Introduction

Welcome to the premiere issue of Material Matters, a technical guide from Sigma-Aldrich dedicated to addressing research needs in materials science and technology. The theme for this issue is polymerization. Innovative polymers are helping advance almost every field of materials science, from alternate energy to organic electronics. Included in this guide are reviews from researchers in relevant technical fields that discuss a subset of some of the tools available to scientists and engineers.

Our mission at Sigma-Aldrich is to inspire and advance your research. I hope that by highlighting the innovations and products featured in this technical guide, we will help generate the next ideas to significantly impact research in polymerization.

Sincerely,

Luke Grocholl, Ph.D.
Materials Science Team
Sigma-Aldrich Corporation

The MatSci eMailbox

Contact us at matsci@sial.com for:
- Comments on this technical guide
- Suggested topics for future technical guides
- New product suggestions
- Spectral and other data to facilitate your research
- Questions for inclusion in a FAQ
- Subscriptions to future issues of Material Matters

The Polymerization Tools Web Site

Visit us at sigma-aldrich.com/poly for:
- Over 1000 monomers for applications from drug delivery to PLEDs
- Guide to thermal initiators with solvent-specific half-life temperature values
- Absorbance spectra of over 250 photoinitiators
- Functional polymers for the synthesis of advanced copolymers
- Comprehensive list of surfactants organized by HLB value
- Cross-linkers, chain transfer agents, plasticizers, and stabilizers for polymer modification

About Our Cover

Central to advances in science and engineering are the dedicated researchers whose ideas drive tomorrow’s technologies. This premiere issue of Material Matters features advanced and unique Sigma-Aldrich materials for polymerization such as monomers, cross-linkers, and functional polymers. The cover depicts how our products combine with your ideas to yield the next generation of nanolithography, fiber optics, flexible LEDs and bioactive polymers for drug delivery. Material Matters—Chemistry Driving Performance.
**Initiator/Stabilizer FAQs**

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Q. How does one choose an appropriate initiator?
In a free-radical addition polymerization, the choice of polymerization initiator depends mainly on two factors: a) its solubility and b) its decomposition temperature. If the polymerization is performed in an organic solvent, then the initiator should be soluble in that solvent, and the decomposition temperature of the initiator must be at or below the boiling point of the solvent. Commonly, AIBN (2,2’-Azobisisobutyronitrile) (441090, dec.102–104°C) and BPO (2,2’-Azobis(2-methylpropionitrile)) (416984, mp 115–119°C) suit these requirements. If the desired polymerization occurs at or below 20 °C, then special, low-temperature free-radical initiators need to be used. Various azo-type initiators can be chosen to satisfy the decomposition temperature requirement.

For emulsion polymerization or polymerization in an aqueous system, a water-soluble initiator like K2S2O8 (379824) or an organic, water-soluble initiator (4,4’-Azobis(4-cyanovaleric acid)) (118168, dec.118–125 °C) would be suitable.

Q. How does one determine the reactivity of a monomer?
Determination of monomer reactivity is not always obvious or straightforward. Researchers rely on their experience and published data on individual monomers. In general, extent of conjugation in the molecular structure can be viewed as indicative of its tendency to form the initial free radical required for propagating a free-radical polymerization. Usually, a more conjugated system is more likely to undergo free-radical polymerization.

Q. When is it necessary to remove a stabilizer prior to polymerization and how does one do so?
To inhibit polymerization during storage, many monomers are provided with a stabilizer as indicated by the label. Usually, it is not necessary to remove stabilizers. They are typically present in ppm level, and the use of a free radical initiator at the polymerization temperature will overwhelm the effect of the stabilizer. In worst-case scenarios, one may need to add extra amounts of initiator to sustain an acceptable polymerization rate. In most cases, once a polymerization initiates, the rate can be sustained without much difficulty. If, however, it is absolutely necessary to remove the stabilizer, column chromatography is the preferred method (for inhibitor removal columns, see products 306312, 311332, 306320).

Q. How does one remove residual initiator, stabilizer, and/or unreacted monomer after polymerization?
It is a common practice to dissolve the polymers in a solvent prior to end use, followed by precipitating the polymer using a cosolvent. Usually, the residual initiators and stabilizers will remain in solution to find its way back into use, followed by precipitating the polymer using a cosolvent. It is a common practice to dissolve the polymers in a solvent prior to end use, followed by precipitating the polymer using a cosolvent. Various azo-type initiators can be chosen to satisfy the decomposition temperature requirement.

