Synthesis of Polypyrrole and Its Derivatives as a Liquid Marble Stabilizer via a Solvent-Free Chemical Oxidative Polymerization Protocol

Musashi Seike, Makoto Uda, Toyoko Suzuki, Hideto Minami, Shinya Higashimoto, Tomoyasu Hirai, Yoshinobu Nakamura, and Syuji Fujii*

ABSTRACT: Solvent-free chemical oxidative polymerizations of pyrrole and its derivatives, namely N-methylpyrrole and N-ethylpyrrole, were conducted by mechanical mixing of monomer and solid FeCl₃ oxidant under nitrogen atmosphere. Polymerizations occurred at the surface of the oxidant, and optical and scanning electron microscopy studies confirmed production of atypical grains with diameters of a few tens of micrometers. Fourier transform infrared spectroscopy studies indicated the presence of hydroxy and carbonyl groups which were introduced during the polymerization due to overoxidation. The polymer grains were doped with chloride ions, and the chloride ion dopant could be removed by dedoping using an aqueous solution of sodium hydroxide, which was confirmed by elemental microanalysis and X-ray photoelectron spectroscopy studies. Water contact angle measurements confirmed that the larger the alkyl group on the nitrogen of pyrrole ring the higher the hydrophobicity and that the contact angles increased after dedoping in all cases. The grains before and after dedoping exhibited photothermal properties: the near-infrared laser irradiation induced a rapid temperature increase to greater than 430 °C. Furthermore, dedoped poly(N-ethylpyrrole) grains adsorbed to the air−water interface and could work as an effective liquid marble stabilizer. The resulting liquid marble could move on a planar water surface due to near-infrared laser-induced Marangoni flow and could disintegrate by exposure to acid vapor via redoping of the poly(N-ethylpyrrole) grains.

1. INTRODUCTION

Polypyrrole (PPy) is a promising conjugated polymer that was reported in a scientific journal for the first time more than 100 years ago,¹,² and has been applied to electrodes, antistatic coating, gas/metal ion adsorbents, sensors, actuators, biomaterials, and models for micrometeorites because of its tunable electrical conductivity, coloration, biocompatibility and environmental stability.³−¹⁶ PPy has been widely synthesized by chemical oxidative polymerization of pyrrole (Py) using ferric chloride (FeCl₃) as an oxidant in aqueous media, which is a simple and cost-effective process. In addition to PPy, PPy derivatives carrying an alkyl group at the N-position of the Py ring, namely poly(N-methylpyrrole) (PMPy) and poly(N-ethylpyrrole) (PEPy), have also received interest because of their potential applications as biosensors, antibacterial agents and anticorrosions, and electrodes.¹⁷−²² Similar to PPy, PMPy and PEPy have been synthesized by chemical oxidative polymerization in liquid media, such as water and chloroform. Here, there are problems with polymerizations of N-methylpyrrole (MPy) and N-ethylpyrrole (EPy) in the liquid media: the polymerizations of the Py derivatives in an aqueous medium resulted in low yields compared with that of Py due to the poor solubility of the monomers in water. The use of organic polymerization media containing halogens causes environmental problems, and production on a large scale are difficult.²¹ Moreover, the chemical synthesis and characterization of PPy derivatives carrying an alkyl group at the N-position have not yet been sufficiently conducted compared with PPy.

Solvent-free polymerization is an environmentally friendly method as it can eliminate the need for any solvent for polymerization.²³ The methodology of solvent-free polymerization has been introduced to chemical oxidative polymerizations, and vapor-phase chemical oxidative polymerization²⁵−²⁷ and direct mixing chemical oxidative polymerization²⁸,²⁹ have been developed. There are a few studies on
sodium hydroxide (NaOH, ≥98%), sodium hydroxide (NaOH, ≥98%), hydrochloric acid (HCl, 37 wt % aqueous solution), and poly(tetrafluoroethylene) powder (PTFE, particle diameter: 200 μm) were purchased from Sigma-Aldrich Co., LLC. N-Ethylpyrrole (EPy, >98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Each monomer was purified by passing through a column containing the aluminum oxide before use. Ferric chloride (FeCl₃, 99%) was received from Nacalai Tesque. Iron(III) chloride hexahydrate (FeCl₃·6H₂O, assay: min. 99.0%) and sulfuric acid (H₂SO₄, assay: min. 95.0%) were obtained from Wako Pure Chemistry, Ltd. pH test paper (046.55) was obtained from As One Co., Ltd. Deionized water (conductivity, less than 0.06 μS cm⁻¹) was prepared using an MFS RFD240NA GA25A-0715 deionized water producing apparatus (Advantec, Osaka, Japan).

2.2. Synthesis of PPy and Its Derivatives. Solvent-free method: PPy and its derivatives were synthesized as follows, according to method previously reported. FeCl₃ powder was prepared by grinding pristine powder utilizing a magnetic stirrer bar for 3 min at 750 rpm in a glass vial (200 mL) under N₂ atmosphere. Py or Py derivative monomers (1.5 g: 2.24 × 10⁻² mol (Py), 1.85 × 10⁻² mol (MPy), 1.58 × 10⁻² mol (EPy)) were then added dropwise to the FeCl₃ powder (monomer/FeCl₃ molar ratio, 1/4). The polymerizations proceeded at 25 °C under N₂ atmosphere for 24 h with stirring, resulting in production of black products. MeOH (~50 mL) was added to the reaction mixture in order to stop the polymerization, and then the mixture was left for 1 h. After removal of the supernatant, the black sediment was dispersed in pure MeOH using an ultrasonic bath (Bransonic M2800-J, Emerson, Japan) for 10 min. Until the supernatant became transparent and colorless, this sedimentation—redispersion cycle was repeated (over 10 times) to remove the remaining monomer, FeCl₃, FeCl₂, HCl, and any MeOH-soluble oligomers. The final products were dried under vacuum at 25 °C for 3 days.

Figure 1. (a) Synthesis strategy of polypyrrole (PPy) and its derivative grains by solvent-free chemical oxidative polymerization using FeCl₃ solid oxidant. Schematic illustrations for (b) light-driven locomotion of a poly(N-ethylpyrrole) (PEPy) grain-stabilized liquid marble (LM) floating on planar air—water surface and (c) HCl vapor-induced disruption of the LM via redoping of PEPy grains.

2. EXPERIMENTAL SECTION

2.1. Materials. Pyrrole (Py, reagent grade, 98%), N-methylpyrrole (MPy, ≥99%), methanol (MeOH, 95%), sodium hydroxide (NaOH, ≥98%), aluminum oxide (activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å), sodium hydroxide (NaOH, ≥98%), hydrochloric acid (HCl, 37 wt % aqueous solution), and poly(tetrafluoroethylene) powder (PTFE, particle diameter: 200 μm) were purchased from Sigma-Aldrich Co., LLC. N-Ethylpyrrole (EPy, >98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. Each monomer was purified by passing through a column containing the aluminum oxide before use. Ferric chloride (FeCl₃, 99%) was received from Nacalai Tesque. Iron(III) chloride hexahydrate (FeCl₃·6H₂O, assay: min. 99.0%) and sulfuric acid (H₂SO₄, assay: min. 95.0%) were obtained from Wako Pure Chemistry, Ltd. pH test paper (046.55) was obtained from As One Co., Ltd. Deionized water (conductivity, less than 0.06 μS cm⁻¹) was prepared using an MFS RFD240NA GA25A-0715 deionized water producing apparatus (Advantec, Osaka, Japan).

