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Communication

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Depolymerization-Powered Autonomous Motors Using Biocompatible Fuel

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S Supporting Information

ABSTRACT: We report the design of autonomous motors powered by the rapid depolymerization reaction of poly(2-ethyl cyanoacrylate) (PECA), an FDA-approved polymer. Motors were fabricated in two different length scales, 3 cm and 300 μm. The motion of the motors is induced by self-generated surface tension gradients along their bodies. The motors are capable of moving in various media, including salt solutions and artificial serum.

Designing micromachines, such as self-powered micromotors, which are capable of converting chemical energy into mechanical motion, is an important problem in science and engineering. These tiny motors are particularly useful in drug delivery,[1] self-assembly, and micromachinery. Several research groups, including ours, have already demonstrated that different mechanisms can be used to power these tiny motors including catalytic reactions,[2−13] ultrasonic resonance,[14,15] light,[16−18] electric,[19,20] and magnetic fields.[21−25] Despite these successes, the obstacles to micromotor design for practical applications remain, such as complicated fabrication procedures, use of toxic chemicals, inability to work in high ionic strength media, etc.

We have recently shown that rapid depolymerization of certain polymers can generate significant fluidic flow.[26,27] On the basis of this phenomenon, we have now devised a motor system which is powered by depolymerization reaction. Motors were fabricated over a length scale ranging from micrometers to centimeters. The fuel used is poly(2-ethyl cyanoacrylate) which is approved by FDA for biomedical applications. Under basic condition, the polymer undergoes a rapid depolymerization reaction and releases nontoxic small molecules.[28,29]

As initial proof of concept, a depolymerization-powered motor was fabricated at the centimeter scale. Shown in Figure 1, the motor was made using a short pipet tip (length approximately 3 cm) with the sharp end sealed by PDMS and the open end loaded with a plug of poly(2-ethyl cyanoacrylate) (PECA) polymer. When this motor is floated on 1 M NaOH solution, the rapid depolymerization of PECA polymer occurs. In our motor design, the depolymerization only occurs on the large open end of the pipet tip and releases small molecules in the vicinity (such as sodium cyanoacrylate, formaldehyde and ethanol: Figure 2), generating a concentration gradient of products which, in turn, powers the movement of the motor at a speed of approximately 9 cm/s (see Supporting Information [SI], video 1 [ja4089549_si_002.avi]). The propulsion mechanism is as depicted in Figure 3. At large length scale/high Reynolds number regime, the phoretic effects (i.e., diffusiophoresis, thermophoresis)[30−34] that power the motion of micromachines no longer play an important role. Typical velocities generated by phoretic mechanisms are in the range of μm/s, 4 orders of magnitudes smaller than that of our motor.[27,35,36]

Figure 1. Schematic demonstration of a PECA-loaded pipet tip motor. The sharp end is sealed with PDMS. and the large opening is sealed with a plug of PECA polymer (green plug).

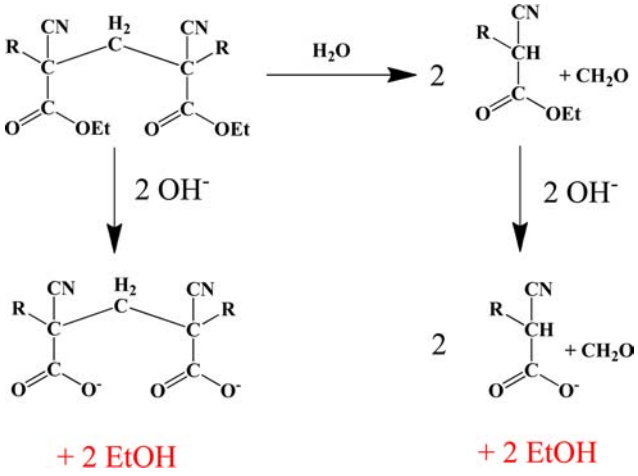

Figure 2. Depolymerization mechanism of PECA in basic solution.

