

Influence of air on polybutadiene used in the preparation of stationary phases for high-performance liquid chromatography

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Abstract

A 100 ml bottle of polybutadiene, PBD, was repeatedly exposed to air over a period of 6 months. Samples were taken at time zero (PBD-0), after 3 months (PBD-3) and 6 months (PBD-6). These samples were sorbed onto HPLC silica by an open-air solution–evaporation procedure, which involved exposure to the atmosphere for 6 days. Portions of the three sets of samples were used to compare self-immobilization and the effects of 100 °C thermal treatments in air or nitrogen on HPLC performance of the resulting phases. It is concluded that self-immobilization is enhanced by prior exposure of sorbed PBD to air and subsequent heating at 100 °C further enhances column performance. The best performance (10^5 plates m^{-1}) resulted from 4 h heating of PBD-6 material in nitrogen.

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1. Introduction

Polybutadiene (PBD) is one of the most popular elastomers widely used in the industry because of its unique, physical properties as elasticity, toughness and durability [1]. The microstructure of the PBD, determined by the content of the *cis*-, *trans*- and vinyl-configurations, is of particular importance since it influences a wide range of physical properties [2]. Several studies have shown that PBD is sensitive to oxygen, heat, UV radiation and gamma radiation, affecting the lifetime of the whole system, i.e., causing deterioration of physical properties [3–6].

Thermal degradation of PBD has been the subject of numerous studies [4,5,7,8]. Studies realized in inert atmospheres, show that at temperatures up to 250 °C, the main process is crosslinking, with preferential consumption of vinyl groups. By heating to 300 °C and above, this crosslinked polymer is decomposed yielding soluble degradation products [4,5]. The results of Chiantore and others [7,8] on the thermal decomposition of PBD containing different ratios of *cis*, *trans* and vinyl confirmed that isomerisation, crosslinking and cyclization are the most characteristic reactions under 250 °C. Fragmentation and

depolymerisation start only at higher temperatures. However, when these studies have been realized in the presence of oxygen, thermal oxidation of PBD occurs: it involves autocatalytic processes which start with peroxide formation followed by decomposition via radical-induced reactions resulting in alcohols, α,β -unsaturated and saturated ketones [9–11]. The thermal oxidation of PBD of different microstructures, measured between 60 and 120 °C, was found to be similar to photooxidation [9,10].

One use of PBD is for the deposition and immobilization on HPLC silica [12–16] and other support materials such as alumina [17–19], titania [20] and zirconia [21–27], to give stable and efficient stationary phases for use in reversed-phase HPLC. Immobilization of PBD by radical initiators such as dicumyl peroxide, followed by thermal treatment, has been extensively studied [12–14, 17,18,20–27]. Other procedures, such as immobilization by gamma radiation [12,15] or microwave radiation [16], have also been studied.

Experiments are reported in the present paper that relate to the self-immobilization and thermal-immobilization of PBD onto HPLC silica without the use of dicumyl peroxide and in the presence or absence of molecular oxygen. The purpose of the work has been to explore whether oxygen, a reactive di-radical species, is a significant participant in the self-immobilization and thermal-immobilization processes.

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2. Experimental

2.1. Materials

Spherical Rainin silica (100-5) (Varian: PK.101-K5) has a mean particle diameter of 5 μm , 0.55 ml g^{-1} specific pore volume and 188 $\text{m}^2 \text{g}^{-1}$ specific surface area. The PBD polymer (mean molar mass of ~ 5000 , 80% 1,4-*cis/trans* and 20% vinyl), catalog No. 38,369-4, was obtained from Aldrich. Hexane (Mallinckrodt, HPLC grade) was used as solvent in the preparation of stationary phases. Filtered methanol (Mallinckrodt, HPLC grade) and water (Milli-Q) were used to prepare the mobile phases. Filtered chloroform (Merck, analytical-reagent grade) and methanol were used for the extraction of excess polymer. The compounds used for the chromatographic testing (uracil, acetone, benzonitrile, benzene, toluene and naphthalene) were analytical-reagent grade and were not further purified.

