Preparation and Application of Polybenzoxazine Adsorption Resin

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ABSTRACT: The synthesis and application of polybenzoxazine adsorption resin was studied. First, the precursor was synthesized by the solventless method. And then a kind of spherical and granular polybenzoxazine resin was obtained using reverse-phase suspension polymerization technique in the process of solidification. Besides, the influence of dispersion medium, the volume ratio of precursor to medium, the solidification temperature, and the agitation speed were studied in detail in the process of polymerization. Second, the spherical shape of the polybenzoxazine resin was identified by scanning electronic microscope and the thermal stability of resin was measured by thermogravimetric analysis. Finally, the adsorption capacity of the spherical resin on pyridine was studied in cyclohexane systems. The correlation coefficient of Langmuir adsorption constant temperature line was bigger than 0.99, which indicated that the equilibrium sorption date was coincident with the Langmuir isotherm equation. And the saturated adsorptive capacity of dried resin achieved 222.2 mg g^{-1}. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1162–1167, 2007

Key words: benzoxazine; spherical resin; reverse-phase suspension polymerization; sorption

INTRODUCTION

Polybenzoxazine is a novel class of phenolic resin. The chemistry of benzoxazine had been studied since 1940s.[1] Recently, many scientists studied not only the reaction mechanism,[2,3] the volumetric expansion[4] effect, and the hydrogen bonding[5,6] during preparation, but also the mechanical property,[7,8] the thermal stability,[9] the flame-retarded performance of polybenzoxazine, and so on.

By transforming the constitution of amine and phenols, various kinds of midbody can be obtained. Scheme 1 shows the representative compounds. In this study, Type 1 was chosen as midbody.

Presently, the means for synthesizing precursor of benzoxazine have two ways: (1) Solvent method[10] and (2) Solventless method. In this study the latter was adopted.

The familiar methods of solidification have three ways: (1) Baking solidification. Precursor was dissolved in some solvent such as chloroform. And then the solution of precursor was baked in oven at a special temperature for several hours. (2) Catalytic solidification. Some catalysts like phenylformic acid were added in precursors and heated in vacuum drying chamber. (3) Subsection solidification. Precursor was solidified by temperature programming.

Suspension polymerization is a popular method in macromolecular synthesis technology by which the monomer is suspended in the water phase by agitation or by adding in some emulsifier. The obtained product was spherical or pulverous. The process of reverse-phase suspension is the same as suspension polymerization while the dispersion medium is oil phase. There is a general characteristic in both suspension and reverse-phase suspension polymerization. Namely, the dispersion medium cannot dissolve the monomer or precursor. We all know that water cannot dissolve the precursor of benzoxazine, either can oil medium. So both suspension and inverse suspension can be used in the synthesis or solidification of benzoxazine. Gu Yi in SiChuan University of China ever prepared spherical precursor of benzoxazine by suspension manner.[11] But the spherical precursor can not be solidified in the suspension system due to the low boiling point of the water. The obtained precursor grain must be polymerized in the baking box.

In this study, spherical polybenzoxazine resin was obtained directly by reverse-phase suspension polymerization. Silicone oil was used as the suspension medium. The precursor was dispersed in the oil with granulometric shape by agitation. Then the mixture was heated to the temperature of solidification. Finally the spherical polybenzoxazine resin was

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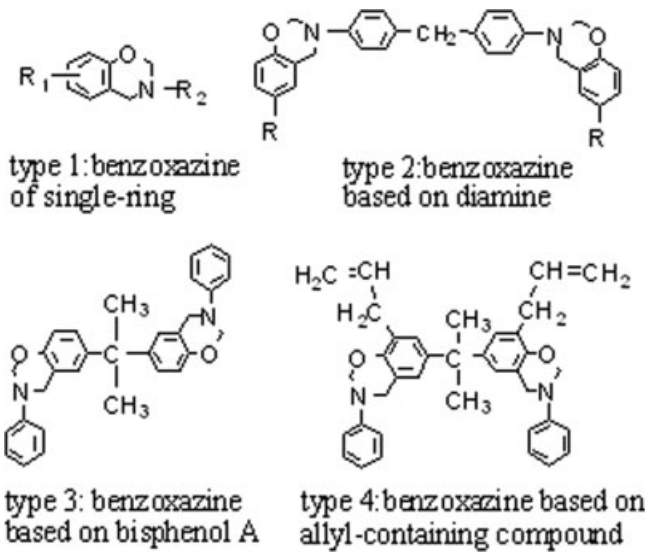


Scheme 1 Types of midbody.

obtained. There is little report on this manner of solidification of benzoxazine precursor before.

