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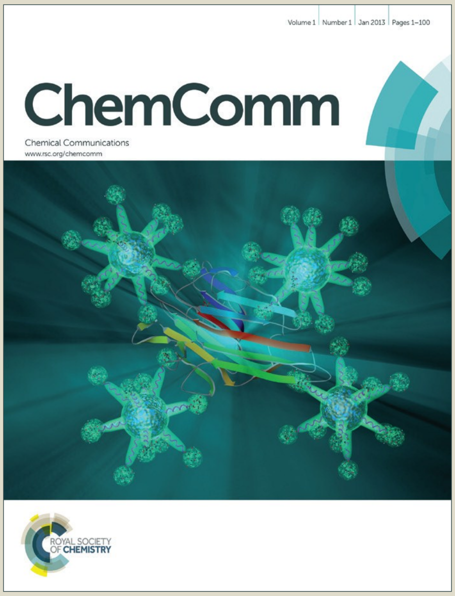

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Liquid marbles as a micro-reactor for efficient radical alternating copolymerization of diene monomer and oxygen

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Liquid marbles have been shown to be a novel micro-reactor to synthesize polyperoxides by the radical alternating copolymerization of the 1,3-diene monomer with oxygen in a good yield. Oxygen gas is effectively absorbed as a comonomer by the large and permeable gas-liquid interface of the liquid marbles.

Alternating copolymerization is a practical and efficient method to use non-homopolymerizable compounds as a comonomer. Epoxy derivatives and olefins including dienes undergo an alternating copolymerization with gases such as carbon dioxide,[1] carbon monoxide,[2] oxygen,[3, 4] and sulfur dioxide.[5] The resulting alternating copolymers are intriguing materials not only from the view point of using non-petroleum resources and the consumption of greenhouse gases, but also from the view point of the formation of main-chain functional polymers by chain polymerization. For instance, the alternating copolymers from oxygen and olefins, so-called polyperoxides, contain peroxy linkages as the main-chain repeating unit and undergo radical chain degradation by various stimuli including heat, UV irradiation, and redox reactions with amines. The functional polyperoxides with well-defined structures, such as the cross-linked polymers,[6-8] the graft polymers,[9] and the block copolymers,[10] were successfully synthesized for application as functional materials, e.g., dismantlable (de-bondable) adhesives[10, 11] biocompatible polymers,[12, 13] thermoresponsive polymers,[14, 15] and surface modifier.[10, 16] In the case of diene monomers, an interesting regiospecificity was also reported, i.e., 2,4-hexadienoates (sorbic esters) undergo a regiospecific 5,4-addition to yield alternating copolymers (polyperoxides) in the presence of excess oxygen and only 5,2-addition to yield non-degradable homopolymers in the absence of oxygen.[17-20] In order to exclusively synthesize polyperoxides from the homopolymerizable diene monomers, a polymerization was performed with oxygen bubbling and vigorous stirring, which are energy consuming processes. An increase in the oxygen-liquid interfacial area is supposed to be an effective and smart solution for the efficient synthesis of polyperoxides.

It is well known that a liquid droplet with high surface energy can be stabilized by solid particles with a low surface energy adsorbed on the gas-liquid interface, and the resulting core-shell type particles are called liquid marbles.[21-26] Recently, liquid marbles have attracted significant attention in view of their potential applications in cosmetics,[27, 28] transport & microfluidics,[29, 30] miniature reactors,[31, 32] personal & health care products,[33] sensors,[34-38] accelerometers, and gas storage.[40] The liquid marbles possess a large specific interfacial area, which leads to easy contact of the liquid droplet to external gases and thus the liquid marbles have been used for gas sensing,[35] heterogeneous hydrogenation reactions,[41] and the interfacial polymerization of a gaseous monomer using an external liquid as a catalyst.[42] In this study, we described the use of a liquid marble as a novel micro-reactor for the effective synthesis of polyperoxides (Fig. 1(a)). To the best of our knowledge, this is the first demonstration of a polymerization in the liquid marbles. The polymerization in the liquid marbles is expected to generate polyperoxides in a good yield with neither stirring the liquid nor oxygen bubbling during the reaction, and has the potential to save manufacturing energy.

