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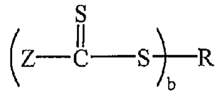
(54) Title: POLYMERISATION AGENT



$$\left(Z-\overset{S}{\overset{\|}{C}}-S\right)_b-R$$

(I)

(57) Abstract: The invention relates to RAFT agents of formula (I) where Z is any group that is a weak lone pair donor and a strong sigma acceptor, R is a group such that the agent can function as a RAFT agent in polymerisation of ethylenically unsaturated monomer, and b is an integer ≥1, with the proviso that when Z is fluorine, R is not $-CH_3$, $-CF_3$, $-CH_2CH_3$, $-nC_3H_7$, $-CF_2NCS$ or $-CH_2CH_2Cl$. The invention also relates to methods for preparing polymers using RAFT agents.

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POLYMERISATION AGENT

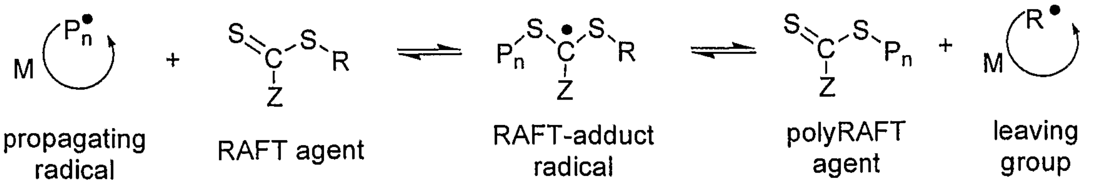
Field of the Invention

The present invention relates generally to agents used in the polymerisation of ethylenically unsaturated monomers to form polymer products. More specifically, the invention relates to a class of reversible addition fragmentation chain transfer agents, and to methods for preparing a polymer using the agents.

Background of the Invention

Polymers have been industrially produced using free radical mediated reactions for over 50 years. Despite being able to effectively produce polymer, early radical polymerisation techniques afforded little if no control over the reaction process. The development of "controlled" or "living" radical polymerisation techniques such as atom transfer polymerisation (ATRP), nitroxide mediated radical polymerisation (NMP) and reversible addition fragmentation chain transfer (RAFT) has in many ways revolutionised free radical polymerisation, enabling homopolymers, random copolymers and block polymers to be produced with a high degree of control and with low polydispersity.

The RAFT technique, as described in International Patent Publication No. WO 98/01478, utilises thiocarbonylthio derivatives (known as “RAFT agents”) as degenerately transferable end groups, and is believed to operate through the chain transfer mechanism depicted below in Scheme 1.



Scheme 1

The ability of a given RAFT agent to function as an efficient chain transfer agent is believed to depend on a complex array of rate constants. In particular, the formation of polymer according to Scheme 1 is believed to be reliant upon equilibria that require high rate constants for the addition of propagating radicals to the RAFT agent and for the fragmentation of the intermediate RAFT-adduct radical, relative to the rate constant for propagation.

Rate constants associated with RAFT polymerisation are believed to be influenced by a complex interplay between stability, steric and polarity effects in the RAFT agent, the RAFT-adduct radical and the polymer product formed. Different factors and structural preferences for the RAFT agent need to be considered in the polymerisation of specific monomers and combinations of monomers. The interplay of factors for a particular system has been largely rationalised on the basis of the results obtained. A clear definition of all factors that influence polymerisation for any particular system has not yet been determined.

While current RAFT technology offers many advantages in being able to produce polymers with a high degree of control and with low polydispersity, the process of selecting a specific RAFT agent for the polymerisation of specific monomer(s) can be complex. Thus according to WO 98/01478, the R group of the RAFT agent should be chosen so as to be a free radical leaving group under the polymerisation conditions and yet, as a free radical leaving group, retain the ability to reinitiate polymerisation. As for the Z group, it should be chosen to give a suitably high reactivity of the C=S group in the RAFT agent towards free radical addition without slowing the rate of fragmentation of the RAFT-adduct radical to the extent that polymerisation is unduly retarded.

Accordingly, in practice the selection of a suitable RAFT agent for a given polymerisation reaction requires careful consideration of the groups R and Z based on the monomer(s) to be polymerised and the reaction conditions that will be used. It will be appreciated that the possible choices are vast. For example, in WO 98/01478 appropriate R groups for a RAFT agent are defined as those selected from "optionally substituted alkyl, an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring, optionally substituted alkylthio, optionally substituted alkoxy, optionally substituted dialkylamino, an organometallic species, and a polymer chain prepared by any polymerisation mechanism". Appropriate Z groups are defined as those selected from "hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxycarbonyl, optionally substituted aryloxycarbonyl (-COOR''), carboxy (-COOH), optionally substituted acyloxy ($-O_2CR''$), optionally substituted carbamoyl ($-CONR''_2$), cyano (-CN), dialyl- or diaryl-phosphonato [$-P(=O)OR''_2$], dialkyl- or diaryl-phosphinato [$-P(=O)R''_2$], and a polymer chain formed by any mechanism".

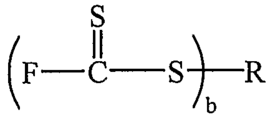
In view of the many permutations of potential R and Z groups, it will also be appreciated that selecting an appropriate R and Z group for a RAFT agent that can effectively control the polymerisation of a specific monomer can be problematic. For example, RAFT agents having an amino or alkoxy Z group may be used in the polymerisation of vinyl acetate but have been found to be ineffective in the polymerisation of styrene. Conversely, RAFT agents having a phenyl Z group may be used in the polymerisation of styrene but have been found to be ineffective in the polymerisation of vinyl acetate.

Having identified appropriate Z and R groups of a RAFT agent for the polymerisation a specific monomer, where a block copolymer is to be prepared it may also be that the selected RAFT agent can only be used to prepare the respective blocks in a specific, and possibly undesirable, order. For example, in the preparation of poly(methyl methacrylate-block-styrene) it may be that the poly(methyl methacrylate) block will need to be prepared first by virtue of the polystyryl propagating species being a poorer free radical leaving group than the poly(methyl methacrylate) propagating species. In other words, in this case it will not be possible to polymerise styrene under the control of the RAFT agent before polymerising the methylmethacrylate.

Accordingly, there remains an opportunity to at least develop an alternative RAFT agent to, and preferably one that is more versatile than, those RAFT agents currently known.

Summary of the Invention

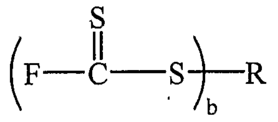
In a first aspect, the present invention provides a RAFT agent of formula (1)



$$\left(F - \overset{\overset{\displaystyle S}{\|}}{C} - S \right)_b - R \qquad (1)$$

where R is a group such that the agent can function as a RAFT agent in the polymerisation of ethylenically unsaturated monomer, and b is an integer ≥1, with the proviso that R is not $-CH_3$, $-CF_3$, $-CH_2CH_3$, $-nC_3H_7$, $-CF_2NCS$ or $-CH_2CH_2Cl$.

In a second aspect, the present invention provides a method for preparing a polymer, said method comprising polymerising one or more ethylenically unsaturated monomers under the control of a RAFT agent of formula (1)



$$\left(\mathrm{F}-\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}-\mathrm{S}\right)_{b}-\mathrm{R}$$

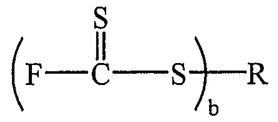
(1)

where R is a group such that the agent can function as a RAFT agent in the polymerisation of the one or more ethylenically unsaturated monomers, and b is an integer ≥1.

In a third aspect, the present invention provides a method of polymerising ethylenically unsaturated monomers to form a polymer, said method comprising:

(a) selecting an ethylenically unsaturated monomer to be polymerised;

(b) providing a RAFT agent of formula (1); and



$$\left(\mathrm{F}-\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}-\mathrm{S}\right)_{b}-\mathrm{R}$$

(1)

(c) polymerising the selected ethylenically unsaturated monomer under the control of said RAFT agent,

wherein the R group is selected such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer and b is an integer ≥1.

The first aspect of the invention is not intended to encompass known compounds falling within general formula (1) that may have utility as a RAFT agent, even though this utility has not been previously described or recognised. The second and third aspects of the invention relate to the use of all suitable RAFT agents of formula (1), including those compounds that may have been described per se in the prior art.

Brief Description of the Drawings

Embodiments of the invention with hereinafter be described with reference to the following non-limiting drawings in which:

Figure 1 depicts the evolution of the full molecular weight distributions with monomer to polymer conversion in a BFDF mediated RAFT polymerisation of styrene at 80°C.

Figure 2 depicts the molecular weight versus conversion plot for the polymerisation of styrene at 80°C using BFDF.

Figure 3 depicts the evolution of the full molecular weight distributions in BFDF mediated RAFT polymerisation of methyl acrylate at 60°C.

Figure 4 depicts the molecular weight versus conversion plot for the polymerisation of methyl acrylate at 60°C using BFDF.

Detailed Description of the Invention

Like conventional RAFT agents, a RAFT agent in accordance with the invention may be used to produce polymers with a high degree of control and with low polydispersity. However, unlike conventional RAFT agents, it is believed that a RAFT agent in accordance with the invention can advantageously be used to polymerise a diverse array of ethylenically unsaturated monomers simply by selecting an appropriate R group. In other words, in the RAFT agents of the invention the fluorine substituent can advantageously function as a "generic" Z group to thereby reduce the potentially complex process of RAFT agent selection to one that simply involves selecting a suitable R group for a given polymerisation. Accordingly, it is believed that RAFT agents of the invention not only offer an alternative to, but are also believed to be more versatile than, conventional RAFT agents. These and other advantages of the invention will be described in more detail below.

As a “RAFT agent”, compounds defined by formula (1) are be capable of taking part in a radical mediated reversible addition fragmentation chain transfer reaction with an ethylenically unsaturated monomer to afford a polymer product. In other words, an ethylenically unsaturated monomer can be polymerised under the control of the “RAFT agent”. By being polymerised "under the control" of the RAFT agent is meant that as a result of reacting with the agent, the ethylenically unsaturated monomer can be polymerised via a RAFT mechanism to form a polymer. In this case, monomer is believed to be polymerised via a RAFT mechanism as depicted in Scheme 1.

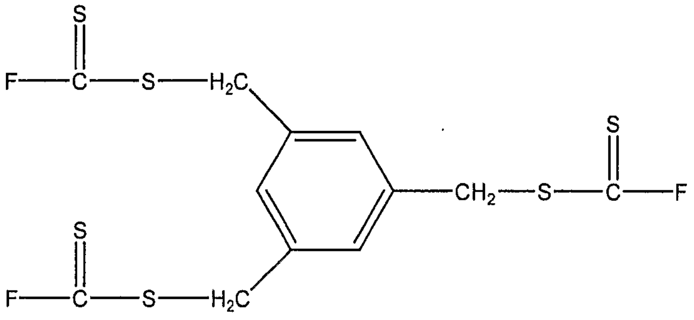
By virtue of the "Z group" in RAFT agents of the invention being in effect predetermined (ie. as –F), the design of such a RAFT agent for use in the polymerisation of a specific monomer is advantageously reduced to the selection of an appropriate R group. In general terms, the R group will be a group such that the agent can function as a RAFT agent in polymerisation of ethylenically unsaturated monomer.

Criteria for the selection of the R group are believed to be similar to that applied to conventional RAFT agents. Accordingly, the R group should be selected such that under the polymerisation conditions it can afford a free radical leaving group that has the ability to reinitiate polymerisation with the selected monomer.

