Novel Poly(β-cyclodextrin) Porous Material as Solid Phase Extraction Sorbent for Aniline Derivatives in Rubber Samples

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Aniline derivates are widely used in rubber products as anti-aging agents, but their biological toxicity causes harm in the use and recycling of rubber products. Therefore, in this study, a high-performance poly(3,4,5,6-tetrafluorophthalonitrile-β-cyclodextrin)(P-TFPN-β-CD) solid-phase extraction (SPE) adsorbent was synthesized and applied to extract and detect aniline derivatives in rubber specimens. After crosslinking with 3,4,5,6tetrafluorophthalonitrile (TFPN), the polymer exhibited mesopores (7.88 nm) and a large specific area (55.2 m²/g). The porous structure significantly improved the extraction efficiency (recovery was between 90.1% and 110.5%) and rate (60% in 10 s) of 4 aniline derivatives (aniline, N-ethyl aniline, 1,2-phenylenediamine, and p-phenylenediamine). With a combined gas chromatographic-flame ionization detector (GC-FID), the extracted aniline derivatives were accurately detected (RSD = 1.60% to 9.90%). Due to the weak interaction between P-TFPN- β -CD and analyte, the prepared poly-TFPN-β-CD SPE adsorbent was regenerated via mild washing with methanol. The high absorption capacities remained after 4 extracting-washing cycles. The novel porous SPE adsorbent showed good extracting and recycling performance for the analysis and detection of aniline compounds in rubber. Thus, it has good prospects for application to improve detection efficiency and reduce cost.

Keywords: Poly (β-cyclodextrin), Adsorbent; Aniline derivatives; Solid-phase extraction; GC-MS

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INTRODUCTION

Rubber is widely used in various products, such as gloves, toys, shoes, seals, and tires due to its excellent elasticity, wear-resistance, and electrical insulation. However, its poor aging resistance hinders its application in daily life; therefore, aniline derivatives, which are stable and effective anti-aging agents, are added to rubber to protect it from damage by free radical reactions (Harrison and Jollow 1987; Müller *et al.* 1997; Janzen *et al.* 2006; Sarafraz-Yazdi and Es'haghi 2006; Oughlis-Hammache *et al.* 2016). However, according to ISO/TR 16178 (2012), aniline derivatives in rubber are considered category 5 critical substances, which are suspected to have an effect on the wearer. Further, they are potentially hazardous materials that can be inhaled or absorbed into the human body through the skin, which can cause tissue hypoxia, met-hemoglobin, and damage to the central nervous system and cardiovascular system (Ryzhakov 2018; Bhuiyan *et al.* 2019; Chaturvedi and Katoch 2020). Moreover, waste rubber products that contain aniline

derivative residues cause soil and water pollution and affect the growth and reproduction of aquatic organisms (Miskam *et al.* 2014). Therefore, accurately detecting the concentration of aniline derivatives in rubber and its waste is conducive to the standardization of rubber quality control. In addition, it provides guidance for improving rubber production methods, which can reduce the damage to the environment and human body caused by over standard samples. For example, Ulsaker and Teien (1979) used gas chromatography/mass spectrometry (GC/MS) to detect the N-ethylaniline in polyethylenebottle-packed intravenous solutions from the rubber part of the two-component closure, and they found that the concentration of N-ethylaniline ranged from 0.1 ppm to 2 ppm. Although GC-MS has high selectivity and sensitivity, it is necessary to eliminate the matrix and interfering compounds *via* solid phase extraction (Guo and Lee 2013; Jamali *et al.* 2013; Miskam *et al.* 2014; Krawczyk and Stanisz 2016; Rajabi *et al.* 2016; Niu *et al.* 2018).

Solid-phase extraction is a useful analytical approach for sample pretreatment prior to gas chromatography analysis. The process is shown schematically in Fig. 1. The first step is to pretreat the column solution to activate it. Then the sample extraction solution containing target object and chaff interferent is loaded to the column. The target object and partial chaff interferent are retained. Then most of the chaff interferent is washed with special solution. The last step is to elute the target object for determination. Amiri *et al.* (2017) prepared magnetic Wells–Dawson heteropoly acid nanoparticles for magnetic solidphase extraction of aromatic amines in water samples with detection limits in the range of 0.003 ng × mL⁻¹ to 0.01 ng × mL⁻¹. The enrichment factors (EFs) ranged from 75 to 113. Relative standard deviations (RSDs) were 4.8% to 8.3%, and the relative recovery values for the spiked water samples ranged from 90.7% to 99.8% (Amiri *et al.* 2017). Nazari *et al.* (2019) synthesized magnetite graphene oxide composites to extract and pre-concentrate aniline, and the limits of detection were 0.341, 0.110, and 0.167 g mL⁻¹ for aniline, phenol, and naphthalene, respectively. The relative standard deviations ranged from 3.3% to 5.7% in 8 repeated extractions. However, these extractants cannot be reused (Nazari *et al.* 2019).