2.2. Synthesis of PPy and Its Derivatives. Solvent-free method: PPy and its derivatives were synthesized as follows, according to method previously reported. FeCl₃ powder was prepared by grinding pristine powder utilizing a magnetic stirrer bar for 3 min at 750 rpm in a glass vial (200 mL) under N₂ atmosphere. Py or Py derivative monomers (1.5 g: 2.24 × 10⁻² mol (Py), 1.85 × 10⁻² mol (MPy), 1.58 × 10⁻² mol (EPy)) were then added dropwise to the FeCl₃ powder (monomer/FeCl₃ molar ratio, 1/4). The polymerizations proceeded at 25 °C under N₂ atmosphere for 24 h with stirring, resulting in production of black products. MeOH (~50 mL) was added to the reaction mixture in order to stop the polymerization, and then the mixture was left for 1 h. After removal of the supernatant, the black sediment was dispersed in pure MeOH using an ultrasonic bath (Bransonic M2800-J, Emerson, Japan) for 10 min. Until the supernatant became transparent and colorless, this sedimentation—redispersion cycle was repeated (over 10 times) to remove the remaining monomer, FeCl₃, FeCl₂, HCl, and any MeOH-soluble oligomers. The final products were dried under vacuum at 25 °C for 3 days.
Solution method: Chemical oxidative precipitation polymerization was conducted in aqueous media to synthesize PPy, PMPy, and PEPy according to the method reported previously. Water (150 g) and monomer (1.5 g) were put in the reaction flask (200 mL). Then an aqueous solution of FeCl₃·6H₂O (14.1 g (PPy), 11.7 g (PMPy) and 9.9 g (PEPy) FeCl₃·6H₂O in 30 g water; monomer/FeCl₃·6H₂O molar ratio, 3/7) was added to the monomer solution. The polymerization proceeded at 25 °C for 24 h with magnetic stirring, which produced black products. The centrifugal purification was conducted via a sedimentation−redispersion cycle (over 10 times) to remove the remaining monomer, FeCl₃, FeCl₂, HCl and any oligomers. After removal of the supernatant, the black sediment was redispersed in water using the ultrasonic bath for 10 min. The black sediments were freeze-dried under vacuum at 25 °C for 3 days.

Dedoping: Each PPy and its grains were dispersed in the aqueous solution of NaOH and left at 25 °C for 3 days with magnetic stirring at 250 rpm to dedope the PPy and its derivatives. The pH of the dispersion was kept at ca. 12 with additional aqueous solution of NaOH during dedoping.

2.3. Measurements. Microscopy Study. The PPy and its derivative grains were observed using an optical microscope and scanning electron microscope (SEM). Details are shown in the Supporting Information.

Other Measurements. Details on laser diffraction (LD) measurements, Fourier transform infrared (FT-IR) spectroscopy, elemental microanalysis, X-ray photoelectron spectroscopy (XPS) analysis, aqueous electrophoresis, conductivity measurements, helium pycnometry, contact angle measurements, thermogravimetric analysis (TGA), UV/vis/NIR spectroscopy, and thermographic analysis are shown in the Supporting Information.

2.4. LM Formation. The water droplet (15 μL) was placed on a dried grain powder bed prepared on a polystyrene dish and was covered with the grains by rolling for 60 s. The hydrophobic dedoped PEPy grains were adsorbed at the air−water surface of the water droplet to create an LM.

2.5. Light-Induced Locomotion of LM. On the basis of the method reported previously, light-induced locomotions of the LMs were studied and numerically analyzed (Supporting Information). Briefly, a near-infrared (NIR) laser (808 nm; output power, ∼200 mW; spot diameter, 1 mm × 5 mm) was manually irradiated to the LM placed on planar air−water surface at an angle of ∼45°, aiming for three-phase contact line formed by the LM surface, air phase, and supporting water phase, using an NIR laser pointer (Changchun New Industries, Optoelectronics Technology, Co. Ltd., China).

2.6. HCl Gas-Responsive Behavior of LM. The LM stabilized with dedoped PEPy grains was placed on a glass slide, and a droplet of HCl aqueous solution (5 μL, 37 wt %) was placed near the LM (the distance between droplet and LM, 2.5 cm), followed by closing the system by placing the Petri dish. After the system was closed, the pH test paper next to the LM changed from yellow (ca. pH 7) to red (ca. pH 2) within 10 s, indicating that the atmosphere around the LM became HCl gas (boiling point, −85 °C).

3. RESULTS AND DISCUSSION

Solvent-Free Chemical Oxidative Polymerization. There have been no reports on solvent-free chemical oxidative
polymerization of Py and its derivatives by mechanical mixing of monomer and oxidant and, therefore, no morphological and chemical characterizations on the products. After addition of the monomers to the FeCl₃ powder, an exothermic reaction occurred and temperatures increased to 350, 213, and 190 °C from 25 °C for PPy, PMPy, and PEPy systems, indicating progress of the polymerization. The yields after the purification were gravimetrically determined to be 74% (PPy), 56% (PMPy), and 63% (PEPy), which were similar to those reported previously for P3HT and PEDOT synthesized by solvent-free polymerization (67 and 52%). As comparison, the yields of PPy, PMPy, and PEPy synthesized by aqueous chemical oxidative polymerization were gravimetrically determined to be 89%, 47%, and 2%. It is noteworthy that higher yields were obtained for the solvent-free system in the cases of PMPy and PEPy, compared with the aqueous polymerization system. This should be due to lower solubility of monomers (especially EPy) in aqueous medium: The monomer could not be completely dissolved and its concentration in aqueous medium was low, leading to low polymerization rate. All products were obtained as black powders after the purification, and optical microscopy studies indicated productions of atypical grains with sizes between a few micrometer and 50 μm (Figure 2a–c). LD studies also confirmed productions of micrometer-sized grains with volume-average diameters of 15 ± 38 μm (PPy), 17 ± 14 μm (PMPy), and 20 ± 17 μm (PEPy) (Figure 2g–i). Submicrometer-sized primary particles were observed on their surfaces in SEM images (Figure 2a–c, inset).

To investigate the mechanism of how the products were obtained as grains, the surface and cross-section of the products obtained by dropping monomers onto solid FeCl₃ powder without stirring were characterized. The FeCl₃ powder consisted of aggregates of micrometer-sized FeCl₃ primary particles (Figure S1), and a micrometer-sized porous structure was formed within the powder. Once the monomers were dropped onto the FeCl₃ solid, the monomers filled the pore space of the FeCl₃ powder. The monomers are expected to be polymerized on the surface of solid FeCl₃ particles, where they contact with each other, and the generated polymer filled the porous space of the FeCl₃ powder (Figure S2). There is a high possibility that the FeCl₃ dissolves into the liquid monomer phase and polymerization also occurs in the continuous monomer phase (Figures S2 and S3). (Note that FeCl₃ could be dissolved into acetone and 1-propanol, which show the similar solubility parameters (18.5 and 24.2 MPa½) with Py (23.1 MPa½), MPy (18.4 MPa½) and EPy (18.3 MPa½)). The polymer nuclei generated in the monomer phase should deposit onto the polymer-coated FeCl₃ particles to decrease interfacial free energy. Cross-sectional SEM observation of the products after the purification (removal of FeCl₃, FeCl₂, HCl, residual monomers, and oligomers) confirmed a micrometer-sized multihollow structure (Figure S4). During the polymerizations, these porous polymer materials were expected to be mechanically broken to the grains by magnetic stirring.

