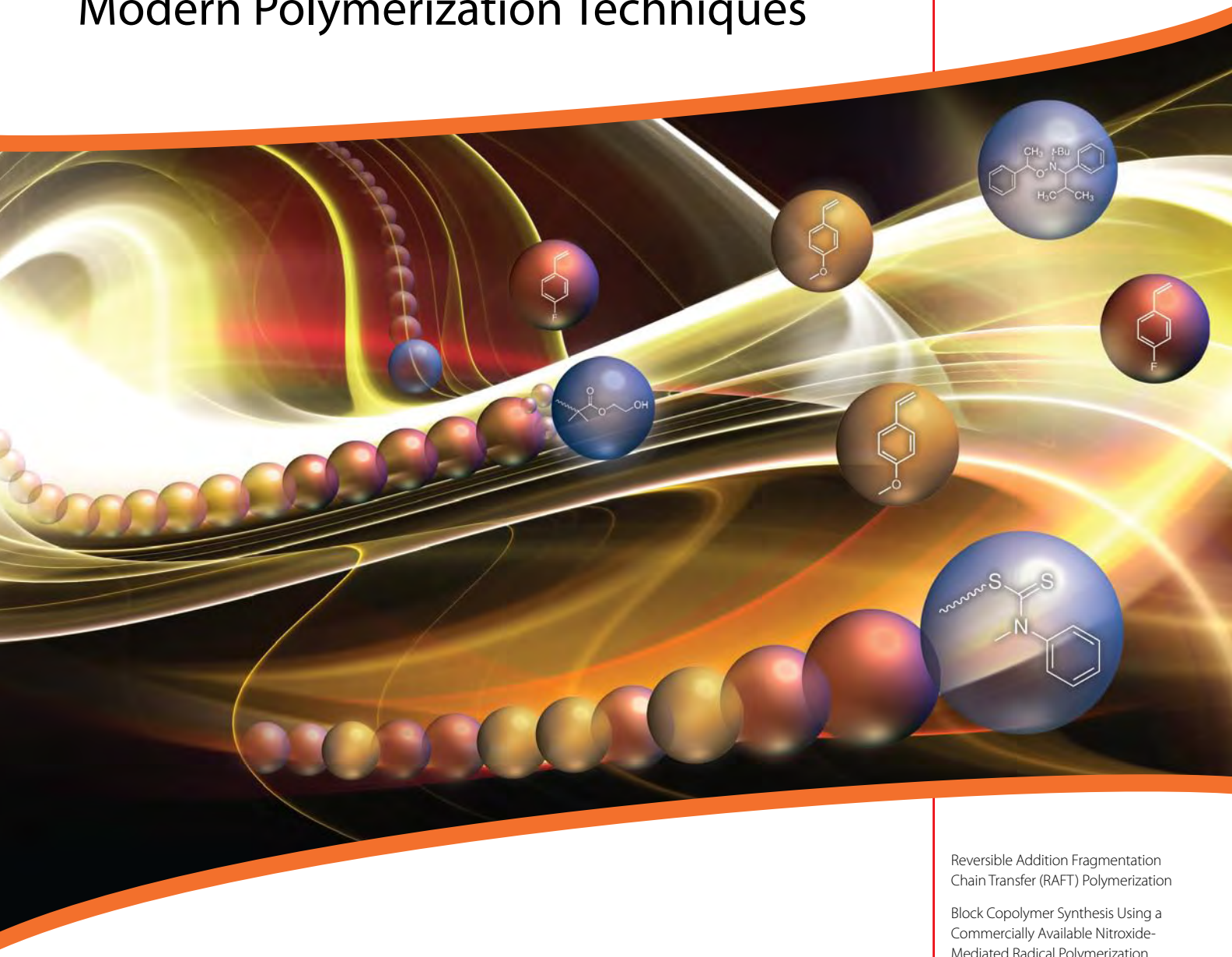
Material Matters™

Volume 5, Number 1 • 2010

ALDRICH Materials Science

Modern Polymerization Techniques



Start living with controlled polymerization

Introduction

Kaushik Patel, Ph.D.
Materials Science
Sigma-Aldrich Corporation

Welcome to the first 2010 issue of ***Material Matters***™ focusing on Modern Polymerization techniques for making polymers with well-defined properties and molecular architectures. With this issue, we are pleased to announce the increased emphasis of Sigma-Aldrich® Corporation on serving you, the customers of Aldrich® Materials Science. Over the coming year we will invest to expand our offer of products for materials research. A significant portion of this investment will be in Polymer Science and includes additional tools for polymer synthesis as well as greater selection of novel polymer materials. The many new products for living radical and electrochemical polymerization presented in this issue are the first result of this investment. Another benefit from this investment is the center of excellence for custom monomer and polymer synthesis announced on p. 8 of this issue. We are committed to supplying you with the highest quality materials needed for your research, so that you can focus on results!

Living and template-assisted polymerization methods developed over the last decade have changed the way we think about polymer materials. We are no longer limited to making simple polymers heterogeneous in terms of their molecular weight and conformation. It is now possible to prepare polymers with precise nanometer scale architectures designed to confer useful properties to the resulting polymer materials that find increased use in applications ranging from advanced coatings to molecular electronics. Three revolutionary methods that give living character to the well-known radical polymerization process are especially powerful: (i) Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization, (ii) Nitroxide-Mediated Polymerization (NMP), and (iii) Atom-Transfer Radical Polymerization (ATRP). Each of the three methods is useful and, in practice, the choice between them often comes down to availability of the necessary reagents. You will find the initiators, ligands, and chain transfer agents needed to carry out all three techniques in product tables that accompany the articles in this issue. A selection of electropolymerizable thiophene and pyrrole monomers useful in the context of template-assisted synthesis of polymer materials is also featured in this issue.

The issue begins with an article by a team of CSIRO researchers who discovered and significantly developed the RAFT process. They provide an overview of the RAFT polymerization technique and explain criteria for choosing a RAFT agent appropriate for a given monomer. In the following article Professor Karen Wooley and her student Nam Lee from Texas A&M University illustrate the NMP process by describing synthesis of a well-defined diblock copolymer using NMP initiators available from Aldrich Materials Science. Professor Krzysztof Matyjaszewski and his colleagues discuss the recently developed improvements to ATRP and also provide practical recommendations regarding the choice of the appropriate reagents. Finally, Professor Kazuo Akagi from Kyoto University reports the recent synthesis of films containing helical polyacetylene which were templated by a chiral liquid crystal.

Each article in this issue is accompanied by a list of monomers available from Aldrich Materials Science. Please contact us at ***matsci@sial.com*** if you need any monomer that is not available in our catalog, or would like custom packaged quantities of monomers for your development work. We welcome your product requests and suggestions as we continue to grow our Polymer Science product offer.

About Our Cover

Methods of living radical polymerization can be used to synthesize polymers with well-defined molecular weight and functional end-groups designed to self-assemble and form nanostructures or to selectively modify surfaces of inorganic solids. Our cover illustrates the "living" growth of polymer chains characteristic of these technologies. An ATRP synthesis of a block copolymer illustrated in the top part of the picture shows the copper initiating species (tiny spheres) close to a hydroxy initiator at the beginning of the growing polymer chain. Below it synthesis of random copolymer is controlled by an attached RAFT agent. The universal NMP initiator is also shown in the blue sphere to the right.

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Vol. 5, No. 1 • 2010

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Joe Porwoll, President
Aldrich Chemical Co., Inc.

Do you have a compound that you wish Sigma-Aldrich® could list to help materials research? If it is needed to accelerate your research, it matters—please send your suggestion to ***matsci@sial.com*** *and we will be happy to give it careful consideration.*

Professor Karen Wooley of Texas – A&M University kindly suggested that we offer the *exo*-5-Norbornene-carboxylic acid (**Aldrich Prod. No. 718149**) as a product in our catalog. This compound is a functional, stereochemically pure monomer used in ring opening metathesis polymerization (ROMP) synthesis of well-defined polymer materials. The pure *exo*- monomer shows faster reaction times,[1] higher conversion ratios, and better control of ROMP synthesis[2] compared to the racemic analog. The carboxylic acid serves as a versatile handle that can be used to prepare a variety of polymers (e.g., glycopolymers) for biomedical applications.[3-5]

exo-5-Norbornenecarboxylic acid

(1*R*,2*S*,4*R*)-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid [934-30-5] $C_8H_{10}O_2$ FW 138.16

718149-1G	1 g
718149-5G	5 g

References

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Polymerization Tools Featured in this Issue

Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization



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Introduction

RAFT (Reversible Addition Fragmentation chain Transfer) polymerization is a reversible deactivation radical polymerization (RDRP) and one of the more versatile methods for providing living characteristics to radical polymerization.[1-7] The historical development of RAFT polymerization at CSIRO has been outlined.[1] Advantages of RAFT polymerization include:

- The ability to control polymerization of most monomers polymerizable by radical polymerization. These include (meth)acrylates, (meth) acrylamides, acrylonitrile, styrenes, dienes and vinyl monomers.
- Tolerance of unprotected functionality in monomer and solvent (e.g., OH, NR_2, COOH, $CONR_2$, SO_3H). Polymerizations can be carried out in aqueous or protic media.
- Compatibility with reaction conditions (e.g., bulk, organic or aqueous solution, emulsion, mini-emulsion, suspension).
- Ease of implementation and inexpensive relative to competitive technologies.

In an ideal living polymerization, all chains are initiated at the beginning of the reaction, grow at a similar rate and survive the polymerization: there is no irreversible chain transfer or termination. If initiation is rapid with respect to propagation, the molecular weight distribution is very narrow and chains can be extended by further adding monomers into the reaction. In a radical polymerization all chains cannot be simultaneously active. In RDRP, such as RAFT polymerization, these attributes are displayed in the presence of reagents that are capable of reversibly deactivating propagating radicals such that the majority of living chains are maintained in a dormant form, and reaction conditions that support a rapid equilibrium between the active and dormant chains (**Figure 1**).

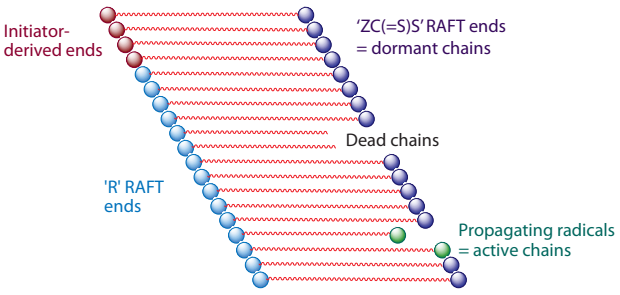


Figure 1. RAFT Polymerization Schematic.[4] The number of chains of each type shown here is not in proportion to that expected for a well-designed experiment. On average, all living chains grow simultaneously and have equal chain length because equilibration of the dormant and active chain ends is rapid with respect to propagation. A RAFT agent is represented as 'ZC(=S)S'.

Under these conditions, molecular weights can increase linearly with conversion, molecular weight distributions can be very narrow (**Figure 2**) and the majority of the polymerization product should comprise of dormant chains.

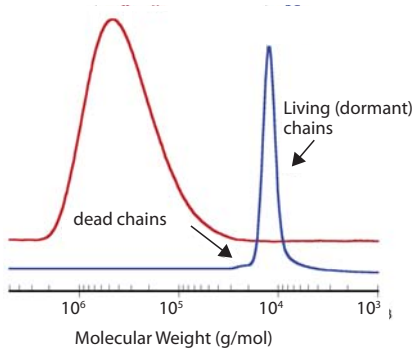
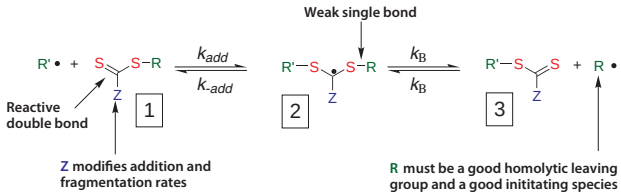


Figure 2. Typical molecular weight distributions for a conventional and a RAFT polymerization of styrene under similar experimental conditions.[4]

The mechanism of chain activation/deactivation in RAFT is shown in **Scheme 1**. The reactions associated with RAFT equilibria are in addition to those (i.e., initiation, propagation and termination) that occur during conventional radical polymerization. In an ideal RAFT process, the RAFT agent should behave as a transfer agent. Termination is not suppressed by the RAFT process. Retention of the thiocarbonylthio groups in the polymeric product is responsible for the living character of RAFT polymerization and renders the process suitable for synthesizing block copolymers and end functional polymers. Removal or transformation of the thiocarbonylthio group may be required for some applications. A number of methods to accomplish the end group removal have been devised and can be readily incorporated into polymer syntheses.[10, 12-16]



Scheme 1. Mechanism for reversible addition-fragmentation chain transfer (RAFT)

Selection of the RAFT agent (ZC(=S)SR) for the monomers and reaction conditions is crucial for the success of a RAFT polymerization experiment. However, this should not be a daunting task. The effectiveness of RAFT agents is determined by the substituents R and Z and guidelines for selection have been proposed (**Figure 3**).[1, 3] Polymerization of most monomers can be well-controlled to provide minimal retardation and a high fraction of living chains by using one of just two RAFT agents. The first class is suited to more activated monomers (MAM) such as methacrylics, e.g., methyl methacrylate (MMA, **Aldrich Prod. No. M55909**), methacrylic acid (MAA, **Aldrich Prod. No. 155721**), hydroxypropyl methacrylamide (HPMAM) and acrylics, e.g., methyl acrylate (MA, **Aldrich Prod. No. M27301**), acrylic acid (**Aldrich Prod. No 147230**), acrylamide (AM, **Aldrich Prod. No. 148660**), acrylonitrile (AN, **Aldrich Prod. No. 320137**), styrene (St, **Aldrich Prod. No. W323306**). The second class of RAFT agents is suited to less activated monomers (LAM) such as vinyl acetate (VAc, **Aldrich Prod. No. V1503**), *N*-vinylpyrrolidone (NVP) or *N*-vinylcarbazole (NVC).

