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Polymer–inorganic selective adsorbents for gas chromatography produced by graft polymerization

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ABSTRACT

The possibilities for a new approach to the development of polymer–inorganic sorbents with improved sorptive separation properties for the gas chromatographic analysis of organic compounds of different classes including strongly polar and high-boiling types are discussed. The method involves graft radical polymerization of vinyl monomers on the solid inorganic surface modified by chemical fixation on it of silicon containing unsaturated polymerizable compounds and hydroperoxides. The influence of the microstructure of polymer layers grafted to inorganic particles on the sorption properties of polymer–inorganic systems in the gas chromatographic separation of sorbates of different natures is shown. The separation properties of polymer–inorganic sorbents are shown to vary on changing the chemical nature of the grafted polymer layer. Possible methods for the direct control of the properties of polymer–inorganic sorbents are proposed. New highly effective and selective sorbents based on homopolymers and copolymers of styrene and some nitrogen-containing monomers were prepared. These sorbents give 2–5 times faster separations of organic sorbates, including aromatic compounds, than well known polymer sorbents.

INTRODUCTION

Selective sorbents providing relatively high separation efficiencies are required for the rapid analysis of high-boiling aromatic compounds by gas chromatography (GC). Chemical grafting of copolymer chains to the surface of dispersive inorganic materials by graft radical polymerization of various vinyl monomers is a promising trend for the development of such sorbents [1]. High thermal resistance, the absence of a background signal and also application of highly sensitive detectors are characteristics of such sorbents.

Methods for graft radical polymerization based on inorganic fillers modified by radical-generating organosilicon compounds were developed recently [2,3]. These methods seem promising for the directed synthesis of dispersive polymer–inorganic materials with prescribed structural and functional properties.

The adsorptive properties of some polymer–inorganic systems were studied in this work. The influence of the microstructure and chemical nature of the grafted polymer layer on the chromatographic properties of sorbents was studied and possibilities of this method for the modification of solid surface were examined as an approach to the directed synthesis of new adsorbents.

EXPERIMENTAL

Polystyrene (PS), polyacrylonitrile (PAN), styrene–acrylonitrile copolymers (SAN) and styrene–N-vinylpyrrolidone (SVP) of various compositions grafted to A-175 Aerosil and AG-57 aluminium oxide surfaces were studied. Polymer–inorganic materials were prepared by graft radical liquid-phase polymerization and copolymer-ization of monomers using Aerosil and aluminium oxide with initiating groups chem-ically fixed on inorganic particles, *e.g.*, hydroperoxide (HP) or polymerizable (metha-cryloyloxymethyl)methylsilane (MS) groups [2,3]. These groups are the propagation sites of macrochains on the inorganic surface:

(MS)

(PH)