Fig. 1. Sketch diagram of solid-phase extraction

Cyclodextrins (CDs), common macrocyclic oligosaccharides with a hydrophobic inner cavity and hydrophilic exterior, can encapsulate small organic molecules into their cavities to form inclusion complexes. Due to their compatibility with various organic compounds and ability to be restored *via* a simple solvent treatment, CDs have been extensively studied and applied in the absorption field (Liu *et al.* 2017; Nojavan and Yazdanpanah 2017; Chen *et al.* 2018; 2019; Jiang *et al.* 2019; Takeo *et al.* 2019; Wu *et al.*

2019; Yazdanpanah and Nojavan 2019). Researchers have demonstrated that modified cyclodextrin has good reusability in the absorption of organic compounds (Zhou et al. 2012; Feng et al. 2016). Feng et al. (2016) prepared Fe₃O₄/hydroxypropyl-β-cyclodextrin polymer magnetic nanomaterials to absorb malachite green, and the absorption rate of the solid-phase extraction agent was 92% and could be used 5 times. After 5 uses, the removal efficiency was above 85% (Xie et al. 2017). Li et al. (2014) prepared anionic βcyclodextrin/Fe₃O₄ microspheres to absorb Cu²⁺, and they could be reused 8 times. After 8 uses, the removal efficiency of Cu^{2+} decreased from 95% to 88.21% (Li *et al.* 2014). Crosslinked β-cyclodextrin polymers typically have low surface areas and poorer absorption performance than conventional extractants. Thus, in this study, 3,4,5,6-tetrafluorophthalonitrile (TFPN) was employed to crosslink CDs to create a porous and layered structure. The resulting cross-linked poly-TFPN-β-CD had a mesoporous structure with a high surface area. It effectively adsorbed and extracted 4 common aniline derivatives (aniline, N-ethyl aniline, 1,2-phenylenediamine, and p-phenylenediamine). In addition, the polymer could be regenerated at least 4 times without substantial reduction in absorption performance via a mild washing procedure. These findings demonstrated the promising application of porous cyclodextrin-based polymers for the accurate and repeatable detection of aniline derivatives in rubber.

EXPERIMENTAL

Materials

β-cyclodextrin, dichloromethane, and anhydrous potassium carbonate (K₂CO₃) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). 3,4,5,6-Tetrafluorophthalonitrile (TFPN) was purchased from Shanghai Macklin Reagent Co. Ltd (Shanghai, China). N,N-dimethylformamide (DMF) was supplied by Aladdin reagent Co. Ltd. (Shanghai, China). Anhydrous tetrafuran (THF) was purchased from Energy Chemical (Shanghai, China). Methanol of chromatographic purity, aniline, N-ethyl aniline, 1,2-phenylenediamine, and p-phenylenediamine (> 99.5%, standard (GC)) were supplied by CATO Research Chemical Inc. (Eugene, OR, USA). The working standard solutions of the four aniline derivatives were freshly prepared by dilution of the stock solutions with methanol to the desired concentrations. The rubber samples were purchased from the local market, positive rubber samples of aniline derivatives were prepared. The rubber samples of less than $3 \text{ mm} \times 3 \text{ mm} \times 5 \text{ mm}$ in size were prepared by immersion in a mixture of 50 mL of standard solution with a concentration of 500 mg/L and 10 mL of isopropanol. Then, after oscillation for 24 h at room temperature under shading conditions and volatilization of the solution under shading conditions, 3 different positive rubber samples of aniline derivatives were obtained. Ultrapure water was prepared via the Milli-Q system (Aubagne, France). All other reagents were of analytical grade and used without further purification.

