer will form a new propagating radical ($P_m^\bullet$). The equilibrium between the active propagating radicals ($P_n^\bullet$

and $P_m^\bullet$) and the dormant polymeric dithio compounds in the presence of monomer provides equal probability for all chains to grow. Hence narrow polydispersity polymers are produced. When the polymerization is complete (or stopped) the vast majority of the chains will contain the dithio end group and these are isolated as stable materials. Reactivation of these in the presence of a second monomer will result in the formation of a block copolymer.



Scheme 3. Mechanism of RAFT polymerization

For RAFT polymerization to function efficiently, the choice of the substituents Z and R in the dithio compound S=C(Z)SR is of critical importance. The requirements (see Scheme 3) are for very fast rates of addition and fragmentation and efficient re-initiation. This translates into very high chain transfer constants for the S=C(Z)SR reagent. The rate of addition of radicals to the C=S double bond is strongly influenced by the substituent Z. We have found that when Z=aryl or alkyl and R is a good homolytic leaving group, (e.g., cumyl) the chain transfer constants of the dithio compound are too high (>50) to be measured by conventional methods (e.g. Mayo plots). On the other hand, when Z=O-alkyl (xanthates) or N,N-dialkyl (dithiocarbamates) the chain transfer constants are only in the range of 0.01-3. For fragmentation to occur efficiently in the desired direction the substituent R must be a good homolytic leaving group, relative to the attacking radical $P_n^\bullet$. For example, the dithio reagent where $R=CH_2Ph$ (and Z=Ph) functions as a suitable chain transfer agent for styryl and acrylyl propagating radicals but not for the methacrylyl propagating radical. The leaving ability of the substituent R must also be balanced with the ability of the radical $R^{\bullet}$ to re-initiate polymerization. The triphenylmethyl radical, for instance, would be an excellent leaving group but would be a poor re-initiator of chains and its use would result in retardation of polymerization. Suitable R groups are tertiary radicals where one substituent is Ph, COOR or CN (e.g. cyanoisopropyl). During chain extension (Scheme 3) the attacking and leaving propagating radicals ($P_n^{\bullet}$ and $P_m^{\bullet}$) are, in essence, identical and therefore would have equivalent rates in both addition and fragmentation.

It should be noted that in RAFT polymerization there will be a small number of polymer chains formed that do not carry the thiocarbonylthio end group and are therefore "dead". The maximum number of dead chains will be equal to the number of initiating radicals derived from the initiator employed in the polymerization. To put it another way, the number of chains carrying the thiocarbonylthio [S=C(Z)S—] end group will be equal to the number of dithio molecules whereas the total number of chains formed will be equal to the number of chains initiated by the radical $R^{\bullet}$ expelled from the dithio compound (see Scheme 3) plus the number produced by the initiator. As a consequence, a high ratio of dithio compound to initiator-derived radicals gives best results, albeit, at the expense of the molecular weight of the final polymer. In addition, a slow rate of initiation is beneficial in that it will reduce the rate of termination by radical-radical reactions. Having said this, RAFT polymerization can be used to prepare narrow polydispersity polymers of moderate to high molecular weight at useful rates of polymerization. For example, the polymerization of 7M methyl methacrylate in benzene with AIBN (0.006M) in the presence of dithio compound (**2**) (0.011M) proceeds to essentially complete conversion (>95%) in 16 hrs at 60 °C to give PMMA of $M_n = 56{,}200$ and $M_w/M_n = 1.12$.

Further evidence for the mechanism shown in Scheme 3 is provided by ^{1}H NMR spectroscopy[19)]. Fig. 3 shows the expected structure and the ^{1}H NMR spectrum of a poly(methyl acrylate) of $M_n = 4700$ and $M_w/M_n = 1.05$ prepared by the solution polymerization of methyl acrylate in the presence of 1-phenylethyl dithiobenzoate (**3**).

The end groups of the polymer, CH(CH$_3$) Ph and S(Ph)C=S, are clearly visible in the spectrum and give different signals to those observed in the ^{1}H NMR spectrum of the chain transfer agent (**3**) (not shown).