A RAFT agent in accordance with the invention may be provided with a diverse array of R groups which include, but are not limited to, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylthio, optionally substituted heterocyclyl, optionally substituted acyl, optionally substituted amino, a linear, branched or crosslinked polymer formed by any polymerisation mechanism, and a solid support such gold, silica and the like. Where such solid supports are used, the RAFT agent will generally be tethered to the solid support via one of the other aforementioned R groups.

With reference to formula (1) "b" is an integer ≥ 1. Where "b" is ≥ 2 the R group may be conveniently defined as a group R^1. In this case, suitable R^1 groups include, but are not limited to, "b"-valent atoms selected from C, S, and O, or "b"-valent moieties selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted acyl, optionally substituted amino, and a linear or branched polymer chain formed by any polymerisation mechanism.

For example, the R^1 group may be tri-valent moiety to which three fluro-thiocarbonylthio substituents can be attached such as in the compound depicted directly below:



RAFT agents in accordance with the invention in which "b" ≥ 2 may be used to prepare polymers having complex architectures including multiblock, branched, star and graft polymers.

Further examples of suitable R groups include, but are not limited to, $-CH_2CH_3$, $-iC_3H_7$, $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-C(CH_3)_2C_6H_5$, $-CH_2COOR^5$, $-CH(CH_3)COOR^5$, $-C(CH_3)_2COOR^5$, $-CH_2CONR^5R^6$, $-CH(CH_3)CONR^5R^6$, $-C(CH_3)_2CONR^5R^6$, $-C(CH_3)_3$, $-CF_3$, $-CF_2R^5$, $-CFR^5R^6$, $-CH_2CHCH_2$, $-CH(CH_3)CHCH_2$, $-C(CH_3)_2CHCH_2$, $-CH_2Cl$, $-CH(CH_3)Cl$, $-C(CH_3)_2Cl$, $-CH_2OR^5$, $-CH(CH_3)OR^5$, $-C(CH_3)_2OR^5$, $-CH_2SO_3R^5$, $-CH(CH_3)SO_3R^5$, $-C(CH_3)_2SO_3R^5$, $-CH_2COR^5$, $-CH(CH_3)COR^5$, $-C(CH_3)_2COR^5$, $-CH_2NR^5R^6$, $-CH(CH_3)NR^5R^6$, $-C(CH_3)_2NR^5R^6$, $-CH_2CN$, $-CH(CH_3)CN$, $-C(CH_3)_2CN$, $-CH_2CH_2OR^5$, $-CH(CH_3)CH_2OR^5$, $-C(CH_3)_2CH_2OR^5$, $-CH_2CH_2Cl$, $-CH(CH_3)CH_2Cl$, $-C(CH_3)_2CH_2Cl$, $-CH(C_6H_5)_2$, $-C(C_6H_5)_3$, $-C(CH_3)(C_6H_5)_2$, $-CCl_3$, $-CCl_2R^5$, $-CClR^5R^6$, and $-ONR^5R^6$, where R^5 and R^6 are independently selected from H, alkyl and aryl.

Preferred R groups include, but are not limited to, $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-CH(CH_3)COOR^5$, $-CH_2CN$, $-CH(CH_3)CN$, and $-C(CH_3)_2CN$, where R^5 is selected from H, alkyl and aryl.

Further examples of suitable R^1 groups include, but are not limited to, dendrimers, cyclodextrins, and hyperbranched polymers.

Compounds of formula (1) may be prepared by any suitable means. However, such compounds may be conveniently prepared in accordance with the method described directly below.

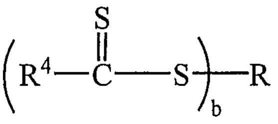
A RAFT agent of formula (1) may be prepared by reacting a compound of formula (2):

$$\left(R^2S\right)_b\!\!-R \qquad (2)$$

with a compound of formula (3):

$$S{=}CR^3R^4 \qquad (3)$$

where R is a group such that the agent can function as a RAFT agent in polymerisation of ethylenically unsaturated monomer, b is an integer ≥1, R^2 and R^3 are any combination of groups that promote the elimination of R^2 and R^3 to form a compound of formula (4):



$$\left(R^4-\overset{S}{\overset{\|}{C}}-S\right)_b\!\!-R \qquad (4)$$

in which R^4 is F or a group which can then be substituted with F.

In the method described directly above, a compound of formula (2) is reacted with a compound of formula (3) such that substituents R^2 and R^3 are eliminated to form a compound of formula (4). The elimination of substituents R^2 and R^3 will generally result in the formation of the addition compound R^2-R^3. Compounds of formula (2) and (3) will generally be combined in a suitable solvent and maintained at a suitable temperature and period of time such that substituents R^2 and R^3 are eliminated and the compound of formula (4) is produced. In some cases it may be appropriate to conduct this elimination reaction under an inert atmosphere such as nitrogen or argon.

For compounds of formula (2), the R group is as previously defined, and the substituent R^2 may be selected from H, or an alkali metal such as K or Na.

A driving force for the reaction between compounds of formula (2) and (3) will generally be the formation of an elimination product through the reaction of substituent R^2 with substituent R^3 (ie. the formation of R^2-R^3). In this case, R^3 will be selected such that it can form the elimination product R^2-R^3. Where R^2 is H, R^3 may be selected from I, Br, Cl, F, a mesylate group, a tosylate group, a phosphite ester group, a chlorosulfite group, and a trifluoromethylate group. Where R^2 is an alkali metal, R^3 may also be selected from I, Br, Cl, F, a mesylate group, a tosylate group, a phosphite ester group, a chlorosulfite group, and a trifluoromesylate group.

Where R^4 in formula (3) is F, the reaction between a compound of formula (2) and formula (3) will generally directly afford a compound of formula (1). Where R^4 in a compound of formula (3) is not F, R^4 should be selected such that subsequent to the formation of a compound of formula (4) it can be substituted with F to provide a compound of formula (1). In this case, R^4 may be selected from I, Br, Cl, a mesylate group, a tosylate group, a phosphite ester group, a chlorosulfite group, and a trifluoromesylate group.

Techniques for substituting such R^4 groups with a fluorine atom may include, but are not limited to, subjecting a compound of formula (4) where R^4 = I, Br, or Cl to a Finkelstein analogous reaction in which the compound is reacted with a metal fluoride, preferably an alkali metal fluoride such as KF or NaF, in an organic solvent in the presence of a cryptant such as 18-crown 6-ether. Such a reaction is preferably performed under anhydrous conditions under an inert atmosphere. with the exclusion of light and at temperatures greater than about 25°C. Where R^4 in a compound of formula (4) is a mesylate, a tosylate, a phosphite ester, a chlorosulfite or a trifluoromesylate group, F substitution may be performed by subjecting the compound to a fluorinating agent such as HF.

Suitable solvents for performing the reaction between a compound of formula (2) and (3) include, but are not limited to, carbon disulfide, chlorinated organic solvents such as $CHCl_3$, CH_2Cl_2 and CH_3Cl, and linear or cyclic ethers such as diethylether and tetrahydrofuran.

Suitable solvents for conducting the fluorination of a compound of formula (4) include, but are not limited to acetonitrile, dimethylsulfoxide (DMSO), dimethyformamide (DMF) and dimethylacetamide (DMA).

Fluorinated dithioester compounds of the type depicted in formula (1) are not widely known. However, compounds of formula (1) where R = $-CH_2CH_3$ and $-nC_3H_7$ have been reported[a] and were prepared in a similar manner to that outlined above. Compounds of formula (1) where R = $-CH_3$, $-CF_2NCS$[b] and $-CH_2CH_2Cl$[c] have also been reported. However, these compounds were not specifically prepared but merely identified as minor (less than 30%) by products in a reaction sequence. A compound of formula (1) where R = $-CF_3$ is also known. Although falling within the general structure of formula (1), these various compounds are not believed to have been identified to date as being useful in the polymerisation of ethylenically unsaturated monomers.

As used herein, the term "alkyl", used either alone or in compound words such as "alkyloxy", "alkylthio", "alkylamino" and "dialkylamino" denotes straight chain, branched or cyclic alkyl, preferably C_{1-20} alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethyl-propyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2,-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methoxyhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethyl-pentyl, 1,2,3,-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, octyl, 6-methylheptyl, 1-methylheptyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyl-octyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-, 2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-,3- or 4-propylheptyl, undecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1-2-pentylheptyl and the like. Examples of cyclic alkyl include mono- or polycyclic alkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, and the like.

As used herein, the term "alkenyl" denotes groups formed from straight chain, branched or cyclic alkenes including ethylenically mono-, di- or poly-unsaturated alkyl or cycloalkyl groups as previously defined, preferably C_{2-20} alkenyl. Examples of alkenyl include vinyl, allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, cyclopentenyl, 1-methyl-cyclopentenyl, 1-hexenyl, 3-hexenyl, cyclohexenyl, 1-heptenyl, 3-heptenyl, 1-octenyl, cyclooctenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 3-decenyl, 1,3-butadienyl, 1-4,pentadienyl, 1,3-cyclopentadienyl, 1,3-hexadienyl, 1,4-hexadienyl, 1,3-cyclohexadienyl, 1,4-cyclohexadienyl, 1,3-cycloheptadienyl, 1,3,5-cycloheptatrienyl and 1,3,5,7-cyclooctatetraenyl.

As used herein, the term "alkoxy" denotes straight chain or branched alkoxy, preferably C_{1-20} alkoxy. Examples of alkoxy include methoxy, ethoxy, n-propoxy, isopropoxy and the different butoxy isomers.

As used herein, the terms "aryl" and "heteroaryl" denote any group which includes or consists of one or more aromatic or heteroaromatic ring respectively, and which is attached via a ring atom, preferably having 6 to 14 carbon atoms. The rings may be mono or polycyclic ring systems, although mono or bicyclic 5 or 6 membered rings are preferred. Examples of suitable rings include but are not limited to benzene, biphenyl, terphenyl, quaterphenyl, naphthalene, tetrahydronaphthalene, l-benzylnaphthalene, anthracene, dihydroanthracene, benzanthracene, dibenzanthracene, phenanthracene, perylene, pyridine, 4-phenylpyridine, 3-phenylpyridine, thiophene, benzothiophene, naphthothiophene, thianthrene, furan, benzofuran, pyrene, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, pyrazine, pyrimidine, pyridazine, indole, indolizine, isoindole, purine, quinoline, isoquinoline, phthalazine, quinoxaline, quinazoline, pteridine, carbazole, carboline, phenanthridine, acridine, phenanthroline, phenazine, isothiazole, isooxazole, phenoxazine and the like, each of which may be optionally substituted.

As used herein, the terms "heterocyclic", "heterocyclyl" and "heterocycl", used either alone or in compound words such as "heterocyclicalkenoyl", heterocycloxy" or "haloheterocyclyl" denote aromatic, pseudo-aromatic and non-aromatic rings or ring systems which contain one or more heteroatoms selected from N, S, and O and which may be optionally substituted. Preferably the rings or ring systems have 3 to 20 carbon atoms. The rings or ring systems may be selected from those described above in relation to the definition of "heteroaryl".