Characterization

Infrared spectra were determined with an AVATAR 360 transform infrared spectrometer (Nicolet, Madison, WI, USA). Morphology was studied with a scanning electron microscope (SU8010, Hitachi High-Technologies Corporation, Ishikawa, Japan). The nitrogen absorption-desorption measurements were performed on an ASAP2020-HD88 analyzer (Micromeritics Co., Ltd., Atlanta, GA, USA). The surface area of poly(β-

cyclodextrin) was calculated by the Brunauer-Emmett-Teller (BET) method (Zhang and Lu 2019). The pore size distribution of the polymer was determined by modeling according to the Brett-Jouner-Halenda (BJH) theory. Solid nuclear magnetic resonance spectrum testing was performed on a Bruker AG 500 MHz AVANCEIII nuclear magnetic resonance spectrometer (Fällanden, Switzerland). Thermogravimetry (TG) was determined with a TGA 2 Mettler Toledo thermal analyzer (Greifensee, Switzerland). Differential scanning calorimetry (DSC) was determined with a DSC 3 Mettler Toledo thermal analyzer (Greifensee, Switzerland). X-ray photoelectron spectroscopy (XPS) was determined with an ESCALAB 250 (Thermo Fisher Scientific, West Sussex, United Kingdom).

Gas chromatographic analysis was performed on an Agilent 7890A equipped with a flame ionization detector (FID) and an HP-5 phenyl methyl siloxan column (30 m × 320 μ m × 0.25 μ m) (Agilent Company, Wilmington, DE, USA). The injection mode was split (5:1). N₂ (99.999%) served as the carrier gas with a constant flow of 1.0 mL × min⁻¹. Further, the column temperature was increased from 50 °C to 260 °C t 4.0 °C × min⁻¹, raised to 280 °C at a rate of 40.0 °C × min⁻¹, and then maintained for 2 min.

Synthesis of the Poly-TFPN-β-CD

The poly(β -cyclodextrin) was synthesized *via* one-pot nucleophilic substitution condensation copolymerization with β -CD and 3,4,5,6-tetrafluorophthalonitrile (TFPN) as the monomers (Fig. 2). β -cyclodextrin (0.52 g, 0.45 mmol), TFPN (0.30 g, 1.50 mmol), and K₂CO₃ were added into a reaction tube. Then, 20 mL of mixed solvent (THF / DMF, 9:1v/v) was added into the tube with dry nitrogen flushing. After 3 min of dry nitrogen flushing, the reaction tube was sealed, and the mixture was stirred at 85 °C for 48 h. The yellow products were precipitated and thoroughly washed with 1N HCl, water (25 mL × 2), THF (25 mL × 2), and CH₂Cl₂ (40 mL). The final product was frozen at -196 °C in a liquid nitrogen bath for 10 min and then dried in a freezer dryer. The yield of the polymer was 37.6% to 40.2%. The synthetic route is shown in Fig. 2.





Solid-Phase Extraction (SPE) and GC-FID Detection

The prepared positive rubber sample was extracted with 10 mL of ethanol *via* an ultrasonic method before testing. Next, 0.45 μ m nyron-66 filter membrane was placed on the bottom of the 0.5 mL syringe, and 10 mg of poly(β -cyclodextrin) was added onto it. Then, another 0.5 μ m nyron-66 filter membrane was placed above the adsorbent poly(β -cyclodextrin). One mL of the analytes was then passed through this thin layer, and the adsorbent layer was washed with 5 mL of methanol. The resulting absorption solution was collected and evaporated to 1 mL, and the analytes were filtered using a 0.22 μ m filter

membrane. Then, the sample was injected into the GC-FID system for further analysis. Finally, the residual adsorbent was washed with an additional 10 mL of methanol to prepare for the next extraction process.

RESULTS AND DISCUSSION

Structural Analysis of Poly-TFPN-β-CD and β-CD

KBr discs samples were prepared. In the FT-IR spectra of the polymer and the crude materials (Fig. 3), the broad OH stretching band around 3450 cm⁻¹ reflected the stretching vibration of multiple OH functional groups of β -CD. The peak at 2894 cm⁻¹ was attributed to the C-H vibration of CH₂, and the peak at 2252 cm⁻¹ was the characteristic signal of the cyano group in 2, 3, 5, 6-tetrafluoroterephthalonitrile (TFPN). The characteristic signals of above functional groups were all observed in the spectrum of the polymer (P-CD), which confirmed the successful synthesis of β -CD polymer. Figures 3b and 3c show the solid-state ¹³C NMR and ¹⁹F NMR of the β -CD polymer, respectively. In the ¹³C NMR spectra (Fig. 3b), the peaks from 140 ppm to 153 ppm were attributed to the signals of the carbon atom of C-F (a) and C-O (b) of the aromatic ring. The peaks at 109.9 ppm and 97.7 ppm were attributed to the signal of the carbon atom of CN (c) and aromatic ring (C-CN, d, Ar) (Fig. 3b). The signal of the carbon atom in the sugar ring appeared at 107.3 ppm and 72.8 ppm. In the ¹⁹F NMR spectra, the peaks at -122.9 and -137.3 ppm belonged to the signal of the signal of the fig. 3c).