Recently, a switchable RAFT agent that can be used to control polymerization of both MAMs and LAMs has been described.[8, 9] Requirements for specific end-functionality or polymer architecture may dictate the use of other RAFT agents.[10, 11]

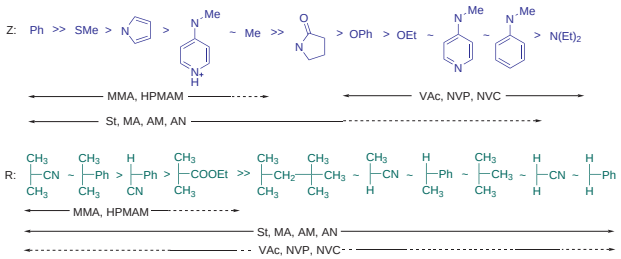


Figure 3. Guidelines for selection of RAFT agents (Z-C(=S)S-R) for various polymerizations.[1, 3] For 'Z', addition rates and transfer constants decrease and fragmentation rates increase from left to right. For 'R', fragmentation rates decrease from left to right. A dashed line indicates limited control (e.g., retardation, high dispersity likely).

With appropriate choice of reagents and polymerization conditions RAFT polymerization can be used in the synthesis of well-defined homo, gradient, diblock, triblock and star polymers, as well as more complex architectures including microgels and polymer brushes. Applications now being reported range from novel surfactants, dispersants, coatings and adhesives, to biomaterials, membranes, drug delivery media, electroactive materials and other fields falling under the nano-technology umbrella.

RAFT Polymerization of 'More-Activated Monomers' (MAMs)

Good control over polymerization of a MAM is observed with trithiocarbonates (Z=S-alkyl, e.g., **4**-**6**). Z is preferably based on a thiol with low volatility. Aromatic dithioesters (Z=aryl, e.g., **9**, **10**) are amongst the most active RAFT agents and show general utility in the polymerization of MAMs.[1, 2] However, the aromatic substituted RAFT agents may give retardation when used in high concentrations and are more sensitive to hydrolysis and decomposition induced by Lewis acids.[17, 18] Alkyl-substituted RAFT agents (**4**-**6**) can be tried if hydrolysis is a concern. The bis(thiocarbonyl) disulfides **7** and **8** are useful as precursors to the tertiary RAFT agents and can be used to form a RAFT agent *in situ* during polymerization.[19]

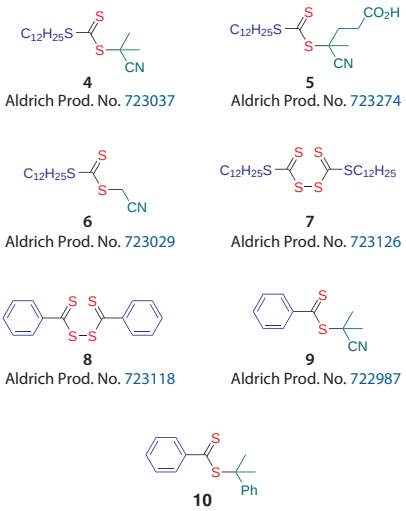


Figure 4. A series of RAFT agents that show good polymerization control for MAMs.

R must efficiently reinitiate polymerization and must be a good homolytic leaving group with respect to the propagating radical.[20] R• must also be efficient in reinitiating polymerization: it should add to monomer rapidly with respect to the rate of propagation. A good choice for the case of acrylates and acrylamides is the RAFT agent **6** with R=cyanomethyl. The choice of 'R' is critical in the case of methacrylates. In some of the most effective RAFT agents R is tertiary cyanoalkyl (e.g., **4**, **5**, **9**). The utility of the RAFT process is illustrated by the following example of RAFT polymerization of methyl methacrylate (MMA). A series of high (80-100%) conversion MMA polymerizations were carried out at 90 °C with 1,1′-azobis(1-cyclohexanecarbonitrile) initiator, and using an ~60-fold range of concentrations of *S*-dodecyl *S*-(2-cyano-4-carboxy)but-2-yl trithiocarbonate **5**.[10] The molecular weight distributions observed after six hours are shown in **Figure 5**. The molecular weights, ranging from 2,600 to 125,000, agree with expectation based on the concentrations of RAFT agent and initiator used.[10] All samples have narrow molecular weight distributions (PDI <1.2).

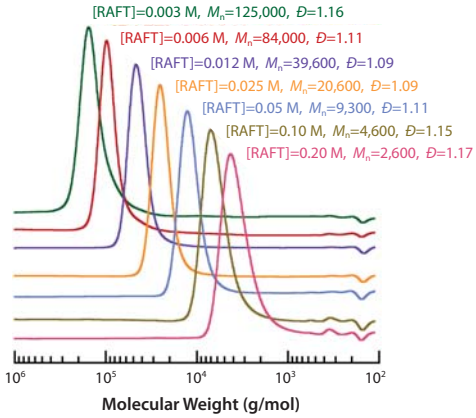


Figure 5. Molecular weight distributions for PMMA formed by high conversion RAFT polymerization of MMA (6.55 M in benzene) with 1,1′-azobis(1-cyclohexanecarbonitrile) (0.0018 M) as initiator and various concentrations of RAFT agent **5** for 6 h at 90 °C.[10]

RAFT Polymerization of 'Less-Activated Monomers' (LAMs)

The less active RAFT agents with Z=NR'$_2$ (dithiocarbamates), Z=OR' (xanthates) and R' = alkyl or aryl offer good control. The more active RAFT agents Z=R (dithioesters) or SR (trithiocarbonates) inhibit polymerization of a LAM. The choice of R group is also critical because most monomers in the class have a high propagation rate constant. Inhibition periods due to slow reinitiation are expected for RAFT agents such as **12** and **13**. One preferred RAFT agent is **11**. Examples of VAc polymerization with **11** are shown in **Table 1**.[7]

Table 1. RAFT Polymerization of Vinyl Acetate[7]

Monomer (M)	RAFT Agent (M×10^2)	Initiator[a] (M×10^3)/ Conditions	Conv %	M_n[b]	M_n (calc)[c]	*PDI*
10.86	11 (4.98)	AIBN (61) 60 °C 16 h	96	22,700	18,000	1.24
7.24	11 (5.06)	ACHN (28) 75 °C 16 h	93	13,400	11,440	1.29
7.24	11 (10.06)	ACHN (28) 75 °C 16 h	95	7,100	5,880	1.25

[a]AIBN: 2,2'-azobis(isobutyronitrile) (**Aldrich Prod. No. 441090**);
ACHN: 1,1'-azobis(cyclohexanecarbonitrile) (**Aldrich Prod. No. 380210**)
[b]number average molecular weight in polystyrene equivalents.
[c]calculated molecular weight based on complete consumption of RAFT agent.

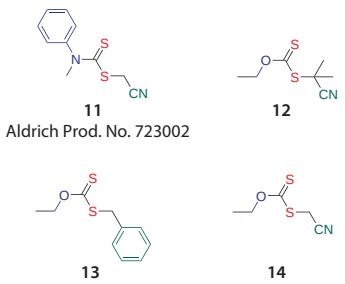
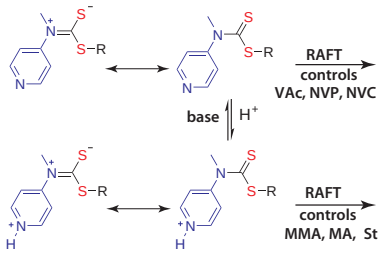


Figure 6. A series of RAFT agents that show good polymerization control for MAMs.

Switchable RAFT Agents

We recently reported on a new class of stimuli-responsive RAFT agents that can be "switched" to offer good control over polymerization of both MAMs and LAMs and thus a more convenient route to polyMAM-*block*-polyLAM polymers with narrowed molecular weight distributions.[9] This approach was demonstrated with the use of 4-pyridinyl-*N*-methyldithiocarbamate derivatives to prepare PMMA-*block*-PVAc and PMA-*block*-PNVC. The *N*-4-pyridinyl-*N*-methyldithiocarbamates provide effective control over polymerization of LAMs (**Scheme 2**) and when protonated also provide excellent control over the polymerization of MAMs.[9]



Scheme 2. RAFT Agent capable of polymerization of both LAMs and MAMs controlled by pH.

Conclusions

Reversible Addition Fragmentation chain Transfer (RAFT) has emerged as one of the most important methods for controlling radical polymerization. RAFT has been shown to be robust and versatile and applicable to the majority of monomers subject to radical polymerization. However, selection of the appropriate RAFT agent for the monomers in tandem with the proper reaction conditions is crucial for successful polymerization.

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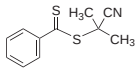
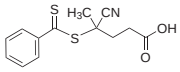
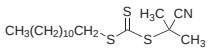
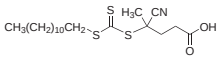
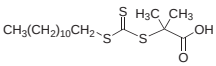
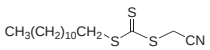
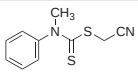
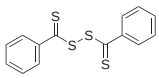
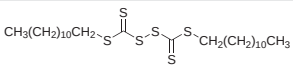
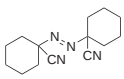
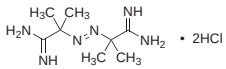
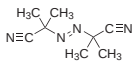
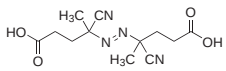
RAFT Agents

For a complete description of available RAFT agents, please visit *sigma-aldrich.com/poly*

Name	Structure	Description	Cat. No.
2-Cyano-2-propyl benzodithioate		RAFT agent for controlled radical polymerization; especially suited for the polymerization of methacrylate and methacrylamide monomers. Chain Transfer Agent (CTA)	722987-1G 722987-5G
4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid			722995-1G 722995-5G
2-Cyano-2-propyl dodecyl trithiocarbonate		RAFT agent for controlled radical polymerization; especially suited for the polymerization of methacrylate, methacrylamide and styrene monomers. Chain Transfer Agent (CTA)	723037-1G 723037-5G
4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid			723274-1G 723274-5G
2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid		RAFT agent for controlled radical polymerization; especially suited for the polymerization of styrene, acrylate and acrylamide monomers. Chain Transfer Agent (CTA)	723010-1G 723010-5G
Cyanomethyl dodecyl trithiocarbonate			723029-1G 723029-5G
Cyanomethyl methyl(phenyl)carbamodithioate		RAFT agent for controlled radical polymerization; especially suited for the polymerization of vinyl ester and vinyl amide monomers. Chain Transfer Agent (CTA)	723002-1G 723002-5G
Bis(thiobenzoyl) disulfide		Precursor for the synthesis of RAFT agents for controlled radical polymerization.	723118-5G
Bis(dodecylsulfanylthiocarbonyl) disulfide			723126-5G

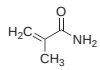
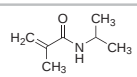
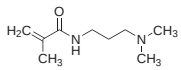
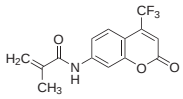
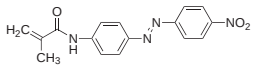
Radical Initiators

For a complete list of available radical initiators, please visit *sigma-aldrich.com/poly*

Name	Structure	Purity	Cat. No.
1,1′-Azobis(cyclohexanecarbonitrile), ACHN		98%	380210-25G 380210-100G
2,2′-Azobis(2-methylpropionamidine) dihydrochloride, AAPH		97%	440914-25G 440914-100G
2,2′-Azobis(2-methylpropionitrile), AIBN		98%	441090-25G 441090-100G
4,4′-Azobis(4-cyanovaleric acid), ACVA		≥98.0%	11590-25G 11590-100G

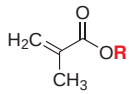
Methacrylamide Monomers

For a complete list of available acrylamides and methacrylamide monomers, please visit *sigma-aldrich.com/acrylic*

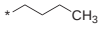
Name	Structure	Purity	Cat. No.
Methacrylamide		98%	109606-5G 109606-250G 109606-500G
N-Isopropylmethacrylamide		97%	423548-5G 423548-25G
N-[3-(Dimethylamino)propyl]meth-acrylamide		99%	409472-250ML 409472-1L
7-[4-(Trifluoromethyl)coumarin] methacrylamide		98%	566225-100MG 566225-500MG
Disperse Orange 3 methacrylamide		-	595845-100MG 595845-1G

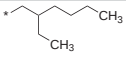
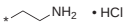
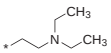
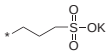
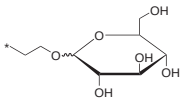
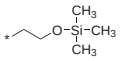
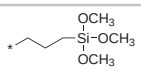
Methacrylate Monomers

For a complete list of available methacrylate monomers, please visit *sigma-aldrich.com/acrylic*

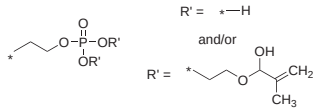
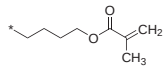
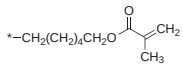
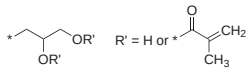
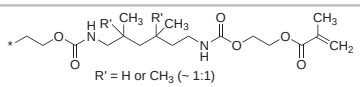
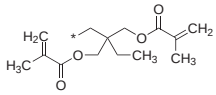


Monofunctional Methacrylate Monomers

Name	R Group	Purity	Additive	Cat. No.
Methacryloyl chloride		97%	monomethyl ether hydroquinone 200 ppm as stabilizer	523216-100ML 523216-1L
Sodium methacrylate	*—Na	99%	-	408212-50G 408212-250G
Methacrylic acid	*—H	99%	monomethyl ether hydroquinone 250 ppm as inhibitor	155721-5G 155721-100G 155721-500G 155721-2KG 155721-3KG 155721-18KG
Methyl methacrylate	*—CH_3	99%	monomethyl ether hydroquinone 10-100 ppm as inhibitor	M55909-25ML M55909-500ML M55909-1L M55909-2L M55909-17L
Ethyl methacrylate		99%	monomethyl ether hydroquinone 15 ppm as inhibitor	234893-100ML 234893-500ML 234893-1L
2,2,2-Trifluoroethyl meth-acrylate		99%	-	373761-5G 373761-25G
Butyl methacrylate		99%	monomethyl ether hydroquinone 10 ppm as inhibitor	235865-5ML 235865-100ML 235865-1L 235865-18L
Hexyl methacrylate	*—$CH_2(CH_2)_4CH_3$	98%	-	462373-500G 462373-1KG
Lauryl methacrylate	*—$CH_2(CH_2)_{10}CH_3$	96%	-	291811-100ML 291811-500ML
Stearyl methacrylate	*—$CH_2(CH_2)_{16}CH_3$	-	monomethyl ether hydroquinone 300-500 ppm as inhibitor	411442-250ML 411442-1L