2.2. Preparation of stationary phase

In an earlier paper [15] it was shown that a 50% loading of PBD on silica particles (1 g PBD to 1 g silica which had been dried at 150 °C for 24 h) produced the best chromatographic parameters. Various batches of PBD-loaded silica were prepared by mixing a solution of PBD in hexane (at a ratio of 1 g PBD per 12 ml of hexane) with a suspension of silica in hexane (1 g silica per 12 ml of hexane). The suspension was stirred for 3 h. After the hexane was slowly evaporated, without stirring, at room temperature the stationary phase remained in storage at room temperature for 6 days.

In the present work, samples of PBD were taken periodically from a reagent bottle initially containing 100 ml of the reagent. The bottle was opened permitting fresh air to enter various times over a period of 6 months. Samples for the present work were taken at time zero (PBD-0), after 3 months (PBD-3) and 6 months (PBD-6). These three samples were sorbed onto three equivalent batches of silica by the above procedure.

Several 3 g quantities of PBD-loaded silicas, prepared from each of the three PBD samples (PBD-0, PBD-3, PBD-6), were put into tubes for the purpose of solvent extraction, column packing and column testing. Other PBD-loaded silica samples were sealed under air in tubes. These sealed tubes were subjected to heat treatments at 100 °C for 1, 2 or 4 h prior to extraction, packing and testing. The other PBD-loaded silica samples obtained from the three batches of PBD were placed in flow-through extraction tubes and heated at 100 °C under a 4 ml min^{-1} flow of high purity N_2 for 1, 2 or 4 h prior to extraction, packing and testing.

2.2.1. Solvent extraction

Tubes containing the non-heated and heated phases were connected to a Waters 510 pump (Milford, MA, USA) for

extraction of all the non-immobilized (excess) PBD. First, chloroform and then methanol were passed through the material at 1 ml min^{-1} for 3 h at ambient temperature, for each solvent. After this procedure, the stationary phase contained in the tube was removed and the solvent was evaporated at room temperature.

2.3. Column packing

Columns (60 mm \times 3.6 mm) were made from type 316 stainless-steel tubing. The internal surface was polished using a technique developed in our laboratory [28]. The columns were downward packed using 10% (w/v) slurries of each stationary phase in chloroform. A constant packing pressure of 34.5 MPa (Haskel packing pump) was used, with methanol as propulsion solvent. Columns were conditioned for 2 h with a mobile phase consisting of methanol and water 70:30 (v/v) at 0.3 ml min^{-1} . Each phase was evaluated chromatographically with duplicate columns.

2.4. Column testing

The chromatographic evaluation of column performance was done with a modular HPLC system equipped with a Shimadzu LC-10 AD pump, a Rheodyne model 8125 injection valve (5 μl loop) and a Shimadzu model SPD-10 AV UV-Vis detector (at 254 nm). Data acquisition used Chrom Perfect for Windows, version 3.52 and Report Write Plus software (Justice Innovations).

The standard sample mixture used in this study contained the solutes: uracil, acetone, benzonitrile, benzene, toluene and naphthalene. The mobile phase was methanol–water (60:40, v/v) or (70:30, v/v) at 0.2 ml min^{-1} for the non-heated and heated phases, respectively. The optimal flow-rate was determined by a van Deemter plot. The column dead time, t_M , was determined using uracil as an unretained compound. Chromatographic performance was evaluated by means of efficiency [plates per meter (N/L)], retention factor (k), resolution (R_s) and asymmetry factor (A_s) measured at 10% of the peak height.