Compared with conventional experiment, the time and the temperature of polymerization were greatly reduced using the reverse-phase suspension polymerization technique and the resultant can be removed from the container easily. Besides, the adsorptive capacity of the polybenzoxazine resin on pyridine was studied. The results reported in the article may contribute to finding a new method of preparing spherical polybenzoxazine adsorption resin and finding further application of the resin in the environmental protection.

EXPERIMENTAL

Materials

Polyformaldehyde, aniline, phenol, cyclohexane, pyridine, 201 methyl-silicone oil, glycerine, methylbenzene, chloroform, and acetone were purchased from Chemical Agent Company Limited of Shanghai. All chemical were used without further purification.

Equipment

Ultraviolet absorption spectrum (Nicolet Evolution 300, USA), thermogravimetric analysis (TG209, German), scanning electronic microscope (S-570, Japan).

Precursor synthesis by the solventless method

The yellow precursor was obtained after the mixture of 38.7 g polyformaldehyde, 60.4 mL aniline, and 39 g phenol was refluxed and heated in the rang of 110–120°C for 30 min in 250 mL round-bottom flask. Then the solution of precursor dissolved in chloroform was washed in turn by 5% aqueous sodium hydroxide and distilled water repeatedly to remove the unreacted phenol and the hydroxide, respectively. Finally, the chloroform was removed by vacuum distillation.

Preparation of spherical benzoxazine adsorption resin

First, the desired quantities of the precursor were dissolved in dioxane. The solution was mixed with dispersion medium (50 mL) in round-bottom flask. Second, the mixture was stirred for about 10 min to obtain latices using motor stirrer. Finally, after the dioxane was extracted from the latices, the remainder was heated at the desired temperature for 20–40 min until the precursor was solidified.

To explore the optimal condition of reverse-phase suspension polymerization, four factors of solidification including volume ratio of precursor to medium, dispersion medium, solidification temperature, and agitation speed were investigated.

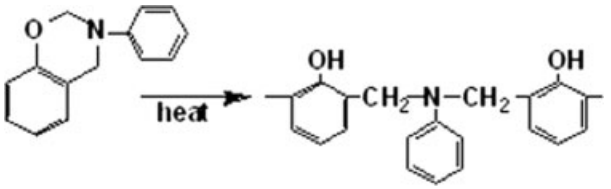
Batch method for adsorption of pyridine in cyclohexane

The obtained spherical and granular polybenzoxazine resin was purified by extractor implement for 12 h using chloroform as eluent. Then the resin was dried in vacuum for 2 h at 60°C.

Dried resin (0.11 g) and 10 mL pyridine solution (in cyclohexane) were vibrated at 25°C for 1.5 h. Two groups of series were used in the process of adsorption. The concentrations of one group were 100, 150, 200, 250, 300, 350, and 400 ppm, respectively. Another group's concentrations were 1, 10, 50, 80, 100, 150, and 200 mg mL^{-1}, respectively. The quantities of adsorbing pyridine were measured by ultraviolet absorption spectrum. It is necessary to explain that the concentrations of the second series were too high to be measured by ultraviolet absorption spectrum, and so before measurement the solution has to be diluted. The adsorption capacity was calculated as follows:

$$Q = V(C_0 - NC_e/W)$$

where Q is the adsorption capacity of the sample (mg pyridine g^{-1} dry adsorbent), V is the volume of solution (mL), C_0 is the concentration of pyridine (mg mL^{-1}) before adsorption, C_e is the concentration of pyridine (mg mL^{-1}) after adsorption, N is the dilution multiple, and W is the weight of dried resin.



Scheme 2 The principle of solidification.

RESULTS AND DISCUSSION

Mechanism of preparation

Benzoxazine rings were capable of undergoing ring-opening solidification as shown in the equation (Scheme 2).

