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Article

Gamma Radiation Effects on Polydimethylsilane Stationary Phases for Use in Packed-Column Gas Chromatographic Analyses

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Este trabalho estudou os efeitos da radiação gama como indutora da imobilização de fases estacionárias líquidas de polidimetilsilicones usadas para separações cromatográficas em colunas recheadas. Testes de extração em solventes mostram que doses moderadas de radiação gama (80-140 kGy) produzem imobilização (90%) da maioria dos polidimetilsilicones testados em suportes do tipo Chromosorb, apesar do efeito da massa molecular ser importante. A estabilidade térmica também aumenta significativamente, possibilitando o uso de altas temperaturas sem perdas por volatilização. Espectros no infravermelho confirmam a presença de fase estacionária no suporte após testes de estabilidade térmica e após lavagem exaustiva com solventes em coluna cromatográfica. O comportamento cromatográfico das fases imobilizadas é igual ou melhor do que o das fases não-irradiadas, exceto no caso de altas doses (300 kGy) de radiação gama. As colunas preparadas com polimetilsilicones imobilizados por radiação gama podem ser usadas com sucesso em análises onde a contaminação da coluna por compostos de alto ponto de ebulição exigem frequente recuperação da mesma.

Gamma radiation induced immobilization of several polydimethylsilane liquid stationary phases for use in packed-column gas chromatographic separations has been studied. Extraction tests show that moderate doses of gamma radiation (80-140 kGy) are sufficient to produce significant (90%) immobilization of most polydimethylsilanes onto Chromosorb supports, although a molecular mass effect is seen. Thermal stability also increases significantly with radiation dose, suggesting higher temperature use with smaller volatility losses. Infrared spectra confirm the continued presence of the stationary phase on the support after thermal stability tests and after exhaustive in-column washing. The column chromatographic behavior of the immobilized phases is equal to or better than that of the unirradiated phases, except for higher doses (300 kGy) of gamma-radiation. Columns prepared from gamma-immobilized polydimethylsilane have been used successfully in analyses where column contamination from high boiling materials requires frequent column recuperation.

Keywords: *gas chromatography, packed columns, immobilized phases, gamma radiation*

Introduction

Liquid polymeric stationary phases used in gas chromatography often present limitations due to volatility or thermal stability, which impose upper temperature limits on their use. One way to alleviate this problem is through chemical bonding of the liquid stationary phase to the support[1], as is done for most HPLC stationary phases. Another way to improve stationary phase stability is by crosslinking reactions which increase the polymer molecular mass. These immobilization processes, which involve bonding between the chains with possible bonding to the support[2], are usually initiated by free radicals produced by heat[3,4], chemical initiators such as peroxides[5,6], azo compounds[7,8] or ozone[9], low temperature plasmas[10], or by ionizing radiation from accelerated electrons[11] or from gamma irradiation[12-17].

These free radical initiated immobilization methods have been very successful in producing modern high temperature capillary columns. However, very little information exists about immobilization of supported liquid stationary phases for use in packed-column gas chromatography[18]. This investigation was undertaken to investigate the properties of several polydimethylsilanes on Chro-

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mosorb supports after immobilization by different doses of gamma irradiation.

Experimental

Materials

The polydimethylsilane liquid phases were dissolved in chloroform for preparing different loadings on Chromosorb W (80-100 mesh) or Chromosorb W-HP (80-100 mesh). Portions of the prepared packings were placed in glass ampoules and sealed under air for irradiation in an industrial irradiation facility operated by IBRAS-CBO (Campinas, Brazil). All solvents and most of the test compounds were p. a. and used without further treatment. When necessary, reagents were purified by conventional methods[19].

Equipment

Two different gas chromatographic systems were used: a Varian 1700 and an Instrumentos Científicos CG 500, both equipped with flame ionization detectors. Packed stainless steel columns were positioned to permit on-column injection.

Infrared spectra were taken on a Perkin-Elmer 399B spectrophotometer while thermogravimetric analyses were carried out on a DuPont model 1090B thermal analyzer with a model 951'thermogravimetric analyzer.

Testing procedures

Solvent extraction of the packings was carried out in a modified Soxhlet apparatus[20] with three solvents (methanol, hexane and chloroform), each for six hours.