Name	R Group	Purity	Additive	Cat. No.
tert-Butyl methacrylate		98%	monomethyl ether hydroquinone 200 ppm as inhibitor	463353-100ML 463353-250ML
Isobutyl methacrylate		97%	monomethyl ether hydroquinone ≤15 ppm as inhibitor	169919-1L 169919-18L
2-Ethylhexyl methacrylate		98%	monomethyl ether hydroquinone ~50 ppm as stabilizer	290807-25ML 290807-1L
2-Hydroxyethyl methacrylate		≥99%	monomethyl ether hydroquinone ≤50 ppm as inhibitor	477028-25ML 477028-100ML
2-Hydroxyethyl methacrylate		97%	monomethyl ether hydroquinone 200-220 ppm as inhibitor	128635-5G 128635-500G 128635-1KG 128635-18KG
Hydroxypropyl methacrylate		97%	monomethyl ether hydroquinone 250-350 ppm as inhibitor	268542-100ML 268542-1L 268542-18L
2-Aminoethyl methacrylate hydrochloride		90%	-	516155-5G 516155-25G
2-(Dimethylamino)ethyl methacrylate		98%	monomethyl ether hydroquinone 2,000 ppm as inhibitor	234907-5ML 234907-100ML 234907-1L
2-(Diethylamino)ethyl methacrylate		99%	phenothiazine 100 ppm as inhibitor	408980-250ML 408980-1L
2-Isocyanatoethyl methacrylate		98%	BHT <0.1% as inhibitor	477060-5ML 477060-50ML
Allyl methacrylate		98%	monomethyl ether hydroquinone 50-185 ppm as inhibitor	234931-100ML 234931-500ML
Glycidyl methacrylate		97%	monomethyl ether hydroquinone 100 ppm as inhibitor	151238-100G 151238-500G
Furfuryl methacrylate		97%	monomethyl ether hydroquinone 200 ppm as inhibitor	411760-25ML 411760-100ML
Benzyl methacrylate		96%	monomethyl ether hydroquinone 50 ppm as inhibitor	409448-250ML 409448-1L
Cyclohexyl methacrylate		≥97%	monomethyl ether hydroquinone ~60 ppm as inhibitor	408964-100ML 408964-250ML
3-Sulfopropyl methacrylate potassium salt		98%	-	251658-100G 251658-500G
Isobornyl methacrylate		-	MEHQ 150 ppm as inhibitor	392111-100ML 392111-500ML 392111-1L
Glycosyloxyethyl methacrylate solution, 5% (w/v) in ethanol		-	-	659576-25ML
Ferrocenylmethyl methacrylate		95%, NMR	Ionol® 46 (Raschig GmbH) as inhibitor	700479-1G
2-(Trimethylsilyloxy)ethyl methacrylate		96%	-	347485-25G 347485-100G
3-(Trimethoxysilyl)propyl methacrylate		98%	-	440159-100ML 440159-500ML

Polyfunctional Methacrylate Monomers

Name	R Group	Purity	Additive	Cat. No.
Phosphoric acid 2-hydroxyethyl methacrylate ester		-	MEHQ 700-1000 ppm	695890-100ML 695890-250ML
1,4-Butanediol dimethacrylate		95%	monomethyl ether hydroquinone 100 ppm as inhibitor	234958-100G 234958-500G
1,6-Hexanediol dimethacrylate		-	hydroquinone 100 ppm as inhibitor	411736-25ML 411736-100ML
Glycerol dimethacrylate, mixture of isomers		85%	monomethyl ether hydroquinone 200 ppm as inhibitor	436895-100ML 436895-500ML
Diurethane dimethacrylate, mixture of isomers		-	topanol 225 ppm ±25 ppm as inhibitor	436909-100ML 436909-500ML
Trimethylolpropane trimethacrylate		-	monomethyl ether hydroquinone 175 ppm as inhibitor	246840-100G 246840-500G

Block Copolymer Synthesis Using a Commercially Available Nitroxide-Mediated Radical Polymerization (NMP) Initiator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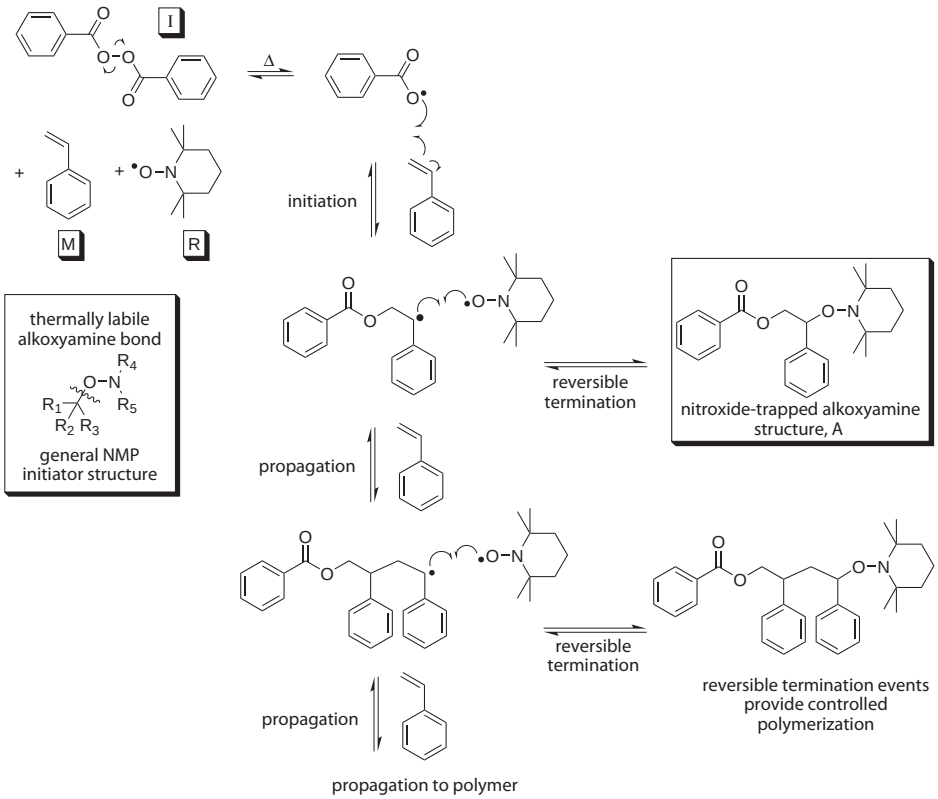
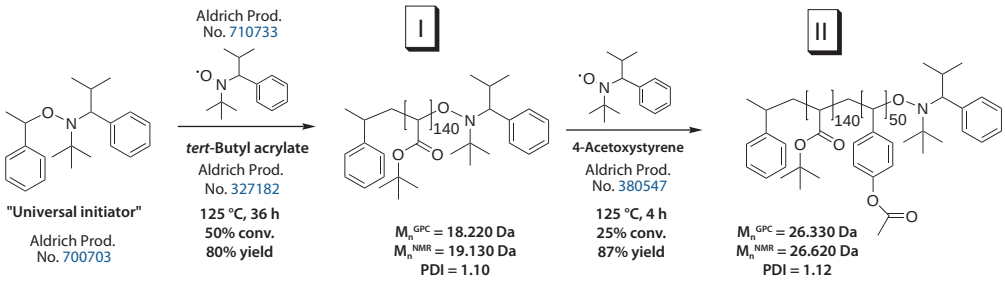
Introduction

Controlled radical polymerization, which provides exquisite tuning of macromolecular size, structure, composition and architecture, with experimental convenience, has become one of the most indispensible tools for polymer chemists. Its emergence in the mid-1990s has greatly advanced the fields of nanoscience and nanotechnology, by providing ready access to complex polymers that serve as building blocks for functional nanostructures with predictable parameters such as the size, morphology, regioselective placement of functionalities, etc. This exceptional polymerization control is due to reversible termination events that mediate the radical concentration and reactivity. The living character of this type of polymerization provides an ability to produce polymers with controlled molecular weight and narrow molecular weight distribution, and, moreover, to chain extend with different monomers and obtain multi-block copolymers. Nitroxide-mediated radical polymerization (NMP) is one of these controlled radical polymerizations that also includes atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT) polymerization. NMP stands out due to its simplicity: the polymerization is thermally initiated in the absence of an external radical source or a metal catalyst. As illustrated in **Scheme 1**, NMP involves a combination of radical initiator (I), monomer (M) and nitroxide radical (R), for trapping of intermediate radical species. For instance, the thermally-promoted homolysis of benzoyl peroxide (**Aldrich Prod. No.** 179981) produces radicals that are capable of initiating the polymerization of styrene monomer. Propagation proceeds to produce polymer chains, while reversible termination events, involving reactions with nitroxide radicals to afford thermally labile alkoxyamines, mediate the availability of the reactive radical species and, thereby, provide control over the polymerization. It is important that the stable nitroxide radicals are capable of the reversible termination reactions, but do not initiate polymerizations.



Scheme 1. Overall mechanism for NMP, illustrated for styrene monomer (M) polymerization initiated by benzoyl peroxide initiator (I) and mediated by TEMPO nitroxide radicals (R). Also shown is the general structure for alkoxyamine-based unimolecular NMP initiators.

One of the most significant advances with NMP was the isolation of an alkoxyamine that could act as a unimolecular agent, providing both the reactive, initiating radical and the stable, mediating nitroxide radical. Initially, nitroxides were employed as additives to reversibly terminate polymer chains initiated by a separate radical source. By using TEMPO to trap a styrenyl radical initiated by benzoyl peroxide (as shown by structure A of **Scheme 1**), Hawker demonstrated an ability to tune the molecular weight, define the end groups, and extend to block copolymers, while maintaining narrow molecular weight distributions. He later developed a universal initiator, which has received broad application in laboratories around the world. A key limitation to the use of this universal initiator remained the challenge of its synthesis. With it now being offered commercially by Aldrich Materials Science, it is expected that NMP will experience a renewed vigor of investigation. With our interest in the construction of nanoscopic objects via the self-assembly of amphiphilic block copolymers in water, we have used the universal initiator (**Aldrich Prod. No. 700703**), in the presence of less than 5 equivalent percent of the corresponding nitroxide (added to assist with capping the propagating chain ends during polymerization), to prepare an amphiphilic diblock copolymer precursor, poly(*tert*-butyl acrylate)-*b*-poly(4-acetoxystyrene) with a controlled molecular weight and a narrow molecular weight distribution (**Scheme 2**).



Scheme 2. Synthesis of poly(*tert*-butyl acrylate) (I) continuing on to create poly(*t*-butyl acrylate)-b-poly(4-acetoxystyrene) (II) using the universal NMP initiator.

Synthesis of Poly(*t*-butyl acrylate)$_{140}$ (**I**)

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, as solutions with the solvent proton as a standard. To a flame-dried 50 mL Schlenk flask equipped with a magnetic stir bar and under N_2 atmosphere, at room temperature, was added (124 mg, 0.381 mmol, **Aldrich Prod. No. 700703**), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (4.19 mg, 0.019 mmol, **Aldrich Prod. No. 710733**), and *tert*-butyl acrylate (10.16 g, 79.6 mmol, **Aldrich Prod. No. 327182**). The reaction flask was sealed and stirred for 10 min at rt. The reaction mixture was degassed through three cycles of freeze-pump-thaw. After the last cycle, the reaction mixture was recovered back to rt and stirred for 10 min before being immersed into a pre-heated oil bath at 125 °C to start the polymerization. After 36 h (kinetic data for conversion shown in **Figure 1**), ^{1}H NMR analysis showed 50% monomer conversion had been reached (**Figure 3**). The polymerization was quenched by quick immersion of the reaction flask into liquid N_2. The reaction mixture was dissolved in THF (**Aldrich Prod. No. 401757**) and precipitated into H_2O/MeOH (v:v, 1:4) three times to afford P*t*BA as a white powder, (4.1 g, 80% yield based upon monomer conversion); M_n^{NMR} = 19,130 g/mol, M_n^{GPC} = 18,220 g/mol, PDI = 1.10. ^{1}H NMR (CD_2Cl_2, ppm): δ 1.43 (br, 1290 H), 1.80 (br, 70 H), 2.21 (br, 160 H), 7.14-7.26 (m, 10 H). ^{13}C NMR (CD_2Cl_2, ppm): δ 28.4, 36.5, 38.0, 42.5, 80.9, 174.4. The GPC data can be seen in **Figure 2**.