Given that our motor is moving at the air/water interface, we propose that the propulsion mechanism is based on surface tension effect, similar to that for camphor boats,[37,38] oil droplets[39,40] or solvent-driven gels.[41,42] According to the mechanism proposed by Vezin *et al.*[29] and Lenaerts *et al.*,[28] with the degradation of PECA in the basic solution, surface active substances (e.g., ethanol[43]) are released from the reactive

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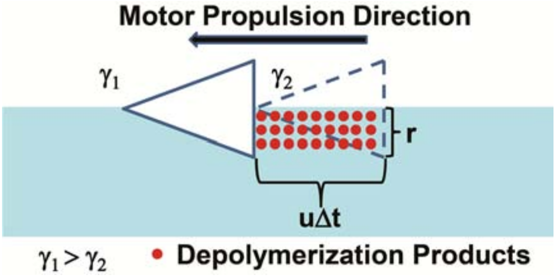

Figure 3. Schematic of the propulsion mechanism. The motor advances with speed u, and moves a total distance of $u\Delta t$ during time interval Δt. The generated depolymerization products lower the local interfacial tension near the large opening of the motor. (γ_1, γ_2 are the surface tension coefficients of the sharp end and open end, respectively).

end (the large open end filled with PECA fuel), lowering local surface tension, and generating a surface tension gradient across the motor which powers the movement of the motor. (Figure 3) Such a gradient of surface tension can give rise to transport for two distinct physical reasons:[44] Asymmetric surface tension force along the contact line and Marangoni convective flow. Due to the nonzero average surface tension gradient, the motor body is subject to a net force pointing toward the end with higher surface tension (the sharp end sealed with PDMS), and moves in that direction in consequence. The surface concentration gradient also results in Marangoni convective flow in the bulk solution which can affect the movement of floaters[38] or direct the motion of submerged objects.[41] The role of ethanol as a surface active substance was confirmed by our control experiment where NaOH/ethanol mixture (v/v = 1/1; NaOH, 1 M) (SI, video 2 [ja4089549_si_003.avi]) was used and the motor remained motionless due to a lack of significant surface tension difference between the two ends.

To further quantify our proposed mechanism, a steady state model was built (see Supporting Information [SI] for details). For simplicity, we assume that ethanol is the primary surface-active product generated by depolymerization and it constitutes a fraction (ω, ~20%) of the product; of course, the other organic products will also be surface active and contribute accordingly. As the motor moves directionally, half-submerged at the air−solution interface with velocity u, its movement is subject to Newton's second law. When terminal velocity is reached:

$$0 = F_{\text{surf}} - F_{\text{vis}} \tag{1}$$

where F_{surf} is the surface tension force, which is caused by the asymmetric surface tension along the contact line, and F_{vis}, the viscous drag force. F_{vis} results from the relative movement between the motor and solution, and therefore is affected by both the motion of the motor and fluid flow.[40] For a 3-cm motor that is moving at a speed around 9 cm/s, Reynolds number is 2700. At high Reynolds number,[45,46]

$$F_{\text{vis}} = \frac{1}{2}\rho(u - v)^2 C_d A$$

where ρ represents the fluid density, v the flow velocity, C_d the resistant coefficient, A the reference area, and in this case: $A = (1/2)\pi r^2$. As for the fluid dynamics and surface active species (ethanol) in the aqueous phase, they are subject to Navier−Stokes equation and convection-diffusion equation at steady states, respectively:

$$\rho v \nabla v = -\nabla p + \nabla \mathbf{T} + f \tag{2}$$

$$\frac{\partial c}{\partial t} = \nabla(D\nabla c) - \nabla(vc) + R \tag{3}$$

where p represents the pressure, $\mathbf{T}$ the stress tensor, f body forces, c concentration of ethanol, D diffusion coefficient of ethanol, and R the "source" of ethanol, i.e. the depolymerization reaction at the open end of the motor.