The precursor of benzoxazine has both hydrophobic group and hydrophilic group. When the oil phase is used as dispersion medium, the precursor appears with spherical micelle by agitation while the majority of hydrophilic group is at the inner of spherical micelle and most of hydrophobic group is outside. Though there was no emulsifier added into the suspending liquid, the micelle was stabilized by agitation. When the suspending liquid was heated, the polybenzoxazine grain resin could be obtained in a spherical shape. That is why we can obtain spherical polybenzoxazine resin by reverse-phase suspension polymerization.

SEM photograph of polybenzoxazine (Fig. 1) showed that the shape of resin was spherical, and the average grain diameter was about 0.9 mm.

Effect of volume ratio of precursor to medium

It was very important to choose appropriate ratio of precursor to medium for solidification. The effect of volume ratio of precursor to medium was studied by taking five different ratios as shown in Table I. It is seen from Table I that the maximum volume ratio of precursor to medium was 5 : 50. The reason that spherical resin cannot be obtained in high ratio may be as follows. The benzoxazine precursor was a very high viscous liquid in room temperature. It can be well distributed to the silicone oil by agitation. But if the consistency was higher than critical consistency in silicone oil, the number of spherical micelle reached the saturation and the precursor had more chance to touch with each other at the moment of solidification, which resulted in the polybenzoxazine resin agglomerations.

Effect of solidification medium

To assess the efficacy of spherical resin synthesis, the effect of solidification medium was studied in the process. Glycerinum, silicone oil, and the mixture of glycerinum and silicone oil as mediums were studied under otherwise similar conditions (volume ratio of precursor to medium, 5 : 50; solidification temperature, 180°C; agitation speed, 200 rpm). The glycerinum and silicone oil have similar density to polybenzoxazine precursor. The result showed that the silicone oil had optimal effect among three mediums.

The viscosity of glycerinum became higher when the temperature was above 100°C. Therefore, the precursors can not be dispersed easily into the glycerinum. And also because the density of the glycerinum is a little bigger than benzoxazine precursor, part of the precursors suspended above the glycerinum in the process of agitation. So after solidification, the product appeared not to be spherical.

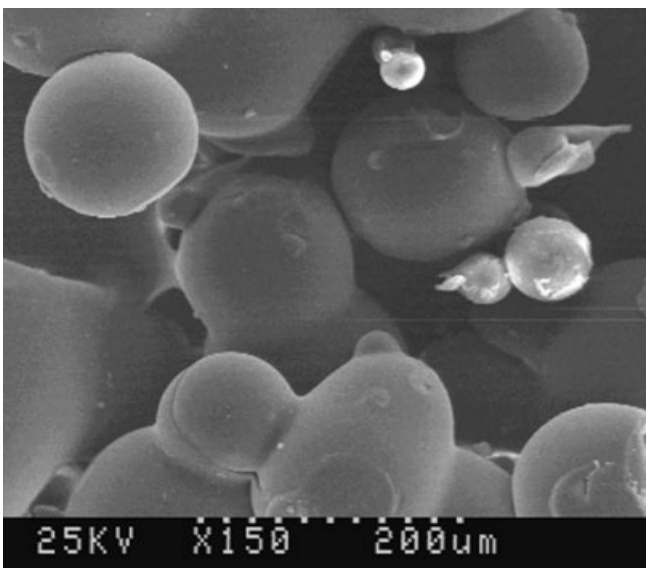


Figure 1 SEM photograph of spherical polybenzoxazine resin.

TABLE I
The Influence of Volume Ratio of Precursor to Medium

Volume ratio of precursor to medium	Solidification result
10 : 50	Agglomerations
7.5 : 50	Part agglomerations
5 : 50	Spherical resin
4 : 50	Spherical resin
3 : 50	Spherical resin

Dispersion medium, silicone oil; solidification temperature, 180°C; agitation speed 200 rpm.

There was a similar consequence in the medium of the mixture of glycerinum and silicone oil.

However, silicone oil not only has similar density to benzoxazine precursors, but also has high steam point. Indeed, silicone oil has great stabilization during the process of solidification. The precursor can be well distributed to the silicone oil in the process of agitation. Moreover, the spherical grains after solidification in the silicone oil can be purified more easily by acetone or chloroform than in other two mediums. So solidification was most effective in silicone oil. The obtained resin that can be purified easily was granular and spherical.

Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the range of 180–210°C as shown in Table II.