Doped PPy and Its Derivatives. To characterize the chemical structure of the products, FT-IR measurements were conducted (Figure 3). In the spectra of PPy and its derivatives (solvent-free), absorption bands originating from C−H out-of-plane deformation vibrations (PPy, 789 cm⁻¹), C−H in-plane deformation vibrations (PPy, 1045 cm⁻¹; PMPy, 1053 cm⁻¹; PEPy, 1062 cm⁻¹), C−N stretching vibration in the Py ring (PMPy, 1447 cm⁻¹; PEPy, 1450 cm⁻¹), and C−C stretching vibration in the Py ring (PPy, 1547 cm⁻¹; PMPy, 1560 cm⁻¹; PEPy, 1560 cm⁻¹) were observed. Furthermore, absorptions due to C−H stretching vibrations assigned to the methyl and ethyl groups bonded to the nitrogen of PMPy and PEPy
were also observed at 2941 cm$^{-1}$ (PMPy) and 2972 cm$^{-1}$ (PEPy), which agreed well with those reported previously.\textsuperscript{39,40} In addition to the characteristic absorptions mentioned above, absorptions near 1700 cm$^{-1}$ and near 3000 cm$^{-1}$, corresponding to carbonyl and hydroxy groups, were observed. These absorptions confirmed that the PPy and its derivatives (solvent-free) were overoxidized.\textsuperscript{41−43} The overoxidation is considered to be caused as the side reaction due to the generated reaction heat during the polymerization (>190 °C) and strong oxidizing ability of the solid FeCl$_3$.\textsuperscript{44} These absorptions due to overoxidation were also observed in the PMPy and PEPy systems (water medium), even though hydrated Fe$^{3+}$ oxidant with mild oxidizing ability was utilized and the temperature increase was suppressed during the polymerization due to heat transfer to the aqueous media (temperature increased only to 24.4 and 23.6 °C for PMPy and PEPy systems). The overoxidation in aqueous media should occur because of the low redox potential of MPy and EPy.\textsuperscript{40} Interestingly, PPy (water medium) did not show these absorptions due to the overoxidation. This should be because of the higher redox potential of Py compared to MPy and EPy\textsuperscript{40} and suppressed temperature increase (25.7 °C). The conjugate lengths of the PPy and its derivatives synthesized by solvent-free and aqueous chemical oxidative polymerizations were characterized by comparing the maximum absorption wavenumbers around 1531−1561 cm$^{-1}$. The wavenumber of maximum absorption around 1531−1561 cm$^{-1}$ is known to increase for the shorter conjugation length caused by introduction of carbonyl group via overoxidation.\textsuperscript{45,46} The maximum absorption wavenumbers of PPy and PMPy were 1547 cm$^{-1}$ (solvent-free) and 1532 cm$^{-1}$ (water medium) for PPy and 1563 cm$^{-1}$ (solvent-free) and 1547 cm$^{-1}$ (water medium) for PMPy. These results indicated that the conjugate lengths of PPy and PMPy synthesized by the solvent-free chemical oxidative polymerization were shorter than those synthesized by the aqueous chemical oxidative polymerization. This means that the overoxidation proceeds easier in the solvent-free chemical oxidative polymerization than aqueous chemical oxidative polymerization. On the other hand, the maximum absorption wavenumbers were 1568 cm$^{-1}$ (solvent-free) and 1591 cm$^{-1}$ (water medium) for PEPy, and the PEPy (water medium) was expected to have a shorter conjugate length. These results might be due to the low solubility of

Table 1. Elemental Microanalysis, Conductivity, and Density Data for Doped and Dedoped PPy, PMPy, and PEPy Materials

| Material          | C (%) | H (%) | N (%) | Cl (%) | Cl/N ratio | Conductivity$^a$ (S·cm$^{-1}$) | Density (g·cm$^{-3}$) |
|-------------------|-------|-------|-------|--------|------------|-------------------------------|----------------------|
| PPy (doped)       | 50.21 | 5.35  | 12.62 | 11.11  | 0.35       | 5.47 ± 0.12 × 10$^{-9}$       | 1.41 ± 0.03          |
| PPy (dedoped)     | 52.43 | 4.65  | 12.45 | 0.58   | 0.02       | <1.41 × 10$^{-11}$           | 1.29 ± 0.01          |
| PMPy (doped)      | 49.05 | 5.43  | 11.15 | 14.06  | 0.50       | 4.21 ± 0.04 × 10$^{-9}$       | 1.76 ± 0.02          |
| PMPy (dedoped)    | 55.01 | 5.56  | 12.36 | 2.91   | 0.09       | <1.41 × 10$^{-11}$           | 1.28 ± 0.01          |
| PEPy (doped)      | 57.05 | 5.90  | 10.92 | 12.83  | 0.46       | 2.65 ± 0.27 × 10$^{-9}$       | 1.37 ± 0.01          |
| PEPy (dedoped)    | 68.34 | 6.90  | 12.25 | 3.49   | 0.11       | <1.41 × 10$^{-11}$           | 1.19 ± 0.01          |

$^a$Measured by a four-point-probe method with an applied voltage of 10 V. $^b$Less than the lower limit of the measurement.
PEPy in aqueous medium, resulting in a shorter critical chain length when the PEPy precipitate is in aqueous medium.

Atomic percentages of C, H, N, and Cl were investigated by elemental microanalysis studies (Table 1). Regarding the PPy, the Cl/N atomic ratio was 0.35, which was in good agreement with the theoretical value calculated assuming the structural formula of PPy. On the other hand, the Cl/N atomic ratios for PMPy and PEPy were 0.50 and 0.46, which were larger than that for PPy. This is presumably because the redox potentials of the MPy and EPy monomers are lower than that of Py, and further positive charges were introduced to PMPy and PEPy by oxidation of these polymers.

XPS studies were conducted to characterize the surface chemistry of the products (Figure 4 and Table 2). As for the results of elemental microanalysis, signals due to C (originating from Py ring and alkyl groups on the Py ring), N and Cl (originating from dopant) were observed. In addition, the signal due to O (originating from hydroxy and carbonyl groups) introduced by overoxidation was also confirmed. The surface Cl/N atomic ratios were estimated to be 0.19 (PPPy), 0.31 (PMPy), and 0.25 (PEPy) (Table 2), which were lower than those estimated by elemental microanalysis. This might be due to the easier dedoping of the chloride dopant from the surface of each product during storage. The Cl/N atomic ratios of PMPy and PEPy were larger than that of PPy, which was the same trend as the results from elemental microanalysis.

Electrophoresis studies were conducted to determine zeta potentials of the products in pH 3–10 aqueous media (Figure 5a–c). In acidic and neutral conditions (pH 3–7), positive zeta potentials were measured, suggesting that the PPy and its derivatives carry positive charges introduced by doping and protonation in water media. The zeta potentials of PPy were ranged between ca. +25 and +10 mV, while those of PMPy and PEPy were ca. +40 mV at and below pH 7. This difference should be based on the difference of doping level (see elemental microanalysis and XPS results). Isoelectric points (IEPs) were 7.7 (PPPy), 8.9 (PMPy) and 9.2 (PEPy) and increased with an increase of the size of the alkyl group on the Py ring. This can be correlated with the strength of the electrostatic interaction between the cations of polymers and the chloride anion. The electrostatic interaction force \( F_e \) can be discussed on the basis of Coulomb’s law (eq 1)

\[
F_e = \frac{1}{4\pi \varepsilon_0 \varepsilon} \frac{q_1 q_2}{r^2}
\]

where \( \varepsilon \) is relative permittivity, \( \varepsilon_0 \) is permittivity of vacuum electric constant, \( q_1 \) and \( q_2 \) are signed magnitudes of the charges, and \( r \) is the distance between the charges. The relative

![Figure 5](https://doi.org/10.1021/acsomega.2c00327) - Figure 5. (a–c) Zeta potential vs pH curves obtained for (a) PPy, (b) PMPy, and (c) PEPy synthesized by solvent-free chemical oxidative polymerization. The solid lines are a guide to the eye, rather than a fit to the data. (d–f) Changes of static water contact angle on pressed pellets made from (d) PPy, (e) PMPy, and (f) PEPy grains with time.
permittivity is expected to decrease with an increase of hydrophobic alkyl group size, leading to stronger electrostatic interaction between charges based on Coulomb’s law and less dedoping. The larger the alkyl group on the Py ring, the lower the dielectric constant of products and the stronger the electrostatic interaction between the charges. Therefore, IEP was expected to increase with an increase of the alkyl group size.