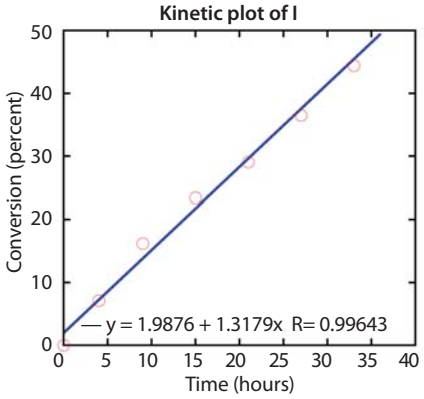


Figure 1. Percent conversion of monomers vs. time

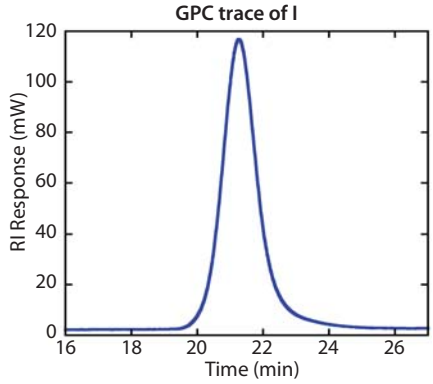


Figure 2. Molecular weight distribution of I. M_n = 18,220 g/mol, PDI = 1.10

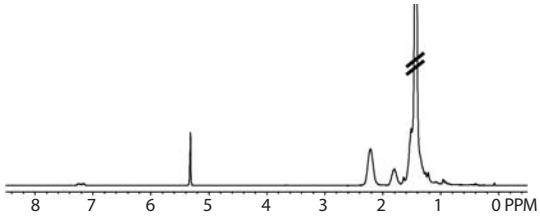


Figure 3. ^{1}H NMR spectrum of I

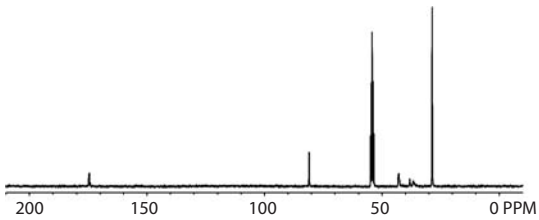


Figure 4. ^{13}C NMR spectrum of I

Synthesis of Poly(*t*-butyl acrylate)$_{140}$-*b*-poly(acetoxystyrene)$_{50}$ (**II**)

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, as solutions with the solvent proton as a standard. To a flame-dried 50 mL Schlenk flask equipped with a magnetic stir bar and under N_2 atmosphere, at room temperature, was added **I** (124 mg, 0.381 mmol), 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (4.19 mg, 0.019 mmol), and 4-acetoxystyrene (10.16 g, 79.6 mmol, **Aldrich Prod. No.** 380547). The reaction flask was sealed and stirred for 10 min at rt. The reaction mixture was degassed through three cycles of freeze-pump-thaw. After the last cycle, the reaction mixture was recovered back to rt and stirred for 10 min before being immersed into a pre-heated oil bath at 125 °C to start the polymerization. After 4 h (kinetic data for conversion shown in **Figure 5**), ^{1}H NMR analysis showed 25% monomer conversion had been reached (**Figure 7**). The polymerization was quenched by quick immersion of the reaction flask into liquid N_2. The reaction mixture was dissolved in THF and precipitated into H_2O/MeOH (v:v, 1:4) three times to afford P*t*BA-*b*-PAS as a white powder, (4.62 g, 87% yield based upon monomer conversion); M_n^{NMR} = 26,620 g/mol, M_n^{GPC} = 26,330 g/mol, PDI = 1.12. ^{1}H NMR (CD_2Cl_2, ppm): δ 1.43 (br, 1500 H), 1.80 (br, 100 H), 2.21 (br, 290 H), 6.36-6.82 (m, 190 H), 7.14-7.26 (m, 10 H). ^{13}C NMR (CD_2Cl_2, ppm, **Figure 8**): δ 21.5, 28.4, 36.5, 38.0, 40.5, 42.6, 80.9, 121.8, 128.9, 143.0, 149.4, 169.7, 174.7. The GPC data can be seen in **Figure 6**.

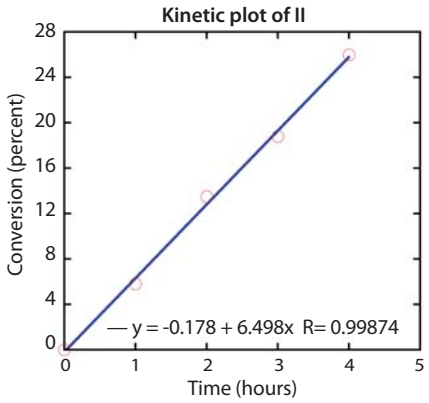


Figure 5. Percent conversion of monomers vs. time

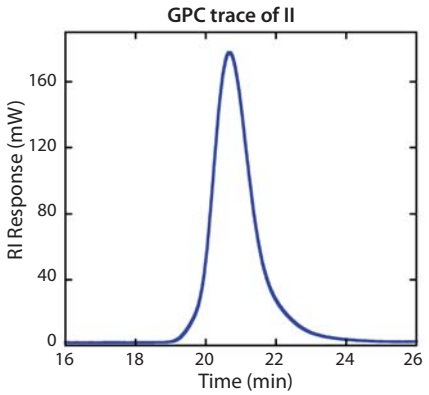


Figure 6. Molecular weight distribution of II. M_n = 26,330 g/mol, PDI = 1.12

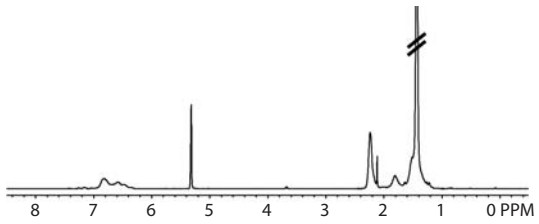


Figure 7. ^{1}H NMR spectrum of II

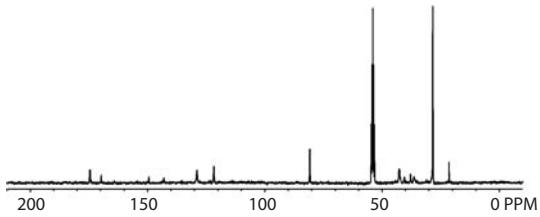


Figure 8. ^{13}C NMR spectrum of II

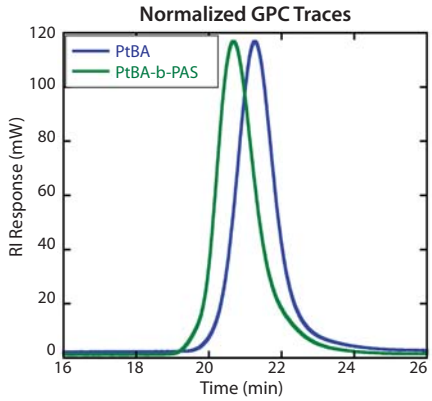


Figure 9. Normalized GPC traces showing molecular weight distributions of polymers I and II.

Conclusions

We have demonstrated a facile preparation of an amphiphilic diblock copolymer precursor with a controlled molecular weight and a low PDI using the universal NMP initiator (**Aldrich Prod. No.** 700703). This required no special apparatus or technique, beyond those employed for standard radical polymerizations, but only synthesis of the corresponding nitroxide (**Aldrich Prod. No.** 710733). The final block copolymer was purified by precipitation to remove excess monomers, and was then deprotected. The morphology and size of the subsequent supramolecularly assembled nanostructures in water depend on the polymer block length and the ratio of the block lengths, each carefully manipulated through monomer conversions, the control over which arises from the universal NMP initiator. With the simplicity of this system, it is expected that NMP will experience a dramatic increase in breadth of application.

Acknowledgments

This material is based upon work supported by the National Heart Lung and Blood Institute of the National Institutes of Health as a Program of Excellence in Nanotechnology (HL080729). N. S. Lee thanks GlaxoSmithKline for their financial support through the ACS Division of Organic Chemistry Graduate Fellowship 2008–2009.

References

(1) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.
(2) Moad, G.; Solomon, D. H.; Johns, S. R.; Willing, R. I. *Macromolecules* **1982**, *15*, 909; Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32; Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
(3) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.
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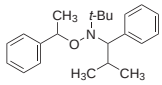
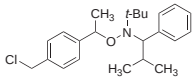
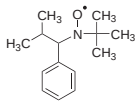
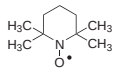
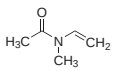
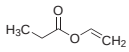
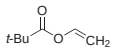
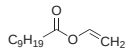
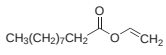
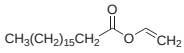
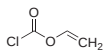
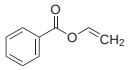
NMP Initiators

For a complete description of available free radical initiators, please visit *sigma-aldrich.com/poly*

Name	Structure	Description	Cat. No.
N-tert-Butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl) hydroxylamine		Universal alkoxyamine initiator for nitroxide-mediated living radical polymerization (NMP initiator). Particularly useful for synthesis of styrene and acrylate polymers and co-polymers.	700703-250MG 700703-1G
N-tert-Butyl-*O*-[1-[4-(chloromethyl)phenyl]ethyl]-*N*-(2-methyl-1-phenylpropyl)hydroxylamine		Functional alkoxyamine initiator for nitroxide-mediated living radical polymerization (NMP initiator). Particularly useful for synthesis of styrene and acrylate polymers and co-polymers.	711268-250MG
2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide		Stable nitroxide radical useful in controlling living radical polymerizations	710733-250MG 710733-1G
TEMPO, 2,2,6,6-Tetramethyl-1-piperidinyloxy		Stable nitroxide radical useful in controlling living polymerizations	426369-1G 426369-5G

Vinyl Amide and Vinyl Ester Monomers

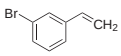
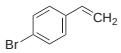
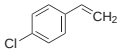
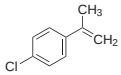
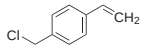
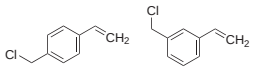
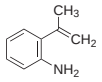
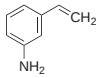
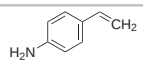
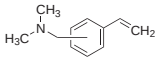
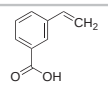
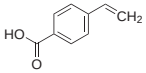
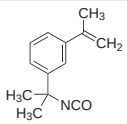
For a complete list of available vinyl monomers, please visit *sigma-aldrich.com/monomers*

Name	Structure	Purity	Additive	Cat. No.
N-Vinylformamide		98%	4-Hydroxy-TEMPO 25-55 ppm as stabilizer	447331-100ML 447331-500ML
N-Methyl-*N*-vinylacetamide		98%	-	255130-100ML 255130-500ML
Vinyl propionate		98%	monomethyl ether hydroquinone <100 ppm as inhibitor	401714-500ML
Vinyl pivalate		99%	monomethyl ether hydroquinone 6-15 ppm as stabilizer	124400-250ML 124400-1L
Vinyl neodecanoate, mixture of isomers		-	monomethyl ether hydroquinone 5 ppm as inhibitor	134481-1L
Vinyl decanoate		95%	-	411795-10G
Vinyl stearate		95%	-	436208-50G 436208-250G
Vinyl chloroformate		99%	BHT 100 ppm as inhibitor	528064-5ML 528064-10ML
Vinyl benzoate		≥99%	hydroquinone 20 ppm as stabilizer	403091-100ML 403091-500ML

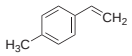
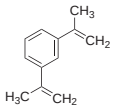
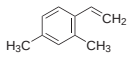
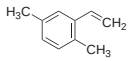
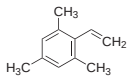
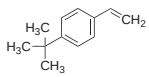
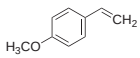
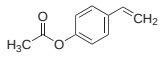
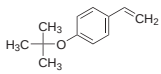
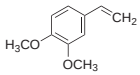
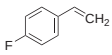
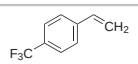
Styrene Monomers

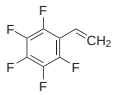
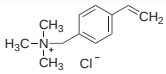
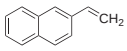
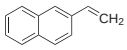
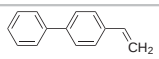
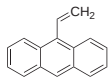
For a complete list of available styrene, functionalized styrere, and substituted styrene monomers, please visit *sigma-aldrich.com/monomers*

Functionalized Styrene Monomers

Name	Structure	Purity	Additive	Cat. No.
α-Bromostyrene		90%	-	292273-5G 292273-25G
2-Bromostyrene		97%	-	132683-1G 132683-5G
3-Bromostyrene		97%	3,5-di-*tert*-butylcatechol 0.1% as inhibitor	132675-1G 132675-5G
4-Bromostyrene		98%	3,5-di-*tert*-butylcatechol 0.1% as inhibitor	124141-10G 124141-25G
2-Chlorostyrene		97%	hydroquinone 0.1% as stabilizer	160679-5G 160679-25G
3-Chlorostyrene		98%	3,5-di-*tert*-butylcatechol 0.1% as stabilizer	C71009-1G
4-Chlorostyrene		97%	4-*tert*-butylcatechol 500 ppm as inhibitor	C71203-10G C71203-50G
4-Chloro-α-methylstyrene		98%	*tert*-butylcatechol 100 ppm as stabilizer	C57200-25G
2,6-Dichlorostyrene		99%	-	D74509-2.5G D74509-10G
4-Vinylbenzyl chloride		90%	*tert*-butylcatechol 500 ppm as inhibitor nitroparaffin 500 ppm as inhibitor	436887-25ML 436887-100ML
Vinylbenzyl chloride	 Mixture of isomers	97%	*tert*-butylcatechol 50-100 ppm as inhibitor nitromethane 700-1100 ppm as inhibitor	338729-25G 338729-100G
2-Isopropenylaniline		≥98%	-	194212-5G 194212-25G
3-Vinylaniline		97%	-	560839-1G 560839-5G
4-Vinylaniline		97%	-	536180-1G 536180-5G
N,N-Dimethylvinylbenzyl-amine, mixture of isomers		97%	-	476382-1G 476382-10G
3-Vinylbenzoic acid		96%	-	523089-5G
4-Vinylbenzoic acid		97%	-	254738-1G 254738-5G
3-Isopropenyl-α,α-dimethyl-benzyl isocyanate		95%	-	361771-250ML 361771-1L

Substituted Styrene Monomers

Name	Structure	Purity	Additive	Cat. No.
α-Methylstyrene		99%	*p-tert*-butylcatechol 15 ppm as inhibitor	M80903-5ML M80903-100ML M80903-1L
Methylstyrene		99%	4-*tert*-butylcatechol ≤50 ppm as stabilizer	522864-250ML 522864-1L
3-Methylstyrene		99%	3,5-di-*tert*-butylcatechol 0.1% as inhibitor	184675-5G
4-Methylstyrene		96%	3,5-di-*tert*-butylcatechol as inhibitor	M80806-10ML M80806-100ML M80806-500ML
1,3-Diisopropenylbenzene		97%	-	255173-250ML 255173-1L
2,4-Dimethylstyrene		97%	*tert*-butylcatechol 100 ppm as inhibitor	262633-5G
2,5-Dimethylstyrene		99%	-	361135-1G 361135-5G
2,4,6-Trimethylstyrene		95%	*tert*-butylcatechol <0.05% as inhibitor	259780-5G
4-*tert*-Butylstyrene		93%	*tert*-butylcatechol 100 ppm as inhibitor	523933-250ML 523933-1L
4-Vinylanisole		97%	-	141003-5G 141003-25G
4-Acetoxystyrene		96%	MEHQ 200-300 ppm as inhibitor	380547-5ML 380547-25ML
4-*tert*-Butoxystyrene		99%	4-*tert*-butylcatechol 200 ppm as inhibitor	455644-10ML 455644-50ML
3,4-Dimethoxystyrene		-	hydroquinone 1% as inhibitor	154466-5G 154466-10G
2-Fluorostyrene		98%	-	290505-5G
3-Fluorostyrene		97%	-	219452-1G 219452-5G
4-Fluorostyrene		99%	*tert*-butylcatechol as inhibitor	155799-1G 155799-10G
2-(Trifluoromethyl)styrene		99%	4-*tert*-butylcatechol 0.1% as inhibitor	369594-1G
3-(Trifluoromethyl)styrene		99%	4-*tert*-butylcatechol as inhibitor	366692-1G
4-(Trifluoromethyl)styrene		98%	4-*tert*-butylcatechol 0.1% as inhibitor	369608-1G
2,6-Difluorostyrene		99%	4-*tert*-butylcatechol 0.25% as inhibitor	374407-250MG 374407-1G