On the basis of experimental observations, the above model can be simplified, and the following rough estimation of the motor speed can be made. When the motor starts moving unidirectionally with a high speed, contribution of convective flow in the aqueous phase to the motor movement is negligible, as shown in SI videos 3 and 4 (ja4089549_si_004.avi and ja4089549_si_005.avi). Such an assumption has also been verified by Kitahata *et al.*[38] Therefore, eq 2 and the convective term in eq 3 can be neglected, and F_{vis} is only related to motion of the motor, (i.e., $F_{\text{vis}} = (^1/_2)\rho u^2 C_d A$). In addition, when the motor is moving with a high speed powered by a rapid depolymerization reaction (reaction rate at the PECA-filled end, $J = 9.43 \times 10^{-2}$ mol·m^{-2}·s^{-1}, see SI for the measurement of depolymerization rate), the contribution from the slow diffusion ($D = 1.24 \times 10^{-9}$ m^2·s^{-1}) to the concentration of ethanol can also be neglected, with chemical reaction as the predominant factor for the change in ethanol concentration. The depolymerization rate is assumed to be constant from time t to $t + \Delta t$, and in that time period the motor moves a total distance of $u\Delta t$, generating $\omega J(1/2)\pi r^2 \Delta t$ mol ethanol (r denotes the radius of the powering end of the motor, and $r = 1$ mm in the system). Since depolymerization reaction is the only contributing factor, concentration of ethanol at the tail of the motor is

$$c = \frac{\left(\omega J \frac{1}{2}\pi r^2 \Delta t\right)}{\left(u\Delta t \frac{1}{2}\pi r^2\right)} = \frac{\omega J}{u}$$

while there is negligible ethanol in solution ahead of the motor.[47] At low concentration of ethanol, the surface tension of the solution has a linear relationship with the local ethanol concentration:[43] $\gamma = \gamma_0 - bc$, where γ is the surface tension of the aqueous solution, γ_0 is the surface tension of water, and b is a constant; therefore, $F_{\text{surf}} = 2rbc$. According to the above assumptions, eq 1 can be rewritten as the following equation:

$$2rbc = \frac{1}{4}\rho u^2 C_d \pi r^2 \tag{4}$$

The solution of the equation

$$u = \sqrt[3]{\frac{8b\omega J}{\rho \pi r C_d}}$$

presents an estimation of motor speed at 15 cm/s. This is in good agreement with the experimental result (9 cm/s), and thus verifies the mechanism proposed. The propulsion force of the motor is approximately 7 μN, as calculated from $F_{\text{surf}} = 2rbc$.

In the next step, we designed a micrometer-sized motor. In addition to size reduction, we also aimed to eliminate the requirement of a strongly basic solution. Anion-exchange beads were chosen for this experiment since they can quickly release OH$^-$ ions which trigger the depolymerization of PECA polymer, thereby obviating the need for a strongly basic solution, In addition, the porous structure of the beads makes them ideal carriers for PECA polymer through simple physical absorption. The smaller motor was fabricated by soaking anion-exchange beads (Amberlite IRA400, hydroxide form) in PECA/acetone solution. When dried, these tiny beads (diameter approximately 300 μm) became loaded with PECA. The PECA-loaded beads were then coated with poly(methyl methacrylate) (PMMA) on one side. (Figure 4). The purpose of the unsymmetrical coating of PMMA was two-fold. First, PMMA coating gives the beads appropriate density so that they float on water. Second, PMMA blocks one side of the beads which enables depolymerization to occur only on the other side, thereby imparting directionality to the movement (Figure 4).

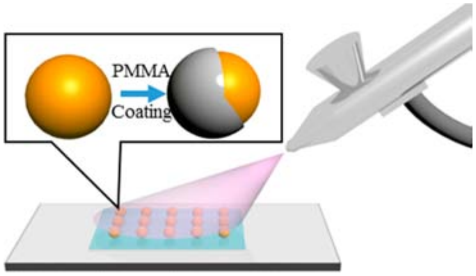

Figure 4. Fabrication process for PECA-loaded Amberlite beads. Amberlite IRA400 (hydroxide form) was first soaked in PECA/acetone solution and recovered by centrifugation. Then the dried PECA-loaded beads were adhered to a strip of double-sided 3 M Scotch tape mounted on a glass slide. A layer of PMMA was carefully coated onto one side of the beads by an airbrush. (Solid yellow spheres represent Amberlite beads, gray shells represent PMMA-coated beads.)