The hydrophilicity–hydrophobicity balance of the doped PPy and its derivatives was studied by measuring the water contact angles on the pressed pellets (Figure 5d–f). It was confirmed that the larger the hydrophobic alkyl group, the higher the contact angle, indicating that hydrophobic alkyl groups were exposed on the surface of the grains.

The electrical conductivities and densities of the PPy and its derivatives were shown in Table 1. The conductivity measurements indicated that the larger alkyl group on the Py ring led to the lower conductivity. In the electrically conducting polymers, the electrical conductivity is realized by moving and hopping of cationic carrier on and between polymer chains. It has been well-known that the side-chain group makes it difficult for the carrier to hop between polymer chains, thereby reducing the conductivity.49 Additionally, the torsion angle between adjacent rings on the polymer backbone, caused by introduction of alkyl groups, has been reported to influence the electronic properties:50,51 methyl and ethyl groups bonded to Py ring could twist the backbone, resulting in lower conductivity. Regarding the density, PMPy had the highest density due to the highest loading amount of the high-density chloride ion dopant in the polymers. The PEPy had lower density than the PPy, despite the higher Cl/N ratio. This should be probably because ethyl group could increase the distance between the polymers, which makes tight packing among polymer chains via \( \pi-\pi \) stacking difficult.52

TGA measurements indicated gradual weight loss with an increase of temperature and residue amounts at 1000 \( ^\circ \)C were 51% (PPy), 58% (PMPy) and 55% (PEPy) (Figure S5). The residue after the TGA measurement should be carbon materials.53 The weight loss around 100 \( ^\circ \)C should be due to the evaporation of absorbed water, and the amount of absorbed water was the smallest for the most hydrophobic PEPy. Noteworthily, the weight losses could be observed around 150–220 \( ^\circ \)C, which was not observed for dedoped PPy (Figure S5). It has been reported that chloride ion dopant could be removed from doped PPy by heating to 165 \( ^\circ \)C in aqueous medium.54 Therefore, the weight loss observed in the doped PPy is expected to be due to dedoping of the chloride ion dopant.

Figure 6. (a) UV–vis–NIR spectra and (b, c) photothermal properties of (b) PEPy grains and (c) LM stabilized with dedoped PEPy grains. Shaded areas in (b) and (c) are irradiation periods with NIR laser light.

PPy-based materials are known to show photothermal properties.55,56 To investigate the light-to-heat photothermal property, pressed pellets made from the doped PPy and its derivatives were irradiated by NIR laser light, and their temperature changes were monitored using a thermograph (Figures 6b and S6). All doped materials showed a temperature increase up to >440 \( ^\circ \)C: 446.8 \( ^\circ \)C (PPy), 587.5 \( ^\circ \)C (PMPy), and 615.8 \( ^\circ \)C (PEPy) within 5 s. After the laser irradiation was stopped, the temperature decreased to room temperature after 20 s. The light-to-heat photothermal property could be explained in terms of NIR absorption and low luminescence efficiency of the PPy and its derivatives.57,58

Dedoped PPy and Its Derivatives. Next, the effects of dedoping on the chemical structure, morphology and bulk/surface chemistry were investigated. LD studies confirmed that there were no/little changes in \( D_n \) values before and after dedoping (PPy, 19 ± 17 \( \mu \)m; PMPy, 17 ± 15 \( \mu \)m; PEPy, 39 ± 71 \( \mu \)m) (Figure 2g–i). SEM studies indicated that there were few changes in the size and shape of grains, whereas the number of submicrometer-sized primary particles was reduced and micrometer-sized particles appeared after dedoping (Figure 2d–f), which is presumably because of the removal of the submicrometer-sized particles attached to the grain surfaces during the dedoping and purification process.

The FT-IR measurements confirmed that hydroxy and carbonyl groups exist in the dedoped PPy derivatives (Figure 3). The maximum absorption wavenumbers around 1531–1561 cm\(^{-1}\) after the dedoping were 1560 cm\(^{-1}\) (PPy), 1593 cm\(^{-1}\) (PMPy), and 1597 cm\(^{-1}\) (PEPy). Compared with the doped sample, the conjugation lengths were shortened in all systems, considering higher wavenumbers. This should be due to the nucleophilic attack of hydroxide ion during the dedoping in NaOH aqueous solution (pH 12), which introduced carbonyl groups that shorten the conjugation length in the products.46,59

Elemental microanalysis studies confirmed that the amounts of chloride ion dopant were reduced by dedoping (Table 1). The numbers of Py rings per one chloride ion dopant were calculated based on the Cl/N ratios: 2.9 rings (doped) and 50.0 rings (dedoped) for PPy, 2.0 rings (doped) and 11.1 rings (dedoped) for PMPy, and 2.2 rings (doped) and 9.1 rings (dedoped) for PEPy. The dedoping degree decreased with an increase of alkyl group length, which could be correlated with the strength of electrostatic interaction between cation on polymer chains and chloride dopant anion, as discussed above.

XPS measurements confirmed that the intensity of the signals of Cl were weakened after the dedoping in all systems (Figure 4 and Table 2). Interestingly, the signals of Cl did not
These results correlated with the UV liquid droplets covered by solid particles adsorbed at the gas dedoping (Figure S6). absorptions at 808 nm were similar before and after the no signi°

After dedoping (Table 1), because of the removal of the high-bonding energy after the dedoping. lower binding energy and remaining of intensity of the higher binding energy after the dedoping.

Both the conductivity and density of the products decreased after dedoping (Table 1), because of the removal of the high-density chloride ion, which works as a dopant to attain electric conductivity. Water contact angles increased after the dedoping in all systems (Figure S5d°f), which should be due to the decrease of concentration of the cation carrier on the polymer chains and the hydrophilic chloride ion dopant.

The dedoped PPy and its derivatives also absorbed NIR light as well as the doped ones, and the maximum temperatures on the surface of each pellet were 421.2 °C (dedoped PPy), 614.0 °C (dedoped PMPy), and 609.2 °C (dedoped PEPy), showing no significant differences compared to the doped samples. These results correlated with the UV°vis°NIR results that the absorptions at 808 nm were similar before and after the dedoping (Figure S6).

LMs Stabilized by Dedoped PEPy Grains. LMs are liquid droplets covered by solid particles adsorbed at the gas°liquid interface and can be easily formed by rolling the droplets on the particle/grain powder bed. The requirement for the particles to function as an LM stabilizer is that surfaces of the particles (and their dry powder) are hydrophobic. Thanks to near-spherical morphology and nonwetting character of the LMs, they can move on both solid and liquid surfaces without disruption. Recently, research on stimuli-responsive LMs, whose stability, structure, shape, and motion can be controlled/tuned by external stimuli, gains increasing interest. Based on their stimuli-responsive characters, potential applications of the LMs have been proposed in areas such as sensors, miniature reactors, microfluidics, pressure-sensitive adhesives, and material delivery carriers. Recently, we succeeded in synthesis of hydrophobic PPy, PANI, and PEDOT grains by aqueous chemical oxidative polymerizations using perfluoralkyl dopants and demonstrated that the dried grain powders can work as an LM stabilizer with a light-to-heat photothermal property. Additionally, the remote locomotion control of LMs on a planar air°water surface was realized by light-induced Marangoni propulsion: anisotropic heat gradient was generated around the LM floating on the water surface by the local NIR-laser irradiation of the LMs. Here, the perfluoralkyl dopants, which have been used as a hydrophobizing agent for PPy, PANI, and PEDOT, show low biodegradability and are known to be a persistent organic pollutant. Therefore, development of perfluoralkyl dopant-free light-responsive LM stabilizers is crucial.