Name	Structure	Purity	Additive	Cat. No.
2,3,4,5,6-Pentafluorostyrene		99%	*p-tert*-butylcatechol 0.1% as inhibitor	196916-25G
3-Nitrostyrene		96%	-	N26601-2.5G N26601-10G
(Vinylbenzyl)trimethylammonium chloride		99%	-	458694-100G 458694-250G
2-Vinylnaphthalene		98%	-	453870-1G
2-Vinylnaphthalene		95%	-	V2909-5G V2909-25G
4-Vinylbiphenyl		-	-	V1805-1G V1805-10G
9-Vinylanthracene		97%	-	V1708-1G V1708-5G

ATRP for Everyone: Ligands and Initiators for the Clean Synthesis of Functional Polymers

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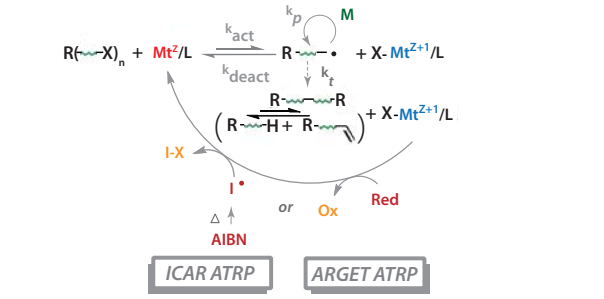
Introduction

Atom transfer radical polymerization (ATRP)[1-4] has emerged as one of the most successful synthetic techniques for the preparation of polymers with predetermined molecular weights, narrow molecular weight distributions, and high degrees of chain end functionalities (**Scheme 1**). The unprecedented control over molecular architecture afforded by the ATRP enables preparation of systematic polymer libraries.[5] **Scheme 1** exemplifies a systematic library of star-shaped polymers, where the polymers in each row have the same arm size and those in each column have the same number of arms. Such libraries can provide important data for understanding the relationships between polymer structure and physical properties or function.

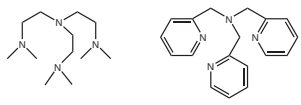


Scheme 1. Schematic illustration of the ATRP (top) and an example of a star-shaped polymer library.

Catalysts for ATRP

ATRP is catalytic process using a metal complex, in which the transition metal Mt can exist in two different oxidation states. The lower oxidation state metal complex Mt^z/L (L is a ligand) reacts with the ATRP initiator (alkyl halide RX) to yield a radical R• and the corresponding higher oxidation state metal complex with a coordinated halide anion X-Mt^{z+1}/L, in a process termed activation, proceeding with the rate constant, k_{act}. The latter complex can transfer the halogen atom back to the radical, re-generating the alkyl halide and the lower oxidation state metal complex. The radicals can react with the monomer M (generating polymer with the rate constant of propagation k_p), with each other (termination with the rate constant, k_t) or with X-Mt^{z+1}/L (deactivation with the rate constant, k_{deact}). The last step, which distinguishes ATRP from conventional radical polymerization, yields the halogen-terminated polymeric dormant state, which can be reactivated in a reaction with Mt^z/L. If the deactivation process is efficient (i.e., high value of k_{deact}) and if all polymer chains are initiated within a short period by appropriate selection of the alkyl halide initiator, the resulting polymer will be characterized by a narrow molecular weight distribution. Additionally, it is desirable to use an active catalyst with a high value of the ratio of k_{act} / k_{deact}, termed the ATRP equilibrium constant, k_{ATRP}, to ensure fast polymerization. The rate constants k_{act} and k_{deact} depend on both the transition metal and the ligand. Rules for the rational selection of active catalysts for ATRP for various reaction media and monomers have been developed.[2, 6]

Various metals and ligands have been successfully employed as catalysts in ATRP, but the most often used are the catalysts based on copper (the two oxidation states are Cu^I and Cu^{II}) and N-containing ligands. One drawback of the classical ATRP is the use of high amounts of the catalyst.[4] The obtained polymers are well-defined in terms of molecular weight distribution and chain-end functionality but require tedious purification to remove the catalyst. Although various methods for catalyst removal have been developed,[2, 7] the extra purification step is associated with longer time needed to obtain the final product, and with generation of waste, both of which increased the cost of the materials prepared by ATRP. However, the use of ligands such as tris[2-(dimethylamino)ethyl]amine (Me_6TREN, **Aldrich Prod. No. 723142**) and tris(2-pyridylmethyl)amine (TPMA, **Aldrich Prod. No. 723134**) alleviates this problem (**Figure 1**). These ligands can be used in new techniques called Activators ReGenerated by Electron Transfer (ARGET)[8, 9] and Initiators for Continuous Activator Regeneration (ICAR)[10] which allow to decrease amount of catalyst to only few, often single-digit, ppm. For comparison, 1,000 to 10,000 ppm were used in traditional ATRP. For many applications, in these new systems the residual copper can be left in the final colorless products. Both techniques employ a reducing agent: a radical initiator such as AIBN in ICAR ATRP;[10] and tin(II) ethylhexanoate[8, 9, 11-13] (**Aldrich Prod. No. S3252**), ascorbic acid,[14] glucose,[9] hydrazine,[10] or Cu(0)[15] in ARGET ATRP. These reducing agents allow for regeneration of the lower oxidation state metal complex, which would normally be irreversibly converted to the higher oxidation state complex due to radical termination by a process dubbed "persistent radical effect".[16]



Me_6TREN
Aldrich Prod. No. 723142

TPMA
Aldrich Prod. No. 723134

Figure 1. Ligands for Cu-mediated ATRP using ppm amounts of catalyst.

The ARGET and ICAR ATRP processes allow chemists to reduce the amount of catalyst more than one thousand times and the polymers obtained are white or colorless. These processes also allow preparation of well-defined block copolymers,[12] polymers with high molecular weight,[11, 17] high chain-end functionality[11] and adjustable molecular weight distribution.[18] In addition, since the level of control in an ARGET and ICAR ATRP is only weakly affected by an excess of reducing agent, the reaction can be successfully carried out in the presence of limited amounts of air.[13] Reactions can be carried out without deoxygenation, in flasks fitted with rubber septa or even in simple jars. This was demonstrated in our laboratory by placing functionalized wafers in one of these vessels and growing very dense polymer brushes (~0.4 chain/nm^2), including block copolymer brushes, without any deoxygenation. ATRP stops after opening the vessel to air but starts again when a sufficient amount of reducing agent is added to the closed flask. This polymerization process does not require any special skills and is especially well-suited for grafting from larger surfaces, but can also be applied for preparation of any other polymer materials. Only very active catalysts derived from Me_6TREN and TPMA can be used in these new techniques. **Figure 2** presents the kinetic plot, evolution of molecular weights and polydispersities with conversion and GPC traces for polymerization of styrene (St) with 50 ppm of $Cu^{II}Br_2$/TPMA catalyst in the presence of AIBN as reducing agent. Molecular weight control is excellent and follows theoretical values based on quantitative initiation. The polymer, after precipitation in hexane, appeared as a white solid powder containing only 5 ppm of the residual catalyst. If more Cu removal is needed, the *ATRP pure*® resin can be used.[5, 19]

Typical ICAR ATRP procedure

The following is a procedure employing very low concentration of copper catalyst that yields well-defined polystyrene macroinitiator (PSt-Br) with degree of polymerization 100. As shown in **Figure 2**, the polymerization is well-controlled: the linear first order kinetic plot of monomer consumption indicates constant number of active species and the increase of molecular weights with conversion is characteristic of a living process. Moreover, the obtained polymer was virtually colorless without the use of any special purification methods other than simple precipitation in hexane.

- Add $CuBr_2$ (7.8 mg, 3.5 × 10^{-2} mmol) and TPMA (10.1 mg, 3.49 × 10^{-2} mmol) to a 10 mL flask equipped with magnetic stirring bar.
- Add DMF (4 mL) to solubilize $CuBr_2$/TPMA. Stir for 10 min to obtain a homogeneous yellowish solution.
- Add St (80.0 ml, 0.698 mmol), AIBN (0.153 g, 0.0931 mmol) and ethyl 2-bromoisobutyrate (0.68 mL, 4.65 mmol) to a 200-mL round bottom flask equipped with a magnetic stirring bar.
- Transfer the catalyst solution to the 200 mL round bottom flask reactor.
- Close the flask reactor with glass adapter (with glass stopcock and a rubber septum). Stir the solution while purging with nitrogen for 1 h.
- Place the flask in an oil bath at 70 °C. To follow the progress of the reaction, samples can be withdrawn with a stainless steel needle. The samples can be analyzed by GC or NMR (monomer conversion) and SEC (molecular weight and polydispersity).
- After 20.5 h*, the monomer conversion reaches 69 %. M_n = 9,700 g/mol, PDI = 1.11. The reactor is opened to air and allowed to cool to room temperature.
- Dilute the polymer with THF (100 mL) and precipitate into 2 L of hexane.
- Dry the produced polymer at 45 °C to constant weight (ca. 24 h).

* Time of the reaction may vary depending on a type of used equipment and purity of chemical reagents.

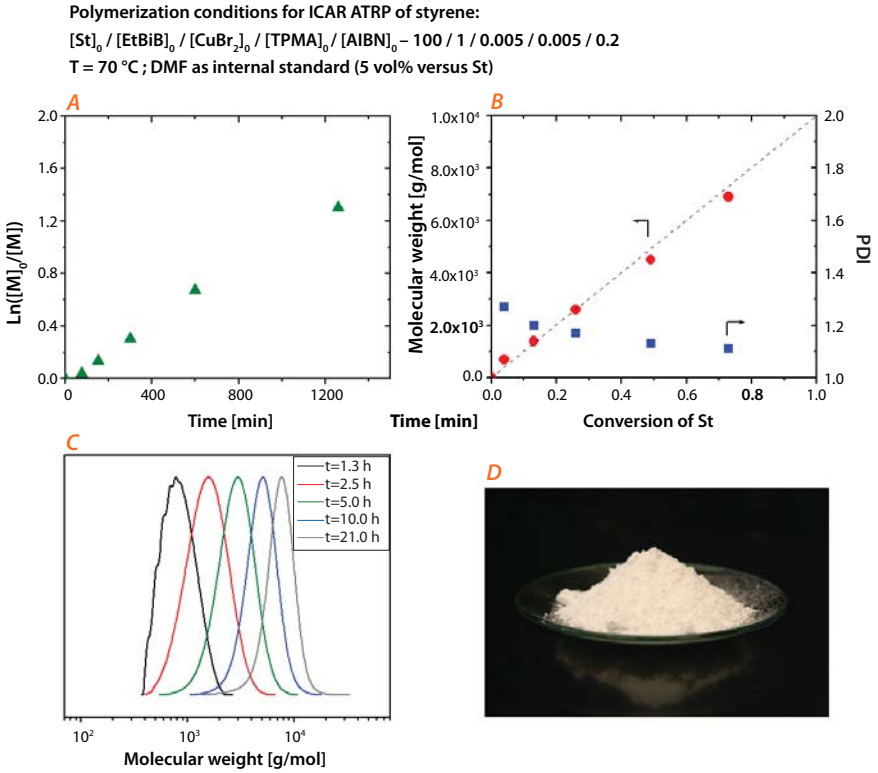
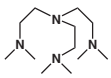
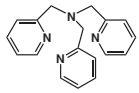
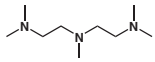
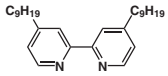


Figure 2. ICAR ATRP of styrene (St) using 50 ppm of catalyst. (a) Kinetic plot (b) Molecular weight and polydispersity as a function of conversion (c) Evolution of GPC traces (d) Photograph of polymer after precipitation in hexane

It is interesting to compare the results of ICAR ATRP employing Me_6TREN or TPMA with the process under similar conditions but with other catalysts, derived from ligands, such as the traditionally used derivatives of 2,2-bipyridine (bpy) (ex., **Aldrich Prod. No.** 482250) or N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, **Aldrich Prod. No.** 369497).

As seen from **Table 1**, only the polymerizations mediated by the complexes of Me_6TREN and TPMA (the first two entries) were well-controlled and yielded polymers with narrow molecular weight distribution.[10] In all cases, only 50 ppm of Cu was employed.

Table 1. ICAR ATRP of St initiated by ethyl 2-bromoisobutyrate (EBiB) in the presence of various Cu-based catalysts.

St / EBiB / CU^{II} / AIBN (60 °C, in anisole, (50 vol % vs. St))	Ligand	Cu (ppm)	Time (min)	Conv. (%)	M_n (theor.)	M_n (SEC)	*PDI*
200/1/0.01/0.1	0.01	50	2760	44	8700	7900	1.12
Me_6TREN							
200/1/0.01/0.1	0.01	50	2880	39	7800	6800	1.09
TPMA							
200/1/0.01/0.1	0.01	50	2880	29	5600	4500	1.62
PMDETA							
200/1/0.01/0.1	0.02	50	2940	36	7200	5600	1.68
dNbpy							

Me_6TREN and TPMA were successfully used in ICAR and ARGET ATRP of various monomers such as styrene,[9-11] methyl acrylate,[15] butyl acrylate,[8] methyl methacrylate,[8, 12] butyl methacrylate,[20] dimethylaminoethyl methacrylate[21] and acrylonitrile.[17, 22] They can also be used in classical ATRP of coordinating monomers such as, for example, 4-vinylpyridine (**Aldrich Prod. No.** V3204). Rate of ICAR ATRP is not affected by the catalysts but it is defined by the rate of decomposition of the radical initiator and can be significantly accelerated at higher temperatures.