Fig. 3. Structural analysis of poly-TFPN-β-CD and β-CD before and after crosslinking; (a) FT-IR spectra of β-CD, poly-TFPN-β-CD, and 3,4,5,6-tetra fluorophthalonitrile (TFPN); (b) The solid ¹³CNMR spectra of poly-TFPN-β-CD; (c) The ¹⁹F NMR spectra of poly-TFPN-β-CD

Thermal Properties of Poly-TFPN-β-CD

Figure 4 shows the TG and DSC curves of β -CD and poly-TFPN- β -CD. There were two decomposition stages of cyclodextrin (Fig. 4a).



Fig. 4. Thermo analysis of β -CD and poly-TFPN- β -CD; (a) TG curves of β -CD and poly-TFPN- β -CD; (b) DSC curves of β -CD and poly-TFPN- β -CD

The first stage may have been the removal of crystal water, and the second stage was the degradation of β -CD at 324 °C. For poly-TFPN- β -CD, there were also two decomposition sections. Similarly, the first stage was the removal of crystal water, although

the proportion of decomposition was relatively small for the hydrophobicity increment of β -CD after modification. The decomposition temperature of poly-TFPN- β -CD was 285 °C. Moreover, because of the introduction of the aromatic compound TFPN, the residual carbon rate of cyclodextrin was greatly increased to 56.0%. The DSC curve is shown in Fig. 4b. An obvious exothermic peak was observed at 111.5 °C, which corresponded to the crystallization temperature of β -CD. After crosslinking with TFPN, the crystallization temperature of poly-TFPN- β -CD increased to 126.6 °C due to the formation of long chain polymers.

Porous Structure of Poly-TFPN-β-CD

The porous structure and specific surface area are important for absorption. Therefore, SEM and BET were carried out to evaluate the porous structure and specific surface area of poly-TFPN- β -CD. Figure 5a shows that the original β -CD had a minimally porous structure. After modification, the multi-layer polymer endowed the product with a more abundant pore structure that could effectively increase the specific surface area. The porous structures of β -CD before and after modification were further verified by BET analysis. The specific surface area of the modified β -CD was 55.2 m² × g⁻¹. In addition, the N₂ nitrogen absorption curve of poly-TFPN- β -CD was a type II curve, which is indicative of a mesoporous structure. The treatment greatly improved the specific surface area of cyclodextrin; thus, its absorption performance was expected to improve. The total pore volume calculated by the single-point absorption method was 0.108 cm³ × g⁻¹. The Barrett Joyner Halenda model (BJH) was applied to calculate the pore size distribution (Zhang and Lu 2019). The pore diameter was 7.88 nm, which indicated that a mesoporous structure formed (Miskam *et al.* 2014).



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Fig. 5. Characterization of the porous structures of poly-TFPN- β -CD; (a) An SEM image of β -CD; (b) An SEM image of poly-TFPN- β -CD; (c) The N₂ absorption (lower line) and desorption (upper line) isotherms of poly-TFPN- β -CD; (d) The cumulative pore volume of poly-TFPN- β -CD obtained by NLDFT analysis

Absorption Properties of Poly-TFPN-β-CD and the Accuracy of the Method

The absorption efficiency of β -CD and poly-TFPN- β -CD for aniline derivatives were determined, and the results are shown in Fig. 6. Poly-TFPN- β -CD adsorbed over 60% of aniline derivatives in 10 s, whereas the absorption capacity of β -CD was always below 40%, which indicated that the absorption efficiency of poly (β -CD) was three times higher than that of β -CD due to its high specific surface area.

To test the accuracy of the method, various concentrations of the standard solutions of 4 aniline derivatives between 1 mg \times L⁻¹ and 100 mg \times L⁻¹ were applied to plot the working curve (n = 3). The concentration of the analytes exhibited a linear relationship with peak area. The linear equation and relative parameters are listed in Table 1. The precision of this method was determined by relative standard deviation (RSD) values. The RSD of this method ranged from 1.61% to 7.64%, which illustrated that the developed method had good reproducibility.