The dedoped PEPy grains adsorbed at the air°water surface of the water droplets (15 μL, 3.0 mm diameter) in an autonomous manner, and LMs were fabricated individually by rolling them on the grain powder bed. On the other hand, LM could not be fabricated using PPy and PMPy grains before and after dedoping and PEPy grains before dedoping, and water droplets were absorbed into the grain powder beds due to their hydrophilic character. The dedoped PEPy grain-stabilized LMs could exist stably even on solid substrates including plastic and glass, independent of hydrophilicity°hydrophobicity balance, as well as on a planar air°water surface (Figure 7a). During and after the evaporation of inner water under ambient conditions, wrinkles were formed on the LM surface (Figure S7), indicating that the dedoped PEPy grains irreversibly adsorbed at the droplet surface. The weight ratio of dedoped PEPy grains and water was 2.8°100 (w/w), determined in a gravimetal approach. The LMs placed on the planar air°water surface were stable for more than 5 min. This stability was realized by the vapor gap bridged with the hydrophobic dedoped PEPy grains between the inner water of the LM and the supporting planar water surface. Here, no hydrophobic dopant is required to prepare hydrophobic LM stabilizer with a photothermal property, which is preferable from the viewpoint of the environment and is advantageous compared to the PPy, PANI, and PEDOT grains doped with the perfluoralkyl dopant.

The light-to-heat transducing photothermal property was introduced into the LM due to the dedoped PEPy grain stabilizer. NIR irradiation induced the rapid increase (within
locomotions of the LM (Movie S2). Another light source to realize Marangoni magnifying glass-focused sunlight could be also utilized as of the NIR laser irradiation could simply determine the heat diffusion to the inner water phase of the LM and the thinner dedoped PEPy grain layer thickness (93 μm) on the LM surface.

**Locomotion Control of Dedoped PEPy Grain-Stabilized LMs.** Research on the remote locomotion control of small objects received interest because of possible applications in material deliveries and microfluidics. The local NIR laser irradiation to the dedoped PEPy grain-stabilized LM realized on-demand locomotion control of the LM on the planar air–water surface. The NIR laser-induced locomotions of the LM were traced as shown in Figure 7a (white arrows indicated the locomotion directions, Movie S1). The direction of the NIR laser irradiation could simply determine the locomotion direction of the LM. It is noteworthy that a magnifying glass-focused sunlight could be also utilized as another light source to realize Marangoni flow-based locomotions of the LM (Movie S2).

Snapshots of the NIR light-driven locomotion of the dedoped PEPy grain-stabilized LM were obtained by thermography (Figure 7b). Before laser irradiation (t = 0 s), the LM was in an equilibrium state in a thermal manner with the surrounding bulk water surface. Once the NIR laser was irradiated, a temperature increase was observed at the laser-irradiated spot on the LM (t = 0.10 s, and then an anisotropic heat flow was generated on the bulk water surface (t ≥ 0.20 s). (Note that the NIR laser irradiation to the pure water does not cause temperature increase.) The line profile of the temperature recorded along the path of LM locomotion (t = 0.20 s in Figure 7b) confirmed that the temperatures of the NIR laser-irradiated point on the LM and of water surface near the LM were 42.3 and 32.5 °C (Figure 7c), which were higher than that of the bulk water surface (24.1 °C). The surface temperature difference between the water near the LM and the bulk water means the same thing as a surface tension difference. The surface tension difference was calculated to be 1.3 mN m⁻¹ (72.1 mN m⁻¹ − 70.8 mN m⁻¹), and the LM could move because of Marangoni flow generated by this surface tension difference.

The average path length per one NIR laser irradiation shot, average maximum velocity, and acceleration were determined to be 21.9 ± 7.1 mm, 17.2 ± 5.4 mm s⁻¹, and 87.2 ± 42.1 mm s⁻² by numerical analysis (Figure 8). The variations in the maximum velocity and acceleration should occur due to the variations in the positioning of the NIR laser light and the thickness of the PEPy grain layer on the LM (Figure S8). These values were on the same order of magnitude as those reported for the NIR light-induced locomotions of PPy and PANI grain-stabilized LMs. The average generated force (F₁) was calculated to be ~1.29 μN based on Newton’s formula (eq 2) using the average mass of the LMs (1.48 × 10⁻⁵ kg).

\[
F₁ = (\text{mass of LM}) \times (\text{average acceleration})
\]

The decay time of the locomotion was 1.10 ± 0.25 s (Figure S9), which was also similar to those determined for the LMs previously reported.

**Stimulus-Responsive Disruption of Dedoped PEPy Grain-Stabilized LMs.** After exposure of the dedoped PEPy grain-stabilized LM placed on a glass slide to the HCl gas in a closed system for approximately 45 s, the LM disrupted and the inner liquid leaked out (Figure S10a). The reason for the disruption of the LM is the redoping of dedoped PEPy with hydrophilic chloride ion dopant. XPS studies confirmed the reintroduction of chloride ions as a dopant to the dedoped PEPy after the redoping (Figure 4c,f). The water contact angle on the pellets decreased from 67° (dedoped) to 32° (redoped) after exposure to HCl gas (Figure S11). These results suggest that the inner liquid penetrated through the hydrophilized redoped PEPy grains attached to the LM surface and that the LM disrupted due to the contact between the inner liquid and the supporting glass slide substrate. In contrast, control experiment using the PTFE grain-stabilized LM resulted in no disruption and the LM maintained their near-spherical shape even after exposure to HCl gas for 30 min (Figure S10b). This should mean that HCl gas does not affect the wettability of the PTFE grains. Another control experiment using H₂SO₄ also resulted in no disruption of the PEPy-stabilized LM even after 10 min, and the surface of LMs formed the wrinkles by evaporation of inner liquid (Figure S12). Because the H₂SO₄ does not evaporate efficiently at room temperature (boiling point, >300 °C), the redoping of dedoped PEPy grains with the hydrophilic sulfate ions is unlikely. These results strongly indicated that the LM stabilized with dedoped PEPy grains responded only to the acidic gas.

4. CONCLUSION

In conclusion, we conducted solvent-free chemical oxidative polymerization by mechanical mixing of monomer and solid oxidant and succeeded in synthesis of PPy and its derivatives in a form of grain. Optical microscopy and SEM studies confirmed that the grains were a few tens of micrometers sized atypical aggregates of primary particles. Elemental microanalyses and FT-IR studies suggested the presence of larger amounts of hydroxy and carbonyl groups in the PPy grains synthesized by solvent-free polymerization compared with those synthesized by polymerization in aqueous medium,
indicating overoxidation to higher degree and shorter conjugation length. XPS studies confirmed that the PPy and its derivative grains were doped with chloride ions, and the chloride ion dopant was successfully removed by dedoping using aqueous solution of NaOH. Water contact angle measurements confirmed that the larger the alkyl group on the nitrogen of Py ring, the higher the hydrophobicity, and that the hydrophobicity increased after the dedoping. The grains exhibited photothermal properties and the NIR laser irradiation induced rapid temperature increase to >430 °C within a few seconds. It is noteworthy that sunlight could also work as one of the light sources, which can induce temperature increase. The easy and simple method developed in this study required only commercially available chemicals and enabled the solvent-free production of conjugated polymers with photothermal property. The solvent-free polymerization is conducted in the gas phase, which could be thought of as very hydrophobic polymerization media. Therefore, the solvent-free polymerization is suitable to synthesize hydrophobic grains, which are difficult to be synthesized in hydrophilic aqueous media. Thanks to the hydrophobic character, the dedoped PEPy grains were able to adsorb to the water droplet surface to stabilize LMs in an autonomous manner. Furthermore, it was demonstrated that the LM exhibited locomotions due to NIR laser/sunlight-induced Marangoni flow on the planar air–water surface and disintegrated by exposure to HCl vapor via redoping of the PEpy grains. This study substantially broadens and extends the scope of application of PPy and its derivatives.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00327.