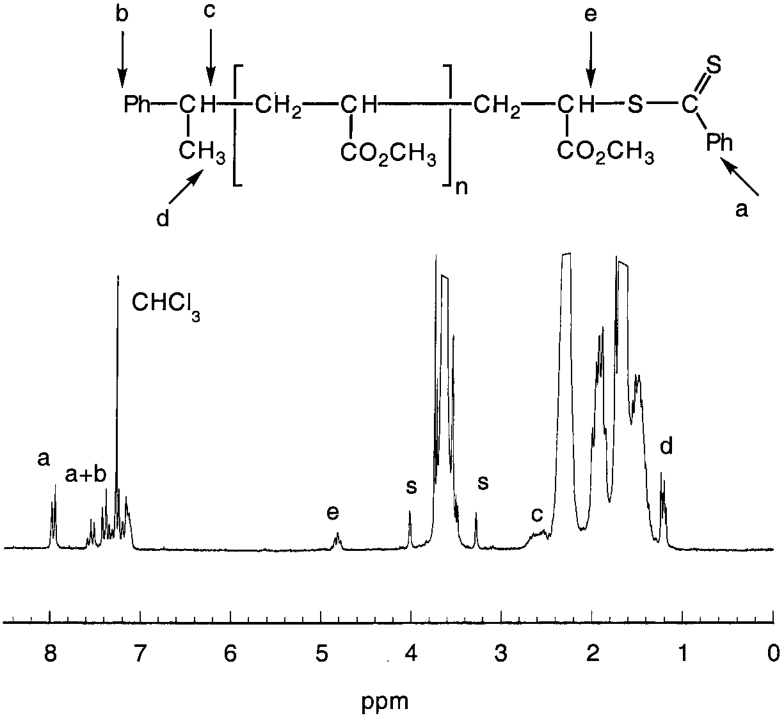


Fig. 3. Structure and ^{1}H NMR spectrum (200MHz, CDCl$_3$) of a poly(methyl acrylate) prepared in the presence of 1-phenylethyl dithiobenzoate(**3**). 'S' are spinning side bands[19)].

Homo and copolymers by RAFT polymerization

Results obtained at various time intervals for the thermal polymerization of styrene at 100°C in the presence of cumyl dithiobenzoate (**2**) are shown in Tab.1. As can be seen, the polymers have narrow polydispersities (M_w/M_n = 1.08-1.12) and the calculated M_n's are very close in value to those determined by GPC. The GPC traces for the data in Tab.1 are shown in Fig. 4 and the linearity of the plot of number average molecular weight versus conversion in Fig. 5.

Tab. 1. Molecular weight/conversion data for the thermal polymerization of styrene at 100 °C in the presence cumyl dithiobenzoate (0.029M)[a)]

Time (hr)	% Conv.	$M_n \times 10^{-3}$	M_w/M_n	$M_n \times 10^{-3}$ (Calc)
2	4.3	1.5	1.12	1.3
6	14.3	5.7	1.08	4.5
20	40.0	13.8	1.08	12.5
64	81.0	25.2	1.12	25.3

[a)] M_n determined by GPC, M_n (Calc) = [St] / [dithioester] x conversion x 104

Results for the RAFT polymerization of various monomers are shown in Tab. 2[19)]. The data demonstrate that RAFT polymerization is applicable to a range of monomers and can be used to prepare both high and low M_n polymers of narrow polydispersity over a wide temperature range. It also shows that it can be applied successfully in an emulsion system. The results in Tab. 3[19)] demonstrate that RAFT polymerization is applicable to functional

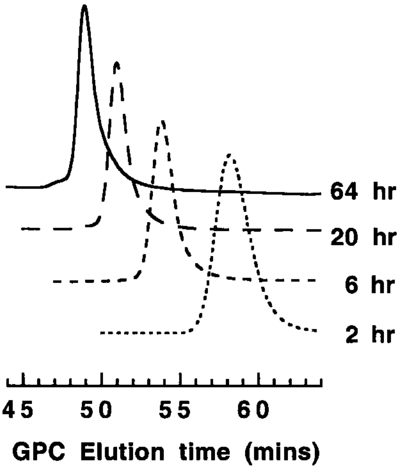


Fig. 4. GPC traces for the data in Tab. 1

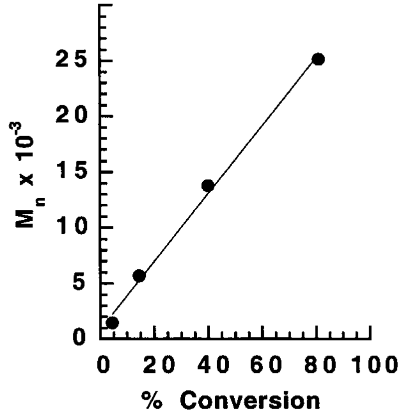


Fig. 5. M_n versus Conversion for the data in Tab. 1

Tab. 2. RAFT polymerization of various monomers using dithio compound (**2**)