where Me : Si , Al

M : $CH=CH_2$ $CH=CH_2$ $CH=CH_2$
         | | |
         C_6H_5 $C\equiv N$
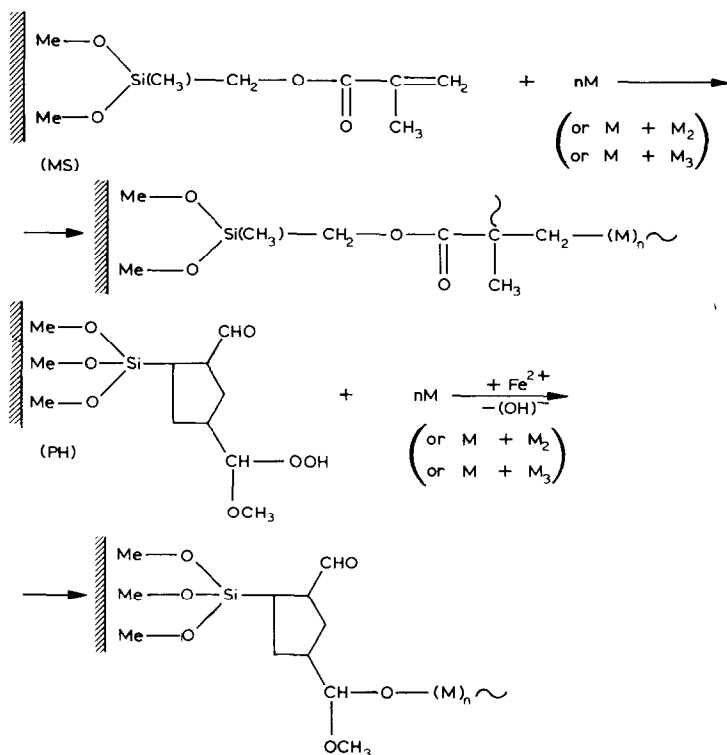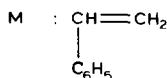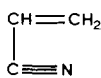
M_1 M_2 M_3
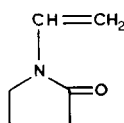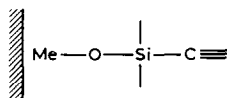
Our methods for graft polymerization allow a solid polymeric layer on a hard surface to be obtained; this layer is chemically bonded with the surface by a resistant bond:

$$\text{Me} - \text{O} - \overset{\textstyle |}{\underset{\textstyle |}{\text{Si}}} - \text{C} \equiv$$

The operating conditions (the nature of the solvent and monomer, temperature, time of polymerization) can change the polymeric layer thickness from 1 to 10–15 nm, and also its chemical composition, molecular weight characteristics and the density of macromolecule fixation on the surface.

The synthesized dispersive products were extracted with a suitable solvent to remove ungrafted copolymer and polymer and were carefully dried. The content of the grafted polymer in the sorbent (q) was determined thermogravimetrically on the ash by burning the sample at 800°C. To determine the molecular weight (MW) of the grafted polymer it was separated from the inorganic support by dissolution in hydrochloric acid. The MW and q values of the sorbents are given in Table I. The adsorbent fraction with 0.16–0.36-mm particles was used. The specific surface area measured by the BET method was 40–50 m^2/g.

Tsvet-110 and Tsvet-165 gas chromatographs with 1.0×0.003 m I.D. glass columns and thermal conductivity and flame ionization detectors were used. Helium was used as the carrier gas at a flow-rate of 30–40 cm^3/min. The separating properties of the adsorbents and their polarities were evaluated from the relative retention times (with respect to n-pentane) (t_R) and separation factors (R) for C$_6$–C$_{10}$ aromatic and aliphatic hydrocarbons and C$_1$–C$_4$ alcohols, including isomers. The specifity or selectivity of the adsorbents was determined from t_R and α values for known pairs of organic compounds with different sorbate–adsorbent reaction types.

RESULTS AND DISCUSSION

Structure of the grafted polymeric layers and chromatographic properties of polymer–inorganic systems of the Aerosil–polystyrene type

The microstructure of the grafted layers was studied by reverse GC using sorbates of different nature. Thermodynamic parameters of sorption were calculated: differential molar free energy (ΔG), the change in sorption entropy (ΔS) and heat of adsorption (ΔQ) (calculated for linear areas of the retention diagrams).

TABLE I

CHARACTERISTICS OF SORBENTS BASED ON PS GRAFTED TO AEROSIL

Sorbent	Relative content of polymer q (g/g Aerosil)	MW · 10^{-3}	Concentration of chains on Aerosil surface (conventional units)	Specific surface area (m^2/g)
PSA-1[a]	0.06	50	1.0	20.4 ± 1.7
PSA-2[a]	0.27	45	2.5	23.2 ± 5.1
PSA-3[a]	0.66	570	1.0	6.8 ± 1.2
PSA-4[b]	0.33	–	–	14.3 ± 5.7