Block Copolymers

Block copolymers continue to remain a subject of intense research and technological interest due to their unusual and useful properties.[23, 24] Current and potential high-technology applications of block copolymers are based on their ability to self-assemble, in bulk as well as in selective solvents, into ordered nanostructures. For example, block copolymers with hydrophilic and hydrophobic segments self-assemble, both in the solid state and in the solution, to generate a variety of nano-scale structures. The structures range from simple micellar or lamellar to complex gyroid. Recent studies on block copolymer self assembly demonstrated that nano-scale morphology is highly dependent on block chain length, chain length ratios, polydispersity index, and block composition. Therefore, it is essential to precisely control the degree of polymerization of each segment in the block copolymer and achieve narrow molecular weight distribution. ATRP is a convenient technique for preparation of block copolymers because the growing polymer chain contains a stable halogen terminated ω-end that can act as an initiator for chain extension.

Figure 3 presents GPC traces of polystyrene-*b*-poly(*t*-butyl acrylate) (PSt-*b*-P*t*BA) as an example of synthesis of a block copolymer library.[5] In order to synthesize these copolymers ICAR and ARGET ATRP were used with similar conditions as described above. This library can be then converted to polymeric surfactants polystyrene-*b*-poly(acrylic acid) (PSt-*b*-PAA) by deprotection of *t*-butyl groups. PSt-*b*-PAA copolymers may be used as polymeric surfactants in many applications such as particle dispersants (organic, inorganic and metals), nano-device delivery vehicles, blend compatibilizers, coatings, surface modifiers, detergents, and emulsifiers. The broad range of compositions and molecular weights provided by each polymeric library synthesized by ATRP allows rapid screening and identification of the optimal structure for the particular application. Several systematic polymeric libraries are now commercially available.[19]

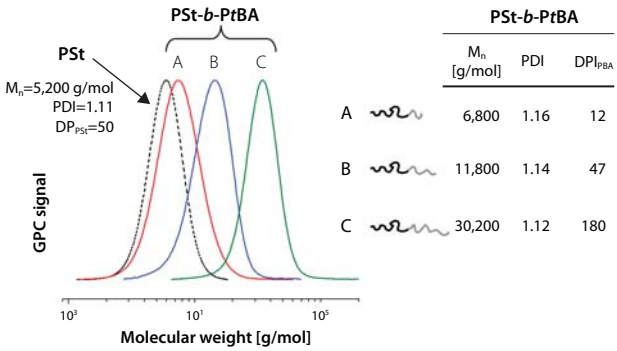


Figure 3. GPC traces and properties of PSt-*b*-PtBA block copolymer library.

Initiators for ATRP

ATRP uses simple initiators, mainly alkyl halides R-X (X = Cl, Br).[1, 25, 26] The number-average molecular weight M_n of polymers prepared by ATRP depends on the initial concentration ratio of monomer (M) to initiator as well as the monomer conversion:

$$M_n = ([M]_0 / [RX]_0) \times Conv \times M_W(M)$$

where $[M]_0$ is the initial monomer concentration, $[RX]_0$ is the initial concentration of alkyl halide, Conv is the monomer conversion, and $M_W(M)$ is the molecular weight of the monomer. The alkyl halides used as initiators can contain either one or numerous halogen atoms. Depending on the exact initiator structure and the number of halogen atoms, the architecture of the prepared polymers can be varied from linear (using alkyl halides with a single halogen atom), to star-like or brush-like (multiple halogen atoms in the initiator). Star polymers can be generated using initiators with alkyl halide groups attached to a single core (**Figure 4**), whereas to obtain brush polymers, the halide groups should be attached along the backbone of a polymer or a large molecule or nanoparticle with a high aspect ratio (e.g., a carbon nanotube).

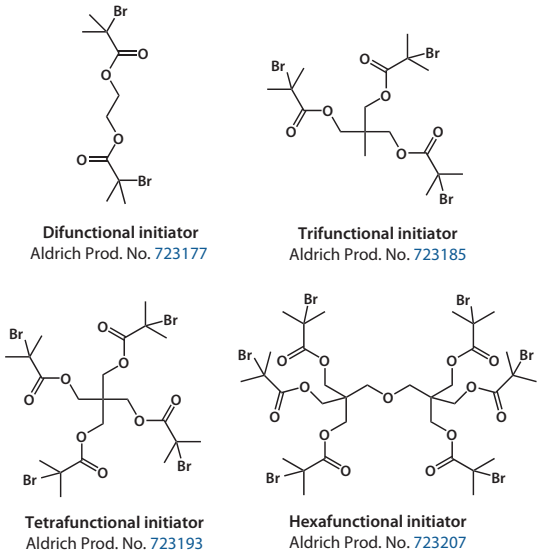


Figure 4. Examples of ATRP initiators yielding polymeric stars.

Four major strategies exist for the synthesis of polymers with functional groups via ATRP: i) direct polymerization of functional monomers, ii) polymerization of "protected" monomers followed by post-polymerization chemical transformations, iii) the use of functional initiators, and iv) substitutions of the terminal halogen atom. The first two approaches yield polymers with multiple functionalities along the backbone whereas the last two yield end-functionalized polymers. **Figure 5** illustrates structures of alkyl halide functional initiators that yield end-functionalized polymers. Groups such as hydroxy are suitable for the synthesis of polymers that can react with molecules, or surfaces with carboxylic acid groups. Allyl group-containing initiators yield polymers that can participate in hydrosilylation or ene reactions with polymers or surfaces containing Si-H or S-H bonds, respectively. Trichlorosilyl groups react with surfaces containing hydroxy or amine groups (including Si-OH bonds), such as those on the surface of silica particles or glass.

Finally, disulfide-containing difunctional initiators yield polymers containing a functional group able to react with gold surfaces, and also gives the polymers the ability to degrade in reducing environments.

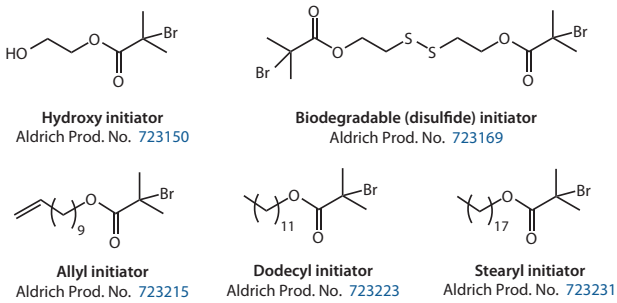


Figure 5. Examples of ATRP initiators that can be used to prepare end-functionalized and disulfide containing polymers.

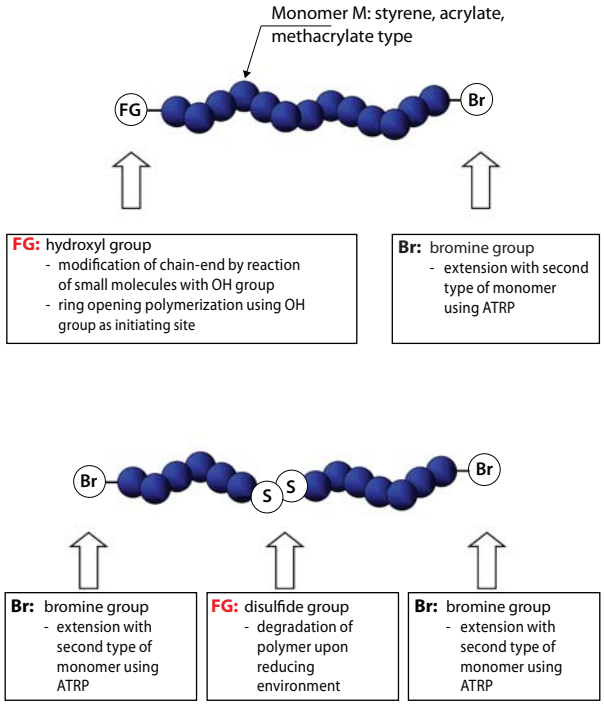


Figure 6. Examples of end-functionalized polymers prepared by ATRP using an initiator with a hydroxy or disulfide functional group (FG).

A much broader variety of functional alkyl halides can be easily custom-synthesized.[1] Several concepts for functional polymer architectures that can be prepared using functionalized ATRP initiators are further illustrated in **Figure 6**. It should be emphasized that the polymers prepared by ATRP contain two chain ends: the α-end (FG) derived from the initiator and the ω-end, which is normally a bromine or chlorine atom. Alkyl halides can participate in a number of nucleophilic substitution reactions, which expands significantly the types of end-functional polymers accessible through ATRP.[25]

Summary

The number of materials and commercial products that use polymers either in a pure form or as a part of more complex mixtures, blends, and composites, is countless. The properties and application of polymers depend not only on the molecular size but also on the molecular shape and composition.[27] Today, ATRP is one of the most powerful polymer synthetic methods which allows control over molecular architecture, as evidenced by over one hundred patent applications, over a thousand journal articles published annually, and also in a number of commercial products made in US, Japan and Europe. Due to recent advancements in initiation processes (ARGET and ICAR ATRP) it is relatively easy to perform any polymerization reaction and the purification of the final products is now easier, while generating a minimum amount of waste.

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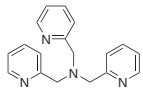
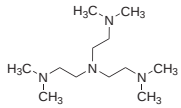
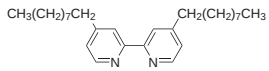
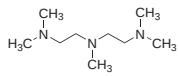
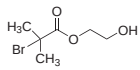
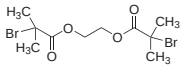
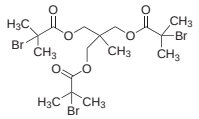
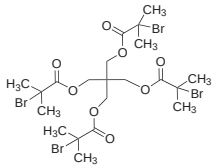
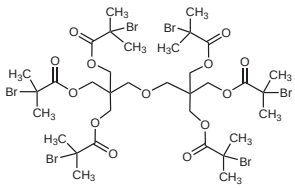
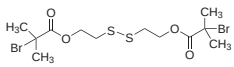
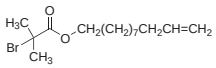
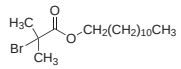
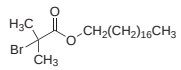
Ligands for ATRP

Name	Structure	Cat. No.
Tris(2-pyridylmethyl)amine, TPMA		723134-250MG 723134-1G
Tris[2-(dimethylamino)ethyl]amine, Me_6TREN		723142-1ML
4,4′-Dinonyl-2,2′-dipyridyl, dNbpy		482250-1G 482250-5G
N,N,N′,N″,N″-Pentamethyldiethylenetriamine, PMDETA		369497-250ML 369497-1L

ATRP Initiators

For a complete description of available ATRP initiators including purities, please visit *sigma-aldrich.com/poly*

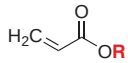
Name	Structure	Description	Cat. No.
2-Hydroxyethyl 2-bromoisobutyrate		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of hydroxy functionalized telechelic polymers. Can be used to modify carboxylate- or isocyanate- modified surfaces, particles or biomolecules.	723150-1G 723150-5G
Ethylene bis(2-bromoisobutyrate)		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of difunctional polymers.	723177-1G 723177-5G
1,1,1-Tris(2-bromoisobutyryloxymethyl)ethane		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of trifunctional polymers.	723185-1G 723185-5G
Pentaerythritol tetrakis(2-bromoisobutyrate)		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of tetrafunctional polymers.	723193-1G 723193-5G
Dipentaerythritol hexakis (2-bromoisobutyrate)		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of hexafunctional polymers.	723207-1G 723207-5G
Bis[2-(2′-bromoisobutyryloxy)ethyl]disulfide		Atom Transfer Radical Polymerization (ATRP) initiator for the preparation of biodegradable polymers as well as polymers that adhere to gold surfaces.	723169-1G 723169-5G
10-Undecenyl 2-bromoisobutyrate		Atom Transfer Radical Polymerization (ATRP) initiator that reacts with surfaces containing S-H bonds. Precursor of various silane-containing polymers and initiators. Hydrosilation with Cl_3SiH yields an initiator that reacts with glass surfaces.	723215-1G 723215-5G
Dodecyl 2-bromoisobutyrate		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of dodecyl functionalized telechelic polymers.	723223-1G 723223-5G
Octadecyl 2-bromoisobutyrate		Atom Transfer Radical Polymerization (ATRP) initiator for the creation of stearyl functionalized telechelic polymers.	723231-1G 723231-5G

Metal Catalysts for ATRP

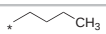
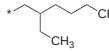
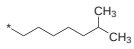
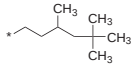
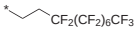
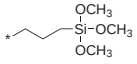
Name	Formula	Purity	Cat. No.
Copper(I) chloride	CuCl	≥99.995% trace metals basis	229628-10G 229628-100G
Copper(II) chloride	$CuCl_2$	99.999% trace metals basis	203149-10G 203149-50G
Copper(I) bromide	CuBr	99.999% trace metals basis	254185-10G 254185-100G
Copper(II) bromide	$CuBr_2$	99.999% trace metals basis	437867-5G 437867-25G
Copper(I) iodide	CuI	99.999% trace metals basis	215554-5G 215554-25G 215554-100G

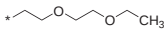
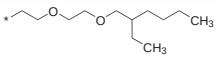
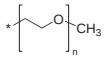
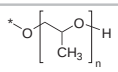
Acrylate Monomers

For a complete list of available acrylate monomers, please visit *sigma-aldrich.com/acrylic*

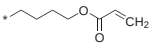
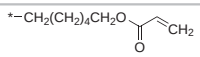
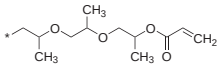
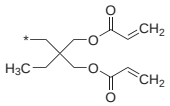
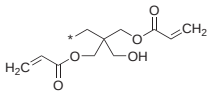
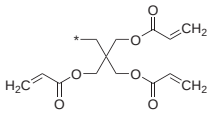
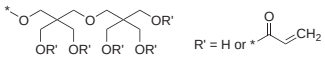