For initiator solubilities and decomposition temperatures, visit our Web site at sigma-aldrich.com/poly.

**Polymer Analysis by NMR**

Sigma-Aldrich Quality Control Team

One of the challenges polymer scientists face is molecular weight (average chain length) determination of their materials. While membrane osmometry, gel permeation chromatography, viscosity analysis and mass spectrometry are typically used for molecular weight determination, the techniques can be time consuming, inaccurate for the molecular weight ranges involved, or require specialized instrumentation. End-group analysis by NMR offers an easy alternative method using an instrument commonly found in many analytical labs. In addition, NMR analysis can also be used to accurately determine monomer ratios for various copolymer.

Scientists at Sigma-Aldrich routinely determine number-average molecular weight (Mn) by 1H NMR end-group analysis for polymers having Mn values under 3000. Sensitivity of the instrument to detect end-group protons will determine the upper limit that can be measured. In order to use this method, the following criteria must be met:

- Identifiable end-group protons distinguishable from repeating monomer-grpoup protons by NMR
- Accurate integration of both end-group and monomer protons
- Knowledge of monomer formula weights

Once the ratio of protons on the end-groups to protons on the polymer chain is determined, using the NMR, simple math can be applied to generate the Mw value.

This example illustrates this method:

437441 Poly(ethylene glycol) diacrylate

## End-Group (Vinyl) Protons

H<sub>2</sub>CC(H)CO-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>O(C)(O)(H)CH<sub>2</sub>

FW= 55.06 (44.05)<sub>n</sub> 71.06

1) Calculation, integral per proton:
Locate the end-group proton signals (ca. 5.8, 6.2 & 6.4 ppm)

\[
\text{integral per proton} = \frac{\text{sum of vinyl proton integrals}}{\# \text{ of protons in the two vinyl end groups}}
\]

\[
= \frac{10.00 + 9.66 + 10.17}{6} = 4.97 \text{ per proton}
\]

2) Calculation, number of repeating monomer units, n:
Locate the OCH<sub>2</sub>CH<sub>2</sub> proton signals (ca. 3.6, 3.7 & 4.3 ppm)

\[
n = \frac{\text{sum of CH<sub>2</sub> proton integrals}}{\# \text{ of CH<sub>2</sub> protons}}
\]

\[
= \frac{(20.79 + 151.87) \times 4}{4.97} = 8.69 \text{ repeating units, } n
\]

3) Calculation, M<sub>n</sub>:

\[
M_n = (\text{FW end groups}) + (\text{FW repeating unit}) \times n
\]

\[
= (55.06 + 71.60) + (44.05) \times 8.69 = 509
\]

Therefore, the M<sub>n</sub> of this polymer is approx. 509
Fluorinated Hyperbranched Polymers

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Mount Pleasant, MI

Fluorocarbon polymers, like small-molecule fluorocarbons, exhibit increased thermal stability, hydrophobicity, lipophobicity, improved chemical resistance, and decreased intermolecular attractive forces in comparison to their hydrocarbon analogs.¹ These properties derive from the fundamental atomic properties of fluorine: high ionization potential, low polarizability, and high electronegativity. Due to the very high electronegativity, C–F bonds are always strongly polarized. The strength of the C–F bond is due to its highly ionic character, which accounts for the thermal stability of perfluorocarbons. The high ionization potential, combined with the low polarizability, leads to weak intermolecular interactions, which in turn leads to low surface energy and low refractive indices for perfluorocarbons. Therefore, perfluorocarbons have been used to create non-stick and non-wettable surfaces with low surface energies.

Linear fluorinated polymers, such as tetrafluoroethylene (Teflon®) exhibit high crystallinity, which increases the melting point even further. That often leads to inhibitory high processing temperatures. For applications such as mold releases or coatings, high crystallinity is often not needed or even unfavorable.

The superior chemical resistance, hydrophobicity, and low adhesive forces can be coupled with improved processibility (high solubility, low viscosity)² by making highly branched fluorocarbon polymers (Figure 1).² The glass transition temperature of these materials is up to 55 °C (depending on molecular weight), but they are thermally stable to 300 °C, which is sufficient for most applications. The contact angle with water for this hyperbranched fluoropolymer is just below 100° (tetrafluoroethylene: 105°), which can be increased to 120° by substituting one-third of the remaining p-fluorines of the structure with longer fluoroalkyl chains.