As used herein, the term "acyl", used either alone or in compound words such as "acyloxy", "acylthio", "acylamino" or "diacylamino", denotes carbamoyl, an aliphatic acyl group an acyl group containing an aromatic ring, which is referred to as aromatic acyl, or a heterocyclic ring, which is referred to as heterocyclic acyl, preferably C_{1-20} acyl. Examples of acyl include carbamoyl; straight chain or branched alkanoyl such as formyl, acetyl, propanoyl, butanoyl, 2-methylpropanoyl, pentanoyl, 2,2-dimethylpropanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, nonadecanoyl and icosanoyl; alkoxycarbonyl such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, t-pentyloxycarbonyl and heptyloxycarbonyl; cycloalkylcarbonyl such as cyclopropylcarbonyl, cyclobutylcarbonyl, cyclopentylcarbonyl and cyclohexylcarbonyl; alkylsulfonyl such as methylsulfonyl and ethylsulfonyl; alkoxysulfonyl such as methoxysulfonyl and ethoxysulfonyl; aroyl such as benzoyl, toluoyl and naphthoyl; aralkanoyl such as phenylalkanoyl (e.g. phenylacetyl, phenylpropanoyl, phenylbutanoyl, phenylisobutylyl, phenylpentanoyl and phenylhexanoyl) and naphthylalkanoyl (e.g. naphthylacetyl, naphthylpropanoyl and naphthylbutanoyl; aralkenoyl such as phenylalkenoyl (e.g. phenylpropenoyl, phenylbutenoyl, phenylmethacryloyl, phenylpentenoyl and phenylhexenoyl and naphthylalkenoyl (e.g. naphthylpropenoyl, naphthylbutenoyl and naphthylpentenoyl); aralkoxycarbonyl such as phenylalkoxycarbonyl (e.g. benzyloxycarbonyl); aryloxycarbonyl such as phenoxycarbonyl and napthyloxycarbonyl; aryloxyalkanoyl such as phenoxyacetyl and phenoxypropionyl; arylcarbamoyl such as phenylcarbamoyl; arylthiocarbamoyl such as phenylthiocarbamoyl; arylglyoxyloyl such as phenylglyoxyloyl and naphthylglyoxyloyl; arylsulfonyl such as phenylsulfonyl and napthylsulfonyl; heterocycliccarbonyl; heterocyclicalkanoyl such as thienylacetyl, thienylpropanoyl, thienylbutanoyl, thienylpentanoyl, thienylhexanoyl, thiazolylacetyl, thiadiazolylacetyl and tetrazolylacetyl;

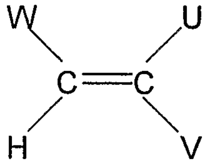
heterocyclicalkenoyl such as heterocyclicpropenoyl, heterocyclicbutenoyl, heterocyclicpentenoyl and heterocyclichexenoyl; and heterocyclicglyoxyloyl such as thiazolylglyoxyloyl and thienylglyoxyloyl.

As used herein, the term "alkynyl" denotes groups formed from straight chain, branched or cyclic alkyne including those structurally similar to the alkyl and cycloalkyl groups as previously defined, preferably C_{2-20} alkynyl. Examples of alkynyl include ethynyl, 2-propynyl and 2- or 3-butynyl.

As used herein, the expression "optionally substituted" means that a group may or may not be substituted with one or more groups selected from, but not limited to, alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, acetyleno, carboximidyl, haloaryloxy, isocyano, cyano, formyl, carboxyl, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, imino, alkylimine, alkenylimine, alkynylimino, arylimino, benzylimino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphonyl, arylsulphonyl, alkylsolphinyl, arylsulphinyl, carboalkoxy, alkylthio, benzylthio, acylthio, sulphonamido, sulfanyl, sulfo and phosphorus-containing groups, alkoxysilyl, silyl, alkylsilyl, alkylalkoxysilyl, phenoxysilyl, alkylphenoxysilyl, alkoxyphenoxysilyl, arylphenoxysilyl, allophanyl, guanidino, hydantoyl, ureido, and ureylene. The expression "optionally substituted" also means that one or more saturated carbon atoms may be substituted for a heteroatom or heterogroup such as O, S, NH and the like.

A RAFT agent of formula (1) may be used in accordance with the invention to prepare a polymer. The invention can advantageously be applied to polymerise a diverse array of monomers that are susceptible to free-radical polymerisation. However, unlike conventional RAFT agents, it is believed that RAFT agents in accordance with the invention may also be used to effectively control polymerisation of stable and unstable monomer radicals without the need to change the "Z group". A more detailed discussion on this advantage is provided below.

Ethylenically unsaturated monomers that may be used in accordance with the method of the invention include, but are not limited to, those with the general formula (5)



(5)

where U and W are independently selected from the group consisting of $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, hydrogen, halogen and optionally substituted C_1-C_4 alkyl wherein the substituents are independently selected from the group consisting of hydroxy, $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CN$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, $-OR^6$, $-SR^6$, $-O_2CR^6$, $-SCOR^6$, and $-OCSR^6$; and

V is selected from the group consisting of hydrogen, R^6, $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, $-OR^6$, $-SR^6$, $-O_2CR^6$, $-SCOR^6$, and $-OCSR^6$;

where R^6 is selected from the group consisting of optionally substituted C_1-C_{18} alkyl, optionally substituted C_2-C_{18} alkenyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aralkyl, optionally substituted heteroarylalkyl, optionally substituted alkaryl, optionally substituted alkylheteroaryl and polymer chains, wherein the substituents are independently selected from the group consisting of alkyleneoxidyl (epoxy), hydroxy, alkoxy, acyl, acyloxy, formyl, alkylcarbonyl, carboxy, sulfonic acid, alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, amino, including salts and derivatives thereof. Preferred polymer chains include, but are not limited to, polyalkylene oxide, polyarylene ether and polyalkylene ether.

Examples of monomers include, but are not limited to, maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerisable monomers, acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in the art would recognise, the choice of comonomers is determined by their steric and electronic properties. The factors which determine copolymerisability of various monomers are well documented in the art. For example, see: Greenlee, RZ. in Polymer Handbook 3rd Edition (Brandup, J., and Immergut, E.H Eds.) Wiley: New York. 1989 pII/53.

Specific examples of useful ethylenically unsaturated monomers include, but are not limited to the following:

methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-butylacrylamide, N-n-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropylacrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, ethylene and chloroprene. This list is not exhaustive.

The polymerisation will usually require initiation from a source of free radicals. The source of initiating radicals can be provided by any suitable method of generating free radicals, such as the thermally induced homolytic scission of suitable compound(s) (thermal initiators such as peroxides, peroxyesters, or azo compounds), the spontaneous generation from monomers (e.g. styrene), redox initiating systems, photochemical initiating systems or high energy radiation such as electron beam, X- or gamma-radiation. The initiating system is chosen such that under the reaction conditions there is no substantial adverse interaction of the initiator or the initiating radicals with the RAFT agent under the conditions of the reaction. The initiator ideally should also have the requisite solubility in the reaction medium.

Thermal initiators are chosen to have an appropriate half life at the temperature of polymerisation. These initiators can include one or more of the following compounds:

> 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyanobutane), dimethyl 2,2'-azobis(isobutyrate), 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-amidinopropane)

dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine), 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-ethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, diisopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite. This list is not exhaustive.

Photochemical initiator systems are chosen to have the requisite solubility in the reaction medium and have an appropriate quantum yield for radical production under the conditions of the polymerisation. Examples include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems.

Redox initiator systems are chosen to have the requisite solubility in the reaction medium and have an appropriate rate of radical production under the conditions of the polymerisation; these initiating systems can include, but are not limited to, combinations of the following oxidants and reductants:

oxidants: potassium, peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide.
reductants: iron (II), titanium (III), potassium thiosulfite, potassium bisulfite.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "the Chemistry of Free Radical Polymerisation", Pergamon, London, 1995, pp 53-95.

The method for preparing a polymer comprises polymerising one or more ethylenically unsaturated monomers under the control of a RAFT agent of formula (1). During the method it is believed that the RAFT agent reacts with an initiating or propagating radical to give, through a RAFT-adduct radical, a new radical that initiates further polymerisation and a polyRAFT agent also of formula (1) with similar characteristics to the original RAFT agent, where R is in effect the former initiating or propagating radical. The reaction conditions for the polymerisation should be chosen such that the ratio of the total number of initiator-derived radicals to the number of RAFT agent molecules is maintained at a minimum value consistent with achieving an acceptable rate of polymerisation. Preferably such a ratio is less than 1:1, more preferably less than 1:10, and most preferably in the range of less than 1:10 to 1:500.

Those skilled in the art will appreciate that in the application of conventional RAFT agents the chain transfer constant is an important parameter of the addition-fragmentation steps that occur in the polymerisation process. A consideration of chain transfer constants for RAFT agents is given in WO 98/01478, the detail of which is believed to be applicable to RAFT agents described herein. Preferably, the transfer constant for the addition-fragmentation chain transfer process that occurs in accordance with the method of the invention is >0.1, more preferably >1, most preferably >10.

For avoidance of any doubt, initiating radicals referred to herein are intended to be those free radicals that are derived from an initiator, or other species, which add to ethylenically unsaturated monomer to produce propagating radicals. Also, propagating radicals are intended to be those radical species that have added one or more ethylenically unsaturated monomer units and are capable of adding further such units.

Polymer prepared in accordance with the method of the invention may be carried out using solution, emulsion, bulk or suspension polymerisation techniques in either batch, semi-batch, continuous, or feed modes.

For heterogeneous polymerisation, it is desirable to choose a RAFT agent which has appropriate solubility parameters. For aqueous emulsion polymerisation reactions, the RAFT agent should preferably partition in favour of the organic (monomer) phase and yet have sufficient aqueous solubility that it is able to distribute between the monomer droplet phase and the polymerisation locus.

The choice of polymerisation conditions will generally be important. The reaction temperature may influence the rate parameters discussed above. For example, higher reaction temperatures can increase the rate of fragmentation. Conditions should be chosen such that the number of polymer chains formed from initiator-derived radicals is minimised to an extent consistent with obtaining an acceptable rate of polymerisation. Termination of polymerisation by radical-radical reaction will lead to chains which contain no active group and therefore cannot be reactivated. The rate of radical-radical termination is proportional to the square of the radical concentration. Furthermore, in the synthesis of block star or branched polymers, chains formed from initiator-derived radicals will constitute a linear homopolymer impurity in the final product. These reaction conditions therefore require careful choice of the initiator concentration and, where appropriate the rate of the initiator feed.

It is also desirable to choose other components of the polymerisation medium (for example, the solvents, surfactants, additives, and initiator) such that they have a low transfer constant towards the propagating radical. Chain transfer to these species will lead to the formation of polymer chains which do not contain the active RAFT group.

As a general guide in choosing conditions for the synthesis of narrow polydispersity polymers, the concentration of initiator(s) and other reaction conditions (solvent(s) if any, reaction temperature, reaction pressure, surfactants if any, other additives) should be chosen such that the molecular weight of polymer formed in the absence of the RAFT agent is at least twice that formed in its presence. In polymerisations where termination is solely by disproportionation, this equates to choosing an initiator concentration such that the total moles of initiating radicals formed during the polymerisation is less than 0.5 times that of the total moles of RAFT agent . More preferably conditions should be chosen such that the molecular weight of polymer formed in the absence of the RAFT agent is at least 5-fold that formed in its presence ([initiating radicals]/[RAFT agent] < 0.2).

Thus, the polydispersity can be controlled by varying the number of moles of RAFT agent to the number of moles initiating radicals. Lower polydispersities are obtained by increasing this ratio; higher polydispersities are obtained by decreasing this ratio.

With these provisos, the method of polymerisation according to the invention is performed under the conditions typical of conventional free-radical polymerisation. Polymerisation according to the method is preferably carried out with temperatures during the reaction in the range -20 to 200°C, more preferably in the range 40-160°C.