[a] Grafting with pH-Aerosil.
[b] Grafting with MS-Aerosil; polymer component is structured.
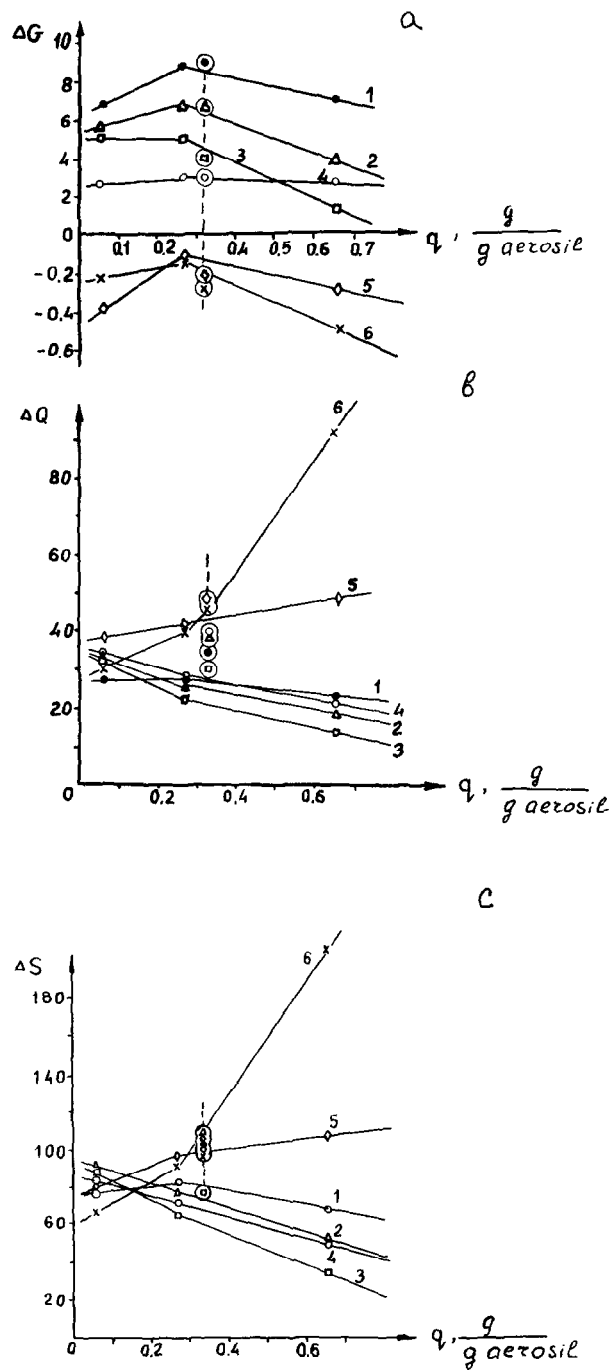
Fig. 1. (a) Differential molar free energy (ΔG), (b) heat of adsorption (ΔQ) and (c) entropy of adsorption (ΔS) *versus* the content of polystyrene grafted to Aerosil for: (1) *n*-pentane, (2) *n*-hexane, (3) cyclohexane, (4) benzene, (5) methyl ethyl ketone and (6) butanol.

Specially prepared PS samples were studied, characterized by the molecular weights of the graft chains and by the density of their fixation on the surface and indirectly reflected in the layer thickness (q) (Table I). The Aerosil–polystyrene system is a suitable model for evaluating surfaces by chromatography because the polymeric component does not contain functional groups for specific sorbate–sorbent reactions.

Studies of the sorption of non-polar compounds showed a small sorptive activity of al the sorbents studied on the basis of ΔG (Fig. 1, curves 1–4 and a high sorption–desorption equilibrium on the basis of ΔQ and ΔS. Sample PSA-4 is excluded (Fig. 1, points encircled); it is grafted in the polymeric layer. When q is increased and when grafts are available in the polymeric layer, the polarity of sorbents with respect to alkanes evaluated as the difference ΔG for n-pentane and n-hexane, is increased (Fig. 1, curves 1 and 2). The nature of curves 2 and 3 in Fig. 1 (hexane–cyclohexane) indicates a space distribution of grafted macrochains which hampers the sorption of hydrocarbons in direct relation to the volume of their molecules.