This material has improved lubricating properties and has been used as an imprinting mold release (Figure 2).⁴ With a mold coated with the hyperbranched polymer, 250 nm circles and 50–60 nm lines can be imprinted without the pattern being destroyed by removing the imprinter.

For coatings applications, the hyperbranched fluorinated polymer has to be cross-linked to make it less brittle (fluorocarbon polymers have not only reduced adhesion, but also reduced cohesion). At the same time, the cross-linking molecule can be used to introduce other properties or additional functional groups.⁵

This family of materials thus combines the superior properties of fluorocarbon polymers with an easy synthesis and processibility, allowing for its use in a variety of applications.

References:

Figure 1. A highly cross-linked fluorinated polymer.

Figure 2. AFM images of a) 250nm punctures in ca. 100 nm thick film of fluoroalkyl-substituted HBFP; b) expelled material adjacent to punctures; c) imprint of 50–60 nm thick lines spaced 210 nm apart. Imprinting: Krchnavek, Dept. of Electrical Engineering, Washington University, St. Louis; AFM: Tomasz Kowalewski, Dept. of Chemistry, Carnegie Mellon University.
Fluorinated Monomers

3,6-Difluorphthalic anhydride, 97%

**C₈H₄F₂O₃**

MW: 184.1

MP: 218–221 °C (lit.)

381128-100MG 100 mg
381128-500MG 500 mg

2-Fluorostyrene, 98%

**C₈H₈F**

MW: 122.14

BP: 29–30 °C (4 mm Hg) (lit.)

290505-1G 1 g
290505-5G 5 g

4-Fluorostyrene, 99%

**C₈H₇F**

MW: 122.14

BP: 67 °C (50 mm Hg) (lit.)

155799-1G 1 g
155799-10G 10 g

Glycidyl 2,2,3,3,3-pentafluoropropyl ether, 97%

**C₆H₁₈F₄O₂**

MW: 188.12

BP: 50 °C (4 mm Hg) (lit.)

474150-5ML 5 mL
474150-25ML 25 mL

Hexafluoroglutaric acid, 97%

**C₅H₂₆F₆O₄**

MW: 240.06

MP: 88-91 °C (lit.)

BP: 134–138 °C (3 mm Hg) (lit.)

196908-5G 5 g
196908-25G 25 g

4,4’-(Hexafluoroisopropylidene)dianiline, 98%

**C₁₅H₁₂F₆N₂**

MW: 334.26

MP: 195–198 °C (lit.)

368148-1G 1 g
368148-5G 5 g

4,4’-(Hexafluoroisopropylidene)diphenol, 97%

**C₁₅H₁₀F₆O₂**

MW: 336.23

MP: 160–163 °C (lit.)

257591-5G 5 g
257591-25G 25 g
257591-100G 100 g

Fluorinated Acrylates

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<th>R</th>
<th>R’</th>
<th>Quantity</th>
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<td>2,2,3,3,3-Pentafluoropropyl acrylate, 98%</td>
<td>H</td>
<td>CF₃CF₂CF₃</td>
<td>470961-5ML</td>
</tr>
<tr>
<td>3,3,4,4,5,5,6,6,7,8,8,9,9,10,10-Heptadecafluorodecyl acrylate, 97%</td>
<td>H</td>
<td>CH₃CH₂(CF₂)₉CF₃</td>
<td>474487-5ML</td>
</tr>
<tr>
<td>Heneicosafluorododecyl acrylate, 96%</td>
<td>H</td>
<td>CH₃CH₂(CF₂)₁₉CF₃</td>
<td>474355-5G</td>
</tr>
<tr>
<td>2,2,2-Trifluoroethyl methacrylate, 99%</td>
<td>CH₃</td>
<td>CH₂CF₃</td>
<td>373761-5G</td>
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<tr>
<td>2-(Trifluoromethyl)acrylic acid, 98%</td>
<td>CF₃</td>
<td>H</td>
<td>369144-1G</td>
</tr>
<tr>
<td>Zonyl® TM fluoromonomer</td>
<td>(CF₃)ₙCF₂, n ~ 7–8</td>
<td>CH₃CH₂</td>
<td>421480-10ML</td>
</tr>
</tbody>
</table>