Monomer	Temp. °C	Initiator	M_n x 10^{-3}	M_w/M_n
MMA	60	Bz_2O_2	47.1	1.04
MMA	60	AIBN	6.3	1.19
BMA[a]	80	ACP[b]	57.7	1.22
BA	60	AIBMe[c]	6.1	1.17
BA[d]	60	AIBN	92.7	1.14
St	110	Thermal	14.4	1.04
St	110	Thermal	88.2	1.16
VBz[e]	150	AB[f]	3.5	1.29
St/AN[g]	100	Thermal	51.4	1.07

[a] Emulsion [b] Azobiscyanopentanoic acid [c] Azobis(methyl isobutyrate)
[d] Using dithio compound (**4**) [e] Vinyl Benzoate [f] Azobismethylpropane
[g] St : AN=62:38 (azeotropic composition)

monomers and can be performed in various solvents including water and dimethyl formamide (DMF).

The copolymerization experiments in Tab. 2 (St/AN) and Tab. 3 (MMA/HEMA) have been used to show that the composition of the copolymers (by NMR) formed in the presence of a dithio reagent are identical to those formed in its absence.

Tab. 3. RAFT polymerization of functional monomers at 60 °C

Monomer	Solvent	Initiator	M_n x 10^{-3}	M_w/M_n	Dithio [a]
DMAEMA[b]	EtOAc	ACP	21.5	1.13	9
AA[c]	DMF	AIBN	13.8	1.23	3
$StSO_3Na$[d]	H_2O	ACP	8.0	1.13	5
DMA[e]	Benzene	AIBN	35.1	1.14	4
MMA/HEMA	EtOAc	AIBN	28.0	1.21	2

[a] See Fig. 1. [b] Dimethylaminoethyl methacrylate [c] Acrylic acid
[d] p-Styrenesulfonic acid sodium salt [e] Dimethyl acrylamide

End - functional polymers

High purity and narrow polydispersity end-functional polymers can be prepared by using a functional dithio reagent in the RAFT process. For example, an α-hydroxypoly(methyl methacrylate) of $M_n = 55{,}300$ and $M_w/M_n = 1.05$ was prepared by heating MMA (7 M in benzene) with AIBN (0.006M) in the presence of dithio compound (**8**) (0.012 M) at 60 °C for 16 hrs (92% conversion). Two further examples of end functional polymers are the poly(dimethylaminoethyl methacrylate) prepared with dithio compound (**9**) and the poly(p-styrenesulfonic acid sodium salt) prepared with dithio compound (**5**) (see Tab. 3).

The thiocarbonylthio end group can also be converted to other functionalities[23,24]. For example, treatment with hydroxide or an amine will produce a thiol-terminated polymer. Indeed, since the thiocarbonylthio moiety is coloured (polymers range in colour from pale yellow to pink depending on the substituents Z and P_n) such chemical transformations can be used to decolourize the polymer. Treatment with NaOCl or H_2O_2 or exposure to ultraviolet light has also been shown to decolourize the polymers.

Gradient copolymers

Narrow polydispersity gradient copolymers can be produced by the RAFT process by suitable monomer feed protocols. However, such polymers can also be made in a batch polymerization by taking advantage of disparate reactivity ratios between monomers. For instance, the copolymerization of an equimolar mixture of MMA and BA ($r_1 \sim 1.7$, $r_2 \sim 0.2$) in the presence of a dithio compound will provide copolymer chains which will be rich in MMA at one end and rich in BA at the other. Tab. 4 shows the results of one such experiment. When a mixture of MMA and BA in the molar ratio of 1 : 0.91 was polymerized with AIBN in the presence of dithio compound (**2**) at 60 °C, the ratio of MMA to BA in the polymer was 1 : 0.45 at 22% conversion and $M_n = 16{,}800$ and reached 1 : 0.80 at 93% conversion and $M_n = 75{,}400$.