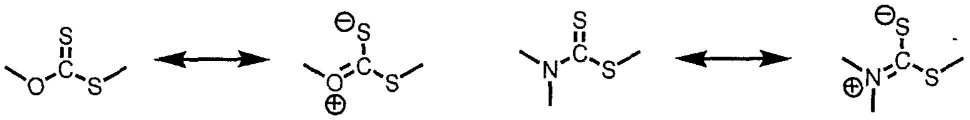
For low polydispersity polymers, the RAFT agent is added before polymerisation is commenced. For example, when carried out in batch mode in solution, the reactor can be charged with RAFT agent and monomer or medium plus monomer. To the mixture is then added the desired amount of initiator and the mixture is heated for a time which is dictated by the desired conversion and molecular weight. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the RAFT agent over the course of the polymerisation process.

In the case of emulsion or suspension polymerisation the medium will often be predominantly water and the conventional stabilisers, dispersants and other additives can be present. For solution polymerisation, the reaction medium can be chosen from a wide range of media to suit the monomer(s) being used.

The method for preparing polymer in accordance with the invention is advantageously less complex than methods for preparing polymer using conventional RAFT agents. In particular, by virtue of the "Z group" in RAFT agents of the invention being in effect predetermined (ie. as –F), the method of the invention is simplified through not having to consider the nature of the "Z group" which must be employed under the conditions of the polymerisation. Accordingly, methods of polymerising ethylenically unsaturated monomers under the control of a RAFT agent to form a polymer product can be rendered less complex by being able to simply provide a RAFT agent of formula (1) where substituent R is appropriately selected for the polymerisation conditions employed.

The ability to only consider the nature of the R group when selecting a RAFT agent can be particularly advantageous where monomers being contemplated for polymerisation have disparate reactivities. For example, conventional RAFT agents that are suited to controlling the polymerisation of monomers with unstable propagating radicals (such as vinyl acetate) are inherently unsuitable for controlling the polymerisation of monomers with stable propagating radicals (such as styrene), and vice versa. This lack of reaction versatility is believed to arise because relative to a conventional RAFT agent suited to controlling polymerisation of monomers with stable propagating radicals, an unstable propagating radical presents as a poor leaving group to the RAFT-adduct radical. By presenting as a poor leaving group, the unstable propagating radical has the effect of unduly retarding or inhibiting polymerisation. To date, this problem has been addressed by employing different RAFT agents with different Z groups.

Specifically, conventional RAFT agents used to control the polymerisation of monomers with unstable propagating radicals address the problem of retardation or inhibition of polymerisation through use of strong lone pair donor alkoxy (e.g. xanthate RAFT agents) or amino (e.g. dithiocarbamate RAFT agents) Z groups. Such Z groups are believed to promote fragmentation of the RAFT-adduct radical by stabilising the "dormant" RAFT fragmentation products via resonance as shown below in Scheme 2.



Scheme 2

However, by stabilising the S=C bond in this manner, the reactivity of S=C bond toward radical addition is significantly reduced and such agents are not sufficiently reactive for controlling the polymerisation of monomers with relatively stable propagating radicals. Accordingly, conventional RAFT agents with a common Z group cannot be used to control the polymerisation of monomers having disparate reactivity, which in turn also renders them inherently unsuitable for the production of well-defined block copolymers from such monomers.

Xanthate and dithiocarbamate RAFT agents used to control vinyl acetate are therefore not suitable for the production of well-defined styrene-vinyl acetate block copolymers.

Moreover, even in vinyl acetate polymerisation, the xanthates and dithiocarbamates do not appear to be as effective in controlling the polydispersity of the resultant polymer when compared with the best dithioesters in styrene or acrylate polymerisations. In the case of vinyl acetate polymerisation, narrow molecular weight distributions have only been reported for low to moderate molecular weights (up to ca.10^4 g mol^{-1})[d], whereas for styrene and many acrylates, control can extend above 10^5 g mol^{-1} [e].

RAFT agents in accordance with the invention are believed to not only be capable of controlling the polymerisation of a diverse array of ethylenically unsaturated monomers, but can achieve this with a common "Z group" (i.e.–F). In particular, a RAFT agent of the invention is believed to be capable of controlling the polymerisation of monomers having disparate reactivities. The RAFT agents may therefore also provide an opportunity to prepare well defined block copolymers from monomers with disparate reactivities such as styrene and vinyl acetate.

The expression "disparate reactivities" in the context of the invention is intended to relate to the relative reactivities of ethylenically unsaturated monomers and as such, the monomers may be conveniently categorised as being either stable or unstable. Stable monomers are considered to be those monomers that provide a stable propagating radical, and unstable monomers are considered to be those that provide an unstable propagating radical. Those skilled in the art will appreciate the types of monomers that may be categorised as stable or unstable.

For convenience, the categorisation of stable and unstable monomers may also be made with regard to the reference reaction shown in Scheme 3.

$$RSC\bullet(CH_3)S\text{-}R \rightarrow RSC(CH_3){=}S + R\bullet$$

Scheme 3

With regard to Scheme 3, R• denotes a propagating radical and stable monomers are considered as those that would give equilibrium (addition) constants below the threshold for rate retardation at 333K, and unstable monomers are considered as those that would give equilibrium (addition) constants above the threshold for rate retardation at 333K.

As used in the context of Scheme 3, the expression "rate retardation" relates to the rate of polymerisation measured with the RAFT agent relative to the rate of conventional free radical polymerisation measured absent the RAFT agent and with all other variables being equal. Accordingly, in this context a rate that is "retarded" is one which is slower than that which can be measured for conventional free radical polymerisation absent the RAFT agent and with all other variables being equal. However, reference to "rate retardation" in the context of Scheme 3 should not be taken to mean that where a polymerisation using a RAFT agent of the invention is retarded, the agent would not be capable of controlling the polymerisation. To the contrary, a polymerisation using a RAFT agent of the invention may exhibit retardation and yet still effectively be controlled by the RAFT agent. A polymerisation that is "unduly retarded" should therefore be considered as one in which polymerisation is so slow that it would be impractical and/or uneconomic to perform.

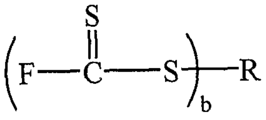
Despite being ineffective in the preparation of copolymers from monomers having disparate reactivities, a conventional RAFT agent may be used to prepare copolymers from monomers having comparable reactivities. However, as discussed above the sequential order in which the block segments of the block copolymer are prepared can be limited. For example, for the synthesis of poly(methyl methacrylate-block-styrene) under batch polymerisation conditions the poly (methyl methacrylate) block is made first in order to produce a block copolymer having a narrow polydispersity.

RAFT agents in accordance with the invention are believed to have an ability to alter the order in which block segments in certain block copolymers are prepared, relative to the order dictated by conventional RAFT agents. For example, it has been reported that for R=benzyl and 1-PhEt in $CH_3SC{\bullet}(CH_3)SR$ and $CH_3SC{\bullet}(Ph)SR$ RAFT-adduct radicals, benyzl presents as a better leaving group than 1-PhEt despite the fact that the latter radical is more bulky and more stable. This counter intuitive trend in the $CH_3SC{\bullet}(CH_3)SR$ and $CH_3SC{\bullet}(Ph)SR$ radicals has been attributed to a homoanomeric effect[f]. Through the unique selection of the "Z group", RAFT agents in accordance with the invention are believed to be capable of influencing the homoanomeric effect and thereby also influence the leaving group ability of the R group. This ability to enhance or diminish the homoanomeric effect, and hence manipulate the leaving group ability without changing the

R group itself, may prove useful in the preparation of block copolymers where the block order of the copolymer could be reversed relative to that dictated by conventional RAFT agents. In this case, it may therefore be possible to select a monomer to form the second block to be polymerised from a group of monomers that could not otherwise be selected if the block copolymer was to be prepared using a conventional RAFT agent (i.e. one disclosed in WO 98/01478).

Accordingly, in a forth aspect the present invention provides a method for preparing a block copolymer, said method comprising the sequential steps of

(a) polymerising a first ethylenically unsaturated monomer under the control of a RAFT agent of formula (1), and



$$\left(F-\overset{\overset{\displaystyle S}{\|}}{C}-S\right)_b\!-R$$

(1)

(b) polymerising a second ethylenically unsaturated monomer under the control of the polyRAFT agent formed in step (a) to provide said block copolymer,

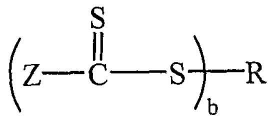
where R is a group such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer, and b is an integer ≥1.

The fourth aspect of the invention relates to the use of all suitable RAFT agents of formula (1), including those compounds that may have been described per se in the prior art.

Without wishing to be limited by theory, it is believed that a number of advantages afforded by the RAFT agents of the invention result from a unique ability of the agents to significantly destabilise the RAFT-adduct radical during polymerisation without stabilising the "dormant" RAFT fragmentation products. By virtue of this ability, RAFT agents in accordance with the invention can promote substantially non-retarded fragmentation of the RAFT-adduct radical and yet can maintain high reactivity of the S=C bond toward radical addition. Through such attributes, it is believed that RAFT agents in accordance with the invention presenting a common "Z group" can be used to control the polymerisation of a diverse array of monomers, including those with disparate reactivities. In other words, despite having a common "Z group", the RAFT agents are believed to be capable of promoting fragmentation of a RAFT-adduct radical formed with an unstable propagating radical, and yet still present a S=C bond having sufficient reactivity to be capable of forming a RAFT-adduct radical with a stable propagating radical.

The mechanism by which the "Z group" in the RAFT agents of the invention imparts such unique attributes is not yet fully understood. However, it is believed that the donor/acceptor properties of the group may play an important role. In particular, in order to obtain the advantages of the invention it is believed that the "Z group" should be a moiety that is a weak lone pair donor and a strong sigma acceptor.

Accordingly, in a fifth aspect the invention provides a RAFT agent of formula (6)

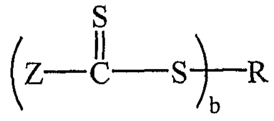


$$\left(Z - \overset{\overset{\displaystyle S}{\|}}{C} - S \right)_b - R \qquad (6)$$

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of ethylenically unsaturated monomer, and b is an integer ≥ 1, with the proviso that when Z is fluorine, R is not $-CH_3$, $-CF_3$, $-CH_2CH_3$, $-nC_3H_7$, $-CF_2NCS$ or $-CH_2CH_2Cl$.

In a sixth aspect, the invention provides a method for preparing a polymer, said method comprising polymerising one or more ethylenically unsaturated monomers under the control of a RAFT agent of formula (6)



$$\left(Z - \overset{\overset{\displaystyle S}{\|}}{C} - S \right)_b - R \qquad (6)$$

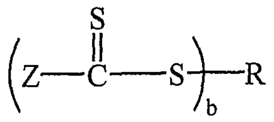
where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of the one or more ethylenically unsaturated monomers, and b is an integer ≥ 1.

In a seventh aspect, the invention provides a method of polymerising ethylenically unsaturated monomers to form a polymer, said method comprising:

(a) selecting an ethylenically unsaturated monomer to be polymerised;

(b) providing a RAFT agent of formula (6); and



$$\left(Z-\overset{\overset{S}{\|}}{C}-S\right)_{b}-R \qquad (6)$$

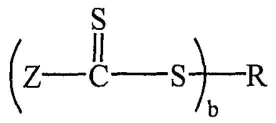
(c) polymerising the selected ethylenically unsaturated monomer under the control of said RAFT agent,

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

wherein the R group is selected such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer and b is an integer ≥1.

In an eighth aspect the invention provides a method for preparing a block copolymer, said method comprising the sequential steps of

(a) polymerising a first ethylenically unsaturated monomer under the control of a RAFT agent of formula (6), and



$$\left(Z-\overset{\overset{S}{\|}}{C}-S\right)_{b}-R \qquad (6)$$

(b) polymerising a second ethylenically unsaturated monomer under the control of the polyRAFT agent formed in step (a) to provide said block copolymer,

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer, and b is an integer ≥1.