For halogenated monomers that result in high and low refractive index polymers, see the Advanced Polymers for Electronic/Optical Devices technical guide. Request your free copy at matsci@sial.com; reference code GGE.
Etch-Resistant Block Copolymers

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Introduction

Block copolymers offer a means of combining the desirable characteristics of different polymers in a new hybrid material. Polymers consisting of hydrophobic and hydrophilic blocks, for example, can be used to encapsulate organic molecules and deliver them into aqueous media. There has been tremendous interest in the self-assembly of block copolymers in nanoscale dimensions, especially in thin-film configuration.

Conventional lithography has its limitations when features of less than 30 nm are desired. Accessibility to a wide range of periodic structures with feature sizes less than 30 nm make block copolymers attractive as templates for nanopatterning. Most of the literature approaches use selective ozonolysis or preferential staining of one block with heavy metals to increase etch selectivity between the blocks. Often, an intermediate silicon nitride (SiN) layer and selective etching of one block over another is required for successful pattern transfer. In general, the use of organic block copolymers is limited at high temperatures because of low thermal/mechanical stabilities. Thus, direct patterning of semiconductors that requires high growth temperature (>500 °C) using organic block copolymers as templates is nearly impossible.

It has been well established that incorporation of silicon (at least 10 wt %) in resist polymers provides improved oxygen–RIE (reactive ion etching) etch resistance. When exposed to oxygen plasma, the silicon-containing polymers are oxidized to silicon oxide that is stable in an O₂ environment. The high etch resistance to oxygen plasma compared to organic polymers makes silicon-containing polymers favorable as bilayer resists to pattern high-aspect ratio structures and to create nanoporous ceramic thin films in a variety of morphologies. In addition, silicon oxide has high thermal and mechanical stability at a temperature greater than 500 °C, making it a long-time dielectric in microchip fabrication. Thus, the possibility of combining acid labile groups and silicon-containing groups in block copolymers offers a new route to directly pattern nanostructured semiconductors.

As the synthesis of silicon-containing block copolymers is quite challenging using traditional living anionic polymerization, post functionalization of polymers is often used to incorporate silicon. Recent advances in controlled living free-radical polymerization (LFRP), including nitroxide-mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT), make it possible to design and synthesize a variety of block copolymers with novel functionalities. The LFRP procedures in general are easier to carry out as they are tolerant to a variety of functionalities and do not require stringent purification of the starting materials, unlike living anionic or cationic polymerization. We had recently applied NMRP towards (i) the synthesis of narrow dispersed silicon-containing homopolymers from three kinds of silicon-containing styrenic monomers, including 4-(pentamethyldisilyl)-styrene (Si₅-St), 4-(bis(trimethylsilyl)-methyl)styrene (Si₅-C₅St), and 4-(pentamethyldisiloxymethyl) styrene (OSi₅-St) (Scheme 1), each containing two silicon atoms to enhance the etch selectivity, and (ii) the synthesis of block copolymers from silicon-containing styrenic monomers with styrene and acid labile acetoxy styrene by sequential monomer addition using an nitroxide unimer initiator. By optimizing conditions such as solvent polarity, temperature of polymerization, and the monomer addition sequence, well-defined narrow dispersed silicon-containing block copolymers were synthesized from the above monomers. Both TEM (transmission electron microscopy) and SAXS (small angle X-ray scattering) data showed that these polymers formed cylindrical, lamellae, or disordered structures depending on the volume ratio between the blocks and their molecular weights. When the silicon-containing block was the major phase and silicon content was greater than 12 wt %, block copolymer morphology and its domain size were well maintained under exposure to oxygen plasma (Figure 1).