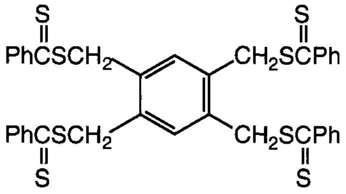
Tab. 4. Gradient MMA/BA copolymer by RAFT polymerization

% Conv.	MMA: BA[a)]	M_n	M_w/M_n
0	1: 0.91	-	-
22	1: 0.45	16,800	1.21
45	1: 0.54	41,600	1.13
93	1: 0.80	75,400	1.21

[a)] Determined by ^{1}H NMR spectroscopy

Star polymers

Star polymers are prepared by using appropriate multiarm dithio compounds. Two examples are structures (**10**) and (**11**) below[20)]. Heating (**10**) (54.5mg) in styrene (10ml) at 100 °C gave four arm polystyrenes of M_n = 25,900 (M_w/M_n = 1.20) and M_n = 67,600 (M_w/M_n = 1.30) after 20 hrs and 64 hrs respectively. Under identical conditions, compound (**11**) (48.9mg) yielded six arm polystyrenes of M_n = 34,100 (M_w/M_n = 1.36) and M_n = 79,600 (M_w/M_n = 1.67) (molecular weight data from GPC). Dithio compounds possessing better homolytic leaving groups (substituents on sulfur) and in which the leaving groups have greater spatial separation than in (**10**) or (**11**) should provide polymers of narrower polydispersities. Examples of these are currently under investigation.



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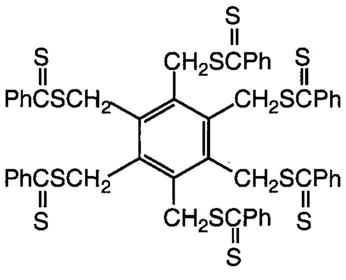

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Block Copolymers

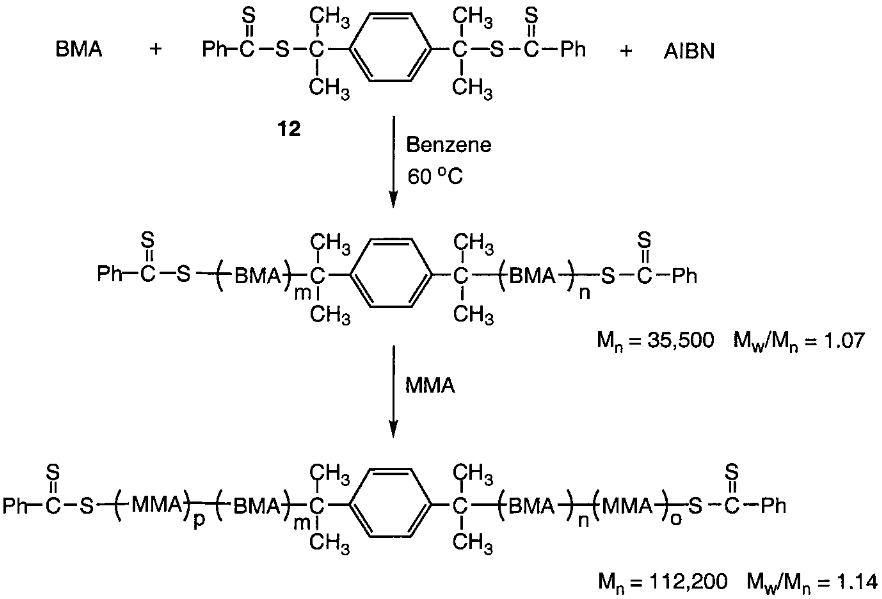
As outlined above, RAFT polymerization proceeds with retention of the thiocarbonylthio group at the chain end of polymers. This allows easy entry to the synthesis of block copolymers by the simple addition of a second (or more) monomer20). Tab. 5 summarizes the results of several such experiments and demonstrates again the utility of the method. All the block copolymers are of narrow polydispersity and both high and low molecular weights are possible. Of considerable interest is the ability to make hydrophilic-hydrophobic block copolymers where the hydrophilic block is composed of polar monomers such as acrylic acid, dimethylaminoethyl methacrylate or ethylene oxide. In this last case, the block copolymer was prepared by converting commercial poly(ethylene oxide) monomethyl ether into a polymeric dithioester and chain extending with styrene. The polymeric dithioester was obtained by esterification of the hydroxyl terminated poly(ethylene oxide) with the carboxyl containing dithio compound (**9**) using dicyclohexyl carbodiimide. It is worthy of note that previous syntheses of poly(ethylene oxide-*block*-styrene) by other living radical techniques gave poorly defined products or very low yields25-28). Likewise, earlier attempts to make poly(St-*block*-DMAEMA) met with only limited success29).