The fifth aspect of the invention is not intended to encompass known compounds falling within general formula (6) that may have utility as a RAFT agent, even though this utility has not been previously described or recognised. The sixth to eighth aspects of the invention relate to the use of all suitable RAFT agents of formula (6), including those compounds that may have been described per se in the prior art.

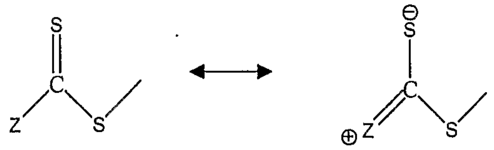
Suitable R groups for RAFT agents of formula (6) are the same as those previously defined for RAFT agents of formula (1).

Those skilled in the art will have an appreciation for what is meant by a Z group being a "weak lone pair donor and a strong sigma acceptor". Nevertheless, to help further qualify what is required by such a Z group, it can be useful to consider certain aspects of the proposed RAFT polymerisation mechanism in more detail.

As reported in a recent high-level *ab initio* study of radical stability in RAFT polymerisation[f], known RAFT-adduct radicals are believed to be relatively stable species due to the necessary presence of the two thiyl substituents (ie. SR and SR' in RSC•(Z)SR'). These thiyl substituents are considered to be strong radical stabilising substituents due to lone pair donation from the sulphur atoms adjacent the carbon radical centre[g h]. Despite many Z groups in conventional RAFT agents also having a lone pair donor capacity, stabilisation of the RAFT-adduct radical is believed to be primarily influenced by the thiyl substituents, with the contribution from any lone pair donating Z group being minor if not negligible. In contrast to the stabilising effect provided to the RAFT-adduct radical through lone pair donation, sigma withdrawal effects are believed to have a destabilising effect on the RAFT-adduct radical. Where the sigma withdrawal effect is greater than the net lone pair donation effect, it is believed that the RAFT-adduct radical can be destabilised to promote fragmentation without stabilising the "dormant" RAFT fragmentation products to the extent where radical addition by relatively stable propagating radicals is reduced or inhibited.

Accordingly, the functional result of the Z group being a "weak lone pair donor and a strong sigma acceptor" is that the destabilising effect of sigma withdrawal by the Z group on the RAFT-adduct radical is greater than the net stabilising effect on the RAFT-adduct radical imparted through lone pair donation from the Z group and the thiyl substituents immediately adjacent the carbon centred radical.

The "weak" lone pair donor property of the Z group can be further qualified with reference to the "strong" sigma acceptor property of the Z group. In particular, the lone pair donor capacity of the Z group should be sufficiently weak so as to not promote stabilisation of the "dormant" RAFT fragmentation products via resonance as shown below in Scheme 4.



Scheme 4

RAFT agents in accordance with this aspect of the invention will therefore have a Z group which provides a strong sigma withdrawal effect that is capable of dominating over any lone pair donor ability of the Z group that may result in stabilisation of the "dormant" RAFT fragmentation products via resonance as shown above in Scheme 4. Such requirements of the Z group can be seen in contrast with xanthate and diothiocarbamate RAFT agents which comprise Z groups that are strong lone pair donors and weak sigma acceptors and favour stabilisation of the "dormant" RAFT fragmentation products via resonance (see Scheme 2).

Suitable Z groups which are believed to destabilise the RAFT-adduct radical without stabilising the "dormant" RAFT fragment products as indicated above through being a weak lone pair donor and strong sigma acceptor include, but are not limited to, -F.

As a further means of evaluating the functional role of Z groups in RAFT agents of the invention, it may be useful to quantitatively consider the stability of certain species present during polymerisation. Such data has been calculated using standard ab initio molecular orbital theory[i] and density functional theory[j] calculations, carried out using GAUSSIAN 98[k], GAUSSIAN 03[l] and MOLPRO 2000.6[m].

The RAFT-adduct radical stability was calculated relative to the reference reaction shown in Scheme 5.

$$CH_3SCH(CH_3)S\text{-}R + CH_3SC{\bullet}(Z)S\text{-}R \rightarrow CH_3SC{\bullet}(CH_3)S\text{-}R + CH_3SCH(Z)S\text{-}R$$

Scheme 5

With reference to the reaction in Scheme 5, a radical that is more stable than $CH_3SC{\bullet}(CH_3)S\text{-}R$ is considered to give rise to a positive value for the enthalpy of the reaction, and a radical that is less stable $CH_3SC{\bullet}(CH_3)S\text{-}R$ is considered to give rise to a negative value for the enthalpy of the reaction. Conventional RAFT agents have been shown to give enthalpy values that are close to or much greater than zero. In particular, enthalpy values ranging from about –5 kJ mol^{-1} up to about 60 kJ mol^{-1} have been calculated[f].

Accordingly, in terms of RAFT-adduct stability it is preferred that Z groups of RAFT agents in accordance with the invention give rise to enthalpy values that are less than -5 kJ mol^{-1}, more preferably less than -10 kJ mol^{-1}. Calculations based on RAFT agents where Z=F give rise to enthalpy values ranging from about -15 kJ mol^{-1} to about -20 kJ mol^{-1}, depending on the nature of R. RAFT-adduct radicals where Z=F are therefore considered to be destabilised relative to all known conventional RAFT-adduct radicals.

With regard to "dormant" RAFT fragmentation products, similar stability calculations may be made relative to the reference reaction shown below in Scheme 6 below.

$$CH_3SC(Z) = S + CH_3\text{-}CH_3 \rightarrow CH_3SC(CH_3) = S + Z - CH_3$$

Scheme 6

Relative to the reference reaction shown in Scheme 6, Z groups that give rise to a positive value for the enthalpy of the reaction are considered to stabilise the S=C bond of the "dormant" RAFT agent, and Z groups that give rise to a negative value for the enthalpy of the reaction are considered to destabilise the S=C bond of the "dormant" RAFT agents.

Relative to the reference reaction shown in Scheme 6, conventional xanthate and dithiocarbamate RAFT agents can be shown to give rise to a high positive enthalpy value (ca.> 40 kJ mol^{-1}). The high positive enthalpy value is believed to result from the strong lone pair donor properties of –OR or $-NR_2$ groups in these compounds which stabilise the S=C bond via resonance.

Relative to the reference reaction shown in Scheme 6, conventional dithioester RAFT agents used to control the polymerisation of stable monomers (eg. where $Z = CH_3$, CH_2Ph, and Ph) can be shown to give rise to enthalpy values that are close to zero (eg. about 0-6 kJ mol^{-1} for $Z = CH_3$, CH_2Ph, and Ph). Such enthalpy values are indicative of the C=S bond not being stabilised via resonance as in conventional xanthate and dithiocarbamate RAFT agents.

Accordingly, in terms of "dormant" RAFT fragmentation product stability it is preferred that Z groups of RAFT agents in accordance with the invention give rise to enthalpy values that are less than 40 kJ mol^{-1}, more preferably less than 15 kJ mol^{-1}, most preferably about 0 to 6 kJ mol^{-1}

Relative to the reference reaction shown in Scheme 6, calculations based on RAFT agents where Z=F give RAFT agents in accordance with the invention where Z = F show enthalpy values that are similar to the aforementioned conventional dithioester RAFT agents (ie. about 6 kJ mol^{-1}). Accordingly, such RAFT agents are considered to not only impart destabilisation to the RAFT-adduct radical, but this can be achieved whilst maintaining a similar high reactivity of the S=C bond relative to the aforementioned conventional dithioester RAFT agents.

Having regard to the discussion herein on the characteristics of a Z group that may afford the advantages of the invention, it is believed that a person skilled in the art could conduct relevant calculations and/or laboratory experimentation to realise other suitable Z groups.

Polymer produced in accordance with the method of the invention can be isolated by stripping off any reaction medium and/or unreacted monomer(s) or through precipitation with a non-solvent. Alternatively, the polymer solution/emulsion can be used in its post reaction form if appropriate to the intended application.

Those skilled in the art will appreciate that polymers formed via a RAFT agent can advantageously be subjected to further polymerisation through reinitiation of a "second" polymerisation reaction. Alternatively, the active RAFT agent head group may be removed through hydrolysis with, for example, an alkaline base.

The invention is believed to be generally applicable in the field of free radical polymerisation and may be used to produce polymers and compositions suitable for use in a diverse array of applications. Such applications include, but are not limited to, coatings (eg. paints and lacquers) used in both industrial and domestic applications, adhesives, fillers, primers, sealants, engineering plastics, compatabilisers, dispersing agents, and rheology control agents.

The invention will now be described with reference to the following non-limiting examples which are included for the purpose of illustrating the invention only, and not to be construed as limiting the generality hereinbefore described.

Examples

Preparation benzyl fluoro dithioformate (BFDF)

Benzyl chloro dithioformate (BCDF): 15.00 g (130 mmol) thiophosgene (Aldrich, 97%) and 16.20 g (130 mmol) benzyl mercaptan (Lancaster, 99%) were dissolved in 30 ml carbon disulfide (Ajax Unilab). The solution was stirred in a flask with a gas outlet for 48 h at room temperature. The HCl gas produced was passed through a bubble counter and subsequently neutralized in alkaline potassium permanganate solution. After the reaction had finished, the solvent was evaporated and the product was distilled in vacuum to yield 13.31 g (50 %) benzyl chloro dithioformate (BCDF, yellow liquid), boiling point 104°C (0.4 mbar). 300 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 4.44 (s 2H CH_2), 7.25-7.40 (m 5H C_6H_5). 75 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 45.45 (1C CH_2), 128.15 (1C *para* C_6H_5), 128.82 / 129.20 (4C ortho/meta C_6H_5), 133.08 (1C -$\underline{C}_6H_5$), 196.35 (1C C=S). IR (ATR) λ^{-1}

[cm^{-1}] = 3085 (vw, CH valence), 3061 (w, CH valence), 3028 (m, CH valence), 2914 (vw, CH_2 valence), 1600 (vw, ar CH valence), 1494 (m, CH rocking), 1452 (m, CH rocking), 1399 (vw (br), CH_2 bending), 1236 (w (br), CH_2 wagging), 1195 (w, CH bending), 1095 (vs, C=S valence), 1070 (m, ar. def), 1028 (w, ar. def), 915 (vw, CH twist), 853 (vw, CH_2 rocking), 824 (w, ar. def.), 770 (vs, as. Cl-C-S valence), 693 (s, CH wagging). UV (CH_2Cl_2): λ_{max} [nm] (log ε) = 307 (4.13).

Benzyl fluoro dithioformate (BFDF): A mixture of 5.81 g (100 mmol) potassium fluoride (Ajax Unilab, >97%, dried in vacuum before use), 0.26 g (10 mmol) 18-crown-6 (Aldrich, 99%), and 30 ml anhydrous acetonitrile (Ajax Univar, >99,5%) was stirred under nitrogen and exclusion of light for 1 h. Subsequently, 9.31 g (46 mmol) benzyl chloro dithioformate (BCDF) were added within 10 min. After the solution was stirred at 40°C for 6 h, the solid content was filtered off and the solvent was evaporated in vacuum. The crude product was distilled at 0.4 mbar and purified via chromatography over silica gel with toluene to yield 4.3 g (50 %) of the pure benzyl fluoro dithioformate (BFDF, pale yellow liquid). 300 MHz ^1H NMR ($CDCl_3$): δ [ppm] = 4.41 (d 2H $^4J_{HF}$=1.1 Hz CH_2), 7.30-7.45 (m 5H C_6H_5). 75 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 43.14 (d 1C $^3J_{CF}$=5.1 Hz CH_2), 128.26 (1C *para* C_6H_5), 128.85 / 129.12 (4C ortho/meta C_6H_5), 133.32 (1C $-\underline{C}_6H_5$), 205.75 (d 1C $^1J_{CF}$=361.9 Hz C=S). 282 MHz ^{19}F NMR ($CDCl_3$): δ [ppm] = 71.56 (s). IR (ATR) λ^{-1} [cm^{-1}] = 3087 (vw, CH valence), 3063 (w, CH valence), 3030 (m, CH valence), 2921 (vw, CH_2 valence), 1602 (vw, ar. C-C valence), 1495 (m, CH rocking), 1453 (m, CH rocking), 1419 (vw (br), CH_2 bending), 1249 (w (br), CH_2 wagging), 1202 (s, CH bending), 1160 (vs, C=S valence), 1070 (m, ar. def), 1013 (m, ar. def), 994 (vs, as. F-C-S valence), 916 (vw, CH twist), 857 (vw, CH_2 rocking), 814 (vw, ar. def.), 764 (m, CH wagging), 693 (s, CH wagging). UV (CH_2Cl_2): λ_{max} [nm] (log ε) = 288 (4.12).