Studies of the sorption of polar compounds indicated an extreme relationships between ΔG and q (Fig. 1, curves 5 and 6); the ΔQ and ΔS values increase when q is increased. Hence the nature of the sorbate–sorbent reaction depends on q: at low q donor–acceptor complex formation is preferred, whereas at high q the formation of hydrogen bonds is preferred. These results mean that the inorganic surface is available for polar sorbates at low filling ratios by macrochains independently of MW and at high densities of macrochain fixation with high MW.

On the basis of these results and of the thicknesses of grafted polymeric layers up to and including 15 nm, as evaluated by electron microscopy, and from calculations (lengths and areas of completely stretched macromolecules, average radius of macromolecular ball), conclusions can be drawn about the conformation of the grafted macrochains and the microstructure of the polymer–inorganic systems [4]. Grafted chains with low and average molecular weights have preferably a spread conformation. When they are tightly fixed on the surface, the inorganic surface is completely blocked by the polymer and, grafts in the polymeric layer also contribute. At high molecular weights the segmental mobility of the grafted chains increases, which gives the possibility of realizing the structure of macromolecular balls with physical overlapping. Dispersive forces of the reaction of balls of grafted PS do not prevent the penetration of polar sorbates to the inorganic surface.

The results allow some recommendations for the direct synthesis of polymer–inorganic sorbents for gas adsorption chromatography to be given. A rigid uniform coating of the surface by the grafted polymer is required in order to obtain an average selectivity and to keep the universality of sorbents. In this case the grafted polymer should have rigid chains and it is recommended to limit the average molecular weights of grafted chains at the maximum density of their fixation on the surface.

Influence of the polymer component of sorbents on their chromatographic characteristics

Based on the above recommendations some polymer–inorganic systems were prepared and analysed. The polymeric component of these systems had graft rigid-chain structures, namely PS, PAN, SAN and SVP of various compositions grafted on the surface of Aerosil and aluminium oxide. The addition of heteroatoms, particularly nitrogen, to macromolecules significantly increases the selectivity of separation

owing to the presence of electronegative adsorption sites in sorption–desorption. Nitro, amino, imido and nitrile groups are known to provide electron-donor adsorption sites of various activity [5–7]. Sorbents such as polysorbnitril, aminopolysorb, polysorbimid and polyacrylonitrile have been used for the selective separation of different classes of organic compounds. Nevertheless, owing to their chemical nature and low thermal stability it is difficult to separate aromatic and high-boiling compounds.

Fig. 2 shows the separation properties of polymer–inorganic sorbents based on Aerosil, characterized by the chemical structure of the grafted polymeric layer (0.3–0.4 g/g filler). All the sorbents studied have good separation properties and different selectivities. Thus PAN sorbents have the highest polarity and selectivity and one can obtain high values of r for a homologous series of organic compound and for the separation of isomers. PS sorbents are less polar and selective than PAN sorbents but they also allow the separation of organic compounds and the time of analysis is half that with PAN sorbents.