The conversion of precursor was found to increase with increase in temperature. However, the increment was not very sharp. Generally, solidification temperature and time are two important factors of conversion percentage, and the conversion increases when the temperature is higher or the solidification time is longer. However, the finished time of reverse-phase suspension polymerization was shorter than that of conventional method. Meanwhile, the color of the products appeared darker with increase in temperature. And, part of the products had a phenomenon of carbonization when the solidification temperature was above 210°C. Therefore, solidification temperature was not an important factor of conversion in this experiment. To avoid carbonization, the precursor was solidified in range of 180–200°C.

TABLE II
Effect of Temperature on Solidification

Solidification temperature (°C)	Solidification time (min)	Conversion (g mL^{-1} precursor)	Products' color
180	40	0.3874	Yellow, Diaphanous
200	25	0.4026	Brown, Diaphanous
210	20	0.4093	Dark brown

Volume ratio of precursors to medium, 5 : 50; dispersion medium, silicone oil; agitation speed, 200 rpm.

Effect of agitation speed

Agitation was very important in this process of reverse-phase suspension polymerization. And speed of agitation played an important role in the sizes of the spherical resin. Table III showed the influence of agitation speed on average grain size.

According to Table III, the granule number of polybenzoxazine per milligram was bigger in higher agitation speed. That means the average grain sizes became smaller and smaller with the increase of agitation speed. The desired grain size can be obtained by changing the agitation speed. We have got pulverous polybezoxazine resin when the agitation speed reached 330 rpm. However, it was also showed in Table III that the solidification time became longer while the agitation speed was faster. The process of solidification required more time to finish in higher stir speed due to energy losing faster in higher speed of agitation.

By reverse-phase suspension polymerization, the spherical and granular polybenzoxazine resin was obtained. In the process of reverse-phase suspension polymerization, the precursor in medium was dispersal in micelle shape and heated homogeneously, and so energy could be made good use of. Compared with conventional method of solidification, the time of polymerization and the temperature of solidification were greatly reduced. In traditional experiment, the time of solidification is 2 h or even more and the temperature is higher than 200°C. In this study the time of polymerization was 30–40 min and the temperature was 180–200°C, respectively. Furthermore, by this means of solidification the polybenzoxazine can be removed fromthe container more easily than conventional solidification.

The thermal stability of spherical and granular polybenzoxazine

The thermal stability of spherical and granular polybenzoxazine was measured by TGA (thermogravi-

TABLE III
The Influence of Agitation Speed

Stir speed (rpm)	Granule number mg $^{-1}$ resin	Finished time (min)	Conversion (g mL^{-1} precursor)
150	59	20	0.4175
200	124	30	0.4051
330	452	45	0.4218

Volume ratio of precursors to medium, 5 : 50; dispersion medium, silicone oil; solidification temperature, 180°C.

metric analysis). The temperature was ramped at 15°C min^{-1} under 90 mL min^{-1} nitrogen.

Figure 2 showed that the sample was almost thermal stability below 200°C and had a sharp mass loss in the range of 250–500°C, which indicated the higher thermal stability of spherical polybenzoxazine resin obtained by reverse-phase suspension solidification than conventional method of solidification. Some kind of low-boiling dissolvent including chloroform and dioxane was encapsulated by spherical polybenzoxazine resin during the process of solidification. That is why there was a gentle loss in the temperature range of 100–200°C.

Adsorption performance of spherical and granular polybenzoxazine resin

Nitrogen in pyridine circle is bonding in sp^2 hybridization. It forms the conjugate system of six electrons. Therefore the pyridine has alkalinity. The nitrogen in pyridine circle can form hydrogen bonding with —OH in polybenzoxazine.

The experiment of adsorption showed that adsorption of polybenzoxazine resin was more effective on high concentration of pyridine than low concentration. Therefore, after the pyridine in cyclohexane was adsorbed in high concentration, the remainder was diluted, and measured by ultraviolet spectra.

According to adsorption isotherm of pyridine (Fig. 3), the adsorptive capacity reached the maximum of about 215 mg g^{-1} when the concentration of pyridine was 100 mg mL^{-1}.