![Scheme 1. Synthesis of macroinitiators and SiBCPs by LFRP at 100 °C.](image)

![Figure 1. Transmission electron micrograph (TEM) images of PAcOSt-PSi₂St (21/79 v/v) before and after O₂ plasma for 10 minutes, showing intact cylindrical morphology.](image)
Silicone-Containing Monomers

**Allytriethoxysilane, 97%**  
**C₆H₃O₃Si**  
MW: 204.34  
BP: 78 °C (21 mm Hg) (lit.)

A6303-5G 5 g  
A6303-25G 25 g

**Diphenylsilanediol, 95%**  
**C₆H₄O₃Si**  
MW: 216.31  
BP: 90 °C (lit.)  
MP: –95 °C (lit.)  
MW: 161.49  
C₅H₅N

D21370-25G 25 g  
D21370-100G 100 g

**Octadecytrichlorosilane, 90+ %**  
**C₁₈H₃₃Cl₃Si**  
MW: 387.93  
BP: 223 °C (10 mm Hg) (lit.)

104817-25G 25 g  
104817-100G 100 g  
104817-500G 500 g

**Poly(dimethylsiloxane), vinyl terminated, viscosity 1,000 centistokes**  
BP: >93 °C (lit.)

433012-100ML 100 mL  
433012-500ML 500 mL

**Trichlorovinylsilane, 97%**  
**C₅H₃Cl₃Si**  
MW: 161.49  
MP: –95 °C (lit.)  
BP: 90 °C (lit.)

104876-5G 5 g  
104876-100G 100 g  
104876-500G 500 g

Styrene Monomers

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<th>Monomer</th>
<th>R</th>
<th>Quantity</th>
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<tbody>
<tr>
<td>Styrene, reagent plus, 99+%</td>
<td>H</td>
<td>240869-5ML</td>
</tr>
<tr>
<td>4-Bromostyrene, 98%</td>
<td>Br</td>
<td>124141-1G</td>
</tr>
<tr>
<td></td>
<td></td>
<td>124141-10G</td>
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<table>
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<th>Monomer</th>
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<td>4-Chlorostyrene, 97%</td>
<td>Cl</td>
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<td></td>
<td></td>
<td>C71203-50G</td>
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<tr>
<td>4-Acetoxy styrene, 96%</td>
<td>O</td>
<td>380547-5ML</td>
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<tr>
<td></td>
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</table>

For an up-to-date list of silsesquioxane monomers, visit our nanomaterials Web site at sigma-aldrich.com/nano.

References:  

For questions, product data, or new product suggestions, please contact the Materials Science team at matsci@sial.com.
Bioactive Hydrogels

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The first report of the synthesis of composite materials comprising conducting polymers and hydrogels was in 1994 by Wallace et al. Their objective was to enhance the porosity and ion-transport properties of hydrogels for controlled drug delivery through electrochemically stimulated release of analytes. Since then, the electrochemical and oxidative polymerization of pyrrole, aniline, and thiophene and their derivatives within hydrogel hosts, such as polyacrylamide, poly(acrylic acid), chitosan, and poly(hHEMA) have been routinely accomplished for biosensor applications and to achieve voltage-stimulated or controlled release. There have also been several studies conducted on the fabrication of polymer blends of hydrogels, such as poly(methyl methacrylate) (PMMA), poly(vinyl methyl ether) (PVME), poly(4-vinylpyridine), and poly(2-hydroxyethyl methacrylate) (p(HEMA)), primarily for the construction of artificial muscles. With hydrogels, high degrees of hydration (ca. 90%) could be reversibly achieved along with biocompatibility, good refractive index matching with water, and relative ease of molecular engineering. In general, the conducting polymer component of these composites retains its electroactive properties.

Brahim et al. have fabricated bioactive polypyrrole-p(HEMA) composites to function as sensing membranes for clinically important amperometric biosensors. A monomer cocktail containing, among other components, the relevant methacrylate monomers, pyrrole or aniline, and photoinitiator was spin-cast onto microfabricated electrodes and first irradiated by UV to effect polymerization of the hydrogel components. This was immediately followed by potentiostatic electropolymerization of the pyrrole/aniline monomer in a phosphate-buffered potassium chloride solution saturated with further monomer. Amperometric enzyme biosensors for the detection of glucose, cholesterol, and galactose were demonstrated, each possessing extensive linear dynamic response ranges, high sensitivities, and prolonged storage stabilities.

Of particular recent interest is the development of bioactive (containing biologically active moieties such as bioactive peptides, growth factors, enzymes and the like) and biosmart (responsive to biologically derived external stimuli) electroconductive hydrogels for implant biocompatibility. A novel polymer composite material consisting of a water-dispersed complex of polypyrrole doped with poly(styrenesulfonate) and embedded in polyacrylamide hydrogel was prepared and evaluated as a matrix for enzyme immobilization. The enzyme glucose oxidase was physically entrapped in the polymer by inclusion in the aqueous phase during emulsion polymerization. The resulting bioactive microparticles (3.5–7.0 µm diameter) were cast onto platinum electrodes and the polymer-modified electrodes used as amperometric glucose biosensors. This configuration displayed rapid response times and efficient screening of interferents.