The retention of both alcohols and hydrocarbons on SAN sorbents containing styrene and acrylonitrile units is much lower than that on PS and PAN sorbents. It is very characteristic for higher members of homologous series. Curves of t_R for organic compounds *versus* content of acrylonitrile units in the graft layer are similar for all classes of compounds studied; an inflection of the curves is observed, with a minimum. The addition of two types of active adsorption sites (π electrons of the benzene ring and unpaired electrons of the nitrile group) and their statistical distribution apparently give favourable conditions for speeding up the sorption–desorption of organic compounds. Thus SAN sorbents can be recommended for the rapid analysis of organic compounds.
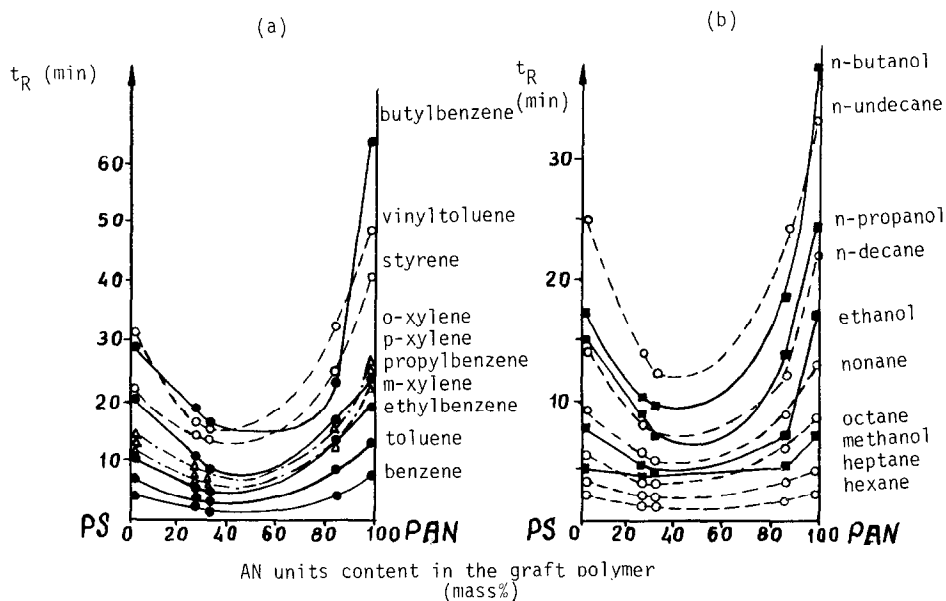

Fig. 2. Relative retention times (with respect to *n*-pentane) of (a) aromatic hydrocarbons and (b) *n*-alkanes (dashed lines) and *n*-alkanols (solid lines) *versus* the composition of the polymer grafted layer.

The replacement of AN units in the grafted polymeric layer with more polar units of N-vinylpyrrolidone significantly changes the chromatographic properties of the sorbent (Table II). SVP sorbents have higher specificity than SAN sorbents.

It is important to consider the chromatographic properties of SAN sorbent in detail and to compare them with those of known polymeric sorbents.

The retention of polar compounds on SAN–Aerosil sorbents (Table III) is proportional to the dipole moment on changing from pentane to acetonitrile and it is relevant to the retention on polysorbnitrile and Chromosorb 104. The t_R values of polar compounds are comparable to those for Chromosorb 104 and they are higher than those for polysorbnitrile. It is important to note that the analysis time using SAN sorbents is several times shorter when all other conditions remain the same. They allow the rapid separation of aliphatic hydrocarbons (up to octane) from water or low-boiling polar compounds such as methanol, ethanol, acetone and diethyl alcohol.

The asymmetry factors of the peaks of aromatic compounds (0.25–0.08) and isomeric alcohols (0.35–0.15) indicate a satisfactory geometric homogeneity of the sorbents. The separation of aromatic hydrocarbons including isomers of butylbenzene is not satisfactory on previously known polymeric sorbents. It should be mentioned that as the parameters of the separation of organic compounds on SAN grafted to Aerosil and aluminium oxide (Table II) are very similar, the nature of the inorganic particle does not have a significant effect on the conditions for complete coating of the particle with the polymeric layer.

Additional functionalization of the solid surface by heat treatment was carried out taking due account of the capability of SAN fixed on the inorganic surface to undergo thermal and chemical transformations [8]. Heat treatment of the sorbents was carried out in a helium flow in chromatographic columns by isothermal stage heating at 200–350°C at 50°C intervals and heating for 4 h in each stage.