A number of compounds with different polarities were used to evaluate the efficiency of each stationary phase, as determined by the retention factor (k), plate number (N), resolution (Rs) and asymmetry factor (As) at 10% of peak height. The chromatographic conditions for each separation, isothermal or with temperature programming, were determined by optimizing resolution of each mixture on an unirradiated column. The mobile phase (N_2) retention time was determined by injecting a mixture of propane and butane (cooking gas) at three different temperatures (60, 110 and 160 °C).

For the thermal stability tests, the column was heated in the chromatograph oven, without the detector connection, for one hour each at successively higher temperature, measuring the efficiency (plate number) of a standard compound (2-butanone) at 60 °C after each step.

The columns were also subjected to successive rinsings at 200 °C[15], injecting one column volume each of acetone, 1:1 acetone-dichloromethane, 4:1 dichloromethane-pentane, 1:1 dichloromethane-pentane and pentane, with the detector disconnected. Following this, the efficiencies of the columns were determined (n-decane and benzyl alcohol) at 110 °C.

Results and Discussion

Solvent extraction removes all of the polydimethylsilane liquid stationary phase (SP) from unirradiated packings. Extraction removes a small amount of the SP from the irradiated packings, quantities which appear directly related to the irradiation dose received (Table 1). Immobilization by radiation was less effective with SP-2100 and DC-200, although even with these packings some immobilization occurred, as shown by the continued presence of the 2960 cm^{-1} band in the infrared spectra (Figs. 1 and 2) after extraction of the irradiated samples. Extraction of unirradiated packings removes the liquid SP and this band disappears.

Low irradiation doses are sufficient to immobilize significant quantities of SE-30, with no dependence on either the initial quantity placed on the support or on whether the support was, or was not, silanized (Table 1). Higher doses increase the quantity immobilized. The fact that the same percentage of SE-30 appears to be immobilized onto the support, independent of the initial quantity of liquid[18] or of the presence of methyl groups from the silanizing reaction on Chromosorb W-HP, suggests that the immobilization is mainly related to crosslinking of the polydimethylsilane

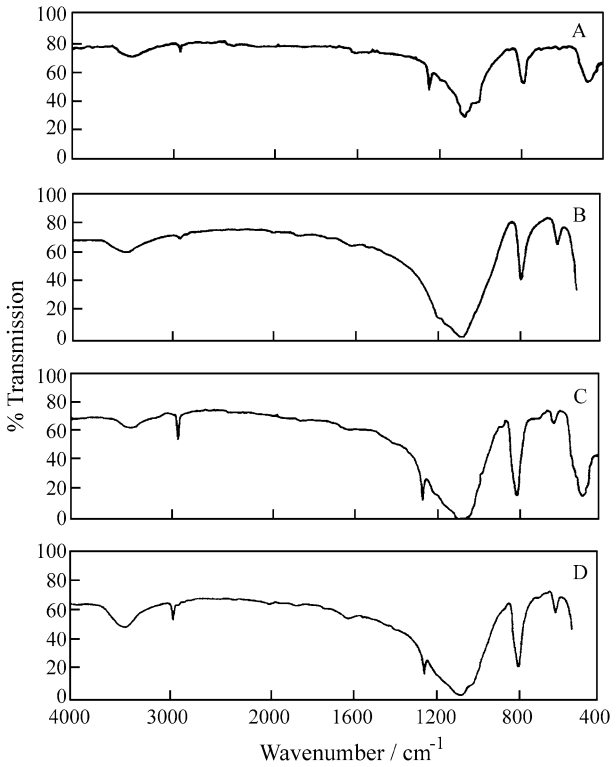

Figure 1. Infrared spectra of 20% SP-2100 on Supelcoport. A: before irradiation or extraction; B: unirradiated packing after extraction; C: packing irradiated to 25 kGy; D: packing irradiated to 25 kGy and subsequently extracted.