Polymerisation of styrene under the control of BFDF

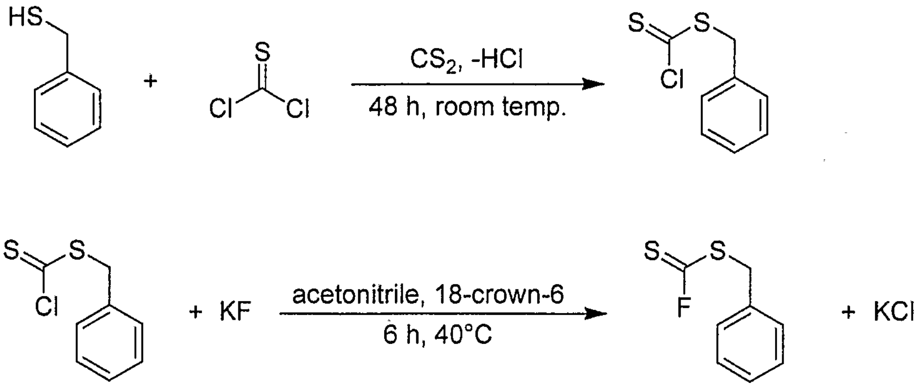
Styrene (Aldrich, 99%) was purified by drying for one day over molecular sieve (4 Å) and subsequent distillation in vacuum. The thermally decaying initiator azobisisobutyronitrile (AIBN, Aldrich, 99%) was purified twice by crystallization from ethanol. A solution of 10.00 g styrene, 57.5 mg BFDF and 12.4 mg AIBN was prepared and mixed thoroughly.

The solution was subsequently subjected to four freeze-pump-thaw cycles to remove any residual oxygen. A small amount of solution was then transferred into a 2 mm optical path length Infrasil cell (Starna Optical) and sealed with a rubber septum. Monomer conversions were determined via on-line Fourier Transform – Near Infra Red (FT-NIR) spectroscopy by following the decrease of the intensity of the first vinylic stretching overtone of the monomer (λ^{-1}(Styrene) = 6134 cm^{-1}). The FT-NIR measurements were performed using a Bruker IFS66\S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF_2 beam splitter and a liquid nitrogen cooled InSb detector. Each spectrum in the spectral region of 8000 to 4000 cm^{-1} was calculated from the co-added interferograms of 50 scans with a resolution of 2 cm^{-1}. For conversion determination, a linear baseline was selected between 6200 and 6100 cm^{-1}. The integrated absorbance between these two points was subsequently used to calculate the monomer to polymer conversion via Beer-Lambert's law. In regular intervals, a small sample was withdrawn from the reaction mixture with an airtight syringe that had been flushed 3 times with nitrogen gas. The sample was transferred into a flask containing THF with hydroquinone as inhibitor and immediately subjected to SEC analysis.

Molecular Weight Analysis

Molecular weight distributions were measured via size exclusion chromatography (SEC) on a Shimadzu modular system, comprising an auto injector, a Polymer Laboratories 5.0 μm bead-size guard column (50×7.5 mm), followed by three PL columns (10^5, 10^4 and 10^3 Å) and a differential refractive index detector. The eluent was tetrahydrofuran (THF) at 40 °C with a flow rate of 1 mL min^{-1}. The system was initially calibrated using narrow polystyrene standards ranging from 540 to $2\cdot10^6$ g mol^{-1}. For methyl acrylate, the resulting molecular weight distributions have been recalibrated using the Mark-Houwink parameters for polymethyl acrylate ($K = 19.5\cdot10^{-5}$ dL g^{-1}, $\alpha = 0.66$). The Mark-Houwink parameters for polystyrene read ($K = 14.1\cdot10^{-5}$ dL g^{-1} and $\alpha = 0.70$).

BFDF was prepared as described above and in accordance with the reaction outlined in Scheme 7.



Scheme 7

The overall yield of both synthetic steps described above was 25 %. According to the ^{1}H NMR data, the BFDF was substantially free of any residual BCDF and the purity was higher than 95 %. The assignment of the IR absorption bands was done by means of density functional theory calculated vibrations at the B3-LYP 6-31G(d) level of theory.

To test the ability of the novel RAFT agent to induce living free radical polymerization, styrene was polymerised using $2.81\cdot10^{-2}$ mol L^{-1} BFDF with AIBN ($[\mathrm{AIBN}]_0 = 6.86\cdot10^{-3}$ mol L^{-1}) as initiator. At 5, 10, 20, 30, and 40 % conversion, samples were taken and the molecular weight distribution was determined.

Figure 1 depicts the evolution of the full molecular weight distributions with monomer to polymer conversion in a BFDF mediated RAFT polymerization of styrene at 80 °C. The distributions are mono-modal and shift to higher molecular weights with increasing conversion. For a more detailed analysis, a molecular weight vs conversion plot is given in Figure 2, with the corresponding M_n values being collated in Table 1 alongside the associated polydispersities, PDI.

Table 1

Conversion %	M_n / g mol^{-1}	M_n^{theo} / g mol^{-1}	*PDI*
5.17	10 000	1 673	1.36
10.75	10 400	3 478	1.36
20.21	12 000	6 539	1.34
30.22	14 000	9 778	1.29
40.51	15 600	13 108	1.27

From Figures 1 and 2 it can be seen that the novel class of RAFT agent induces living/controlled behaviour. However, Figure 2 also shows that an initial increase to high molecular weight material occurs. Such behaviour has been observed before and has been termed hybrid behaviour.[n] Hybrid behaviour is frequently observed when the addition rate coefficient to the initial RAFT agent is too low in comparison with the propagation rate coefficient or the propagating radical, PSTY, leaves the adduct radical in preference to the R-group, i.e. Bz. Assuming that the rate of the reverse reaction between the leaving group R·and the polymeric RAFT agent is negligible, the chain transfer constant, $C_{tr} = k_{tr} / k_p$, can be estimated via the degree of polymerization of the polymer formed instantaneously, DP_n^{inst}, using equation (1).

$$C_{tr} = \frac{[M_0]}{(DP_n^{inst} - 1) \cdot [RAFT_0]} \tag{1}$$

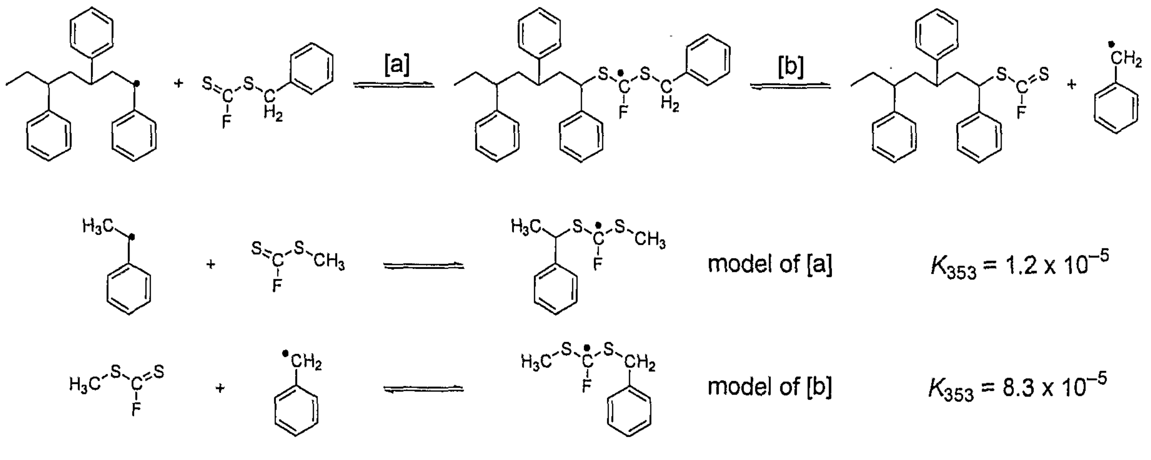
Extrapolation of the determined molecular weights to zero conversion yields a DP_n^{inst} value of 92. Thus, via equation (1), a value of 3.4 for C_{tr} is returned, indicating a relatively slow transfer.

For a more detailed analysis, whether the slow transfer is caused by a slow monomer addition or a poor leaving group, further molecular orbital studies were undertaken. The equilibrium constant at 80°C was calculated for the model addition-fragmentation reaction (1), for R = 1-PhEt and R = Bz.[o]

$$\bullet R + S{=}C(F)SCH_3 \rightarrow R{-}SC\bullet(F)S{-}CH_3 \qquad (1)$$

These two systems were selected to model the two steps, (a) and (b), of the chain transfer reaction that occurs during the initial equilibration period in the RAFT process as shown below in Scheme 8. Although only the thermodynamics have been considered in the present case, it has been reported elsewhere that these radical additions to C=S bonds are virtually barrier less, and the trends in the kinetics follow those in the thermodynamics.[P] The calculated equilibrium constants (L mol^{-1}) for each of the reactions are displayed in Scheme 8, from which it is seen that, on a thermodynamic basis, the 1-PhEt group has a 7-fold preference for fragmentation over the Bz group, consistent with the observed hybrid behaviour.

These results are consistent with comments above on the Z group being able to diminish the homoanomeric effect and thereby reverse ordering of the leaving group ability for 1-PhEt and Bz groups.



Scheme 8

Methyl acrylate was also polymerised in a similar manner to that of styrene. The resulting polymer was characterised as described above. Results of the polymerisation were similar to that outlined above for styrene (see below).

Polymerisation of methyl acrylate under the control of BFDF

Methyl acrylate (99%, Aldrich, M = 86.06 g mol^{-1}) was freed from the inhibitor by percolating over a column of activated basic alumina. The thermally decaying initiator azobisisobutyronitrile (AIBN, Aldrich, 99%) was purified twice by crystallization from ethanol. A solution of 5.00 g methyl acrylate, 14.6 mg BFDF (purity approx. 90 %) and 3.1 mg AIBN was prepared and mixed thoroughly. The solution was subsequently subjected to four freeze-pump-thaw cycles to remove any residual oxygen. A small amount of solution was then transferred into a 2 mm optical path length Infrasil cell (Starna Optical) and sealed with a rubber septum. Monomer conversions were determined via on-line Fourier Transform – Near Infra Red (FT-NIR) spectroscopy by following the decrease of the intensity of the first vinylic stretching overtone of the monomer (λ^{-1}(methyl acrylate) = 6169 cm^{-1}). The FT-NIR measurements were performed using a Bruker IFS66\S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF_2 beam splitter and a liquid nitrogen cooled InSb detector. Each spectrum in the spectral region of 8000 to 4000 cm^{-1} was calculated from the co-added interferograms of 12 scans with a resolution of 2 cm^{-1}. For conversion determination, a linear baseline was selected between 6240 and 6100 cm^{-1}. The integrated absorbance between these two points was subsequently used to calculate the monomer to polymer conversion via Beer-Lambert's law. In regular intervals, a small sample was withdrawn from the reaction mixture with an airtight syringe that had been flushed 3 times with nitrogen gas. The sample was transferred into a flask containing THF with hydroquinone as inhibitor and immediately subjected to SEC analysis.