For implantable biosensing applications, the synthesis of hydrogel composite polymers consisting of cross-linked p(HEMA) with incorporated polypyrrole and/or polyaniline chains are rendered “bioactive” by the covalent immobilization of oxidoreductase enzymes. Enzymes were first “monomerized” by hetero-bifunctional coupling of the amines of the lysine residues of the enzyme (typically 1:2) with acryloyl(polyethylene glycol)N,N,N′,N′-tetraacyl (PEG-NHS). This allowed the covalent immobilization of the tethered oxidoreductase enzyme within the hydrogel milieu. To provide for stabilization of the immobilized enzymes, polyoxyethylene glycol(2000) monomethacrylate (PEGMA) was also included in the monomer cocktail at 0.5 mol %. Together these components allowed photolithographically defined, spin-cast membranes formed on microlithographically defined electrodes to recognize and amperometrically respond to the enzyme's substrate and achieve approximately one year of retained enzyme activity (ca. 80%). For implant biocompatibility, the synthesis of the monomer 2-methacryloyloxyethyl phosphorylcholine (MPC) (Figure 1) was accomplished by the coupling of HEMA with 2-chloro-2-oxo-1,3,2-dioxaphospholane (COP). When incorporated into the hydrogels at the level of 5–10 mol %, this monomer conferred nonthrombogenicity, reduced protein adsorption, and supported cell viability. Mimicking the zwitterionic head group of the outer leaflet of cell membranes, phosphorylcholine, the phosphorylcholine moiety confers the molecular equivalent of “stelt” to the polymer when the biosensor is implanted. When cultured with muscle fibroblasts and endothelial cells, these highly porous hydrogel composites support the migration and mobility of cells within its 3-D network; a property that will render these materials appropriate for the fabrication of nerve electrodes and cellular interfaces as the polymer mimics the biological structures that enable cells to grow.

One challenge faced by the use of electroactive polymers as components of hydrogels for mammalian implantation is the potential toxicity. Early work has established polypyrrole as bio-benign. However, to address this issue, bi-functional monomers of pyrrole such as 2-methacryloyloxyethyl pyrrolidinylbutyrate (MPB) (Figure 2) and aniline that may be UV-polymerized, and hence, covalently coupled into the hydrogel network and also oxidatively polymerized with imbibed free pyrrole or aniline monomer to form the electroactive polymer component were developed. In this way, an interpenetrating network of the electroactive polymer is formed within the preformed hydrogels network that serves as the reactor. Studies are ongoing to evaluate the potential cytotoxicity and biocompatibility of these polymers.

References:

Figure 1. Structure of 2-methacryloyloxyethyl phosphorylcholine

Figure 2. Structure of 2-methacryloyloxyethyl pyrrolidinylbutyrate
Monomers for Bioactive Polymers

Benzy 2-ethyl acrylate, 99%
C₁₀H₁₄O₃
MW: 190.24
589136-250MG 250 mg

Benzy 2-propyl acrylate, 99%
C₁₀H₁₄O₂
MW: 204.26
590126-250MG 250 mg

1,6-Bis(p-acetoxycarbonylphenoxy)hexane, 97%
C₁₆H₁₆O₆
MW: 442.46
657174-1G 1 g
657174-5G 5 g

1,3-Bis(4-carboxyphenoxy)propane, 97%
C₁₆H₁₄O₆
MW: 316.31
655538-SG 5 g

1,6-Bis(p-carboxyphenoxy)hexane, 90%
C₁₆H₁₄O₆
MW: 358.39
655546-SG 5 g

2-Chloro-1,3,2-dioxaphospholane-2-oxide
C₆H₅ClO₄P
MW: 142.48
MP: 12–14 °C (lit.)
BP: 89–91 °C at 0.8 mm Hg (lit.)
377953-1G 1 g
377953-5G 5 g

2-Ethylacrylic acid, 98%
C₅H₈O₂
MW: 142.2
BP: 176 °C (lit.)
589128-250MG 250 mg

Ethyl 2-propyl acrylate, 99%
C₈H₁₄O₂
MW: 142.2
BP: 141 °C (lit.)
590118-250MG 250 mg

