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The Synthesis of New Solid-phase Microextraction Adsorption Material and Its Adsorption Performance

Fu Shuang*, Xia Chunhui, Li Hongmei and Xu Feng

College of Pharmacy, Qiqihar Medical University, Qiqihar 161006, China

Abstract: This article uses three kinds of monomers: the styrene, butyl acrylate and Vinyltriisopropoxysilane, synthesized the solid phase micro extract coating adsorption material, carries on the structure characterization and the physical performance test. Takes it as the solid phase micro extract coating, carries on the inspection to its adsorbability, the experiment obtains the detection limit of the benzene which is 0.21 μ g/L; The detection limit of the toluene is 30 μ g/L; The detection limit of the m-Xylene is 0.55 μ g/L. Indicated the adsorptivity of this polymer has more effection toward the small molecular aromatic hydrocarbon as the solid phase micro extract coating adsorption material, and the limit of detection is lower compared to the commodity extract coating, there are some promotion and adoption value.

Keywords: Adsorptivity, solid phase micro extract coating, structure attribute.

1. INTRODUCTION

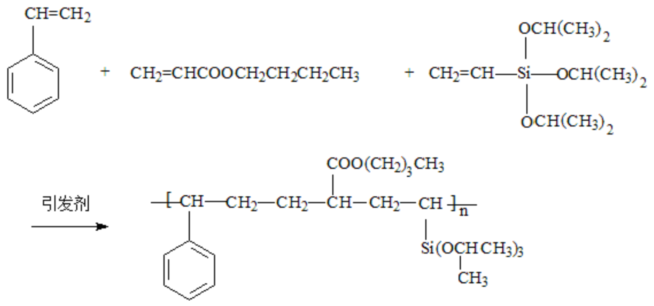
The solid phase micro extract (Solid-Phase microextraction, SPME) is the most popular sample pretreatment method in the chromatograph analysis, this method is a combination of extraction, concentration, desorption and sample injection, the sensitivity is high and the operation is simple, the solid phase micro extract technology is coating the organic high polymer material on a quartz fiber surface as the extract coating, then extract the organic molecules and do the preenrichment, carries on the hot desorption directly in the gas chromatography sample injector, increased the analysis speed and the sensitivity. The coating is the core of the solid phase micro extract technology, a variety of new coating material and the preparation technology which come recently years has further opened up the solid phase micro extract technology application scope, synthesized the new solid phase micro extract adsorption material is the topic which the very many scientific research worker craved [1-6]. The literature [7] synthesis polymers, served as the solid phase micro extract coating the adsorption material which combining with the quartz fiber well and cohesiveness are good, can add this polymer as the solid phase micro extract coating in the benzene with water or the toluene and the adsorption is good, but xylene adsorptivity is not very ideal, myself tried to find out the polymer monomer, the polymerization proportion and the experimental condition once more and finally obtain the phenylethylene–n-butyl acrylate–Vinyltriisopropoxysi-lane terpolymer as the solid phase micro extract adsorption material, and takes it as the solid phase micro extract coating to determine the adsorptivity to the Benzenes, the determination result demonstrated this polymer has the better adsorptivity to the benzene class aromatic hydrocarbon, it worth the further research and the promotion.

2. EXPERIMENTAL PART

2.1. Main Instruments and Reagent

GC-122 gas phase chromatograph, flame ionization detector (Shanghai Exact sciences Limited company); Nicolet 380 Fourier transformation infrared spectroscope (Shanghai kui Yuan scientific instrument limited company); Pyris D iamond TG /DTA thermal analysis meter (American PE Corporation); Scanning probe microscope (Shanghai Zhuo Lunwei nanometer science and technology limited company); Euler viscosity medicinal preparation (Shanghai Ping Xuan Scientific instrument Limited company); 20mL screwtop extractionflask (Dongguan spectrum sign experiment equipment science and technology limited company); The building-up reactions installment (assembles voluntarily); Styrene (AR), acrylic acid Ding ester (AR), ethenyl three isopropoxy silicon hydride (AR); Nonyl phenol polyethyleneoxide ether (0P-10, AR), lauryl sodium sulfate (AR), persulfuric acid ammonia (AR), ferrous sulfate (AR); Benzene (AR), toluene (AR), m-xylol (AR).