To fabricate the liquid marbles, 2-hydroxyethyl sorbate (HES) and lycopodium (Fig. 1(b)) were used as a hydrophilic liquid and a hydrophobic solid particle, respectively. As shown in Fig. 1(c), the

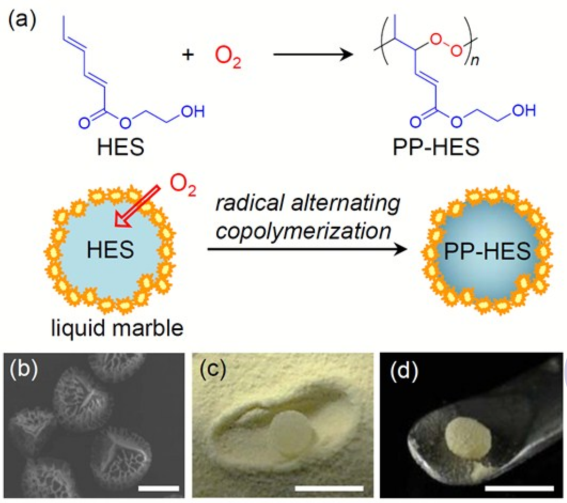

Fig. 1. (a) Schematic illustration of radical alternating copolymerization of HES and oxygen, (b) SEM image of a lycopodium (scale bar = 20 μm), (c) photograph of the liquid marble consisting of 15 μL HES droplet with lycopodium powder (scale bar = 5 mm), and (d) photograph of the polymerized liquid marble at 40 °C for 48 h (scale bar = 5 mm).

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Electronic Supplementary Information (ESI) available: experimental details, ^1H NMR, time-conversion plot, GPC data, and reaction scheme. See DOI: 10.1039/x0xx00000x

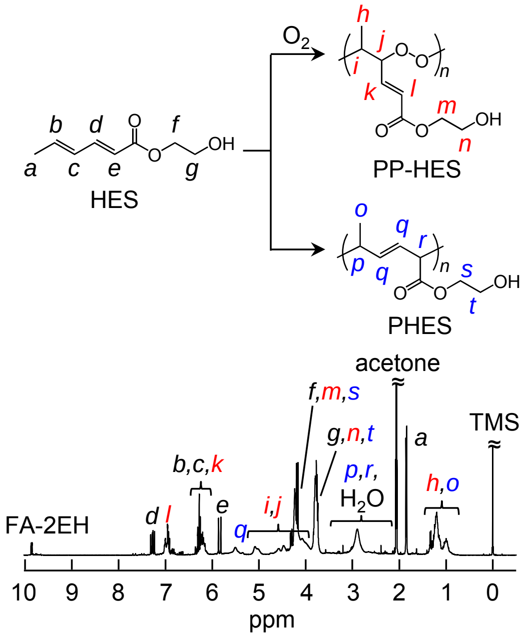

Fig. 2. ^{1}H NMR spectrum of the products obtained by radical alternating copolymerization in a liquid marble at 40 °C for 48 h measured in acetone-d_6.

stable and near-spherical liquid marble with a diameter of a few mm was formed by just rolling the 15-μL HES droplet on the lycopodium powder. A stable liquid marble was also formed on lycopodium using the HES droplet containing up to 1.1 wt% 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMVN) as a radical initiator, and later studies were carried out using the HES containing 1.1 wt % AMVN.