Characterizations of the PPy and its derivative grains, locomotion analysis method (PDF)
Marangoni flow-based locomotion of the LM (AVI)
Marangoni flow-based locomotion of the LM (AVI)

AUTHOR INFORMATION

Corresponding Author
Syuji Fujii — Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan; Nanomaterials Microdevices Research Center, Osaka Institute of Technology, Osaka 535-8585, Japan; orcid.org/0000-0003-2562-9502; Email: syuji.fujii@oit.ac.jp

Authors
Musashi Seike — Division of Applied Chemistry, Environmental and Biomedical Engineering, Graduate School of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan
Makoto Uda — Division of Applied Chemistry, Environmental and Biomedical Engineering, Graduate School of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan
Toyoko Suzuki — Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan; orcid.org/0000-0002-5505-7405
Hideto Minami — Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe 657-8501, Japan; orcid.org/0000-0001-6173-6597

University, Kobe 657-8501, Japan; orcid.org/0000-0001-6173-6597

Shinya Higashimoto — Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan
Tomoyasu Hirai — Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan; Nanomaterials Microdevices Research Center, Osaka Institute of Technology, Osaka 535-8585, Japan; orcid.org/0000-0002-6441-5163
Yoshinobu Nakamura — Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, Osaka 535-8585, Japan; Nanomaterials Microdevices Research Center, Osaka Institute of Technology, Osaka 535-8585, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00327

Author Contributions
Musashi Seike: Conceptualization, Methodology, Investigation. Makoto Uda: Methodology, Investigation. Toyoko Suzuki: Methodology, Investigation. Hideto Minami: Methodology, Investigation. Shinya Higashimoto: Methodology, Investigation. Tomoyasu Hirai: Methodology, Investigation. Yoshinobu Nakamura: Methodology, Investigation. Syuji Fujii: Conceptualization, Methodology, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Funding
This work was supported by a Grant-in-Aid for Scientific Research (B) (JSPS KAKENHI Grant Nos. JP16H04207 and JP20H02803), Scientific Research on Innovative Areas “Engineering Neo-Biomimetics (JSPS KAKENHI Grant No. JP15H01602), “New Polymeric Materials Based on Element-Blocks (JSPS KAKENHI Grant No. JP15H00767), and Private University Research Branding Project (Type A: Osaka Industrial Technology Platform).

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We express our gratitude to Mr. Shun Mukai (Osaka Institute of Technology) for UV/vis/NIR studies.