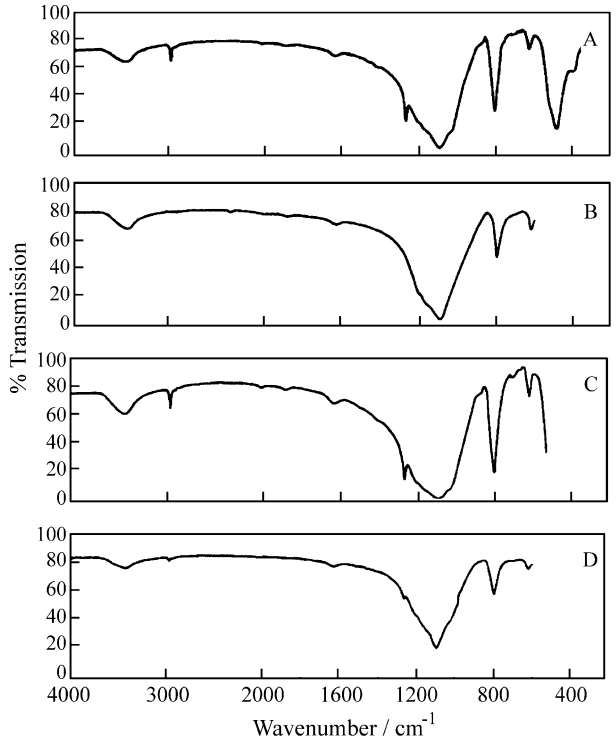

Figure 2. Infrared spectra of 14% DC-200 on Chromosorb W-HP. A: before irradiation or extraction; B: unirradiated packing after extraction; C: packing irradiated to 260 kGy; D: packing irradiated to 260 kGy and subsequently extracted.

chains rather than to formation of chemical bonds to the support.

The different percentages of immobilization observed, comparing SE-30 and DC-200, may be related to their different molecular masses, since SE-30 has a mass of about 1.0 - 2.5 x 10^6 daltons while DC-200 has a range of only 1.6 - 6.7 x 10^4 daltons[21]. Thus, to fully immobilize DC-200 would require much more crosslinking than is needed with SE-30.

In contrast to the results obtained by extraction, thermogravimetry on the several packings did not indicate significant differences between unirradiated and irradiated packings (Table 2). On the other hand, thermal stability tests carried out on packed columns indicate significant increases in the temperature maximum of the irradiated (immobilized) packings, in comparison to unirradiated packings. The temperature maximum usually indicated[22] for SE-30 is 300 °C, for DC-200, 250 °C and for SP-2100, 350 °C. As shown in Table 3, the immobilized packings have useful temperature ranges up to 50 °C higher than these values.

In order to see how much liquid stationary phase remained after this heat treatment, a portion of the packing was removed from the column after the 400 °C step for extraction. For the unirradiated packing, 62% of the quantity initially present was extracted after the heat treatment, indicating that part of the liquid SP had decomposed and/or volatilized, since infrared spectra taken after the extraction did not show the presence of residual polydimethylsilane. No evidence of volatilization was obtained for the irradiated phases after the heat treatment; both the extraction tests and the infrared spectra were the same as before the 400 °C thermal treatment.

Extensive column rinsing of radiation immobilized SE-30 packings did not significantly change their efficiencies, nor did it modify the infrared spectra (Fig. 3). Extraction of the unirradiated packing after rinsing removed 78% of the quantity originally present, indicating that up to 22% had been washed off in the rinsing test. By contrast, no change was observed in the amount extracted (and in the subsequent infrared spectra) for irradiated phases after the rinsing test. This enhanced stability property, which permits extensive rinsing of a packed column, has proved very useful in column recuperation when injecting reaction product mixtures having a wide range of properties and

Table 1. Percentages of the liquid phases immobilized by different irradiation doses.

Liquid phase / support	Radiation dose (kGy)	%Extracted* (total)	% immobilized (total)
14% SE-30 / Chromosorb	0	100	0
	30	28	72
	80	15	85
	130	12	88
	250	12	88
17% SE-30 / Chromosorb W-HP	0	100	0
	40	37	63
	100	16	84
	180	16	84
	280	15	85
	360	11	89
	440	9	91

Table 2. Thermogravimetry on immobilized packings.

Liquid phase	Radiation dose (kGy)	% mass loss	Temperature range (°C) of mass loss	
			Initial	Final
14% SE-30 / Chromosorb W	0	15	368	494
	30	15	374	476
	80	15	376	476
	130	14	400	494
	250	14	400	476
14% DC-200 / Chromosorb W-HP	0	15	330	560
	140	15	340	556
	260	10	358	550
20% SP-2100 / Supelcoport	0	18	362	478
	25	16	363	474

Table 3. Thermal stability, as determined by column efficiency, after heating at different temperatures in the chromatograph oven.