The polymerization of HES in the liquid marbles was carried out under atmospheric oxygen in a sealed vessel at 40 °C (Fig. S1, ESI). As shown in Fig. 1(d), the shape of the liquid marbles was maintained after the polymerization for 48 h. The ^{1}H NMR spectrum of the products after the 48-h polymerization is shown in Fig. 2. The characteristic peaks assignable to the polyperoxide of HES (PP-HES), the homopolymer of HES (PHES), unreacted HES, and a trace amount of fumaraldehyde 2-hydroxyethyl ester (FA-2HE) as one of the degradation products of PP-HES,[8] were detected (Fig. S2, ESI). Acetaldehyde (boiling point = 21 °C) as the other degradation product of PP-HES was not detected due to its evaporation during the polymerization.[8] The consumption ratio of HES and the conversion to PP-HES and PHES are plotted versus the polymerization time in Fig. 3. PP-HES was the main product for any polymerization time and the conversion to PP-HES reached ca. 50 % after the 48-h polymerization. The conversion to FA-2HE was less than 5% throughout the polymerization showing that the degradation of PP-HES is a minor reaction (Fig. S3, ESI). In contrast, when the polymerization in the liquid marbles was carried out under an argon atmosphere instead of oxygen for 48 h, PP-HES was not formed and only PHES was generated with a 23.3 % conversion (Table 1). These results clearly show that the monomer within the liquid marbles absorbed the external gas during the polymerization. Interestingly, the consumption ratio of HES under the oxygen atmosphere was 72.6 % and much higher than that in the argon atmosphere, i.e., 23.3%. It is expected that under the oxygen atmosphere, the polymerization was not only initiated by the primary radical from AMVN but also by the oxygen-centered radical from PP-HES (Scheme S1, ESI). This consideration is substantiated by the fact that the decomposition product of PP-HES, i.e., FA-2HE, was detected by the ^{1}H NMR. The result that the consumption ratio of HES continuously increased even after 5 half-life times of AMVN (= ca. 15 h, calculated by the decomposition rate constant of AMVN at 40 °C = 6.6×10^{-5} s^{-1}; k_d [s^{-1}] = $1.36 \times 10^{16}\exp(-11$ [kJ/mol]/RT)[43] is also explained by the initiation from PP-HES (Fig. 3).

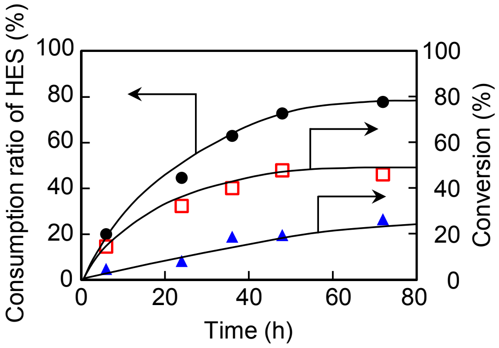

Fig. 3. Consumption ratio of HES (●) and conversion vs time plots for radical polymerization of HES and O$_2$ in a liquid marble (15 μL) at 40 °C: Conversions to PP-HES (□) and PHES (▲).

The GPC curves of the products obtained under an oxygen atmosphere were bimodal and the relative intensities of the peaks in the higher molecular weight region increased with the increasing polymerization time (Fig. 4). PHES obtained under the argon atmosphere resulted in a unimodal GPC curve and the M_n value was 1.64×10^4 with the peak top at log M = 4.3 (Fig. S4, ESI). It is then expected that in Fig. 4, the peaks above log M = 4.0 come from PHES, and the main peaks with the peak tops at around log M = 3.5 correspond to PP-HES. The molecular weights of PP-HES are on the order of 10^3 and are similar to those for PP-HES obtained by the solution polymerization of HES with oxygen bubbling and stirring, and the polyperoxides from other olefins under different conditions.[17, 20, 44] During the copolymerization of olefins including the 1,3-diene monomer with oxygen, frequent chain transfer of the oxygen-centered radical as one of the propagating radicals results in the formation of polyperoxides with a relatively low molecular weight. The same phenomenon is expected for the polymerization in the liquid marble. The shift in the main peak to the lower molecular weight region with the increasing polymerization time is attributed to the moderate decomposition of PP-HES during the polymerization. PP-HES obtained in the liquid marble underwent thermal degradation by heating at 100 °C in the same manner as the polyperoxides obtained by the conventional solution polymerization.[18]