Monofunctional Acrylate Monomers

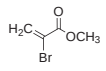
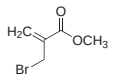
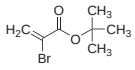
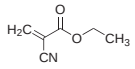
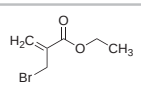
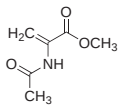
Name	R Group	Purity	Additive	Cat. No.
Sodium acrylate	*—Na	97%	-	408220-25G 408220-100G
Methyl acrylate	*—CH_3	99%	monomethyl ether hydroquinone 100 ppm as inhibitor	M27301-5ML M27301-250ML M27301-1L M27301-2L M27301-18L
Ethyl acrylate		99%	hydroquinone monomethyl ether 15-20 ppm as inhibitor	E9706-100ML E9706-1L E9706-2L
Butyl acrylate		≥99%	monomethyl ether hydroquinone 10-55 ppm as inhibitor	234923-100ML 234923-1L 234923-18L
Hexyl acrylate	*—$CH_2(CH_2)_4CH_3$	98%	hydroquinone 100 ppm as inhibitor	408905-25ML 408905-100ML
Lauryl acrylate	*—$CH_2(CH_2)_{10}CH_3$	90%	monomethyl ether hydroquinone 60-100 ppm as inhibitor	447315-100ML 447315-500ML
Octadecyl acrylate	*—$CH_2(CH_2)_{16}CH_3$	97%	-	409693-250G 409693-1KG
tert-Butyl acrylate		98%	monomethyl ether hydroquinone 10-20 ppm as inhibitor	327182-5ML 327182-100ML 327182-1L
Isobutyl acrylate		≥99%	monomethyl ether hydroquinone 10-20 ppm as stabilizer	436305-250ML 436305-1L
2-Ethylhexyl acrylate		98%	monomethyl ether hydroquinone 10 ppm as inhibitor	290815-25ML 290815-1L 290815-3L 290815-18L
Isooctyl acrylate		-	monomethyl ether hydroquinone 75-125 ppm as inhibitor	437425-100ML 437425-500ML
3,5,5-Trimethylhexyl acrylate		-	monomethyl ether hydroquinone 15-20 ppm as inhibitor	424021-25ML
1*H*,1*H*,2*H*,2*H*-Perfluorodecyl acrylate		97%	monomethyl ether hydroquinone 100 ppm as inhibitor	474487-5ML 474487-25ML
2-Hydroxyethyl acrylate		96%	monomethyl ether hydroquinone 200-650 ppm as inhibitor	292818-250ML 292818-1L 292818-18L
Hydroxypropyl acrylate, mixture of isomers		95%	hydroquinone monomethyl ether 200-650 ppm as inhibitor	370932-1L 370932-18L
4-Hydroxybutyl acrylate		90%	hydroquinone 300 ppm as inhibitor monomethyl ether hydroquinone 50 ppm as inhibitor	275573-25G
2-Carboxyethyl acrylate		-	-	552348-50ML 552348-500ML
2-(Dimethylamino)ethyl acrylate		98%	monomethyl ether hydroquinone 1,000 ppm as inhibitor	330957-100ML 330957-500ML
Isobornyl acrylate		-	MEHQ 200 ppm as inhibitor	392103-100ML 392103-500ML 392103-1L
Pentabromophenyl acrylate		96%	-	592552-5G
Pentabromobenzyl acrylate		98%	-	640263-1G 640263-5G
3-(Trimethoxysilyl)propyl acrylate		92%	BHT 100 ppm as inhibitor	475149-5ML 475149-25ML

Name	R Group	Purity	Additive	Cat. No.
Di(ethylene glycol) ethyl ether acrylate		≥90%	monomethyl ether hydroquinone 1000 ppm as inhibitor	408298-5ML 408298-250ML 408298-1L
Di(ethylene glycol) 2-ethylhexyl ether acrylate		-	monomethyl ether hydroquinone 500 ppm as inhibitor	407542-100ML
Poly(ethylene glycol) methyl ether acrylate		-	BHT 300 ppm as inhibitor MEHQ 100 ppm as inhibitor	454990-250ML 454990-1L
Poly(propylene glycol) acrylate		-	MEHQ 200-400 ppm as inhibitor	469815-100ML 469815-500ML

Polyfunctional Acrylate Monomers

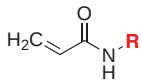
Name	R Group	Additive	Cat. No.
1,4-Butanediol diacrylate		hydroquinone ~75 ppm as inhibitor	411744-25ML 411744-100ML
1,6-Hexanediol diacrylate		monomethyl ether hydroquinone 100 ppm as inhibitor	246816-100G 246816-500G
Tri(propylene glycol) diacrylate, mixture of isomers		monomethyl ether hydroquinone 250 ppm as inhibitor	246832-100G 246832-500G
Trimethylolpropane triacrylate		monomethyl ether hydroquinone 100 ppm as inhibitor	246808-5G 246808-100G 246808-500G
Pentaerythritol triacrylate		monomethyl ether hydroquinone 300-400 ppm as inhibitor	246794-100G 246794-500G
Pentaerythritol tetraacrylate		monomethyl ether hydroquinone 350 ppm as inhibitor	408263-5ML 408263-100ML 408263-250ML
Dipentaerythritol penta-/hexa-acrylate		monomethyl ether hydroquinone 500 ppm as inhibitor	407283-100ML 407283-500ML

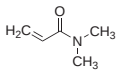
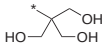
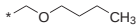
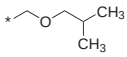
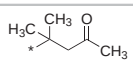
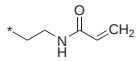
α-Substituted Acrylate Monomers

Name	Structure	Purity	Cat. No.
Methyl α-bromoacrylate		98%	588466-1G
Methyl 2-(bromomethyl)acrylate		97%	302546-1G 302546-5G
tert-Butyl 2-bromoacrylate		95%	588458-1G
Ethyl 2-cyanoacrylate		-	E1505-5G E1505-10G
Ethyl 2-(bromomethyl)acrylate		98%	425222-1G 425222-5G
Methyl 2-acetamidoacrylate		98%	317519-1G 317519-5G

Acrylamide Monomers

For a complete list of available acrylamide and methacrylamide monomers, please visit *sigma-aldrich.com/acrylic*



Name	R Group	Purity	Additive	Cat. No.
N,N-Dimethylacrylamide		99%	monomethyl ether hydroquinone 500 ppm as stabilizer	274135-5ML 274135-100ML 274135-500ML
Acrylamide		≥99%	-	A8887-100G A8887-500G A8887-1KG A8887-2.5KG
N-Isopropylacrylamide		97%	-	415324-10G 415324-50G
N-*tert*-Butylacrylamide		97%	-	411779-100G
N-(Hydroxymethyl)acrylamide solution		-	monomethyl ether hydroquinone 30 ppm as inhibitor	245801-5G 245801-100G 245801-1KG
N-Hydroxyethyl acrylamide		97%	monomethyl ether hydroquinone 3,000 ppm as stabilizer	697931-100ML
N-[Tris(hydroxymethyl)methyl] acrylamide		93%	-	364959-5G 364959-25G
N-(Butoxymethyl)acrylamide		-	hydroquinone monomethyl ether 100 ppm as inhibitor	461067-100ML
N-(Isobutoxymethyl)acrylamide		-	monomethyl ether hydroquinone 200 ppm as inhibitor	436534-100ML
Diacetone acrylamide		99%	-	222348-5G 222348-100G 222348-500G
N,N'-Ethylenebis(acrylamide)		-	-	358878-5G
N-Phenylacrylamide		99%	-	530042-10G

Asymmetric Polymerization in a Chiral Liquid Crystal Reaction Field

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Introduction

It is well known that polyacetylene is a one-dimensional conjugated macromolecule and a good representative for conducting polymers.[1] Pristine polyacetylene is a typical semiconductor, but its electrical conductivity can be amplified by over 14 orders of magnitude through doping.[2,3] The maximum conductivity reported to date is more than 10^5 S/cm,[4] which is comparable to those of copper and gold. It has been generally accepted that polyacetylene has a planar structure, irrespective of cis and trans forms, due to the strong π-conjugation between the sp^2 hybridized carbon atoms in the polymer chain. If it were possible to modify such a planar structure of polyacetylene into a helical one,[5,6] one might expect novel electromagnetic and optical properties.[7,8] Here, we present a modern polymerization method for acetylene in an asymmetric reaction field using a chiral nematic liquid crystal (N*-LC) which is also called a cholesteric LC, which demonstrates the formation of a polyacetylene film comprised of helical chains and fibrils.[6,9-14] Polymerization that results in helical geometry from primary to higher-order spiral morphology is discussed.

Chiral Dopants and N*-LCs

The N*-LC to be used as an asymmetric solvent is prepared by adding a small amount of chiral compound, which serves as a chiral dopant, into a nematic LC (**Figure 1**). The formation of a N*-LC is recognized when the Schlieren texture characteristic of the nematic LC changes into a striated Schlieren or a fingerprint texture as seen under a polarized optical microscope (POM). The distance between the striae corresponds to half the helical pitch of the N*-LC. Note that as the degree of twisting in the N*-LC increases, the observed helical pitch is reduced.

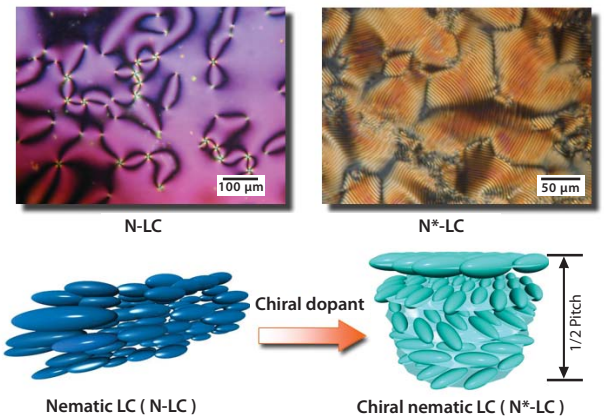

Figure 1. Chiral nematic LC (N*-LC) induced by an addition of chiral dopant into nematic LC. Schlieren texture (left) and fingerprint texture (right) are observed for nematic and chiral nematic LCs, respectively, in polarized optical microscope.

The helical pitch of the N*-LC can be adjusted by two methods: changing the concentration or changing the twisting ability of the chiral dopant. It should be noted however that changing the concentration of the chiral dopant affects the mesophase temperature region of the N*-LC. Namely, it becomes narrower as the dopant concentration increases, eventually resulting in destruction of the mesophase when the concentration reaches a critical value. As a result, the alternative approach of using a chiral compound with greater twisting ability is employed. Axially chiral binaphthyl derivatives are good candidates for chiral dopants,[15] since they have been reported to possess larger twisting abilities than asymmetric carbon containing chiral compounds.[16] (*R*)- & (*S*)-1,1′-bi-naphthyl-2,2′-di-[*para*-(*trans*-4-*n*-pentyl-cyclohexyl)phenoxy-1-hexyl]ether were synthesized through Williamson etherification reactions of optically pure (*R*)-(+)- and (*S*)-(-)-1,1′-bi-2-naphthols respectively which have been functionalized with phenyl-cyclohexyl derivatives. These materials will be referred to as (*R*)- and (*S*)-PCH506-Binol (**Figure 2**). The substituent is composed of a phenyl-cyclohexyl (PCH) moiety, an *n*-pentyl group (5 carbon chain), and a hexamethylene chain linked with an ether-type oxygen atom, [-$(CH_2)_6$O- , 06], and thus abbreviated as PCH506.

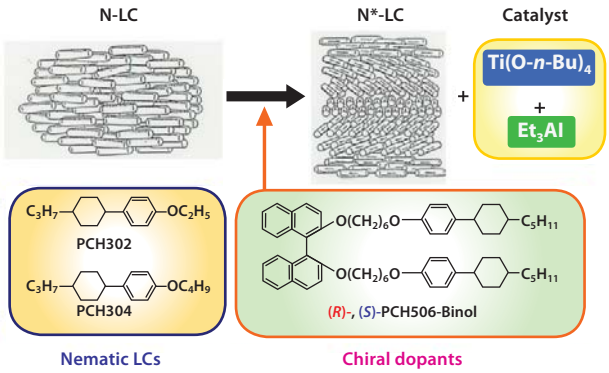

Figure 2. Construction of asymmetric reaction field for acetylene polymerization by dissolving Ziegler-Natta catalyst, Ti(O-*n*-Bu)$_4$ – AlEt$_3$, into the chiral nematic LC. The N*-LC includes an axially chiral binaphthyl derivative, (*R*)- or (*S*)- 2,2′-PCH506-Binol.

To prepare an induced chiral nematic LC, 5-14 weight % of (*R*)- or (*S*)-PCH506-Binol was added as a chiral dopant to an equimolar mixture of the nematic LCs 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene (PCH302) and 4-(*trans*-4-*n*-propylcyclohexyl) butoxybenzene (PCH304). The PCH506 substituent group in the (*R*)- and (*S*)-PCH506-Binol enhances the miscibility between the nematic LC mixture and the binaphthyl derivative used as the chiral dopant. Usage of a similar substituent with a shorter methylene spacer such as PCH503 or normal alkyl substituent gave insufficient miscibility, yielding no chiral nematic phase. In polarizing optical micrographs of the mixture of PCH302, PCH304, and (*R*)-PCH506-Binol (abbreviated as *R*-1) and that of PCH302, PCH304, and (*S*)-PCH506-Binol (abbreviated as *S*-1), a striated Schlieren or a fingerprint-type texture, characteristic of chiral nematic LC phases, is observed (**Figure 1**).