Liquid phase / support	Radiation dose (kGy)	Theoretical plate number after heat treatment to given temperature				
		200 °C	250 °C	300 °C	350 °C	400 °C
14% SE-30 / Chromosorb W	0	1200	1200	900	900	700
	250	1200	1200	900	900	1200
27% SE-30 / Chromosorb W-HP	0	700	700	600	500	400
	280	1500	1400	1200	900	800
14% DC-200 / Chromosorb W-HP	0	1300	1300	1200	---	---
	260	600	600	600	---	---

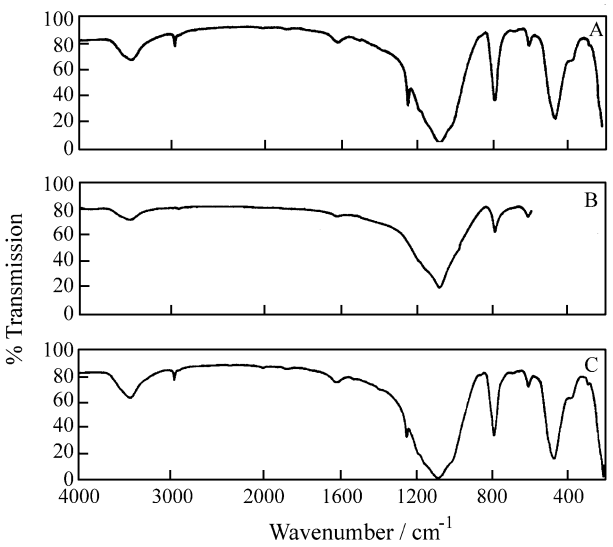

Figure 3. Infrared spectra of 14% SE-30 on Chromosorb W. A . before irradiation or extraction; B: unirradiated packing after the rinsing test; C: packing irradiated to 80 kGy, after the rinsing test.

including high boiling materials where frequent column recuperation is required[23].

Several different synthetic mixtures were analyzed on the packed columns. In the packing containing DC-200, both the plate number and the asymmetry factor were

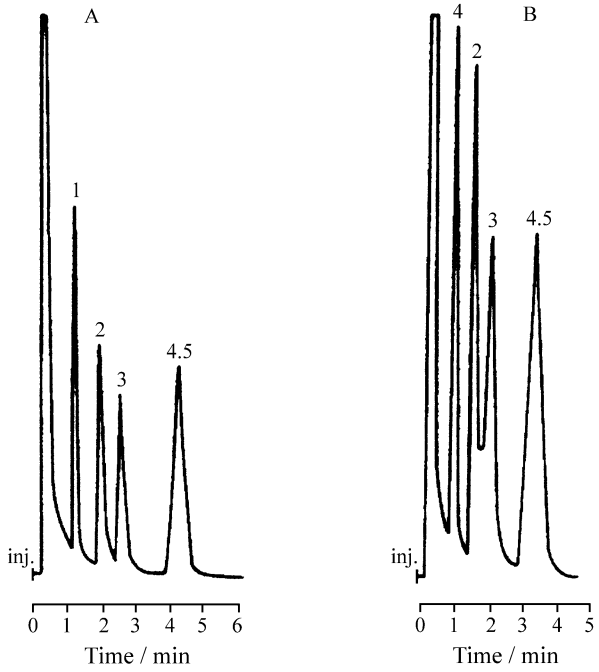

Figure 4. Chromatograms obtained with 14% DC-200 on Chromosorb W-HP. Column: 1.2 m x 2.0 mm (id); mobile phase: N_2 at 30 mL/min; T_{col} = 110 °C; T_{inj} = 220 °C; T_{det} = 270 °C; 1 = 2-pentanone; 2 = aniline; 3 = 2 ethyl-1-hexanol; 4 = n-undecane; 5 = methyl octanate. A: unirradiated packing; B: packing irradiated to 260 kGy.

poorer after irradiation, although no change in resolution was observed (Fig. 4). On the other hand, the immobilization of SP-2100 produced a packing with better chromatographic characteristics (Fig. 5). With SE-30 the chromatographic behavior appears to depend on the test compound, as summarized in Table 4.