Glycosyloxyethyl methacrylate, 5% (w/v) solution in ethanol
C₁₂H₂₀O₈
MW: 292.28
659576-25ML 25 mL
659576-25MG 25 mg

2-Propylacrylic acid, 99%
C₆H₉NO
MW: 111.14
BP: 92–95 °C (11 mm Hg) (lit.)
V3409-5G 5 g
V3409-250G 250 g
V3409-1KG 1 kg
V3409-18KG 18 kg

For a comprehensive list of hydrogel hosts such as polyacrylamide, poly(acrylic acid), chitosan and poly(HEMA), as well as functionalized PEGs (linear, 4-arm and 6-arm), visit sigma-aldrich.com/biocomp.

Cross-linkers

Cross-linking is the formation of chemical links between molecular chains to form a three-dimensional network of connected molecules. The strategy of covalent cross-linking is key to the formation of hydrogels. It is also used in several other technologies of commercial and scientific interest to control and enhance the properties of the resulting polymer system or interface, such as thermosets and coatings.

DVB, 85% (535583)

For a complete list of cross-linkers, visit us at sigma-aldrich.com/biocomp and scroll down to cross-linkers.
Anionic Polymerization

Prof. Roderic P. Quirk
Ms. Manuela Ocampo
Maurice Morton
Institute of
Polymer Science
The University of
Akron, Akron, OH

Living anionic polymerization, especially using alkyllithium initiators, has been demonstrated to be a convenient and useful method to make well-defined polymers with low degrees of compositional heterogeneity and with control of the major structural variables that affect polymer properties. Living polymerizations are chain-reaction polymerizations that proceed in the absence of the kinetic steps of chain termination and chain transfer. For a living polymerization, one initiator molecule generates one polymer molecule; thus, it is possible to calculate and control the number average molecular weight ($M_n$) of the final polymer via the stoichiometry of the reaction using the following relationship.

$$M_n = \frac{g \text{ of monomer consumed}}{\text{moles of initiator}}$$

Given a comparable or faster rate of initiation relative to propagation, it is possible to obtain narrow molecular weight distribution polymers, i.e., $M_n/M_w \leq 1.1$. Due to the absence of termination and transfer steps, the product after complete monomer consumption is a reactive, polymeric organolithium compound. The living nature of alkyllithium-initiated anionic polymerizations using suitable monomers provides versatile methods for the preparation of well-defined block copolymers by sequential addition of monomers, chain-end functionalized polymers by reaction of the living chain ends with appropriate monomers and/or electrophilic terminating agents, and branched polymers by linking reactions with multi-functional linking agents.

The monomers that can be polymerized anionically are classified into two categories: (a) unsaturated monomers with one or more double bonds, such as vinyl (e.g., styrenes, vinylpyridines, alkyl methacrylates), dienes (e.g., isoprene, 1,3-butadiene) and carbonyl-type monomers (e.g., formaldehyde); and (b) heterocyclic monomers (e.g., epoxides, thiiranes, lactones, lactams, and siloxanes). In the case of vinyl monomers, the presence of electron-withdrawing substituents (e.g., X, Y) in the double bond is generally required to stabilize the negative charge that develops in the transition state as shown below.

$$R^* + H_2C\equiv C\equiv CH_2 \rightarrow R^* - H_2C\equiv C\equiv CH_2$$

### Organolithium Initiators

Of all alkali metals, lithium is unique in that it exhibits the highest electronegativity, the smallest covalent and ionic bond radii, along with low-lying, unoccupied p-orbitals available for bonding. Organolithium compounds are unique among organoalkali compounds in exhibiting properties characteristic of both covalent and ionic compounds. Thus, they are aggregated in solution, in the solid state and in the gas phase, and they are generally soluble in hydrocarbon solution. In general, the initiation of anionic polymerization of styrene and diene monomers is effected with alkyllithium compounds such as sec-butyllithium and $n$-butyllithium.

### Experimental Methods

Due to the reactivity of organolithium compounds and other carbanionic species toward impurities such as oxygen, moisture or carbon dioxide, it is necessary to exclude these contaminants from the reaction environment by the use of an inert gas atmosphere or high vacuum techniques.
High Vacuum Techniques The use of high vacuum techniques provides the most effective experimental method to exclude impurities from the reaction system. In order to attain high vacuum, the combination of a mechanical pump and an oil diffusion pump (Z220418) is used in conjunction with a two-stage glass manifold as shown in Figure 1.