Acetylene Polymerization in N*-LC

At first it should be noted that although each component (PCH302 or PCH304) shows a LC phase, the LC temperature region is very narrow, i.e., less than 1 to 2 °C. This would be unsuitable for acetylene polymerization in a nematic LC or N*-LC reaction field, because the exothermal heat evolved during the acetylene polymerization would raise the temperature inside the reaction flask, and destroy the LC phase creating an isotropic one. Hence, an appropriate LC mixture is prepared by mixing the two LC components in equal amounts. In the LC mixture, the nematic-isotropic temperature, T_{N-I}, is raised while the crystalline-nematic temperature, T_{C-N}, is lowered. In fact, the mixture exhibited the LC phase in the 20 to 35 °C region. Subsequently, the change of T_{N-I} upon an addition of Ti(O-*n*-Bu)$_4$ - AlEt$_3$ catalyst was examined through DSC measurement. Even after taking into account the effect of supercooling for LCs, the catalyst solution consisting of the LC mixture and the chiral dopant had an available temperature range for polymerization from 5 to 25 °C. This sufficiently wide temperature region enabled us to perform the acetylene polymerization in the N*-LC phase.

The Ziegler-Natta catalyst consisting of Ti(O-*n*-Bu)$_4$ and Et$_3$Al was prepared using the (*R*)- or (*S*)-chiral nematic LC as a solvent (**Figure 2**). The concentration of Ti(O-*n*-Bu)$_4$ was 15 mmol/L, and the mole ratio of the cocatalyst to catalyst, [Et$_3$Al] / [Ti(O-*n*-Bu)$_4$], was 4.0. The catalyst solution was aged for 30 min at room temperature. During the aging, the N*-LC containing the catalyst showed no noticeable change in optical texture, and only a slight lowering of the transition temperature by 2 to 5 °C. The transition temperature between the solid and chiral nematic phases was 16 to 17 °C, and that between the chiral nematic and isotropic phases was 30 to 31 °C. No solidification was observed down to -7 °C as a result of supercooling. Thus the (*R*)- and (*S*)-chiral nematic LCs are confirmed to be chemically stable in the presence of the catalyst. It is therefore suitable to employ these LCs as an asymmetric solvent for acetylene polymerization. Acetylene gas (99.9999 % purity) was used without further purification. The polymerization temperature was kept between 17 to 18 °C to maintain the chiral nematic phase, by circulating cooled ethanol through an outer flask covering the flask. The initial acetylene pressure was 11.6 to 22.6 Torr and the polymerization time was between 10 to 43 minutes. After polymerization, the polyacetylene films were carefully removed from the container and washed with toluene several times under argon gas at room temperature. The films were dried under vacuum on a PTFE sheet and stored in a freezer at -20 °C.

Characterization of Helical Polyacetylene Film

Scanning electron microscope (SEM) images of the polyacetylene films show that multiple domains of spiral morphology are formed (**Figure 3**), and each domain is composed of a helical structure of fibrils with one-handed twist direction (**Figure 3 inset**). The multi-domain type fibril morphology of polyacetylene seems to replicate that of the N*-LC used in the interfacial acetylene polymerization.

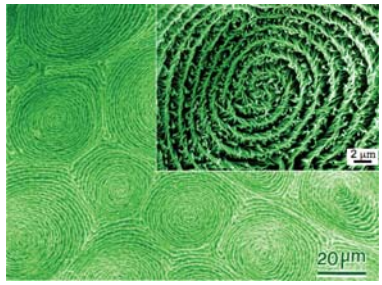

Figure 3. Hierarchical spiral morphology of helical polyacetylene film. The figure and inset show scanning electron microscope (SEM) photographs of multi domain type spiral morphology and right-handed screwed bundles of fibrils in a domain, respectively.

Closer observation of SEM images indicates that helical polyacetylenes synthesized in the (*R*)- and (*S*)-chiral N*-LCs form the twisted bundles of fibrils and even screw-shaped fibrils with counterclockwise and clockwise directions, respectively. This result implies that the twist direction of helical polyacetylene is controllable by choosing the helicity, i.e., chirality of the dopant, when the N*-LC induced by the chiral dopant is employed as an asymmetric polymerization solvent. The helical pitch of the N*-LC depends on the helical twisting ability of the chiral dopant, as well as its concentration and optical purity. This means that the helical pitch of the polyacetylene chain can be also varied by changing helical twisting ability of the chiral dopant. Another axially chiral dopant, (*R*)- or (*S*)-6,6′-PCH506-2,2′-Et-Binol[14,15] gave a shorter helical pitch of N*-LC by 0.3 µm than the corresponding (*R*) or (*S*)-PCH506-Binol. Acetylene polymerization using these types of highly twisted N*-LCs, designated (*R*-2)- and (*S*-2)-chiral nematic LCs, afforded clearer spiral morphologies consisting of helical bundles of fibrils (**Figure 4**). Namely, these bundles are aligned parallel to each other in the microscopic regime, and forms spiral morphologies in the macroscopic regime. It is noteworthy that the higher order structures observed in **Figure 3** resemble the helical self-assembled microstructure of biological molecules such as lipids, which are rarely formed in synthetic polymers. This validates the use of N*-LC as a template polymerization medium for controlling a higher order structure of synthetic polymer.

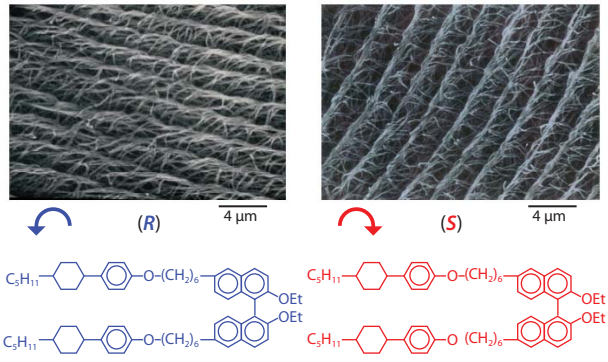

Figure 4. SEM photographs of helical polyacetylene films synthesized in the N*-LCs including (*R*)- 6,6′-PCH506-2,2′-Et-Binol. The left- and right-handed screw directions of helical polyacetylenes are determined by the chirality of the chiral dopants with *R*- and *S*-configurations, respectively.

The bundles of fibrils for helical polyacetylenes synthesized in the (*R*-2)- and (*S*-2)-N*-LCs are twisted counterclockwise and clockwise, respectively (**Figure 4**). The hardness of helical polyacetylene are opposite to those of the corresponding (*R*-2)- and (*S*-2)-N*-LC whose directions are confirmed to be clockwise and counterclockwise, respectively, through the miscibility test with cholesteryl oleyl carbonate (**Aldrich Prod. No. 151157**). This is the same situation as the case of the (*R*-1)- and (*S*-1)-N*-LCs including (*R*)- and (*S*)-PCH506-Binol. In circular dichroism (CD) spectra of the polyacetylene thin films synthesized under the (*R*-2)- and (*S*-2)-chiral nematic LCs, positive and negative Cotton effects are observed respectively in the region from 450 to 800 nm corresponding to π -> π^* transition of polyacetylene chain, despite the absence of chiroptical substituent in side chains. This indicates that the polyacetylene chain itself is helically twisted. It is evident that the above Cotton effect is not due to the chiral dopant [(*R*)- or (*S*)- 6,6′-PCH506-2,2′-Et-Binol], because the Cotton effect of the chiral dopant is only observed at shorter wavelengths such as 240 ~ 340 nm. From these results, it can be concluded that left-handed (counterclockwise) and right-handed (clockwise) helical polyacetylene chains are formed in (*R*)- and (*S*)-chiral nematic LCs, respectively, and that these helical chains are bundled through van der Waals interactions to form helical fibrils with the opposite helical directions to those of the N*-LCs. The bundles of fibrils further form the spiral morphology with various sizes of domains (**Figure 5**).

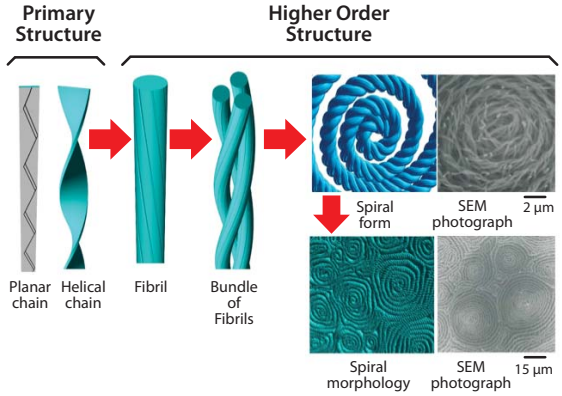

Figure 5. Super-hierarchical helical structures from primary to higher order in helical polyacetylene.

The present helical polyacetylene films have high trans content of 90%, and become highly conductive upon iodine doping. In fact, the electrical conductivities of the doped films are 1.5 ~ 1.8 × 10^3 S/cm at room temperature, which are comparable to those of metalic materials. The iodine-doped polyacetylene showed the same Cotton effect as that of non-doped polyacetylene, although the CD peak was slightly shifted to shorter wavelengths. This indicates that the helical structure is preserved even after iodine doping. Furthermore, CD and X-ray diffraction measurements showed that the helical structure was also preserved after heating up to 150 °C (which corresponds to the isomerization temperature from cis to trans form). It is well-known that the most stable structure of polyacetylene is the planar one. However, since the polyacetylene is actually insoluble and infusible, the helical structure formed during the polymerization can be preserved even if it is washed by toluene (**Aldrich Prod. No. 244511**) or thermally heated below the isomerization temperature. In other words, the insolubility and infusibility characteristics of polyacetylene are important for preserving the meta-stable helical structure.[17] Lastly, it is worth noting that the present polymerization method using the N*-LC (i.e., cholesteric LC) as an asymmetric reaction field has profound versatility for the synthesis of helical π-conjugated polymers that do not contain chiral substituents in side chains. In fact, very recently, a number of helical conjugated polymers such as polybithiophene, polyethylenedioxythiophene derivatives, and phenylene-thiophene copolymers were synthesized through chemical and/or electrochemical polymerizations in N*-LCs environments.[18-20]

Conclusion

We present current progress in the synthesis and also the novel properties of conjugated polymers by focusing on helical polyacetylene with super-hierarchical structure.[14] Interfacial polymerization of acetylene was carried out in asymmetric reaction field consisting of a N*-LC and a Ziegler-Natta catalyst. Since the N*-LC is composed of a nematic LC and a chiral compound such as axially chiral binaphthyl derivative with *R*- or *S*-configuration, the helical directions of polyacetylene chain and fibril bundles and even the spiral morphology are determined by the chirality of the chiral dopant. The helical directions of the fibril and the bundle of the fibril in helical polyacetylene were found to be opposite to that of the N*-LC. The hierarchical spiral morphology involving the primary and higher order structures is generated in a synthetic polymer such as polyacetylene by using N*-LC as an asymmetric polymerization solvent.

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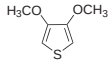
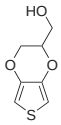
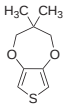
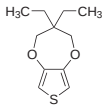
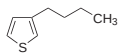
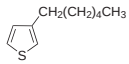
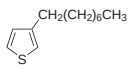
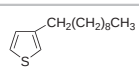
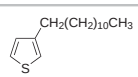
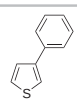
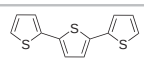
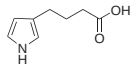
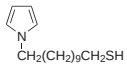
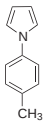
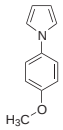
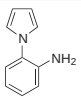
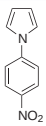
Thiophene and Pyrrole Monomers

Thiophene and pyrrole monomers are easily polymerized electrochemically or using simple chemical polymerization methods to form electroactive polymers. These polymerizations can be carried out in liquid crystal templates, similar to the methodology described in the article by Professor Akagi. Here we list a selection of thiophene and pyrrole monomers.

For a complete list of available thiophene and pyrrole monomers and other synthetic tools, please visit *sigma-aldrich.com/synthetic*

Name	Structure	Purity	Cat. No.
Thiophene		≥99%	T31801-5G T31801-100G T31801-500G
3,4-Dimethoxythiophene		97%	668257-5G
3,4-Ethylenedioxythiophene		-	483028-10G
Hydroxymethyl EDOT		97%	687553-500MG
3,4-Propylenedioxythiophene		97%	660485-100MG 660485-500MG
3,4-(2,2-Dimethylpropylenedioxy)thiophene		97%	660523-500MG
3,4-(2′,2′-Diethylpropylene)dioxythiophene		97%	669210-250MG
3-Methylthiophene		≥98.0%, GC	69370
3-Thiopheneethanol		99%	228796-5G 228796-25G
3-Butylthiophene		96%	510424-1G 510424-5G
3-Hexylthiophene		≥99%	399051-1G 399051-5G
3-Octylthiophene		97%	424285-1G 424285-5G
3-Decylthiophene		97%	456357-5G
3-Dodecylthiophene		97%	456365-1G 456365-5G
3-Phenylthiophene		95%	399043-1G
2,2′-Bithiophene		97%	241636-10G
2,2′:5′,2″-Terthiophene		99%	311073-1G

Name	Structure	Purity	Cat. No.
Pyrrole		98%	131709-25ML 131709-100ML 131709-500ML
3,4-Ethylenedioxypyrrole		-	648310-2ML 648310-10ML
3,4-Propylenedioxypyrrole		-	648329-2ML 648329-10ML
Methyl 1*H*-pyrrole-3-carboxylate		97%	685399-250MG 685399-1G
4-(3-Pyrrolyl)butyric acid		95%	682578-100MG 682578-500MG
N-Methylpyrrole		99%	M78801-100ML
1-(Dimethylamino)pyrrole		99%	247790-5G
1-(2-Cyanoethyl)pyrrole		≥99%	C91352-25G
1*H*-Pyrrole-1-propanoic acid		97%	687545-1G
11-(1*H*-pyrrol-1-yl)undecane-1-thiol		96%	717223-1G
1-Phenylpyrrole		99%	131474-10G
N-Benzylpyrrole		97%	566322-5G
1-(4-Methylphenyl)-1*H*-pyrrole		97%	452963-5G
1-(4-Methoxyphenyl)-1*H*-pyrrole		97%	452955-1G 452955-5G
1-(2-Aminophenyl)pyrrole		≥98%	196940-1G 196940-10G
1-(4-Nitrophenyl)-1*H*-pyrrole		97%	447358-1G 447358-5G

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