Table 1. Results of radical polymerization of HES in the liquid marbles (15 μL) and glass tubes.[a]

reactor	interfacial area (mm^2/mL)	atmosphere	polymerization time (h)	consumption ratio of HES (%)[b]	Conversion (%)[b] PP-HES	PHES	FA-2HE
liquid marble	2000	O$_2$	48	72.6	47.7	19.6	5.2
liquid marble	2000	Ar	48	23.3	0	23.3	0
glass tube	13	O$_2$	6	7.4	1.5	5.8	0.12
glass tube	13	O$_2$	48	20.5	1.8	18.6	0.15

[a]HES with 1.1 wt% AMVN was polymerized at 40 °C. [b]Determined by ^{1}H NMR.

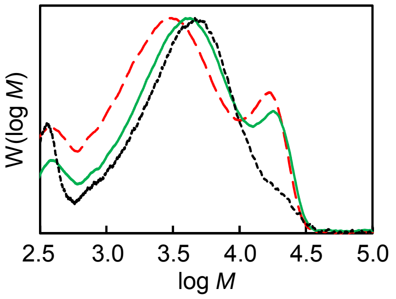

Fig. 4. GPC curves of the reaction mixture obtained by the copolymerization of HES and O_2 in the liquid marble at 40 °C for 6 (····), 36 (—), and 72 h (---).

The effect of the specific interfacial areas on the conversion to PP-HES was investigated by employing the liquid marbles formed by 3, 5, and 15 µL of the HES with AMVN (specific interfacial area = 1600, 2000, and 2800 mm^2/mL, respectively, assuming a sphere) (Fig. 5). As the control experiments, the polymerization was also carried out in glass tubes with different diameters, i.e., 4, 10, and 15 mm, using the 1-mL HES with AMVN (gas-monomer interfacial area = 13, 79, and 180 mm^2/mL, respectively). In the liquid marbles, PP-HES was the main product regardless to the specific interfacial areas and the conversion to PP-HES increased with the increasing specific interfacial areas, whereas the conversion to PHES was almost constant. In stark contrast, in the glass tubes, PHES was the main product, although the conversion to PP-HES increased with an increase in the gas-monomer interfacial areas. To obtain PP-HES as the main product at the same level as in the liquid marbles, a glass tube having a diameter greater than at least 45 mm is required to polymerize 1 mL of HES based on the calculation of the gas-monomer interfacial area. Considering the surface tension and viscosity of the monomers, it appears difficult to spread the monomers all over the wide glass tube, and the liquid marbles are an excellent micro-reactor to achieve a significantly large specific interfacial area.

In order to obtain information about the diffusion of oxygen within the liquid marbles, the conversion to PP-HES in each section of the liquid marble, i.e., the surface layer, center part, and complete liquid marble, were separately investigated. The polymerized liquid marble (15 µL) at 40 °C for 48 h was dipped in deuterated acetone for 10 s to dissolve the surface layer. The other polymerized liquid marble (15 µL) was frozen by liquid nitrogen and cleaved in half and the products at the center was collected. The results of the ^{1}H NMR analysis are summarized in Table 2. On the surface layer, the conversion to PP-HES reached 67.3% without the formation of PHES. Whereas, at the center, the conversion to PP-HES (= 41.1%) was much lower than that obtained on the surface layer and significant amount of PHES (= 21.7%) was formed. These results indicated that most of the oxygen absorbed from the gas-liquid interface was consumed in the surface layer because the addition of carbon-centered radicals to oxygen is much faster than that to the 1,3-diene monomer, i.e., HES.[18] This consideration is supported by the results obtained in the glass tube with the diameter of 4 mm (gas-monomer interfacial area = 13 mm^2/mL) at different polymerization times (Table 1). The conversion to PP-HES after 6-h and 48-h polymerizations was almost the same, i.e., 1.5 and 1.8%, respectively, whereas the conversion to PHES increased from 5.8 to 18.6% with the increasing polymerization time from 6 to 48 h. These results showed that PP-HES was formed during the early stage of the polymerization using the initially adsorbed oxygen, and thereafter, only the homopolymerization of HES proceeded under limited oxygen. Although PP-HES is rubbery due to its low glass transition temperature (= -4.2 °C), the oxygen permeability of PP-HES is expected to be lower than that for liquid HES,[45, 46] and this may be one of the reasons for the suppression of oxygen diffusion to the center part.