In addition, Langmuir isotherm equation is as follows:

$$C_e/Q = 1/(K_b \times A_s) + C_e/A_s$$

where K_b is the bonding constant (mL mg^{-1}), A_s is the saturated adsorptive capacity (mg g^{-1}). According to Langmuir adsorption constant temperature line (Fig. 4), the Langmuir isotherm equation was obtained as follows:

$$C_e/Q = 0.0045C_e + 0.0292$$

So we calculated the saturated adsorptive capacity (A_s) was 222.2 mg g^{-1} dried resin, and the bonding constant (K_b) was 0.154 mL mg^{-1}. The correlation coefficient of Langmuir adsorption constant temperature line was bigger than 0.99, which means that the equilibrium sorption date of the spherical resin on pyridine in cyclohexane system was coincident with the Langmuir isotherm equation.

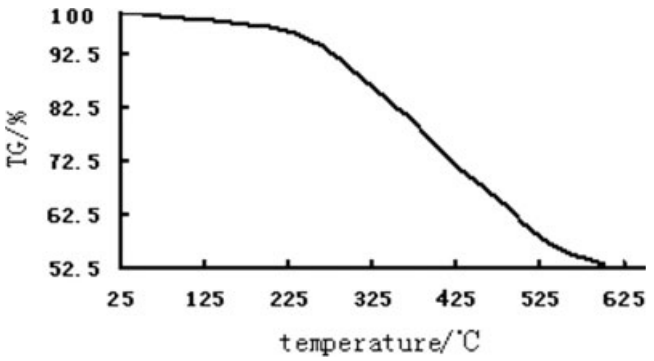


Figure 2 Thermogravimetric analysis of spherical and granular polybenzoxazine.

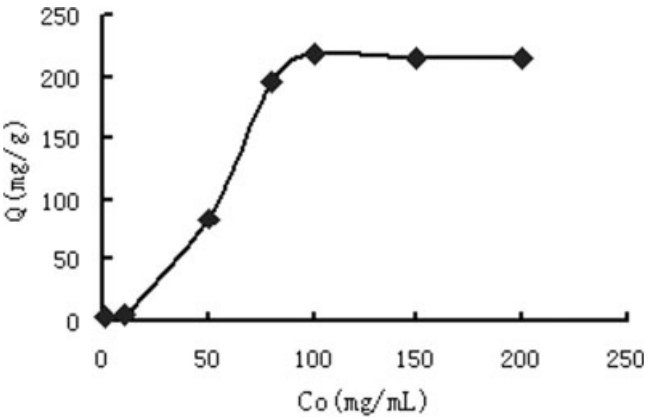


Figure 3 Adsorption isotherm of pyridine.

CONCLUSIONS

The spherical and granular polybenzoxazine resin was obtained in the range of 180–200°C for 30–40 min by reverse-phase suspension solidification. Compared with conventional method of solidification, the time and the temperature of reverse-phase suspension solidification were greatly reduced.

In the process of reverse-phase suspension solidification, we discovered that the dispersion medium

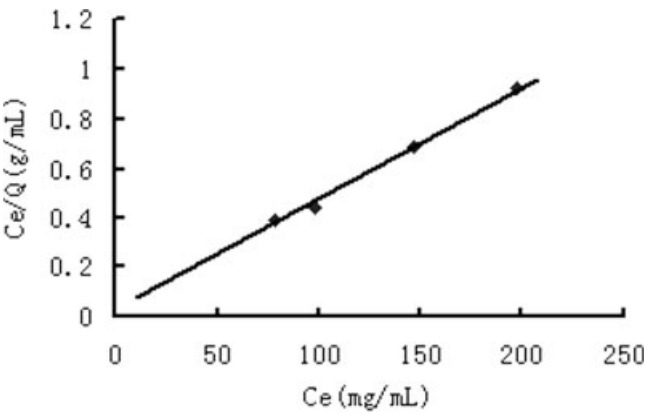


Figure 4 Langmuir adsorption constant temperature line.

and the volume ratio of precursor to medium had great influence on the formation of granular resin. The result showed that silicon oil had the optimal effect during the process of solidification among three mediums (silicon oil, glycerin, and the mixture of silicon oil and glycerin), and the maximum volume ratio to obtain the spherical resin was 5 : 50 (Precursor : Silicon oil).

Stir speed was one of the important factors that impact on the average grain size. The size of the resin became smaller with the increase of stir speed.

The equilibrium sorption date of the spherical resin on pyridine in cyclohexane system was coincident with the Langmuir isotherm equation.

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