Effects of Cross-Linking Density on Interfacial Polymerization and Scaffold Formation in Functionalized Polymer Beads

Kristin M. Hutchins,†,‡ Chih-Yi Lee,§ Binbin Luo,§ Qian Chen,§,‡ and Jeffrey S. Moore*†,‡,

†The Beckman Institute for Advanced Science and Technology, ‡Department of Chemistry, and §Department of Materials Science and Engineering, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: Particles that are functionalized with complementary groups, which undergo bimolecular or co-initiation reactions via contact between particles, may act as blood-clotting mimics and find use in self-healing systems. Here, we show that modifying the cross-linker identity and density during particle synthesis affords polymer beads that exhibit differences in their ability to take up the monomer. The beads are functionalized with complementary co-initiator groups based on benzyol peroxide or dimethylaniline, which, when brought into physical contact, co-initiate polymerization of the surrounding monomers. During polymerization, the beads take up the liquid monomer and polymerization occurs at the interface of the complementary-functionalized beads to afford a scaffold composed of beads and new polymer. However, the robustness of the scaffold is dependent on the identity and density of the crosslinker that is incorporated into the bead matrix. Beads synthesized with lower degrees of crosslinking exhibit higher swelling capabilities and yield scaffolds with more beads and polymer connected to each other following interfacial polymerization. The findings presented here provide insight into how polymer bead properties affect interfacial reactions and will guide the design of new self-healing motifs.

Functionalized particles that respond to their external environment through physical and/or chemical changes are of interest in sensing, drug delivery, and catalysis. Such particles often undergo swelling and/or deswelling in response to an applied stimulus, which results in behaviors such as degradation, changes in characteristic spectral features, and catalytic activity. Particle swelling has also been demonstrated to influence the effectiveness of solid-phase synthesis, whereby swelling allows nearly all reactive sites within the particle to be chemically accessible.

We recently reported a radical polymerization initiated by physical contact between polystyrene (PS) beads functionalized with complementary co-initiator groups, namely, benzyol peroxide (BPO) and dimethylaniline (DMA). The initiation mechanism is believed to involve attack of the peroxide by DMA in an SN2 process, followed by homolytic cleavage that affords an anilinium radical cation and benzyol radical, and then decarboxylation to yield a phenyl radical that initiates polymerization (see Scheme S2 in the Supporting Information (SI)). Polymerization of a vinyl monomer (i.e., methyl acrylate (MA)) was triggered via interfacial contact between beads functionalized with complementary BPO or DMA groups. The beads were synthesized using a small amount of crosslinker (ca. 0.4 mol %) and are able to swell in the liquid monomer during interfacial polymerization. Polymerization between beads afforded a “clot-like” scaffold composed of beads and polymer. During our initial studies, we discovered that the beads are capable of swelling in organic solvents and liquid monomers, which we expected would affect their ability to interact with each other during the co-initiation, polymerization, and scaffold formation steps. Swellability in polymers and hydrogels is often determined by the amount and type of crosslinker utilized during synthesis. Our interest in self-healing materials and applications prompted us to investigate the different intricacies of reactive particles in an effort to optimize the initiation and synthesis of new materials at particle interfaces. Specifically, we were interested in determining what effects changing both the cross-linker identity and density would have on the ability of the beads to swell in the monomer (i.e., increase interfacial contact) and initiate polymerization at their interfaces, as well as the robustness (e.g., amount of beads connected) of the scaffolds that would be formed (see Scheme 1). We expect that our findings will aid in the design of materials for novel self-healing strategies.

Herein, we demonstrate that complementary-functionalized beads with low percentages of ethylene glycol dimethacrylate (EGDMA) crosslinker swell most in the monomer and form robust scaffolds during interfacial polymerization (Scheme 1). Beads incorporating higher percentages of divinylbenzene (DVB) crosslinker swell the least in the monomer and do...
not form scaffolds. We synthesized BPO- and DMA-functionalized PS beads of ca. 500 μm diameter using suspension polymerization, as reported.\textsuperscript{13} However, the identity and amount of crosslinker was varied during the polymerization step (see the SI). The crosslinkers utilized include the original crosslinker (0.3 mol % EGDMA),\textsuperscript{13} as well as 1.0 mol % EGDMA, 0.9 mol % DVB, and 2.0 mol % DVB. The functionalized beads were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (see the SI).

To determine the effect of the cross-linker identity and density on the ability of the beads to take up monomer, images of the BPO- and DMA-functionalized beads were collected with an optical microscope, and the diameters of 10 beads with each crosslinker and functional group were measured in their dry (nonswollen) state. Each bead was swollen in neat MA for a period of 30 min. Images of each bead were taken in the swollen state, surrounded by a drop of MA, the diameters were measured, and the swelling ratios calculated (see Chart 1, as well as Tables S2–S5 in the SI). The beads with 0.3 mol % EGDMA as the crosslinker displayed the largest swelling ratios in MA, while the beads with 2.0 mol % DVB swelled the least in MA. The beads synthesized with either 1.0 mol % EGDMA or 0.9 mol % DVB as the crosslinker exhibited similar swelling ratios in MA. When the crosslinker is identical, the BPO- and DMA-functionalized beads generally swell to a similar degree in MA. The beads synthesized with a smaller amount of crosslinker swelled more than beads synthesized with a greater amount of the identical crosslinker. Thus, to maximize bead swellability in a reactive MA monomer, a low molar amount of crosslinker was found most effective. We note that when the EGDMA crosslinker was decreased to 0.17 mol %, the beads did not withstand deprotection conditions.