Tab. 5. A-B diblock copolymers by RAFT polymerization

A-Block	M_n	A-B Diblock	M_n	M_w/M_n
MMA	55,000	MMA-St	112,500	1.20
MMA	3,200	MMA-MAA	4,700	1.18
BzMA	1,800	BzMA-DMAEMA	3,500	1.06
St	20,300	St-DMA	43,000	1.24
DMAEMA[a)]	63,600	DMAEMA-St[a)]	103,900	1.28
BA	33,600	BA-AA	52,400	1.19
EO[b)]	750	EO-St	7,800	1.07

[a)] GPC with DMF as eluent [b)]Dithioester terminated poly(ethylene oxide) (see text)

A-B-A triblock copolymers can be prepared by RAFT polymerization in two different ways. The first is to chain extend an A-B diblock with monomer A. The second, and more efficient way, is to make use of a difunctional dithio chain transfer agent so as to grow the central B block in two directions. An example of this strategy is shown in Scheme 4. Thus, the difunctional chain transfer agent (**12**) was converted to a poly(butyl methacrylate) (M_n = 35,500 , M_w/M_n = 1.07) with thiocarbonylthio groups at each chain end and this was extended with MMA to give the A-B-A triblock of M_n = 112,200 and M_w/M_n = 1.14. Both steps were performed at 60 °C with AIBN as initiator and benzene (25%) as solvent. Fig. 6 shows the GPC traces of the poly(butyl methacrylate) and the MMA-BMA-MMA triblock copolymer prepared as in Scheme 4.



Scheme 4. Synthesis of a MMA-BMA-MMA triblock copolymer

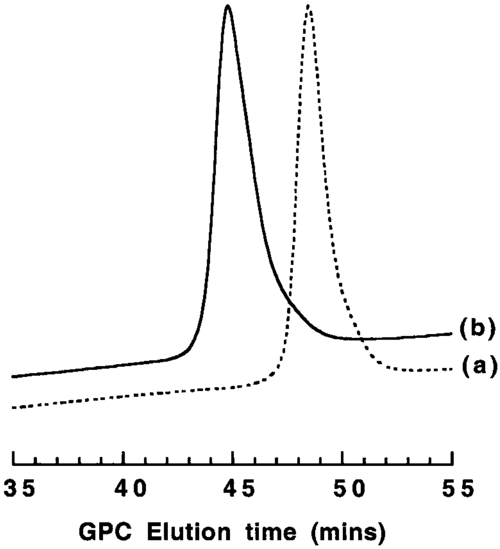


Fig. 6. GPC traces of polymers produced as in Scheme 4, (a) poly(butyl methacrylate), (b) MMA-BMA-MMA triblock

In RAFT polymerization, the order of constructing the blocks of a block copolymer is important. The first block should be the one which provides the better (or equivalent) homolytic leaving group since in the fragmentation step (see Scheme 3) the propagating radical from the second monomer must displace the propagating radical from the first. For example, in the synthesis of a methacrylate-acrylate diblock, the methacrylate block should be prepared first.

Conclusion

Free radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization) mediated by thiocarbonylthio compounds is a process of exceptional effectiveness and versatility. It can be used to prepare a wide range of narrow polydispersity polymers of predetermined molecular weight and of various architectures including block, star and gradient copolymers. At the same time, it offers most of the advantages of conventional free radical polymerization.

Acknowledgment

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