Continuous dimethyldioxirane generation for polymer epoxidation†

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Post-polymerization modification of commodity polymers yields new applications for materials already produced industrially. Incorporation of small amounts of epoxides into unsaturated polymers such as polybutadiene expands their use for grafting and compatibilization applications, but controlled epoxidation of these polymers in a safe, scalable manner presents a challenge. Herein we describe the development of a reactor for the continuous flow generation and use of dimethyldioxirane (DMDO) and its application to the low-level epoxidation of unsaturated polymers. A continuous stirred tank reactor (CSTR) prevents reactor clogging by allowing solid precipitates to settle, enabling the pumping of a homogeneous solution of oxidant. Modification of relative concentrations, flow rates, and temperatures achieves variable epoxidation levels. This method has been demonstrated on gram scale.

Post-polymerization modification vastly expands the properties and applications of simple commodity polymers such as polyolefins.1,2 Polymer epoxidation can alter properties such as solubility, aggregation, and thermal stability, as well as providing functional handles for further modification.3–5 Low epoxidation levels are particularly useful for compatibilization and grafting applications, as minimal backbone alteration preserves polymer properties while providing functional handles for novel modifications. For example, pure poly(lactic acid) (PLA) is brittle at room temperature, but can be strengthened by blending with rubber. However, since PLA is immiscible with common rubbers like polybutadiene (PBD), modifications allowing reactive compatibilization improve the properties of the resultant polymer blend.6 Sun et al. report PLA toughening from acrylonitrile-butadiene-styrene (ABS) rubber containing a small (1%) amount of glycidyl methacrylate (GMA), which contains epoxides that react with PLA end groups.7 Similar effects have been observed for PLA toughened with methyl methacrylate-butadiene block copolymers with added GMA.8

Direct use of epoxidized PBD removes the need for copolymerization with a compatibilizer like GMA, and low-level epoxidation of polybutadiene is particularly valuable, as high epoxidation levels cause an increase in glass transition temperature that negatively impact the toughness of the resulting PLA blends.9 Unfortunately, typical peracid epoxidation methods7,4 necessitate storage and use of hydrogen peroxide or an organic peroxide reagent, which is costly and hazardous on scale.10 Safe, sustainable epoxidation methods are desirable for the large-scale production of polymer with low-level epoxide incorporation.

To circumvent the issues of storing hydrogen peroxide solutions, dimethyldioxirane (DMDO) can be employed. DMDO epoxidation has been demonstrated for unsaturated polymers in batch.11–14 DMDO is generated from acetone and solid, commercially available Oxone® (active ingredient potassium monoperoxy sulfate) in a buffered aqueous solution.15 Due to the inherent instability and hazards of storage and use of organic peroxides, DMDO is typically prepared in situ or immediately before use. Its preparation is low-yielding and requires a hazardous distillation procedure to isolate it as a solution in acetone.16,17 On-demand generation of DMDO is desirable for large-scale applications, such as polymer oxidation at industrial scale, to avoid the hazards of using large amounts of organic peroxides.

Reports of dioxirane generation in continuous flow are promising, as synthesis in flow is ideally suited for on-demand generation and use of hazardous reagents.18,19 The first use of DMDO continuous flow was reported in 2018 by McCluskey et al., who epoxidized a variety of alkenes in 60–98% yield.20 However, the use of acetone as solvent limits the generality of this method for substrates such as higher olefin polymers that are insoluble in acetone. Methyl(trifluoromethyl)dioxirane (TFDO) has also been generated in continuous flow and used for aliphatic C–H oxidation.21 Unfortunately, the use of acetone to replace trifluoroaceton in the system reportedly

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caused precipitation. A robust, scalable protocol for DMDO
generation and use in continuous flow for epoxidation of non-
polar polymers has yet to be developed.

We envisioned a modular continuous flow reactor in which
DMDO would be generated, reacted with a polymer dissolved
in organic solvent, and then quenched at the output. This
system design both minimizes the amount of DMDO present
at any one time in the system, and allows tuning of experi-
mental variables such as temperature and residence time so
different levels of epoxide incorporation can be targeted. In
particular, we focused on low (<20%) levels of epoxide incor-
poration for the purposes of this investigation, due to the com-
patibilization and grafting applications mentioned above.

Our initial design plan combined three inputs (Oxone®
solution, base solution, and acetone solution) in a cross-mixer
to make DMDO, and then added the polymer solution at a
T-mixer (Fig. S1, ESI†). However, we observed rapid formation
of white solids that led to clogging in this system. We hypothe-
sized that the solid precipitation was due to the high concen-
trations of inorganic salts combined with acetone at the cross-
mixer. Oxone® is a triple salt, and it contains one mole of less
soluble, inactive salts (KHSO₄, K₂SO₄) for every one mole of
active salt (KHSO₅). We sought a method to mix the reagents
for DMDO formation that would allow a homogeneous oxidant
solution to be pumped forward without clogging due to the
precipitation of undesired salts.

Handling solid–liquid mixtures in continuous flow is an
ongoing challenge in the field.22 To address this challenge in
our system, we designed a simple continuous stirred tank
reactor (CSTR) that would pre-mix the reagents to produce
DMDO while allowing the undesired solids to settle to the
bottom (Fig. 1).