As shown in Figs. 6 and 7, resolution improved after irradiation for SE-30 on Chromosorb W-HP, even through neither the retention times nor the plate numbers changed significantly. This improvement is related to the irradiation dose received. However, as indicated in Fig. 7c, both retention time and resolution decreased after a high dose. This may be related to a higher degree of crosslinking, which has produced a much more viscous phase, or to radiation decomposition of the SP.

It thus appears that, for each liquid stationary phase-support combination, there is an optimal dose which results in a high percentage of liquid stationary phase being immobilized without causing so much crosslinking that the phase

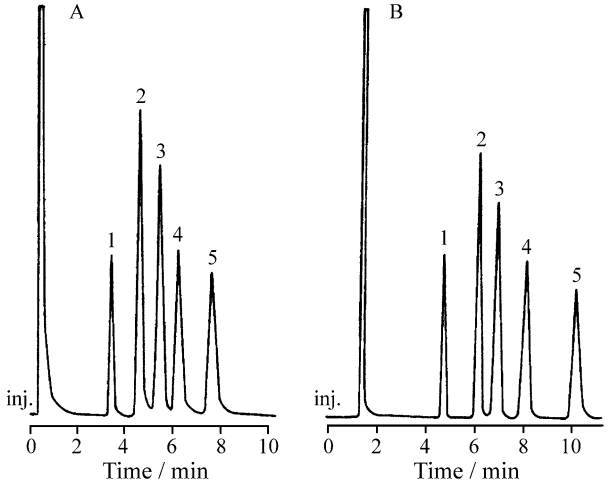

Figure 5. Chromatograms obtained with 20% SP-2100 on Supelcoport. Column: 1.7 m x 1.5 mm (id); mobile phase: N_2 at 30 mL/min; T_{col} = 110 °C; T_{inj} = 160 °C; T_{det} = 160 °C; 1 = methyl hexanoate; 2 = aniline; 3 = n-decane; 4 = benzyl alcohol; 5 = m-cresol. A: unirradiated packing; B: packing irradiated to 25 kGy.

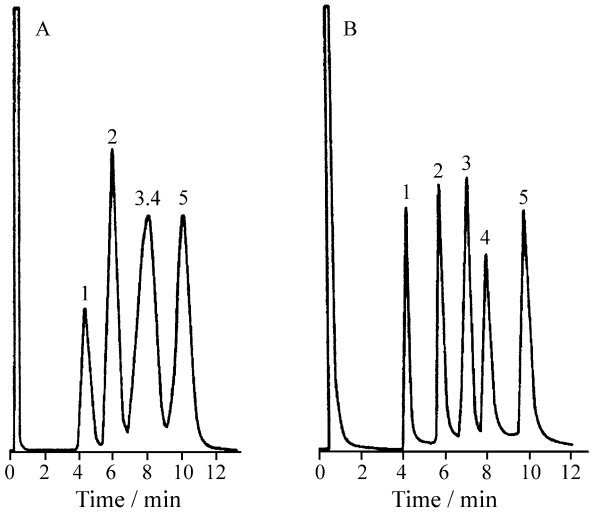

Figure 6. Chromatograms obtained with 27% SE-30 on Chromosorb W-HP. Column: 1.7 m x 1.5 mm (id); mobile phase: N_2 at 30mL/min; T_{col} = 110 °C; T_{inj} = 160 °C; T_{det} = 160 °C; 1 = methyl hexanoate; 2 = aniline; 3 = n-undecane; 4 = benzyl alcohol; 5 = m-cresol. A: unirradiated packing; B: packing irradiated to 180 kGy.

Table 4. Theoretical plate number for 14% SE-30 on Chromosorb W, without irradiation and after several irradiation doses for different test compounds.

Test compound	Theoretical plate number				
	O kGy	30 kGy	80 kGy	130 kGy	250 kGy
n-decane	2200	1100	1000	1100	1300
Benzene	2000	1200	1000	900	200
Toluene	2000	1100	400	900	500
Methyl hexanoate	900	1300	800	200	1300
2-butanone	1000	1600	400	1400	900
2-pentanone	1600	1600	400	1400	1200
Ethanol	1100	400	400	400	400
Cyclohexanol	1700	1100	800	1500	1000
Benzyl alcohol	500	1200	1000	800	1200
m-cresol	1200	1000	1000	1100	1100
Pyridine	1300	1500	800	700	900
Aniline	1700	1400	1400	1600	1000
Bromopentane	900	1000	800	800	1100
Sec-butyl iodide	1000	900	800	1000	600