Table II shows a significant change in the polarity of SAN sorbents after their heat treatment and an improvement in the parameters for the chromatographic separation of different organic compounds. The selectivity of the sorbents for the separation of alcohols, ketones and aliphatic hydrocarbons is significantly increased, the efficiency and selectivity of the separation of high-boiling, difficult to separate hydrocarbons are increased, the separation factor becomes 1.2–1.3 times higher, and the height equivalent to a theoretical plate becomes 1.3–3 times lower. In some instances the values for the separation of pairs of compounds increase by 20–30%. The range of operating temperatures is increased, the upper limit reaching 300–350°C.

The proposed procedure gives the possibility of separating high-boiling polar compounds which could not previously be separated by gas adsorption chromatography. This is very important because at present the separation of high-boiling compounds in complex mixtures is difficult because heat-resistant sorbents are not available.

In comparison with known liquid stationary phases for GC, polymer–inorganic sorbents have three advantages. First, they have a fairly high heat stability (300–350°C). Second, there is no background signal, which allows high-sensitivity detectors to be used. The third advantage is the possibility of analysing mixtures of organic compounds of several classes. The combination of these three properties significantly extends the applications of available sorbents. It should be noted that the chroma-

TABLE II

CHROMATOGRAPHIC CHARACTERISTICS OF SAN AND SVP SORBENTS

Content of acrylonitrile and vinylpyrrolidone units in polymer is 25 wt.%. Content of SAN grafted to Aerosil is $9 \cdot 10^{-4}$ g/m^2 and to alumina $13 \cdot 10^{-4}$ g/m^2, content of grafted SVP is $13 \cdot 10^{-4}$ g/m^2.

Sorbent type	Compounds being separated	Initial inorganic support	Analytical conditions		Selectivity, α		Separation factor, R		Height equivalent to a theoretical plate (mm)	
			Column temperature (°C)	Analytical period (min)	Before heating	After heating	Before heating	After heating	Before heating	After heating
SAN	Decane–undecane	Aerosil	150	3.0	1.67	1.75	1.60	2.35	4.0	1.5
	Decane–undecane	Al$_2$O$_3$	150	5.0	1.60	2.05	2.09	2.40	2.9	2.1
	n-Butylbenzene–tert.-butylbenzene	Aerosil	150	4.5	1.40	1.45	1.15	1.20	3.3	2.9
	n-Butylbenzene–tert.-butylbenzene	Al$_2$O$_3$	250	7.0	3.25	3.70	1.39	2.70	2.5	1.7
	Benzylacetone–acetophenone	Aerosil	150	7.5	No separation	1.80	No separation	2.00	No separation	3.4
	n-Butanol–sec.butanol	Aerosil	150	1.5	1.40	1.20	0.60	1.00	22.0	11.4
	Heptane–n-propanol	Aerosil	150	2.0	2.70	4.00	1.21	2.00	-	-
	Benzene–cyclohexane	Aerosil	150	1.0	2.05	2.20	1.13	1.68	7.3	5.0
	Acetone–isopropanol	Aerosil	150	1.0	1.20	1.50	-	0.52	45.0	16.0
	Dodecane–tetradecane	Aerosil	150	13	2.7	2.95	3.5	3.9	3.0	2.4
	Butyl phenyl ketone–isobutyl phenyl ketone	Aerosil	200	7.0	No separation	1.3	No separation	1.0	No separation	2.7
SVP	Diphenyl–diphenylmethane	Aerosil	250	2.0	No separation	1.1	No separation	0.3	No separation	0.9
	Heptane–propanol	Aerosil	150	2.1	2.00	-	4.40	-	11.7	-
	Acetone–isopropanol	Aerosil	150	0.7	1.10	-	0.70	-	12.9	-
	n-Butanol–sec.butanol	Aerosil	150	1.8	1.60	-	2.90	-	9.9	-
	p-Xylene–m-xylene	Aerosil	150	3.6	1.11	-	1.12	-	3.2	-