REFERENCES

(1) Angeli, A. Sopra il nero del pirrolo. Nota preliminare. Atti. Accad. Naz. Lincei Cl. Sci. Fis. Mater. Re. 1915, 24, 3–6.
(2) Rasmussen, S. C. Conjugated and Conducting Organic Polymers: The First 150 Years. ChemPlusChem. 2020, 85 (7), 1412–1429.
(3) Skotheim, T. A.; Elsenbaumer, R. L.; Gardiner, J. R. Handbook of Conducting Polymers; 2nd ed.; NetLibrary, Inc.: Boulder, 1998; p 1120.
(4) Guimard, N. K.; Gomez, N.; Schmidt, C. E. Conducting polymers in biomedical engineering. Prog. Polym. Sci. 2007, 32 (8–9), 876–921.
(5) Balint, R.; Cassidy, N. J.; Cartmell, S. H. Conductive polymers: towards a smart biomaterial for tissue engineering. Acta Biomater. 2014, 10 (6), 2341–2353.
(6) Ateh, D. D.; Navsaria, H. A.; Vadgama, P. Polypyrrrole-based conducting polymers and interactions with biological tissues. J. R. Soc. Interface 2006, 3 (11), 741–52.
(7) Alshehri, S. A.; Al-Yasari, A.; Marken, F.; Fielden, J. Covalently Linked Polyoxometalate–Polypyrrrole Hybrids: Electropolymer Ma-
tials with Dual-Mode Enhanced Capacitive Energy Storage. Macromolecules 2020, 53 (24), 11120–11129.
(8) Okuzaki, H.; Funasaka, K. Electromechanical Properties of a Humidio-Sensitive Conducting Polymer Film. Macromolecules 2020, 53 (22), 8307–8311.
(9) Saoudi, B.; Jammul, N.; Chehimi, M. M.; Jaubert, A.-S.; Arkam, C.; Delamar, M. XPS study of the adsorption mechanisms of DNA onto polypyrrole particles. Spectroscopy 2004, 18, 519–535.
(10) Von Tumader, D.; Morávková, Z.; Minisy, I. M.; Hromádková, J.; Bober, P. Electropolymerized polypyrrole/safranin-O films: Capacitance enhancement. Polymer 2021, 230, 124099.
(11) Fuji, S.; Armes, S. P.; Jeong, A.; Rendoch, R.; Warren, S.; McArthur, S. L.; Burchell, M. J.; Postberg, F.; Srama, R. Synthesis and Characterization of Polypyrrole-Coated Sulphur-Rich Latex Particles: New Synthetic Mimics for Sulphur-Based Micrometeorites. Chem. Mater. 2006, 18 (11), 2758–2765.
(12) Fielding, L. A.; Hillier, J. K.; Burchell, M. J.; Armes, S. P. Space science applications for conducting polymer particles: synthetic mimics for cosmic dust and micrometeorites. Chem. Commun. 2015, 51 (95), 16886–16899.
(13) Stejskal, J.; Trchova, M.; Kasparyan, H.; Kopecky, D.; Kolska, Z.; Prokes, J.; Krivka, I.; Vajdak, J.; Humplícek, J. Pressure-Sensitive Conducting and Antibacterial Materials Obtained by in Situ Dispersion Coating of Macroporous Melamine Sponges with Polypyrrole. ACS Omega 2021, 6 (32), 20895–20901.
(14) Liu, S.; Masurkar, N.; Varma, S.; Avrutsky, I.; Reddy Arava, L. M. Experimental Studies and Numerical Simulation of Polypyrrole Trilayer Actuators. ACS Omega 2019, 4 (4), 6434–6442.
(15) Oh, W. C.; Fatema, K. N.; Liu, Y.; Jung, C. H.; Sagadevan, S.; Biswas, M. Polypyrrole-Bonded Quaternary Semiconductor Liquid-Box211-Graphene Nanocomposite for a Narrow Band Gap Energy Effect and Its Gas-Sensing Performance. ACS Omega 2020, 5 (28), 17337–17346.
(16) Du, L.; Gao, P.; Meng, Y.; Liu, Y.; Le, S.; Yu, C. Highly Efficient Removal of Cr(VI) from Aqueous Solutions by Polypyrrole/Monodisperse Latex Spheres. ACS Omega 2020, 5 (12), 6651–6660.
(17) Liu, Y.; Xiong, H.; Huang, H.; Li, L.; Huang, Y.; Yu, X. Fabrication of poly(N-methylpyrrole) nanotubes for detection of dopamine. Polym. Bull. 2018, 75 (6), 2357–2368.
(18) Prezyna, L. A.; Qiu, Y. J.; Reynolds, J. R.; Wnek, G. E. Interaction of cationic polypeptides with electroactive polypyrrole/poly(styrenesulfonate) and poly(N-methylpyrrole)/poly(styrenesulfonate) films. Macromolecules 1991, 24 (19), 5283–5287.
(19) Elilab, F.; Gumustekin, S.; Ozkazanc, H.; Ozkazanc, E. Poly(N-methylpyrrole) with high antibacterial activity synthesized via solvent-free synthesis, coating and morphogenesis of conductive polymer materials through spontaneous generation of activated monomers. Chem. Commun. 2014, 50 (80), 11840–11843.
(20) Yan, S.; Sato, K.; Suzuki, J.; Imai, H.; Oaki, Y. Amorphous 2D materials containing a conjugated-polymer network. Chem. Commun. 2019, 2 (1), 97.
(21) Fernandez, F. D. M.; Khadka, R.; Yim, J.-H. A comparative study between vapor phase polymerized PPY and PEDOT - Thermoplastic polyurethane composites for ammonia sensing. Polym. 2021, 127, 13463.
(22) Kumar, A.; Singh, R.; Gopinathan, S. P.; Kumar, A. Solvent free chemical oxidative polymerization as a universal method for the synthesis of ultra high molecular weight conjugated polymers based on 3,4-propylenedioxyphenichines. Chem. Commun. 2012, 48 (40), 4905–7.
(23) Huang, J.; Moore, J. A.; Acquaye, J. H.; Kaner, R. B. Mechanochemical Route to the Conducting Polymer Polyaniiline. Macromolecules 2005, 38 (2), 317–321.
(24) Inoue, H.; Hiroi, T.; Hanouchi, H.; Oyama, K.; Mayama, H.; Nakamura, Y.; Fujii, S. Poly(3-hexylthiophene) Grains Synthesized by Solvent-Free Oxidative Coupling Polymerization and Their Use as Light-Responsive Liquid Marble Stabilizer. Macromolecules 2019, 52 (2), 708–717.
(25) Inoue, H.; Shimogama, N.; Seike, M.; Oyama, K.; Muiak, S.; Higashimoto, S.; Hiroi, T.; Nakamura, Y.; Fujii, S. Poly(3,4-ethylenedioxythiophene) Grains Synthesized by Solvent-Free Chemical Oxidative Polymerization. Chem. Lett. 2019, 48 (8), 968–970.
(26) Fuji, S.; Matsuzawa, S.; Nakamura, Y.; Ohtaka, A.; Teratani, T.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H. Synthesis and characterization of polypyrrole-palladium nanocomposite-coated latex particles and their use as a catalyst for Suzuki coupling reaction in aqueous media. Langmuir 2010, 26 (9), 6230–6239.
(27) Paven, M.; Mayama, H.; Sekido, T.; Butt, H.-J.; Nakamura, Y.; Fujii, S. Light-Driven Delivery and Release of Materials Using Liquid Marbles. Adv. Funct. Mater. 2016, 26 (19), 3199–3206.
(28) CRC handbook of chemistry and physics: Chapman and Hall/CRCNetBASE: Boca Raton, FL, 1999; p CD-ROMs.
(29) Asaumi, Y.; Rey, M.; Oyama, K.; Vogel, N.; Hiroi, T.; Nakamura, Y.; Fujii, S. Effect of Stabilizing Particle Size on the Structure and Properties of Liquid Marbles. Langmuir 2020, 36 (44), 13274–13284.
(30) Asaumi, Y.; Rey, M.; Vogel, N.; Nakamura, Y.; Fujii, S. Particle Monolayer-Stabilized Light-Sensitive Liquid Marbles from Polypyrrole-Coated Microparticles. Langmuir 2020, 36 (10), 2695–2706.
(31) Ciric-Marjanovic, G.; Mentus, S.; Pasti, I.; Gavrilov, N.; Krstic, J.; Travs-Sejdic, J.; Strover, L. T.; Kopeckà, J.; Moravkovà, Z.; Trchovà, M.; Stejskal, J. Synthesis, Characterization, and Electrochemistry of Nanotubular Polypyrrole and Polypyrrole-Derived Carbon Nanotubes. J. Phys. Chem. C 2014, 118 (27), 14770–14784.
(32) Omastova, M.; Trchova, M.; KovaROVÁ, J.; Stejskal, J. Synthesis and structural study of polypyrrole prepared in the presence of surfactants. Synth. Met. 2003, 138 (3), 447–455.
(33) Sišková, M.; Asaumi, Y.; Uda, M.; Seike, M.; Oyama, K.; Higashimoto, S.; Hiroi, T.; Nakamura, Y.; Fujii, S. Dodecyl sulfate-doped polypyrrole derivative grains as a light-responsive liquid marble stabilizer. Polym. J. 2020, 52 (6), 589–599.
(34) Ishii, K.; Sato, K.; Oaki, Y.; Imai, H. Highly porous polymer dendrites of pyrrole derivatives synthesized through rapid oxidative polymerization. Polym. J. 2019, 51 (1), 11–18.
(35) Liang, W.; Lei, J.; Martin, C. R. Effect of synthesis temperature on the structure, doping level and charge-transport properties of polypyrrole. Synth. Met. 1992, 52 (2), 227–239.
(36) Leg, J.; Martin, C. R. Infrared investigations of pristine polypyrrole — Is the polymer called polypyrrole really poly[(pyrrole)-co-hydroxypyrrrole]? Synth. Met. 1992, 48 (3), 331–336.