Reagents were pumped via syringe pump into a small tank
(a flask, stoppered syringe, test tube, or other vessel of similar
size). Under slow stirring, the undesired solids settled to the
bottom of the reactor. The liquid phase of the mixture, con-
taining a solution of water, acetone, base, Oxone®, and
DMDO, could then be pumped forward to react with the poly-
mers. We quickly learned that filtration was necessary to
ensure that finely divided solids did not clog the tubing; a
simple piece of filter paper tied to the tubing using Teflon
tape was sufficient for this purpose (see Fig. S2 in ESI†). Using
common materials (flasks, filter paper, Teflon tape), a simple
CSTR efficiently pre-mixed the reagents for DMDO formation
while preventing solids from clogging narrow-diameter tubing
and fittings.

DMDO is typically generated using NaHCO₃ as a base to
buffer the aqueous solution, as DMDO is formed most effi-
ciently at neutral or slightly alkaline pH.15 However, we observed
that using sodium bicarbonate to generate DMDO in flow
caused precipitation of sodium salts and evolution of carbon
dioxide gas. Excess precipitation of salts caused clogging,
while gas evolution and cavitation from clogging caused incon-
sistencies in residence time due to the formation of gas slugs
in the plug flow reactor. While the CSTR improves solid hand-
ling, generating less solid overall aids in the performance of
the system over long runs and avoids wasting reagents that are
added but precipitate out due to solubility issues. Thus, we
sought to identify a superior base for the generation of DMDO
in continuous flow (Table 1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>pH</th>
<th>Gas evolution</th>
<th>Solid formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7 M Na₂CO₃</td>
<td>5.0</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>2</td>
<td>0.5 M K₂HPO₄</td>
<td>5.5</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>3</td>
<td>1.0 M K₂HPO₄</td>
<td>6.0</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>4</td>
<td>0.5 M K₃PO₄</td>
<td>6.0</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>5</td>
<td>1.0 M K₃PO₄</td>
<td>7.0</td>
<td>Medium</td>
<td>Medium</td>
</tr>
</tbody>
</table>

* pH in CSTR tested by pH strip after system equilibration. * Gas and
solid observed and compared qualitatively.

While 1.0 M K₃PO₄ yielded the highest pH at steady state
(entry 5), further reactions with this base concentration
showed no epoxidation, possibly due to the degradation of
Oxone®. Thus, 0.5 M K₃PO₄ (entry 4) was chosen, yielding a
pH of 6.0 in the CSTR and producing a minimal amount of
solid and gaseous byproducts.

We then modified the setup to contain only two inputs
rather than three to use fewer pumps and minimize the
amount of excess salt introduced into the system. Our goal was
to combine the base and acetone reagents into one solution.
Due to the limited solubility of inorganic bases in acetone,
higher heat caused a decrease in epoxidation (Fig. 3a). We thereby investigated the epoxidation of Z-polypentadiene (Z-PBD) at similar conditions (Table 4). This difference is likely due to the greater substitution, and therefore greater nucleophilicity, of the Z-PBD alkene. Indeed, DMDO epoxidation of Z-PBD in the presence of Z-PBD has been achieved in batch due to the chemoselectivity for greater alkene substituents.
Communication

Conflicts of interest

There are no conflicts to declare.

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Table 4 Comparison of epoxidation levels by polymer

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>[Polymer] (g L⁻¹)</th>
<th>tₚ (min)</th>
<th>Epoxidation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low MW PBD</td>
<td>10</td>
<td>1.25</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>PIP</td>
<td>10</td>
<td>1.25</td>
<td>17</td>
</tr>
</tbody>
</table>

Reaction conditions: Room temperature, ethyl acetate, 3:1 flow rate ratio of DMDO solution to polymer solution.

We next worked to produce a larger sample of epoxidized polymer to demonstrate the reaction on gram scale. A new flow reactor was constructed using peristaltic pumps for all reagents, circumventing the limited volume of syringe pumps and allowing longer run times and therefore production of larger samples (Fig. S3, ESI†). Reaction time was decreased slightly from 1.25 min to 1 min and flow rates were increased to a total of 2 mL min⁻¹ with a 3:1 DMDO to polymer solution ratio. The larger system was used to produce a 1.28 g sample of 1% epoxidized low MW PBD in a total run-time of 90 minutes (see ESI section 5.4† for full experimental details). These larger-scale experiments correspond to over 0.8 g of product per hour in a benchtop reactor without distilling DMDO or producing large quantities of peroxides at one time. The low polymer concentrations required for higher epoxidation samples constrain the throughput of those polymers in this reactor, but a larger-scale flow reactor, albeit outside the scope of this investigation, would alleviate this constraint.

A safe and operationally simple continuous flow method for the generation of DMDO has been developed using a bench-scale CSTR. The reactor design prioritizes usability and safety by limiting the amount of DMDO generated at one time and using simple parts. This reactor has been applied to the oxidation of unsaturated polymers, including PBD and PIP. The system described herein provides advantages for the safety, scalability, and modularity of polyolefin epoxidation. Further investigations may include increased scale and throughput and targeting higher epoxide incorporation for different applications.

References


