MODEL-BASED DESIGN OF REACTION CONDITIONS FOR SEGMENTED COPOLYMER SYNTHESIS BY COMBINING STEP- AND CHAIN-GROWTH POLYMERIZATION

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POLYMER CONJUGATION

Functional groups within polymer backbone: 

Conjugation of macromolecular building blocks

Applications: *e.g.* introducing automated degradability in polymer chains

Research questions:
- *adjustable segment length*?
- *synthesis strategy*?
- *reaction conditions*?

=> *model-based design*
2 PHASE SYNTHESIS STRATEGY

1) Step-growth polymerization:
   light-induced Diels-Alder reaction

2) Chain-growth polymerization:
   RAFT polymerization

bifunctional ortho-methyl benzaldehyde (AA)

bisfumarate bearing a trithiocarbonate group (BB)
MULTI-SCALE MODELING STRATEGY


Derboven et al. Macromolecules 2015, 48, 492

KINETIC MONTE CARLO METHOD

Start 

input:

- Reactions
- Temperature T
- Initial number of molecules \( n_{Ao}, n_{Bo}, \ldots \)
- Intrinsic kinetic parameters \( k_{chem}, f_{chem} \)
- Diffusion parameters for calculation of \( D_{AB} \)
- Total polymerization time \( t_{Tot} \)

Calculation of:

- Volume \( V = f(T, n_{Ao}, n_{Bo}, \ldots) \)
- Concentrations \( C = f(n_{Ao}, n_{Bo}, \ldots, V, N_A) \)
- Apparent “Monte Carlo rate coefficients” for each reaction \( v \)
  \( k_{app,MC}^v = f(k_{chem}, D_{AB}, V, N_A) \)

End

t = t_{Tot}?

yes

Update of:

- Number of molecules: \( n_A, n_B, \ldots \)
- \( t = t + \tau \)

Random selection of:

- Reaction channel (\( \mu \))
- Chain length

Random selection of:

\[ \sum_{v=1}^{\mu-1} P(v) \leq r_2 \leq \sum_{v=1}^{\mu} P(v) \]

Calculation of:

- Monte Carlo reaction rates:
  \( R(v) = k_{app,MC}^v n_A n_B \)
- Time between two reactions:
  \( \tau = -ln(r_1) \left[ \sum_v R(v) \right]^{-1} \)
- Reaction probabilities:
  \[ P(v) = R(v) \left[ \sum_v R(v) \right]^{-1} \]

Composite binary trees

OUTLINE

Light-induced step-growth polymerization
- Experimental observations
- Theoretical framework
- Rate coefficients in view of design
- Design step-growth precursor toward high molar masses

Chain extension by RAFT polymerization
- Experimental observations
- Theoretical framework
- Rate coefficients in view of design
- Design toward microstructural control

Conclusions
EXPERIMENTAL OBSERVATIONS

Main:

\[
\text{AA} + \text{BB} \xrightarrow{k_{\text{main}}} \text{P1}
\]

\[
\begin{align*}
\text{Monomer stability} & \\
\text{AA} & \xrightarrow{\text{hv}}, \text{DCM, RT} & \text{BB} & \xrightarrow{\text{hv}}, \text{DCM, RT}
\end{align*}
\]

Side:

\[
\text{AA} + \text{AA} \xrightarrow{k_{\text{diff-AA}}} \text{P2}
\]

\[
\begin{align*}
\text{Monomer stability} & \\
\text{AA} & \xrightarrow{\text{hv}}, \text{DCM, RT} & \text{BB} & \xrightarrow{\text{hv}}, \text{DCM, RT}
\end{align*}
\]

Gegenhuber et al. Macromolecules 2017 50, 6451

\[
\text{R} = \text{H, Ph}
\]

\[
\text{Photoenol}
\]
THEORETICAL FRAMEWORK AND RATE COEFFICIENTS

$k_{\text{main}}$ via small molecule study

$k_{\text{self, AA}}$ via monomer stability test
DESIGN STEP-GROWTH PRECURSOR TOWARD HIGH MOLAR MASSES