(37) Thiéblemont, J. C.; Gabelle, J. L.; Planche, M. F. Polypyrrole overoxidation during its chemical synthesis. Synth. Met. 1994, 66 (3), 243–247.
(44) Niemi, V. M.; Knuuttila, P.; Österholm, J. E.; Korvola, J. Polymerization of 3-alkylthiophenes with FeCl3. Polymer 1992, 33 (7), 1559−1562.
(45) Tabáčiarová, J.; Míčušik, M.; Fedorko, P.; Omastová, M. Study of polypyrrole aging by XPS, FTIR and conductivity measurements. Polym. Degrad. Stab. 2015, 120, 392−401.
(46) Seike, M.; Asuma, Y.; Kawashima, H.; Hirai, T.; Nakamura, Y.; Fujii, S. Morphological and chemical stabilities of polypyrrole in aqueous medium for 1 year. Polym. J. 2022, 54, 169.
(47) Armes, S. P. Optimum reaction conditions for the polymerization of pyrrole by iron(III) chloride in aqueous solution. Synth. Met. 1987, 20 (3), 365−371.
(48) Pei, Q.; Qian, R. Protonation and deprotonation of polypyrrole chain in aqueous solutions. Synth. Met. 1991, 45 (1), 35−48.
(49) Papathanassiou, A. N.; Grammatikakis, J.; Sakellis, L.; Sakkopoulos, S.; Vittoratos, E.; Dalas, E. Hopping charge transport mechanisms in conducting polypyrroles: Studying the thermal degradation of the dielectric relaxation. Appl. Phys. Lett. 2005, 87 (15), 154107.
(50) Leclerc, M.; Guay, J.; Diao, L. H. Synthesis and characterization of poly(alkylanilines). Macromolecules 1989, 22 (2), 649−653.
(51) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. Organic polymers based on aromatic rings (polyparaphenylene, polypyrrole, polythiophene): Evolution of the electronic properties as a function of the torsion angle between adjacent rings. J. Chem. Phys. 1985, 83 (3), 1323−1329.
(52) Uda, M.; Higashimoto, S.; Hirai, T.; Nakamura, Y.; Fujii, S. Synthesis of poly(alkylamine)s by aqueous chemical oxidative polymerization and their use as stimul-responsible liquid marble stabilizer. Polymer 2021, 212, 123295.
(53) Oyama, K.; Seike, M.; Mitamura, K.; Watase, S.; Suzuki, T.; Omura, T.; Minami, H.; Hirai, T.; Nakamura, Y.; Fujii, S. Monodisperse Nitrogen-Containing Carbon Capsules Fabricated from Conjugated Polymer-Coated Particles via Light Irradiation. Langmuir 2021, 37 (15), 4599−4610.
(54) Thiéblemont, J. C.; Planche, M. F.; Petrescu, C.; Bouvier, J. M.; Bidan, G. Stability of chemically synthesized polypyrrole films. Synth. Met. 1993, 59 (1), 81−96.
(55) Lim, F.; Duan, Q.-Y.; Wu, F.-G. Conjugated Polymer-Based Photothermal Therapy for Killing Microorganisms. ACS Appl. Polym. Mater. 2020, 2 (10), 4331−4344.
(56) Gupta, N.; Chan, Y.-H.; Saha, S.; Liu, M.-H. Recent Development in Near-Infrared Photothermal Therapy Based on Semicontacting Polymer Dots. ACS Appl. Polym. Mater. 2020, 2 (10), 4195−4221.
(57) Li, F.; Winnik, M. A.; Matvienko, A.; Mandelis, A. Polypyrrole nanoparticles as a thermal transducer of NIR radiation in hot-melt adhesives. J. Mater. Chem. 2007, 17 (40), 4309−4315.
(58) Au, K. M.; Chen, M.; Armes, S. P.; Zheng, N. Near-infrared light-triggered irreversible aggregation of poly(oligo(ethylene glycol) methacrylate)-stabilized polypyrrole nanoparticles under biologically relevant conditions. Chem. Commun. 2013, 49 (89), 10525−10527.
(59) Beck, F.; Braun, P.; Oberst, M. Organic Electrochemistry in the Solid State-Overoxidation of Polypyrrole. Berichte der Bunsengesellschaft für physikalische Chemie 1987, 91 (9), 967−974.
(60) Kang, E. T.; Neoh, K. G.; Tan, K. L. X-ray photoelectron spectroscopic studies of electroactive polymers. In Polymer Characteristics; Springer: Berlin, 1993; pp 135−190.
(61) Perruchot, C.; Chehimi, M. M.; Delamar, M.; Lascelles, S. F.; Armes, S. P. Surface Characterization of Polypyrrole-Coated Polystyrene Latex by X-ray Photoelectron Spectroscopy. Langmuir 1996, 12 (13), 3245−3251.
(62) Aussillous, P.; Quéré, D. Properties of liquid marbles. Proc. Math. Phys. Eng. Sci. 2006, 462 (2067), 973−999.
(63) McHale, G.; Newton, M. I. Liquid marbles: topical context within soft matter and recent progress. Soft Matter 2015, 11 (13), 2530−2546.
(64) Lobel, B. T.; Thomas, C. A.; Ireland, P. M.; Wanless, E. J.; Webber, G. B. Liquid marbles, formation and locomotion using external fields and forces. Adv. Powder Technol. 2021, 32 (6), 1823−1832.
(65) Fujii, S.; Yusa, S.; Nakamura, Y. Stimuli-Responsive Liquid Marbles: Controlling Structure, Shape, Stability, and Motion. Adv. Funct. Mater. 2016, 26 (40), 7206−7223.
(66) Dupin, D.; Armes, S. P.; Fujii, S. Stimulus-Responsive Liquid Marbles. J. Am. Chem. Soc. 2009, 131 (15), 5386−5387.
(67) Bormashenko, E. Liquid Marbles, Elastic Nonstick Droplets: From Minireactors to Self-Propulsion. Langmuir 2017, 33 (3), 663−669.
(68) Ooi, C. H.; Nguyen, N.-T. Manipulation of liquid marbles. Microfluid. Nanofluid. 2015, 19 (3), 483−495.
(69) Fujii, S.; Sawada, S.; Nakayama, S.; Kapp, M.; Ueno, K.; Shitajima, K.; Butt, H. J.; Nakamura, Y. Pressure-sensitive adhesive powder. Mater. Horiz. 2016, 3 (1), 47−52.
(70) Nguyen, N.-K.; Ooi, C. H.; Singh, P.; Jin, J.; Sreejith, K. R.; Phan, H.-P.; Nguyen, N.-T. Liquid Marbles as Miniature Reactors for Chemical and Biological Applications. Adv. Funct. Mater. 2021, 31 (35), 2011198.
(71) Sazcek, J.; Yao, X.; Zvikovíc, V.; Mamlouk, M.; Wang, D.; Praman, S. S.; Wang, S. Long-Lived Liquid Marbles for Green Applications. ACS Appl. Mater. Interfaces 2020, 12 (36), 42183−42202.
(72) Avramescu, R. E.; Ghica, M. V.; Dina-Pirvu, C.; Udeanu, D. I.; Popa, L. Liquid Marbles: From Industrial to Medical Applications. Polym. 2018, 23 (5), 1120.
(73) Kawashima, H.; Mayama, H.; Nakamura, Y.; Fujii, S. Hydrophobic polypyrroles synthesized by aqueous chemical oxidative polymerization and their use as light-responsive liquid marble stabilizers. Polym. Chem. 2017, 8 (17), 2609−2618.
(74) Kawashima, H.; Paven, M.; Mayama, H.; Butt, H. J.; Nakamura, Y.; Fujii, S. Transfer of Materials from Water to Solid Surfaces Using Liquid Marbles. ACS Appl. Mater. Interfaces 2017, 9 (38), 33351−33359.
(75) Uda, M.; Kawashima, H.; Mayama, H.; Hirai, T.; Nakamura, Y.; Fujii, S. Locomotion of a Nonaqueous Liquid Marble Induced by Near-Infrared-Light Irradiation. Langmuir 2021, 37 (14), 4172−4182.
(76) Kawashima, H.; Okatani, R.; Mayama, H.; Nakamura, Y.; Fujii, S. Synthesis of hydrophobic polyanilines as a light-responsive liquid marble stabilizer. Polymer 2018, 148, 217−227.
(77) Shimogama, N.; Uda, M.; Oyama, K.; Hanochi, H.; Hirai, T.; Nakamura, Y.; Fujii, S. Hydrophobic poly(3,4-ethylenedioxythiophene) particles synthesized by aqueous oxidative coupling polymerization and their use as near-infrared-responsive liquid marble stabilizer. Polym. J. 2019, 51 (8), 761−770.
(78) Olsen, G. W.; Butenhoff, J. L.; Zobel, L. R. Perfluoroalkyl chemicals and human fetal development: An epidemiologic review with clinical and toxicological perspectives. Reprod. Toxicol. 2009, 27 (3), 212−230.
(79) Sonkar, R.; Kay, M. K.; Choudhury, M. PFOS Modulates Interactive Epigenetic Regulation in First-Trimester Human Trophoblast Cell HTLR-8/SVneo. Chem. Res. Toxicol. 2019, 32 (10), 2016−2027.
(80) Wang, H.; Pumera, M. Fabrication of Micro/Nanoscale Motors. Chem. Rev. 2015, 115 (16), 8704−8735.
(81) Xu, L.; Mou, F.; Gong, H.; Luo, M.; Guan, J. Light-driven micro/nanomotors: from fundamentals to applications. Chem. Soc. Rev. 2017, 46 (22), 6905−6926.
(82) Villa, K.; Pumera, M. Fuel-free light-driven micro/nanomachines: artificial active matter mimicking nature. Chem. Soc. Rev. 2019, 48 (19), 4966−4978.