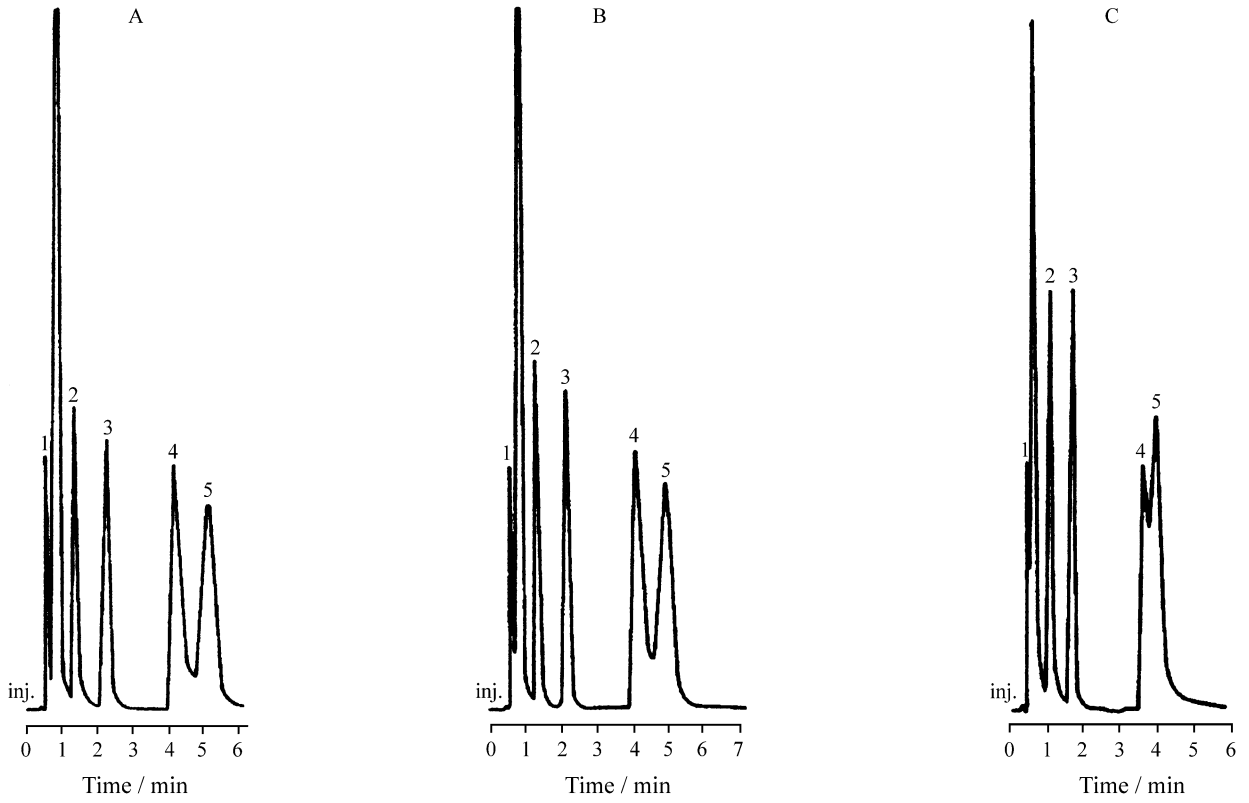

Figure 7. Chromatograms obtained with 14% SE-30 on Chromosorb W. Column: 1.7 m x 1.5 mm (id); mobile phase: N_2 at 30 mL/min; T_{col} = 60 °C; T_{inj} = 120 °C; T_{det} = 120 °C; 1 = ethanol; 2 = 2-butanone; 3 = benzene; 4 = pyridine; 5 = sec- butyl iodide. A: unirradiated packing; B: packing irradiated to 130 kGy; C: packing irradiated to 250 kGy.

becomes too viscous to show good chromatographic behavior, or promoting polymer degradation. Irradiation immobilization of liquid stationary phases on supports can be carried out before packing the column, permitting an extraction test to evaluate the degree of immobilization obtained. Such immobilized packings show enhanced stability at higher temperatures and permit rinsing the column for recuperation, when it becomes contaminated, without losing characteristic chromatographic properties.

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