Equimolar conditions, \( r = \frac{N_{A,0}}{N_{B,0}} = 1 \quad [\text{AA}]_0 = [\text{BB}]_0 = 0.02 \text{ mol L}^{-1} \)

\[
X_W = \frac{1 + p_A}{1 - p_A}
\]

No high molar mass chains
Off-stoichiometric conditions, \( r = \frac{N_{A,0}}{N_{B,0}} = 1.75 \)

\[ [AA]_0 = 0.07 \text{ mol L}^{-1}; [BB]_0 = 0.02 \text{ mol L}^{-1} \]
DESIGN STEP-GROWTH PRECURSOR TOWARD HIGH MOLAR MASSES

Incorporation of AA homopolymer after depletion of BB

Longer AA homopolymer chains if excess of AA

Stage 1
Stage 2
DESIGN STEP-GROWTH PRECURSOR TOWARD HIGH MOLAR MASSES

$p_A = 0.1$

$p_A = 0.45$

$p_A = 0.8$

$r = 1$

$r = 1.75$
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Precursor copolymer

- solubility
- still copolymer
- time for $p_A$

Retention time / min

normalized RI response

$M_w / \text{kg mol}^{-1}$

$r$

$M_w$ (exp.)

trendline

6 h

Precursor copolymer

Segmented copolymer

P1
# THEORETICAL FRAMEWORK

## DORMANT CHAINS

<table>
<thead>
<tr>
<th>Precursor polymer</th>
<th>After chain growth</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D_{AAA}</strong> <em>(n=4n)</em></td>
<td><strong>D_{A0}</strong> <em>(n=3n+k)</em></td>
</tr>
<tr>
<td><strong>AABB</strong></td>
<td><strong>AABB</strong></td>
</tr>
<tr>
<td><strong>BB</strong></td>
<td><strong>BB</strong></td>
</tr>
</tbody>
</table>

## MACRORADICALS

<table>
<thead>
<tr>
<th><strong>D_{mAAA}</strong> <em>(n=4n+k)</em></th>
<th><strong>R_{m0}</strong> <em>(n=4n+k)</em></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AABB</strong></td>
<td><strong>AABB</strong></td>
</tr>
</tbody>
</table>

## Bivariate

1. Chain length
2. Number of RAFT moieties
Step-growth polymer precursor for $r = \frac{N_A,0}{N_B,0} = 1.5$

$[\text{Styrene}]_0 = 8.74 \text{ mol L}^{-1}$

$[\text{AIBN}]_0 = 4.85 \times 10^{-3} \text{ mol L}^{-1}$

Step-growth polymer precursor for $r = \frac{N_A,0}{N_B,0} = 1$

$[\text{Styrene}]_0 = 8.74 \text{ mol L}^{-1}$

$[\text{AIBN}]_0 = 4.85 \times 10^{-3} \text{ mol L}^{-1}$
Step-growth precursor

$X_{\text{styrene}} = 1\%$

$X_{\text{styrene}} = 3\%$

$X_{\text{styrene}} = 6\%$

$N_{A,0} = 1.5$

RAFT groups well-located

Incorporation of styrene

Chain extension $\sim \# \text{RAFT}$

$\rightarrow$ Multisegment copolymers with on average 70 monomer units per segment
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CONCLUSIONS

- **Step-growth polymerization** of benzaldehyde and fumarate monomers containing a trithiocarbonate **RAFT moiety** employing **light-induced Diels Alder chemistry** is introduced.

- Unconventional **off-stochiometric conditions** necessary to compensate for the unavoidable **homopolymerization of the benzaldehyde monomer**.

- The step-growth precursor polymer is **successfully** employed as a **multifunctional CTA** for RAFT polymerization, leading to a **well-defined segmented copolymer**.

- **Polymer synthesis** and **advanced kinetic modeling** strategies are combined to identify optimal synthetic conditions and to predict their structural composition.
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