TABLE III

RELATIVE RETENTION TIMES (t_R) (WITH RESPECT TO n-PENTANE) OF POLAR COMPOUNDS

Column temperature, 150°C

Compound	Polarizability × 10^{-3} (nm^3)	Dipole-moment, D	t_R (min)					
			SAN–Aerosil adsorbent[a]			Polymer adsorbents		
			1	2	3	Polysorb-I	Polysorbnitrile	Chromosorb 104
Water	1.49	1.84	3.7	3.5	2.7	0.1	1.8	2.3
Methanol	3.23	1.67	5.2	4.4	3.0	0.2	1.5	2.0
Ethanol	5.03	1.70	7.6	5.0	4.3	0.4	2.7	3.9
Acetonitrile	–	3.94	6.0	7.6	6.0	0.6	6.2	7.3
Acetone	6.32	2.73	9.0	6.2	4.7	0.7	3.7	4.6
Diethyl ether	9.02	1.17	–	1.7	–	0.9	1.3	1.5
Pentane	9.95	0	1.0	1.0	1.0	1.0	1.0	1.0

[a] 1,2 = SAN grafted to MS-Aerosil; 3 = SAN grafted to HP-Aerosil. Content of grafted polymer: (1) 0.17, (2) 0.33, (3) 0.13 g/g Aerosil.

TABLE IV

RELATIVE RETENTION TIMES (t_R) AND SELECTIVITIES (α) OF COMPOUNDS WITH DIFFERENT GEOMETRIC STRUCTURES AND SIMILAR BOILING POINTS

Column temperature, 150°C.

Compound	B.p. (°C)	Mol.wt.	SAN–Aerosil adsorbent[a]						t_R (min)		
			t_R (min)			α			Polysorb	Polysorbnitril	Chromosorb 104
			1	2	3	1	2	3			
Propanol	60	97.8	12.0	8.5	5.0	1.5	1.85	1.67	1.0	4.9	5.6
Isopropanol	60	82.4	8.0	4.6	3.0				0.8	3.9	3.7
n-Butanol	74	117.5	18.0	10.0	8.3	1.38	1.14	1.19	2.8	10.2	11.3
Isobutanol	74	106.5	13.0	8.8	7.0				2.2	8.3	8.9
sec.-Butanol	74	99.5	12.0	7.6	6.7	2.0	1.29	1.43	1.8	6.7	7.3
tert.-Butanol	74	82.8	6.0	5.9	4.7				1.2	3.8	4.0
n-Pentane	72.1	36.1	1.0	1.0	1.0	1.1	1.1	1.1	1.0	1.0	1.0
Isopentane	72.1	27.8	1.1	1.1	1.1				0.8	—	—
n-Propylbenzene	120	159.0	20.0	12.2	6.6	1.05	1.30	1.0		Not separated	
Isopropylbenzene	120	152.0	19.0	9.4	6.6					Not separated	
n-Butylbenzene	134	183.0	34.0	18.2	12.0	1.42	1.38	1.36		Not separated	
Isobutylbenzene	134	172.8	24.0	12.9	8.8					Not separated	
sec.-Butylbenzene	134	173.3	32.0	14.0	9.2	1.39	1.33	1.06		Not separated	
tert.-Butylbenzene	134	169.0	23.0	10.5	8.7					Not separated	

[a] See Table III.

tographic properties of SAN–Aerosil sorbents 1, 2 and 3 (Tables III and IV) prepared by different processes depend on different microstructures of the grafted polymeric layers.

CONCLUSION

This study of the separation properties of different dispersive polymer–inorganic systems prepared by graft radical copolymerization and polymerization of styrene and some nitrogen-containing vinyl monomers to inorganic dispersive materials has shown the possibility of achieving directed variations of the chromatographic properties of sorbents by changing the chemical nature and microstructure of the grafted polymeric layer at the polymerization stage or using its thermal and chemical transformations.

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