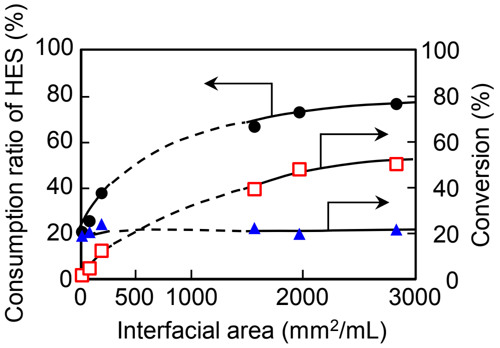

Fig. 5. Consumption ratio of HES (●) and conversion vs gas-liquid interfacial area plots for radical copolymerization of HES and O_2 in the glass tubes (diameter = 4, 10, and 15 mm, interfacial area < 200 mm^2/mL) and in the liquid marbles (volume = 3, 5, and 15 µL, interfacial area > 1500 mm^2/mL) under oxygen atmosphere at 40 °C for 48 h: Conversion to PP-HES (□) and PHES (▲).

Table 2. Conversion dependence on the sections in the liquid marble (15µL).[a]

location	consumption ratio of HES (%)[b]	Conversion (%)[b]		
		PP-HES	PHES	FA-2HE
surface[c]	81.7	67.3	0	14.4
center[d]	67.9	41.1	21.7	5.1
complete	71.4	46.1	18.7	6.5

[a] HES with 1.1 wt% AMVN was polymerized at 40 °C for 48 h. [b]Determined by ^{1}H NMR. [c]A liquid marble was dipped in acetone-d_6 for 10 s. [d]A frozen liquid marble was cleaved and the center part was collected by a pick.

In summary, it was demonstrated that the liquid marbles can work as an efficient and convenient micro-reactor to synthesize polyperoxides by absorbing external oxygen as a comonomer through the large and permeable gas-liquid interface. The copolymerization in the liquid marbles resulted in polyperoxides in good yield without oxygen bubbling and stirring, and the technique has the potential to reduce manufacturing energy. The method described here is simple and applicable to the other alternating copolymerization systems with gases[1, 2, 5] and the polymer reaction with gases such as the reversible trap-release system of carbon dioxide.[47, 48] Polyperoxide derivatives are known as degradable functional materials and the application of the polymerized liquid marbles containing polyperoxide to functional adhesives are currently under investigation.

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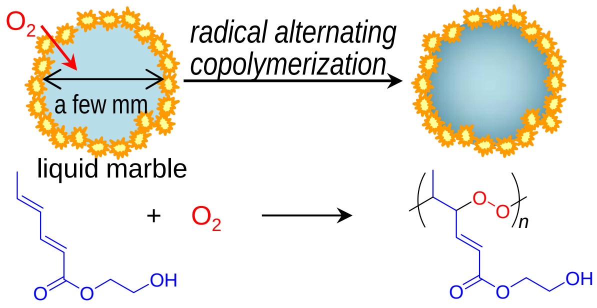

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