Figure 3 depicts the evolution of the full molecular weight distributions in BFDF mediated RAFT polymerisation of methyl acrylate at 60°C. The distributions are mono-modal and shift to higher molecular weights with increasing conversion. For a more detailed analysis, a molecular weight vs conversion plot is given in Figure 4, with the corresponding M_n values being collated in Table 2 alongside the associated polydispersities, PDI.

Table 2

Conversion %	M_n / g mol^{-1}	M_n^{theo} / g mol^{-1}	*PDI*
3.20	6 800	2 200	1.16
10.96	18 600	7 670	1.12
15.47	23 200	10 800	1.16
27.50	39 900	19 200	1.23

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[o] Equilibrium constants (353 K, L mol^{-1}) were calculated at the G3(MP2)-RAD//B3-LYP/6-31G(d) level of theory using the standard textbook formulae, based on the

statistical thermodynamics of an ideal gas under the rigid-rotor / harmonic oscillator approximation.

[p] Coote, M. L. *J. Phys. Chem. A* 2005, *109(6)*, 1230–1239

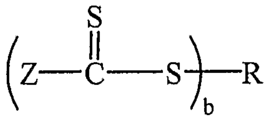
Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in any country.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A RAFT agent of formula (6)



$$\left(Z-\overset{\overset{\displaystyle S}{\|}}{C}-S\right)_b-R \qquad (6)$$

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of ethylenically unsaturated monomer, and b is an integer ≥ 1, with the proviso that when Z is fluorine, R is not $-CH_3$, $-CF_3$, $-CH_2CH_3$, $-nC_3H_7$, $-CF_2NCS$ or $-CH_2CH_2Cl$.

2. The RAFT agent according to claim 1, wherein Z is fluorine.

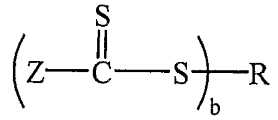
3. The RAFT agent according to claim 1, wherein R is selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylthio, optionally substituted heterocyclyl, optionally substituted acyl, optionally substituted amino, a linear or branched polymer chain formed by any polymerisation mechanism, and a solid support.

4. The RAFT agent according to claim 1, wherein R is selected from $-CH_2CH_3$, $-iC_3H_7$, $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-C(CH_3)_2C_6H_5$, $-CH_2COOR^5$, $-CH(CH_3)COOR^5$, $-C(CH_3)_2COOR^5$, $-CH_2CONR^5R^6$, $-CH(CH_3)CONR^5R^6$, $-C(CH_3)_2CONR^5R^6$, $-C(CH_3)_3$, $-CF_3$, $-CF_2R^5$, $-CFR^5R^6$, $-CH_2CHCH_2$, $-CH(CH_3)CHCH_2$, $-C(CH_3)_2CHCH_2$, $-CH_2Cl$, $-CH(CH_3)Cl$, $-C(CH_3)_2Cl$, $-CH_2OR^5$, $-CH(CH_3)OR^5$, $-C(CH_3)_2OR^5$, $-CH_2SO_3R^5$, $-CH(CH_3)SO_3R^5$, $-C(CH_3)_2SO_3R^5$, $-CH_2COR^5$, $-CH(CH_3)COR^5$, $-C(CH_3)_2COR^5$, $-CH_2NR^5R^6$, $-CH(CH_3)NR^5R^6$, $-C(CH_3)_2NR^5R^6$, $-CH_2CN$, $-CH(CH_3)CN$, $-C(CH_3)_2CN$, $-CH_2CH_2OR^5$, $-CH(CH_3)CH_2OR^5$, $-C(CH_3)_2CH_2OR^5$, $-CH_2CH_2Cl$, $-CH(CH_3)CH_2Cl$, $-C(CH_3)_2CH_2Cl$, $-CH(C_6H_5)_2$, $-C(C_6H_5)_3$, $-C(CH_3)(C_6H_5)_2$, $-CCl_3$, $-CCl_2R^5$,

$-CClR^5R^6$, and $-ONR^5R^6$, where R^5 and R^6 are independently selected from H, alkyl and aryl.

5. The RAFT agent according to claim 1, wherein R is selected from $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-CH(CH_3)COOR^5$, $-CH_2CN$, $-CH(CH_3)CN$, and $-C(CH_3)_2CN$, where R^5 is selected from H, alkyl and aryl.

6. A method for preparing a polymer, said method comprising polymerising one or more ethylenically unsaturated monomers under the control of a RAFT agent of formula (6)



$$\left(Z-\overset{\overset{\displaystyle S}{\|}}{C}-S\right)_b-R \qquad (6)$$

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of the one or more ethylenically unsaturated monomers, and b is an integer ≥1.

7. The method according to claim 6, wherein Z is fluorine.

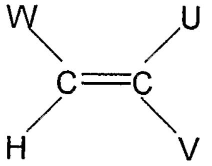
8. The method according to claim 6, wherein R is selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylthio, optionally substituted heterocyclyl, optionally substituted acyl, optionally substituted amino, a linear or branched polymer chain formed by any polymerisation mechanism, and a solid support.

9. The method according to claim 6, wherein R is selected from $-CH_2CH_3$, $-iC_3H_7$, $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-C(CH_3)_2C_6H_5$, $-CH_2COOR^5$, $-CH(CH_3)COOR^5$, $-C(CH_3)_2COOR^5$, $-CH_2CONR^5R^6$, $-CH(CH_3)CONR^5R^6$, $-C(CH_3)_2CONR^5R^6$, $-C(CH_3)_3$, $-CF_3$, $-CF_2R^5$, $-CFR^5R^6$, $-CH_2CHCH_2$, $-CH(CH_3)CHCH_2$, $-C(CH_3)_2CHCH_2$, $-CH_2Cl$, $-CH(CH_3)Cl$, $-C(CH_3)_2Cl$, $-CH_2OR^5$, $-CH(CH_3)OR^5$, $-C(CH_3)_2OR^5$, $-CH_2SO_3R^5$, $-CH(CH_3)SO_3R^5$, $-C(CH_3)_2SO_3R^5$, $-CH_2COR^5$, $-CH(CH_3)COR^5$, $-C(CH_3)_2COR^5$, $-CH_2NR^5R^6$, $-CH(CH_3)NR^5R^6$, $-C(CH_3)_2NR^5R^6$,

$-CH_2CN$, $-CH(CH_3)CN$, $-C(CH_3)_2CN$, $-CH_2CH_2OR^5$, $-CH(CH_3)CH_2OR^5$, $-C(CH_3)_2CH_2OR^5$, $-CH_2CH_2Cl$, $-CH(CH_3)CH_2Cl$, $-C(CH_3)_2CH_2Cl$, $-CH(C_6H_5)_2$, $-C(C_6H_5)_3$, $-C(CH_3)(C_6H_5)_2$, $-CCl_3$, $-CCl_2R^5$, $-CClR^5R^6$, and $-ONR^5R^6$, where R^5 and R^6 are independently selected from H, alkyl and aryl.

10. The method according to claim 6, wherein R is selected from $-CH_2C_6H_5$, $-CH(CH_3)C_6H_5$, $-CH(CH_3)COOR^5$, $-CH_2CN$, $-CH(CH_3)CN$, and $-C(CH_3)_2CN$, where R^5 is selected from H, alkyl and aryl.

11. The method according to claim 6, wherein the one or more ethylenically unsaturated monomers are selected from those with the general formula (5)



(5)

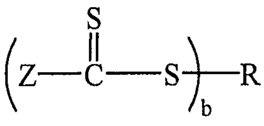
where U and W are independently selected from the group consisting of $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, hydrogen, halogen and optionally substituted C_1-C_4 alkyl wherein the substituents are independently selected from the group consisting of hydroxy, $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CN$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, $-OR^6$, $-SR^6$, $-O_2CR^6$, $-SCOR^6$, and $-OCSR^6$; and

V is selected from the group consisting of hydrogen, R^6, $-CO_2H$, $-CO_2R^6$, $-COR^6$, $-CSR^6$, $-CSOR^6$, $-COSR^6$, $-CONH_2$, $-CONHR^6$, $-CONR^6_2$, $-OR^6$, $-SR^6$, $-O_2CR^6$, $-SCOR^6$, and $-OCSR^6$;

where R^6 is selected from the group consisting of optionally substituted C_1-C_{18} alkyl, optionally substituted C_2-C_{18} alkenyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted aralkyl, optionally substituted heteroarylalkyl, optionally substituted alkaryl, optionally substituted alkylheteroaryl and polymer chains, wherein the substituents are independently selected from the group consisting of alkyleneoxidyl (epoxy), hydroxy, alkoxy, acyl, acyloxy, formyl, alkylcarbonyl, carboxy, sulfonic acid, alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, amino, including salts and derivatives thereof.

12. A method for preparing a block copolymer, said method comprising the sequential steps of

(a) polymerising a first ethylenically unsaturated monomer under the control of a RAFT agent of formula (6), and



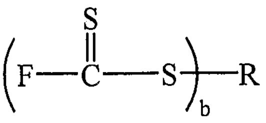
$$\left(Z-\overset{\overset{S}{\|}}{C}-S \right)_b\!-R \qquad (6)$$

(b) polymerising a second ethylenically unsaturated monomer under the control of the polyRAFT agent formed in step (a) to provide said block copolymer,

where Z is any group that is a weak lone pair donor and a strong sigma acceptor,

R is a group such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer, and b is an integer ≥1.

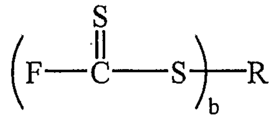
13. A RAFT agent of formula (1)



$$\left(F-\overset{\overset{S}{\|}}{C}-S \right)_b\!-R \qquad (1)$$

where R is a group such that the agent can function as a RAFT agent in the polymerisation of ethylenically unsaturated monomer, and b is an integer ≥1, with the proviso that R is not $-CH_3$, $-CF_3$, $-CH_2CH_3$, $-nC_3H_7$, $-CF_2NCS$ or $-CH_2CH_2Cl$.

14. A method for preparing a polymer, said method comprising polymerising one or more ethylenically unsaturated monomers under the control of a RAFT agent of formula (1)

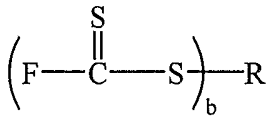


$$\left(F-\overset{\overset{\displaystyle S}{\|}}{C}-S\right)_{b}\!\!-R \qquad (1)$$

where R is a group such that the agent can function as a RAFT agent in the polymerisation of the one or more ethylenically unsaturated monomers, and b is an integer ≥1.

15. A method for preparing a block copolymer, said method comprising the sequential steps of

(a) polymerising a first ethylenically unsaturated monomer under the control of a RAFT agent of formula (1), and



$$\left(F-\overset{\overset{\displaystyle S}{\|}}{C}-S\right)_{b}\!\!-R \qquad (1)$$

(b) polymerising a second ethylenically unsaturated monomer under the control of the polyRAFT agent formed in step (a) to provide said block copolymer,

where R is a group such that the agent can function as a RAFT agent in the polymerisation of the ethylenically unsaturated monomer, and b is an integer ≥1.