2.2. Building-up Reactions Principle



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*Address correspondence to this author at the College of Pharmacy, Qiqihar Medical University, Heilongjiang, 161006, P.R. China; Tel: 15846289920; E-mail: fsjt1980@163.com

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2.3. Polymer Synthesis

Under the nitrogen protection, adds 30mL aqueous solution including 1g OP-10 and the 0.25g lauryl sodium sulfate to the reaction bulb, adds 5ml styrene and 5 mL the butyl acrylate, emulsifies 20min, elevates temperature slowly to 72 ℃, adds 3 mL 3% persulfuric acid ammonia liquor solution, stirs 10 min.

Add 5mL styrene and 5 mL butyl acrylate in the separating funnel, adds by drops to the reaction bulb about 20 min, continues to react for 1 h.Lower the temperature of reaction bulb to 65 ℃, joins 3 mL 3% ammonium persulfate and the 3mL 0.1% ferrous sulfate water-soluble fluid, 5 mL styrene, 5mL butyl acrylate and 1.2mL Vinyltriisopropoxy-silane mixed monomer, adds by drops with the separating funnel to the reaction bulb in 0.5 h, continues to react for 1h.Rise the reaction bulb temperature to 78 ℃ and continue to react with the constant temperature for 1h.After the reaction finished, use the methyl alcohol to Precipitthe polymer, after the lavation and the vacuum drying finally obtain the white solid with viscoelasticity.

2.4. The Structure of the Polymer Characterization

Take 0.5g polymer dissolved in 5ml Tetrahydrofuran solution, take a little coated in Infrared salt pieces, analysis the structure of the polymer by doing the infrared spectrogram, ascertain the exist of styrene and butyl acrylate. Analyzed the polymer with scanning electron microscopy, X-ray probe analysis method, prove the existing way of vinyltriisopropoxy silane in the polymer.

2.5. The Test of the Highest use Temperature of the Polymer

Accurate take 50-60mg the polymer, put in the platinum plate,let the plate hanged inside the furnace(do not touch the furnace wall),add farmar to make the balance come to balance, set the temperature range of 20℃--600℃; set the heating rate of 5℃/min; Use pyris Diamond TG/DTA to test it, determine the highest temperature.

2.6. The Test of the Intrinsic Viscosity of Polymer

When the chemical composition, solvent and temperature of polymer is determined, viscosity value associated only with the molecular weight of polymer. $[\eta]=KM\alpha$($[\eta]$ is intrinsic viscosity, M is viscosity average molecular weight, K and a are constant), the intrinsic viscosity of the visible polymer compounds can be reacted by it's viscosity average molecular weight .

The preparation of the solution: weight the polymer 0.25g (accurate to 0.0001g), dissolved it with Tetrahydrofuran solution, constant-volume in 25ml volumetric flask, shake well, set aside .

The test of the out of time of the solvent: adjust the thermostatic bath to 25℃. On viscometer tube top two sets of medical rubber tube, put in constant temperature water tank, let the capillary is perpendicular to the surface, and the water immersion on line. Move to take 10 ml of Tetrahydrofuran solution into the viscometer, with suction ears ball to suction to ball line two centimeters of above, then loosen the suction ears to make it free fall, write down the time the solution flows between the two scribed line, that's out of time .Repeat more than three times, the error is less than 0.2 seconds, take the average value as the t0.

The test of the out of time of the solution: moves 10ml of polymer solution injected in viscosity meter with a pipette, then prescribed it's viscosity as 1.Measured the out time as t1, repeat three times and take the average ;moves 5ml Tetrahydrofuran solution again, and the viscosity of the polymer in viscometer becomes 2/3, mix it with the suction ear ball updraught, measure it and get t2. As the same way, add 5ml, 10ml,15ml tetrahydrofuran in turn, it's viscosity is1/2,1/3,1/4,and get t3, t4, t5, and calculation η_{sp}/C、$Ln\eta_r$ by intrinsic viscosity of extrapolation method $[\eta]$.

2.7. The Test of Capacity and Heat Resistance Performance of Polymer and Silica Fiber

The test of the ability of combined with quartz fiber: dissolved the polymer in tetrahydrofuran, make it into the dilute solution, after several times coating and drying, make it come to 100um thickness of quartz fiber extraction. And then, put the extraction head at 70℃ water cut the top of the empty bottle top, takes it out after 1h, hangs it in the middle of 300℃ oven, 1h's late, to observe the status of the coating, then put the extraction head into water again, last 1h at room temperature. And then hangs it in the middle of 300℃ oven, 1h's late, to observe the status of the coating.