The standard chromatographic curve under optimum conditions is shown in Fig. S1. In former research, when Fe₃O₄/hydroxypropyl- β -cyclodextrin polymer magnetic nanomaterials were used for solid-phase extraction, the LOD of malachite green was 5.6 mg/L (Feng *et al.* 2016). In this study, the LOD of aniline derivatives was better. Liu *et al.* (2012) determined the LOD of aniline, o-tolidine, o-toluidine, and 3-aminophenol in

environmental water by capillary electrophoresis with on-line concentration, and they found that LOD ranged from 0.29 mg/L to 0.44 mg/L. In this research, the LOD of aniline was greatly increased.



Fig. 6. The absorption efficiency of 10 mg of poly-TFPN- β -CD or 10 mg β -CD with a concentration of 100 mg × L⁻¹ four aniline derivatives

Analyte	Linear Equation	R2	LOD	RSD	Recovery
			(mg/kg)	(%)	(%)
Aniline	Y = 2.113 × 107c -2.5 × 105	0.9952	0.05	3.62	90.1 to
					103.4
N-ethylaniline	Y = 1.031 × 106c -3.6 × 104	0.9967	2.6	7.64	92.6 to
-					110.5
1,2-Phenylenediamine	Y = 1.336 × 108c -2.8 × 106	0.9938	0.05	1.61	90.4 to
-					94.0
N-phenyl-p-	Y = 7.968 × 107c -1.8 × 104	0.9942	0.05	2.12	92.7 to
phenylenediamine					98.9

To evaluate the applicability of this method in practical matrix, 3 kinds of aniline derivatives in commercial rubber (purchased from a local market in Fuzhou, China) were analyzed.

Because no analyte was detected in the rubber samples tested, standard solutions were added to the commercial rubber samples to identify the recovery rates when using this method. The results are summarized in Tables 2, 3, and 4. Relative recovery ranged from 86.8% to 110.5%, and the RSD values of 1.61% to 9.91% were indicative of the high accuracy of this method.

The recovery and RSD results in Tables 2, 3, and 4 showed that this method had good precision in real sample testing. The results showed that the poly-TFPN- β -CD-based solid-phase extraction material was suitable for use in practical testing in various fields.

Analyte	Additive Concentrations (mg/L)	Detected Concentrations (mg/L)	Recovery (%)	RSD (%)
Aniline	0.0182	0.0172	94.32	3.62
	0.0450	0.0406	90.11	9.18
	0.100	0.1034	103.4	8.67
N-ethylaniline	0.0520	0.0575	110.51	7.64
	0.100	0.0939	93.98	6.98
	0.250	0.2316	92.64	9.91
1,2-Phenylenediamine	0.025	0.0226	90.40	1.61
	0.035	0.0311	89.00	3.80
	0.075	0.0696	92.80	7.81
N-phenyl-p- phenylenediamine	0.0260 0.035 0.070	0.0257 0.0324 0.0667	98.91 92.67 93.48	2.21 2.61 7.08

Table 2. Results of the Determination of Four Aniline Derivatives in Rubber Nipple (n = 6)

Table 3	. Results o	f the De	etermination	n of Four	Aniline	Derivative	s in E	Baby (Car ⁻	Tire
(Recycle	ed Rubber) (n = 6))					-		

Analyte	Additives Concentration (mg/L)	Detected Concentration (mg/L)	Recovery (%)	RSD (%)
Aniline	0.0182	0.0177	97.25	3.72
	0.0450	0.0425	94.44	9. 81
	0.100	0.0920	92.00	8.67
N-ethylaniline	0.0520	0.0532	102.31	6.85
	0.100	0.0954	95.40	7.74
	0.250	0.229	91.60	3.82
1,2-Phenylenediamine	0.025	0.0225	90.00	1.981
	0.035	0.0354	101.14	4.82
	0.075	0.0719	95.87	6.52
N-phenyl-p- phenylenediamine	0.0260 0.035 0.070	0.0271 0.0355 0.0687	104.23 101.43 98.14	1.95 3.82 5.09

Table 4. Results of the Determination of Four Aniline Derivatives in Rubber Sole (n = 6)

Analyte	Additives Concentration (mg/L)	Detected Concentration (mg/L)	Recovery (%)	RSD (%)
Aniline	0.0182	0.0169	92.86	4.03
	0.0450	0.0419	93.11	7.16
	0.100	0.0940	94.00	3.25
N-ethylaniline	0.0520	0.0501	96.35	5.29
	0.100	0.0914	91.40	5.31
	0.250	0.217	86.80	9.01
1,2-Phenylenediamine	0.025	0.0219	87.60	4.15
	0.035	0.0327	93.43	3.37
	0.075	0.0733	97.73	6.18
N-phenyl-p- phenylenediamine	0.0260 0.035 0.070	0.0265 0.0332 0.0667	101.92 94.86 95.29	6.42 2.84 5.91

