Liquid marbles as a micro-reactor for efficient radical alternating
copolymerisation of diene monomer and oxygen

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**Experimental Details**

**Materials**

2-Hydroxyethyl sorbate (HES) was prepared according to the method described in the literature.\(^1\) 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) was recrystallized from methanol. Commercially available lycopodium (Sigma-Aldrich) was used as received. All other commercial chemicals were used as received without further purification.

**Preparation of Liquid Marbles**

Lycopodium was selected as the solid stabilizer for the hydrophilic liquid, HES, because the formation of liquid marbles using lycopodium and hydrophilic liquids is well established and a number of researches using lycopodium-based liquid marbles have been reported.\(^2\) A liquid droplet with a given volume, typically 15 μL, was dropped on the lycopodium powder using a micropipette and was rolled over on the powder. Stability of the liquid marbles was visually judged.

**Polymerization of HES in a Liquid Marble**

A typical polymerization procedure was as follows. The milled AMVN crystals by a mortar were added to HES and the mixture was stirred at room temperature for 15 min. A given volume of the mixture was dropped on lycopodium powder in a Schlenk flask under oxygen flow to form the liquid marble (Fig. S1(a)). The Schlenk flask was sealed with a rubber stopper and connected to the oxygen balloon. The liquid marble containing the mixture of HES and AMVN was polymerized at 40 °C for a predetermined time under oxygen atmosphere (Fig. S1(b)). After the polymerization, the reaction mixture was dissolved in acetone-\(d_6\) and subjected to the \(^1\)H NMR spectroscopy. The consumption ratio of HES and the conversion to PP-HES, PHES, and degradation products were determined by the relative peak intensities of the characteristic \(^1\)H NMR peaks. When the liquid marbles more than two were polymerized, a desiccator was used instead of a Schlenk flask.

**Polymerization of HES in a Glass Tube**

A typical polymerization procedure was as follows. To a glass tube (diameter = 4, 10, and 15 mm), 1 mL of HES containing 1.1 wt % AMVN was added and the glass tube was purged with oxygen gas. The polymerization was carried out at 40 °C for 48 h. The polymerization mixture was subjected to the \(^1\)H NMR spectroscopy. The consumption ratio of HES and the conversion to PP-HES, PHES, and degradation products were determined by the relative peak intensities of the characteristic \(^1\)H NMR peaks.

**Measurements**

The number- and weight-average molecular weights (\(M_n\) and \(M_w\)) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and
calibration with standard polystyrenes. The $^1$H NMR spectra were recorded by a Bruker AV300N spectrometer.

**Stability of the liquid marble**

The liquid marble formed by using HES containing 1.1wt% AMVN was stable on the lycopodium powder. However, the one formed by using HES containing 2.0wt% AMVN was not able to form a stable liquid marble even on the lycopodium powder. In both cases, AMVN was not completely dissolved in HES and it seems that the existence of undissolved AMVN have negative effect on the stability of the liquid marbles. When 2,2’-azobis(valeronitrile) (AVN) was used instead of AMVN, 9.1wt% AVN completely dissolved in HES, and the mixture formed a stable liquid marble on lycopodium.

The liquid marbles consisting of HES and HES containing 1.1wt% AMVN were not stable on the other solid substrates such as glass and stainless steal. After the polymerization at 40 °C for 48 h, the liquid marble turned stable and was able to be transferred to glass and stainless steal.
Fig. S1. Schematic illustration of the formation of liquid marbles (a) and polymerization at 40 °C (b).
Figure S2. $^1$H NMR spectra of (a) HES, (b) PP-HES, (c) PHES, and (d) the reaction mixture polymerized in a liquid marble at 40 °C for 48 h measured in acetone-$d_6$ with full identification. PP-HES and PHES were prepared by the separate experiments.
Fig. S3. Consumption ratio of HES (●) and conversion vs time plots for radical polymerization of HES in a liquid marble (15 µL) under oxygen atmosphere at 40 °C: Conversions to PP-HES (□), PHES (▲), and FA-2HE (◇).

Fig. S4. GPC curve of PHES obtained in the liquid marble under argon atmosphere at 40 °C for 48 h: The 15 µL HES mixture containing 1.1 wt% AMVN was used.
Scheme S1. Fate of oxygen-centered radicals formed by the homolysis of polyperoxide.

Reference