The test of thermal performance: coupled extraction head with gas chromatograph to investigate the thermal stability of the coating. Install a 2 meters long empty chromatographic on the gas chromatograph, set the initial temperature of the gasification chamber as 100℃, set the termination temperature as 240℃,the rate of heating is 5℃ every 5minutes, set the oven temperature as 200℃, set the FID detector temperature as 240℃, observe the change of chromatographic peak baseline, to realize the thermal stability of the coating.

2.8. Self-made Solid-phase Microextraction Device

Homemade SPME device: Take a 15cm long optical quartz fiber, get ride of the layer on the surface of the polyester with concentrated sulfuric acid, and then inserted the quartz fiber 0.25kg/L polymer in tetrahydrofuran solution coating repeatedly, make it become 1cm long and 100um thick coating, combine it with the 5uL microsyringe into the device of 5L SPME.

Device as shown in Fig. (**1**).

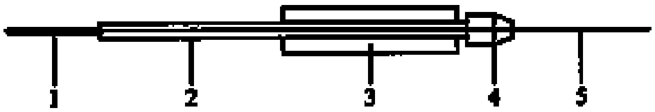

Fig. (1). Self-made solid-phase microextraction device.

(1-coating 2-outer casing 3-Glass syringe casing 4-Sealed knob 5-Quartz fiber and inner casing).

2.9. The Test of Adsorption Ability of Polymer Coating of Benzene Class Aromatics

2.9.1. The Chromatographic Conditions

The chromatographic column is 2m×3mm i.d. Stainless steel column; and acid red supporter filled within 8% SE-30/202(60-80 mesh) ; the temperature of injection port is 190℃;the column temperature is 190℃;the detector temperature is 220℃;the sensitivity is 1010 ; the attenuation is 0; the nitrogen as carrier gas; the flow rate of the carrier gas is 40ml/min; the flow rate of the hydrogen is 40ml/min;the flow rate of the air is 400ml/min.

2.9.2. The Conditions of Extraction

The extraction of head: 100μm; The extraction bottle: 15ml; The extract content: 5ml; The extraction temperature: 45℃ (water bath); The equilibrium time:25min; The extraction time: 25min; The dosage of salting-out agent (NaCl): 0.5g; The desorption temperature:190℃; The desorption time:2min; keep the bath temperature and the stirring speed are constant.

3. THE RESULTS AND DISCUSSION

3.1. The Choice of the Conditions of Polymer Synthesis

Based on the thermal stability of polymers, and fiber bonding force, viscoelasticity as the main factors to test the target extraction ability, the optimal reaction conditions determined by the orthogonal experiment method is: the volume ratio of styrene and butyl acrylate is 1:1; the mass fraction of vinyl silane three isopropyl oxygen radicals to monomer is 5%; the temperature of adding organic silicon is 65℃;the mass fraction of initiator $(NH_4)_2S_2O_4$ is 3%; the mass fraction of $FeSO_4$ is 0.1% ; under this condition the production rate is 74%.

3.2. The Structure Characterization of the Polymer

The test results carried out on the polymer by infrared spectrum scanning is as shown in Fig. (**2**).

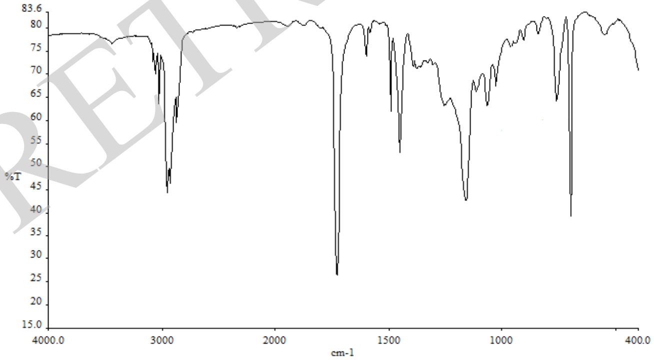

Fig. (2). The infrared spectrum scanning of the polymer.