Regeneration of Absorption Ability

In practical application, the regeneration of the extraction capacity of SPE is of great economic and environmental importance. The interaction between the poly-TFPN- β -CD-based solid-phase extraction material and analyte was weak. Thus, the weak interaction allowed the adsorbed aniline derivates to be easily removed from poly-TFPN- β -CD material for reuse *via* a mild washing method. Four solvents (methane, ethanol, dichloromethane, and acetone) were used to study the regeneration ability of poly-TFPN- β -CD.

The absorption capacity of poly-TFPN- β -CD washed with methanol was closest to that of the original poly-TFPN- β -CD, so methanol was chosen as the regenerant. The effects of washing time on the absorption capacity of poly-TFPN- β -CD was studied, and methanol was used as the regenerant. Figure 6b exhibits the poly-TFPN- β -CD had approximately the same absorption capacity for aniline derivatives over 4 absorption-desorption cycles, which indicated that the developed poly-TFPN- β -CD had high regeneration ability.

To reveal the regeneration mechanism of poly-TFPN- β -CD, exhaustive tests, including SEM, BET, and XPS, were carried out. The morphology of poly-TFPN- β -CD after regeneration (Fig. 7c) showed that the pore structure of poly-TFPN- β -CD remained after the regeneration process, which indicated the persistent absorption ability of poly-TFPN- β -CD.

The porous structure of poly-TFPN- β -CD after regeneration was further studied by BET. The specific surface area of poly-TFPN- β -CD after regeneration was 55.0 m² × g⁻¹, which was approximately the same as that of the original poly-TFPN- β -CD. In addition, the N₂ nitrogen absorption curve of poly-TFPN- β -CD after regeneration was a type II curve, which was indicative of a mesoporous structure. The results of XPS showed that the surface element compositions were largely unchanged before and after regeneration, which demonstrated that all the aniline derivatives adsorbed were eluted.



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Samples Percentage (%) Chemical species	Poly-TFPN-β-CD	Regenerated poly-TFPN- β-CD		
C1s	48.92	51.86		
VC	7.04	4.73		
C-CF ₂	3.62	3.21		
O1s	21.71	21.96		
N1s	5.55	5.92		
BN	0.64	0.7		
F1s	6.28	5.99		
CF ₂	6.25	5.61		

Fig. 7. (a) The absorption capacity of poly-TFPN-β-CD and β-CD for aniline derivatives in 4 absorption-desorption cycles; (b) The regeneration ability of poly-TFPN-β-CD; (c) The SEM image of regenerated poly-TFPN-β-CD; (d) The N₂ absorption (lower line) desorption (upper line) isotherms of poly-TFPN-β-CD. S_{BET} is the Brunauer–Emmett–Teller (BET) surface area (in units of $m^2 \times g^{-1}$) of poly-TFPN-β-CD calculated from the N₂ absorption isotherm, and P and P₀ are the equilibrium and saturation pressures of N₂ at -196 °C, respectively; (e) The XPS spectra of poly-TFPN-β-CD and regenerated poly-TFPN-β-CD; (f) The surface composition of poly-TFPN-β-CD and regenerated poly-TFPN-β-CD

CONCLUSIONS

- 1. In this study, a porous poly-TFPN- β -CD adsorbent was successfully prepared by crosslinking with 3,4,5,6-tetrafluorophthalonitrile (TFPN) for solid-phase extraction.
- 2. The modified poly-TFPN- β -CD showed a multi-porous structure and a large specific surface area of 55.2 m² × g⁻¹.
- 3. The porous SPE adsorbent was coupled with GC-FID to analyze aniline derivatives in prepared positive rubber samples. Poly-TFPN- β -CD polymers showed an improved absorption efficiency (highest 96.4%), a fast absorption rate (≤ 10 s) and high accuracy (RSD ranged from 1.60% to 9.90%).
- 4. Further, poly-TFPN- β -CD polymers also had a high regeneration ability, as they could be regenerated four times.
- 5. Therefore, for this porous material, high absorption property and good regeneration performance were achieved simultaneously.
- 6. The method in this study is expected to have great potential for absorbing and detecting aniline pollutants in rubber. In addition, the good regeneration property of this adsorbent is conductive to wider commercial application.

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