When the PECA-loaded beads were floated on 1 M NaCl solution, the ion-exchange process started immediately. OH^- ions were released, and Cl^- ions were bonded to the polymer backbone. (Figure 5). The increase in local pH triggers the depolymerization of PECA present in the beads. Since this depolymerization reaction happens on the unprotected side of the bead, the soluble depolymerization products generate surface tension gradients which push the bead to move at an average speed 160 mm/s (approximately 500 body lengths per second) (see SI, video 5 [ja4089549_si_006.avi]). After the experiment (1 bead in 5 mL of solution), the pH of the bulk solution had increased from 5.8 to 6.3. Since the anion-exchange function of Amberlite works regardless of the anionic species present in solution, we repeated the same experiment in 1 M KNO_3 and in 1 M K_2SO_4. In both cases, the motors moved at a speed similar to that in NaCl solution, (average speeds of 210 and 130 mm/s for KNO_3 and K_2SO_4, respectively).

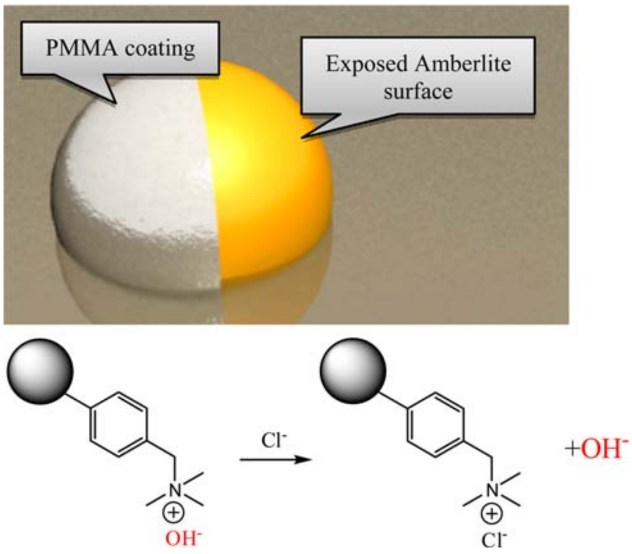

Figure 5. Schematic representation of PECA-loaded Amberlite micromotor on 1 M NaCl solution. When in contact with Cl^- ions, the unprotected Amberlite surface releases OH^- ions which trigger the depolymerization of PECA.

Several control experiments were carried out to establish the requirements of both PECA and a high local pH for the motors to function. The increase in pH can be alleviated by using a buffer solution, and the same experiment when performed in a pH 7.4 phosphate buffer saline showed very little motor motion compared to that in 1 M NaCl although both had the same anion concentration; (10 mm/s in pH 7.4 buffer vs 160 mm/s in 1 M NaCl) (see SI, video 6 [ja4089549_si_007.avi]). We also used Tera-gel beads (inert polystyrene beads with no ion-exchange ability) instead of Amberlite IRA400 as the carrier for PECA polymer. When added to 1 M NaCl, the PECA-loaded Tera-gel bead remained motionless, whereas the same beads moved in 1 M NaOH. To highlight the importance of in situ generation of OH^- from ion-exchange beads, we performed another experiment using Amberlite IRA400, chloride form beads. These beads have the same structure as the IRA400 hydroxide form beads, except the OH^- groups are substituted by Cl^- groups. As a result, the PECA-loaded beads did not move when exposed to 1 M NaCl solution (SI, video 7 [ja4089549_si_008.avi]). In order to rule out electrophoretic motion arising from the ion-exchange process,[28] we carried out an experiment in 1 M NaCl; however, without preloading the Amberlite IRA400 beads with PECA polymer. The bead remained stationary despite the ongoing ion-exchange process.

In conclusion, we have shown that it is possible to use a depolymerization reaction to power autonomous motor systems. The motors work at both centimeter and micrometer scales. The observed speed was up to 660 body lengths per second for the microscale motor. The propulsion is due to a surface tension gradient arising from the products of the depolymerization reaction. The motors use an FDA-approved biocompatible polymer as fuel and can work at physiological pH range and in high ionic strength environment. This opens up the possibility of their use in biological systems. As an example, triggered release of a specific drug can occur if it is either embedded in the PECA polymer or loaded inside the motor and sealed with PECA.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of motor fabrication, determination of depolymerization rate, modeling, and videos (ja4089549_si_002.avi−ja4089549_si_008.avi). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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