Through analysis the infrared spectrum, in1600cm-1, 1450cm-1, 1453cm-1 (the vibration of benzene ring skeleton) and 695cm-1 (aromatic hydrogen plane bending vibration) absorption proves the existence of benzene; in 1680-1620cm-1 has no absorption peak of C=C, proves that styrene has polymerization; in the 1731cm-1 (C=O stretching vibration) and 1162cm-1 (C=C-O stretching vibration), the strong absorption peak is the characteristic of ester absorption, and proves the existence of ester, in 1066cm-1 (Si-O-C stretching vibration) and 963cm-1 (Si-C stretching vibration) has absorption peak, proved that the existence of organic silicon.

The results of analysis the polymer carried out by scanning electron microscopy, X-ray probe is as shown in Fig. (**3**).

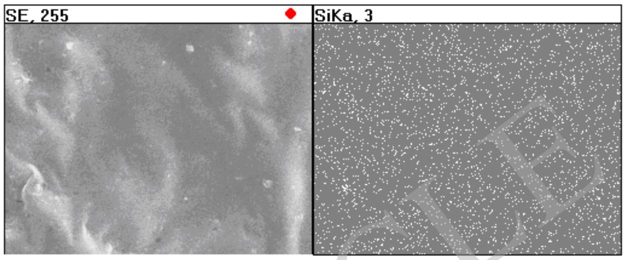

Fig. (3). The analysis diagram of scanning electron microscopy,X-ray probe of polymer.

Though electron microscopy, X-ray probe we can analysis this polymer silicon is evenly distributed. Further proves that the polymer vinyl silane, three isopropyl oxygen radicals is converged on styrene and butyl acrylate polymer rather than on the adsorption, further evidence that the polymer is the result of three kinds of monomer polymerization.

An analysis to result of the thermal performance test on polymer is as shown in Fig. (**4**).

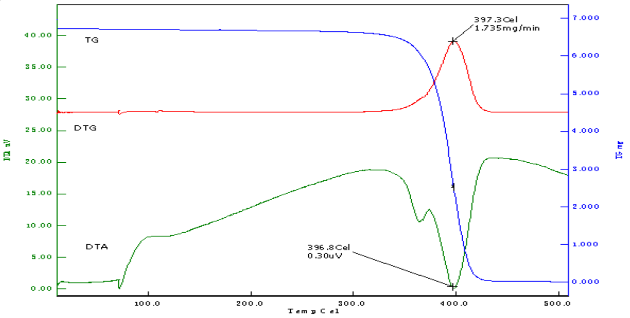

Fig. (4). The curve of polymer’s thermogravimetric/differential thermal.

By thermogravimetric/differential thermal curve analysis shows that the highest temperature of the polymer can be set to 330℃, and the transition temperature of the polymer glass transition is 65℃.

An analysis to result of the intrinsic viscosity determination of polymer is as shown in Fig. (**5**).

By Iimη sp/C = IimLnη r/C = [η],we can know that when C → 0,η sp/C and Lnη r/C to a point which is [η]. Determine ηsp/C and Ln ηr/C to the point that is y=1.6971, namely the polymer [η] of 1.6971.

3.3. An Analysis to Results of Polymer Coating Combined with the Ability to Quartz Fiber and Thermal Performance Test

Combined with quartz fiber capacity test results: according to section 1.7, repeating 20 times, the polymer coating has no obvious change in the appearance. It is visible that the polymer and fiber binding force strong, good film-forming, high and low temperature resistance, resistance to water.

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The results of thermal performance test: when the gasification chamber temperature to 240℃, the extraction coating doesn't change; and the chromatography workstation baseline is very stable, that is conform to the requirements of the solid phase microextraction and heat-resistant coating performance conditions.

3.4. An Analysis to the Result of the Adsorption Performance Test Uses for the Self-made Solid-phase Microextraction Device to Substance Such as Benzene

Take six 100 ml volumetric flasks, compound containing benzene, toluene, xylene between 0, 10, 20, 30, 40 and 50 µg/L aqueous solution, application of self-made solid-phase microextraction device between benzene, toluene, xylene 0.00 µg/L ~ 50.00 µg/L range for headspace extraction, were measured three times, the curve equation of linear regression and correlation coefficient respectively: benzene h = 0.0077 + 0.0085 c, r = 0.9926, the lowest detection limit is 0.21µg/L; Toluene h = 0.0057 0.0057, r = 0.9890, the lowest detection limit is 0.30µg/L; Meta-xylene h = 0.0047 + 0.0519 c, r = 0.9793, the lowest detection limit is 0.55µg/L,the measured chromatograms and linear relationship between three kinds of materials are as shown in Fig. (**5**), Fig. (**6**).