To evaluate the co-initiation, interfacial polymerization, and scaffold formation ability of the beads with different crosslinkers, we performed contact-initiated polymerization experiments (see the SI). Equal amounts of BPO- and DMA-functionalized beads were placed in a weighing bottle, neat MA was added, and the beads were left to react for a period of 90 min. Unreacted MA monomer was rinsed away, and the beads were allowed to dry under ambient atmosphere. The bead scaffolds were analyzed via stereomicroscope imaging and confocal Raman microscopy (see Figures S6 and S7 in the SI).

Comparison of the scaffolds formed utilizing beads with 0.3 mol % EGDMA and 2.0 mol % DVB reveals the effects of bead swellability on interfacial polymerization/scaffold formation for the two extreme cases. Images of the bead scaffolds following the contact-initiated polymerization reaction demonstrate that beads with 0.3 mol % EGDMA as a crosslinker are strongly held in an aggregated scaffold (Figure 1a, as well as Video S1 in the SI). Specifically, nearly all of the beads utilized in the reaction are physically attached in one large scaffold. On the other hand, beads synthesized with 2.0 mol % DVB as a crosslinker are not held in a robust scaffold following the interfacial polymerization. Instead, in these samples, there are numerous instances where ca. 2–6 beads are physically attached to each other (Figure 1d), indicative of successful

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**Chart 1. Swelling Ratios\textsuperscript{a} of BPO- and DMA-Functionalized Beads in MA\textsuperscript{b}**

\[ \text{Swelling ratio} = \left( \frac{\text{swollen particle diameter}}{\text{dry particle diameter}} \right)^3 \]

\textsuperscript{a}The swelling ratio is equal to the cube of the swollen particle diameter divided by the cube of the dry particle diameter.

\textsuperscript{b}Abbreviations: EGDMA (ethylene glycol dimethacrylate), DVB (divinylbenzene). An average of 10 beads is reported for each sample.
polymerization, but no large scaffold is formed. The beads that were synthesized with either 1.0 mol % EGDMA or 0.9 mol % DVB crosslinkers exhibit scaffold formation abilities similar to each other (see Figures 1b and 1c). In both of these cases, a few smaller aggregates formed during interfacial polymerization. However, there are a significant number of defects wherein beads are not attached to a main scaffold in both instances, which did not occur in the case of beads incorporating 0.3 mol % EGDMA crosslinker. Confocal Raman microscopy was performed for each sample at the interface of two physically connected beads (see Figure S7). In all cases, regardless of incorporated crosslinker, a unique signal at ca. 1730 cm$^{-1}$, indicative of poly(methyl acrylate) (PMA), was present (see Figure S6).

Overall, the identity and amount of crosslinker incorporated into the BPO- and DMA-functionalized polymer beads affects their ability to swell in reactive monomer. This difference in swellability is manifested in the interfacial polymerization reaction and scaffold formation. Beads with a low molar amount of EGDMA crosslinker that exhibit high swelling ratios in MA monomer, thus increasing their interfacial contact, form robust scaffolds with nearly all beads attached to one main aggregate (see Video S1, Video S2 is the control). The beads synthesized with a higher molar amount of DVB crosslinker exhibit the lowest swelling ratios in MA monomer and do not form sturdy scaffolds. Regardless of the crosslinker, all complementary-functionalized particles are able to successfully co-initiate polymerization of MA. For implementation in a self-healing system, wherein contact between complementary particles would initiate the synthesis (i.e., polymerization) of new material, utilizing a smaller amount of crosslinker would allow beads that produce more robust scaffolds that could act in a manner similar to blood clot formation at damaged sites. In instances where numerous small defects are present, utilizing medium percentages of crosslinker (e.g., 1 mol %) would result in the formation of multiple smaller scaffolds that could seal damaged areas.

■ CONCLUSIONS

In summary, we have demonstrated that the crosslinker utilized in polymer bead synthesis directly affects the ability of the bead to swell in the monomer. While all the beads are able to initiate polymerization at their interfaces, beads with a low molar amount of EGDMA crosslinker swell the most in the liquid monomer and form robust, aggregated scaffolds. On the other hand, beads with a high molar amount of DVB crosslinker swell the least in the monomer and do not yield large scaffolds following interfacial polymerization. Beads synthesized with ca. 1% EGDMA or DVB crosslinker swell to a similar extent in monomer and produce small scaffolds via interfacial polymerization. These studies provide insight into the design of effective dual-initiator systems for application in self-healing systems.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b00771.

- Experimental details, DRIFT and Raman spectra, and swelling data (PDF)
- Video S1 of interparticle polymerization (AVI)
- Video S2 of interparticle polymerization control (AVI)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jsmoore@illinois.edu.

ORCID
Kristin M. Hutchins: 0000-0001-8792-2830
Qian Chen: 0000-0002-1968-441X
Jeffrey S. Moore: 0000-0001-5841-6269

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Notes
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