In order to achieve the desired levels of purity for controlled anionic polymerization, all monomers, reactants, and solvents should be purified, dried, and degassed, preferably on the vacuum line. Solvents are distilled directly into the requisite glass reactors (Figure 2) via D followed by flame sealing from the vacuum line. Ampules B, E, and F contain monomers or functionalizing agents. Ampule C contains a terminating agent such as degassed methanol. Ampule A is equipped with a degassed methanol tube, and it is used to remove a base sample of the living polymer.

Schlenk Line and Glove Box Techniques are often suitable for carrying out many living anionic polymerization procedures. Alkyl lithium-initiated polymerizations are somewhat forgiving for carrying out many living anionic polymerization procedures. Schlenk Line and Glove Box Techniques are often suitable for carrying out many living anionic polymerization procedures. Alkyl lithium-initiated polymerizations are somewhat forgiving for carrying out many living anionic polymerization procedures.

Safety Considerations
Vacuum traps should be vented while warming because of the possibility of trapped, liquefied gases. Hydrocarbon solutions of alkyl lithium compounds are air- and moisture-sensitive; they should be either handled under an inert atmosphere or using syringes and recommended procedures for handling air-sensitive compounds. Carbon dioxide extinguishers should not be used because RLi compounds and many other organometallic compounds react with carbon dioxide exothermically. An all-purpose fire extinguisher, or one designed specifically for combustible metals, should be available when working with these organometallic compounds and alkali metals.

Monomers for Anionic Polymerization

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
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<tbody>
<tr>
<td>Vinylidene chloride, 99%</td>
<td>H</td>
</tr>
<tr>
<td>163023-100G</td>
<td>Cl</td>
</tr>
<tr>
<td>163023-500G</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid, 99%</td>
<td>H</td>
</tr>
<tr>
<td>147230-5G</td>
<td>O(CH₂)₃</td>
</tr>
<tr>
<td>147230-100G</td>
<td></td>
</tr>
<tr>
<td>147230-500G</td>
<td></td>
</tr>
<tr>
<td>Methyl acrylate, 99%</td>
<td>H</td>
</tr>
<tr>
<td>M27301-5ML</td>
<td>O(CH₂)₃</td>
</tr>
<tr>
<td>M27301-250ML</td>
<td></td>
</tr>
<tr>
<td>Ethyl acrylate, 99%</td>
<td>H</td>
</tr>
<tr>
<td>E9706-5ML</td>
<td>O(CH₂)₂</td>
</tr>
<tr>
<td>E9706-100ML</td>
<td></td>
</tr>
<tr>
<td>Butyl acrylate, 99%</td>
<td>H</td>
</tr>
<tr>
<td>234923-5ML</td>
<td>O(CH₂)₂</td>
</tr>
<tr>
<td>234923-100ML</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxyethyl acrylate, 96%</td>
<td>H</td>
</tr>
<tr>
<td>292818-5ML</td>
<td>O(CH₂)₂</td>
</tr>
<tr>
<td>292818-250ML</td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-3-phenoxypropyl acrylate</td>
<td>H</td>
</tr>
<tr>
<td>407364-100ML</td>
<td></td>
</tr>
<tr>
<td>407364-500ML</td>
<td></td>
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<tr>
<td>N,N-Dimethylacrylamide, 99%</td>
<td>H</td>
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<tr>
<td>274135-5ML</td>
<td>O(CH₂)₂</td>
</tr>
<tr>
<td>274135-100ML</td>
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</tr>
<tr>
<td>274135-500ML</td>
<td></td>
</tr>
<tr>
<td>N-isopropylacrylamide, 97%</td>
<td>H</td>
</tr>
<tr>
<td>415324-10G</td>
<td>O(CH₂)₂</td>
</tr>
<tr>
<td>415324-50G</td>
<td></td>
</tr>
</tbody>
</table>

For questions, product data, or new product suggestions, please contact the Materials Science team at matsci@sial.com.

References

For the manipulation of air-sensitive compounds, see also Aldrich Technical Bulletins AL-134, AL-136, AL-164, and AL-166.