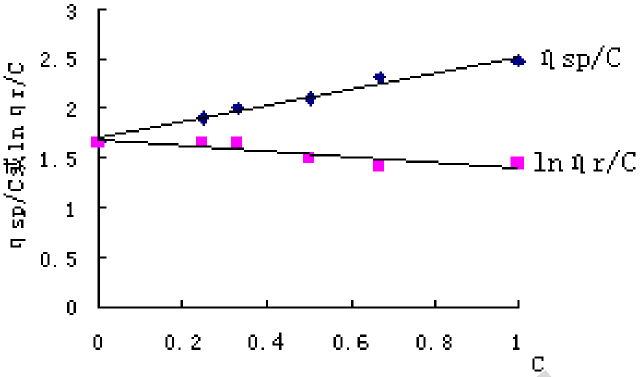

Fig. (5). The polymer η sp/C of C and Ln η r/C of C diagram.

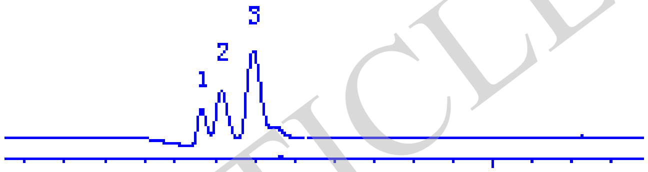

Fig. (6). The chromatograms of the self-made solid-phase microextraction device for the determination of the water containing benzene, toluene, xylene.

（the peak 1：Benzene; the peak 2: toluene; the peak 3: meta-xylene）.

As a result, the coating of benzene, toluene and meta-xylene SPME GC extraction effect is good, and high sensitivity; comparing with goods extraction head which is reported in the literature [7], its effect is better than that of PDMS and PA goods extraction head.

The test of the precision and the detection limit is as shown in Table **1**.

3.5. Compared with Goods Extraction Head

Compared with goods extraction head, the self-made extraction head (100 Lm) and goods extraction head (including 100 µm PDMS and 85 µm PA) extract and

Table 1. Precision and detection limitof the method.

Compound	Found (µg /L)	RSD (%, n=6)	Dtection limit(µg /L)
Benzene	8. 75	0. 94	0.21
Toluene	21. 17	1. 16	0.30
xylene	16. 29	1. 08	0.55

Table 2. Comparison of coating.

Compound	Peak area A(mm2)	Peak area A(mm2)	Peak area A(mm2)
	Our coating	PDMS	PA
Benzene	8. 75	0. 94	0.21
Toluene	21. 17	1. 16	0.30
xylene	16. 29	1. 08	0.55

chromatography analysis of the preparation of the mixed sample solution (concentration respectively 10μg/L). The chromatographic peak area (A mm2) measured were compared, the determination results are shown in Table **2**.

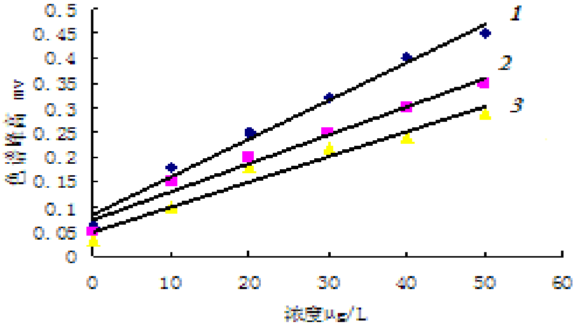

Fig. (7). Methods of linear relationship.

(the peak 1： Benzene; the peak 2: toluene; the peak 3: meta-xylene)

CONCLUSION

With the monomer of styrene, butyl acrylate and Vinyl silane three isopropyl oxygen radicals, synthetic ternary copolymer. Combining the polymer with fibers to make solid phase microextraction coating, the experiments show that this coating has good thermal stability, and fiber binding force strong, good film forming, good flexibility, high and low temperature resistance, water resistance, strong for aromatics adsorption force. Application of more than one hundred times, it does not have falls off phenomenon, and it has certain promotion and use value.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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