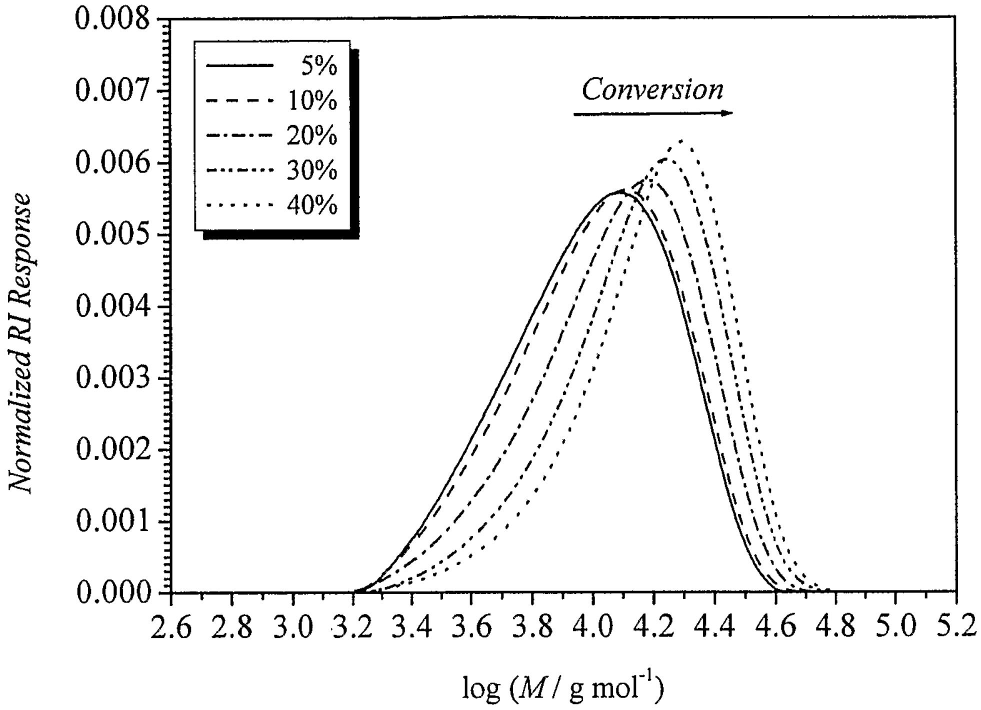

Normalized RI Response
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
5%
10%
20%
30%
40%
Conversion
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
log (M / g mol-1)

Figure 1

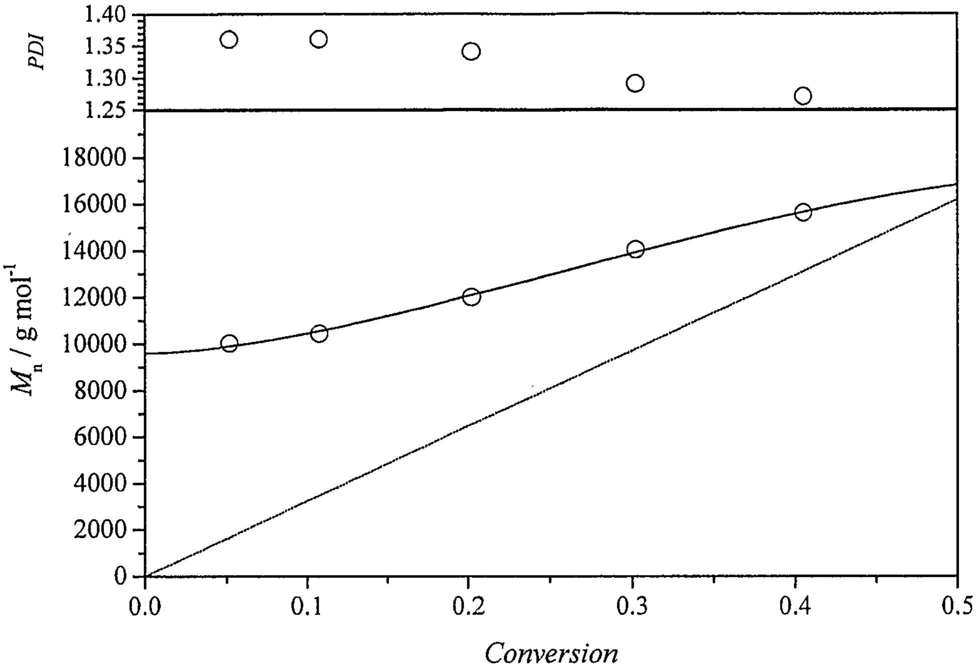

PDI
1.40
1.35
1.30
1.25
M_n / g mol^{-1}
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0.0
0.1
0.2
0.3
0.4
0.5
Conversion

Figure 2

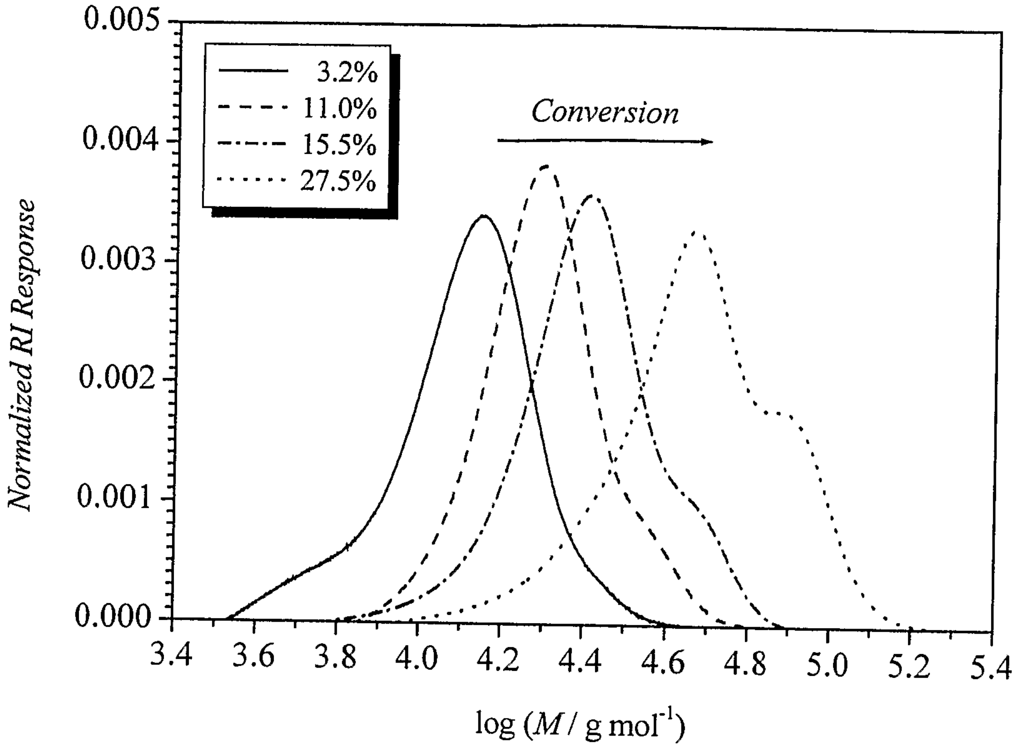

0.005
0.004
0.003
0.002
0.001
0.000
Normalized RI Response
3.2%
11.0%
15.5%
27.5%
Conversion
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
log (M / g mol^{-1})

Figure 3

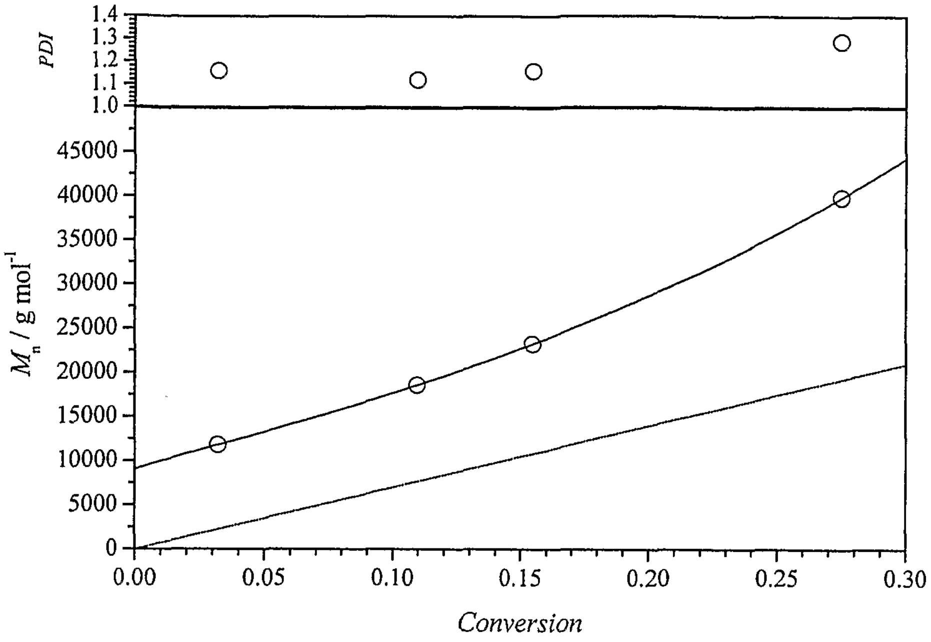

PDI
1.4
1.3
1.2
1.1
1.0
M_n / g mol^{-1}
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Conversion

Figure 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2005/001729

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C07C 327/36 (2006.01) *C08F 2/38* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN Files Registry, CA: substructure search with Z as fluorine, see box II. Keyword search, Espace: raft, polymer*, dithio*.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstract 141:277134 & CHAN B. et al, Australian Journal of Chemistry, 2004, vol. 57, no. 7, pages 659-663, "Understanding metal-free catalytic hydrogenation: A systematic theoretical study of the hydrogenation of ethene." Registry number 216440-79-8.	1-5, 13
X	Chemical Abstract 102:23827 & OBVIVAL'NEVA A. A. et al, Khimicheskaya Fizika, 1982, vol. 2, pages 254-259, "Formation of electron-excited molecules in the reactions of fluorine atoms with carbon disulfide." Registry number 94035-71-9.	1-5, 13
A	US 2003/0191262 A1 (McCORMICK C. L. et al) 9 October 2003. See entire document.	

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 8 December 2005	Date of mailing of the international search report 19 DEC 2005
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **Frances Roden** Telephone No : (02) 6283 2239

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2005/001729

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2003/0199653 A1 (McCORMICK III C. L. et al) 23 October 2003. See entire document.	
A	WO 1998/001478 A1 (E. I. DU PONT DE NEMOURS AND COMPANY) 15 January 1998. See entire document. Cited in the application.	
A	STENZEL M. H. et al, Macromolecular Chemistry and Physics, 2003, vol. 204, pages 1160-1168, "Xanthate mediated living polymerization of vinyl acetate: A systematic variation in MADIX/RAFT agent structure." See entire document. Cited in the application.	
A	RIZZARDO E. et al, American Chemical Society Symp, Ser. 2000, vol. 768, pages 278-296, "Synthesis of defined polymers by reversible addition-fragmentation chain transfer: The RAFT process." See entire document. Cited in the application.	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2005/001729

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: **1-12 (in part)**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
A full substructure search of these claims was not possible as no indication or support is given in the specification as to what Z may be, other than fluorine. The search was therefore limited to compounds where Z is F.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2005/001729

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2003191262	AU	2003230548	US	6855840	US	2003195310
		WO	2003/066685				
US	2003199653						
WO	1998/001478	AU	36033/97	BR	9710219	CA	2259559
		CN	1228787	CN	1500813	CN	1673216
		EP	0910587	KR	2000023688	NZ	333277
		US	2004171777				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX