

Synthesis of Molecularly Imprinted Polymer Particles by Suspension Polymerization in Silicon Oil

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Abstract: Molecularly imprinted polymers using 2,4-dichlorophenoxyacetic acid (2,4-D) as templates were prepared by suspension polymerization in silicon oil. The polymer particles exhibited regular shape in the micro-scale range. The adsorbing experiments indicated that the imprinted polymer particles possessed higher affinity to 2,4-D than the non-imprinted polymer particles.

Keywords: Molecularly imprinted polymer, particles, suspension polymerization, silicon oil.

Molecular imprinting is a method to prepare polymers with recognition site of desired and predetermined selectivity¹. Molecularly imprinted polymers (MIP) are prepared by copolymerizing functional and cross-linking monomers in the presence of a molecular template. The synthesized MIP possess micro-cavities with a three-dimensional structure complementary in both shape and chemical functionality to that of the templates, and are able to rebind the templates. They have been successfully used in many fields, such as separation processes (chromatography, capillary electrophoresis, solid-phase extraction and membrane separations), immunoassays, antibody mimics, sensors, catalysis and artificial enzymes².

The classical method of preparing MIP is bulk polymerization followed by grinding to particles. They are irregular, polydisperse and usually include a large portion of fine particulate material. Extensive sieving and sedimentation to achieve a narrower size distribution and to remove fine particles make time and labor wasting. So many methods have been developed to directly prepare spherical MIP particles, such as suspension polymerization^{3,4}, precipitation polymerization⁵, and emulsion polymerization⁶. Water and liquid perfluorocarbon^{3,4} have been generally used as dispersion phase in suspension polymerization, however, a small amount of water diffusing into the organic phase is enough to destroy the hydrogen bonds and liquid perfluorocarbon is too expensive proverbially. Liquid paraffin was also used as dispersing phase⁷. But especial dispersing device was required, the pre-polymerization mixture must be dispersed by vigorous stirring (8000 rpm). On the other hand, the viscosity of liquid

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paraffin was not high enough that fast polymerization would cause the droplets to congregate.

In this letter, silicon oil was applied for the first time as dispersion phase to synthesize MIP particles by suspension polymerization.

Experimental

0.75 mmol 2, 4-dichlorophenoxyacetic acid (2,4-D), 3 mmol 4-vinylpyridine (4-VP), 15 mmol ethyleneglycol dimethacrylate (EGDMA) and 1 mmol azobisisobutyronitrile (AIBN) were dissolved in 3 g acetonitrile. 50 mL silicon oil was purged with a stream of nitrogen gas for 15 min. The pre-polymerization mixture was added and was dispersed at 800 rpm for 5 min, and then polymerized under UV-radiation at 366 nm for 24 h without stirring. The synthesized particles were filtered and washed with petroleum ether and toluene. To extract 2,4-D from the polymer networks, the particles were washed with MeOH-pyridine (90/10, v/v) (12×4 h) and MeOH (3×4 h). At last the particles were dried in vacuum at 50°C overnight. The non-imprinted polymer particles were prepared and treated in the same manner without 2, 4-D.

100 mg of MIP particles were placed in a 25 mL conical flask, and mixed with 10 mL 2,4-D acetonitrile solution with specific initial concentrations ranging from 0.2 to 5.0 mmol/L. After the conical flasks were shaken for 24 h, the solution was centrifuged at 4000 rpm for 5 min. The concentration of free 2,4-D in the solution was measured by UV spectrophotometry at 285 nm. In addition, the adsorbing amount of 2,4-D to the non-imprinted polymer particles was also determined.

Figure 1 SEM photographs of imprinted polymer particles (a, b) and non-imprinted polymer particles (c, d)

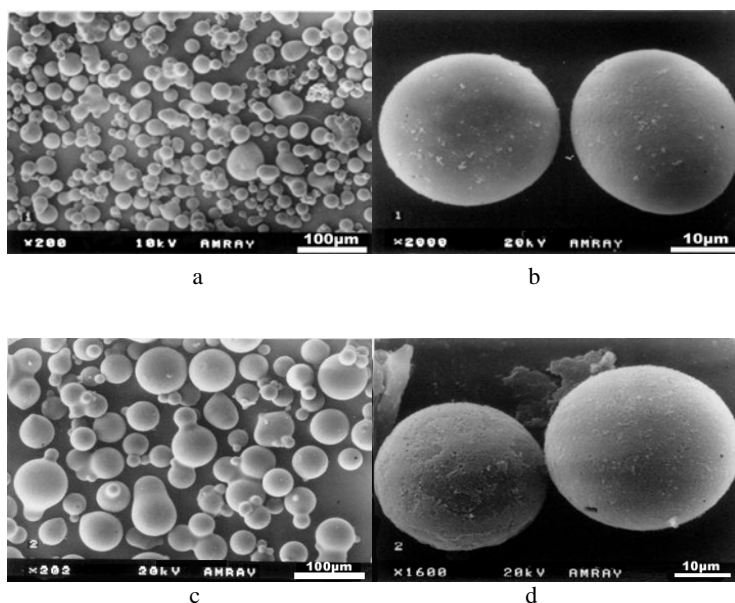
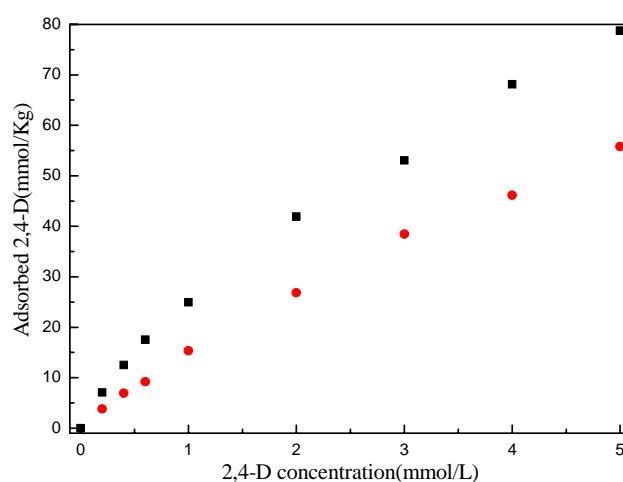


Figure 2 Adsorbing curves of imprinted polymer particles (■) and non-imprinted polymer particles (●)



Results and Discussion

In this study, a novel suspension polymerization method was applied to prepare MIP particles in silicon oil. **Figure 1** showed SEM photographs of typical particles, which exhibited regular shape in the micro-scale range.

Key to the success of this method was to select a suitable dispersion phase. Because there were no stirrer, surfactant or stabilizer during the polymerization, dispersion phase with high viscosity was required in order to avoid dispersed droplets getting together. The coefficient of kinematic viscosity of silicon oil used in the experiments was more than $300 \text{ mm}^2/\text{s}$, which is much higher than conventional liquid medium, such as water, liquid paraffin and perfluoro-(1,3-dimethylcyclohexane). So the silicon oil could resist the movement of the droplets to avoid congregation of particles. On the other hand, the density of pre-polymerization droplets (approximately 0.9 g/mL) was a little lower than that of silicon oil (0.965 g/mL), so the droplets rose slowly in silicon oil. During the polymerization, the density of droplets gradually turned high and the movement of droplets turned slow. After the density of polymerized droplets turned higher than that of silicon oil, they began to sink in silicon oil reversely. Consequently the suspension time of droplets was protracted and congregation was avoided. In addition, other reasons that silicon oil was suitable as dispersing phase due to its nonpolarity, insolubility with pre-polymerization mixture and low cost.

The adsorbing curves of the synthesized particles were measured with 2,4-D acetonitrile solution with concentration ranging from 0.2 to 5.0 mmol/L. The experimental results were shown in **Figure 2**. It could be seen that the adsorbing amount of MIP particles was higher than that of non-imprinted polymer particles. As concentration of 2,4-D was 1.0 mmol/L; the adsorbing amount of MIP particles was 24.93 mmol/Kg while that of non-imprinted polymer particles was 15.36 mmol/Kg.

The high adsorption of 2,4-D might result from the imprinted cavities in the polymer networks and the functional groups on cavities produced by templates 2,4-D.

Conclusion

In the present work, silicon oil was applied to prepare MIP particles using 2,4-D as templates by suspension polymerization. The advantages of silicon oil as dispersion phase are high viscosity; suitable density; nonpolarity, insolubility with pre-polymerization mixture and low cost. The adsorbing experimental results indicated that the MIP particles possessed higher affinity to 2,4-D than the non-imprinted polymers particles.

Acknowledgments

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References

1. G. Wulff, *Angew. Chem., Int. Ed. Engl.*, **1995**, *34*, 1812.
2. M. J. Whitcombe, E. N. Vulfson, *Adv. Mater.*, **2001**, *13*, 467.
3. R. J. Ansell, K. Mosbach, *J. Chromatogr. A*, **1997**, *787*, 55.
4. J.P. Lai, X.Y. Lu, C.Y. Lu, *et al*, *Anal. Chim. Acta*, **2001**, *442*, 105.
5. L. Ye, R. Weiss, K. Mosbach, *Macromolecules*, **2000**, *33*, 8239.
6. N. Perez, M. J. Whitcombe, E. N. Vulfson, *Macromolecules*, **2001**, *34*, 840.
7. H. Kempe, M. Kempe, *Macromol. Rapid Commun.*, 2004, *25*, 315.

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