2.5. Physical and chemical characterization of PBD and stationary phases

2.5.1. Gel permeation chromatography

Samples of the PBD-0 and PBD-6 were analyzed by GPC to determine if there was degradation or crosslinking of the chains during the time that the bottle of PBD was stored. The GPC was performed in a Waters chromatograph equipped with a model 510 pump, model 410 refraction index detector, model U6K injector and Millennium software for data acquisition. The conditions of the analyses involved columns of the America Polymer Standards Corporation 1000–20 000, 300 mm \times 7.8 mm i.d.; an injection volume of 250 μl ; detector at 40 °C and tetrahydrofuran as the mobile phase at a flow-rate of 1.0 ml min^{-1} , while the injection

solutions were prepared at concentrations of 0.5% (v/v) in tetrahydrofuran.

2.5.2. Nuclear magnetic resonance

Samples of the PBD-0 and PBD-6 were analyzed by ^{13}C NMR spectra to identify some oxidation products. ^{13}C NMR spectra of PBD measured in C_2HCl_3 in an INOVA-500 spectrometer (Varian) at 500 MHz, at ambient temperature. A spectral width of 31.5 kHz, 45 °C pulse, pulse repetition time of 2 s and 512 scans were used.

2.5.3. Infrared spectroscopy

Infrared spectra were obtained of the PBD-0, the PBD-6, the silica and the all stationary phases, non-heated and immobilized by thermal treatment in the presence of air or in pure nitrogen, using a BOMEM FT-IR model DA-8 instrument.

2.5.4. Percent carbon

The percent carbon was obtained by elemental analysis of each stationary phase after column packing using a model CHN-2400 Perkin-Elmer analyzer.

3. Results and discussion

3.1. Characterization of PBD

During the time that the PBD was repeatedly exposed to air over a period of 6 months we observed an increase of the viscosity of the PBD. Samples of the PBD at time zero (PBD-0) and 6 months (PBD-6) were submitted to analysis by gel permeation chromatography, infrared spectroscopy and nuclear magnetic resonance for ^{13}C . The data obtained by GPC are shown in Table 1. We can observe that a small increase of mean molar mass of PBD occurred after 6 months. Considering that the oxidation occurred during the storage of the bottle, it is generally assumed that oxidation results in multiple scissions to cause the formation of final products like carboxylic acids or volatile compounds [29]. Viscosity and other molecular measurements confirm this point. However, radical recombination can also occur to result in an increase of molar mass and possible crosslinking [29]. During the crosslinking reactions, the average molar mass of the chains increases, thus causing the sample to become gradually insoluble in solvents for the linear polymer [29].

Table 1

GPC analysis of PBD at time zero (PBD-0) and after repeatedly exposed to air over a period of 6 months (PBD-6)

Analysis of PBD	GPC parameters	
	Mean molar mass (Mn)	Polydispersity (D)
PBD-0	8213	1.1
PBD-6	8653	1.1

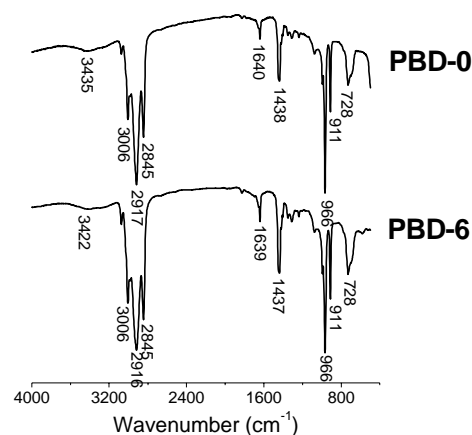


Fig. 1. IR spectra of PBD-0 and PBD-6.

The crosslinking can improve the thermal and mechanical properties [30]. The intermolecular crosslinking results in the formation of a three-dimensional network and, consequently, causes partial insolubilization of the polymer [6].

In the infrared analysis, both spectra of PBD-0 and PBD-6 are similar (Fig. 1). These spectra show the identification of the bands associated with *cis*- and *trans*-CH=CH and vinyl CH=CH₂ structural groups of the PBD. The regions of 3330–2600 and 1700–1600 cm⁻¹ are assigned to the =CH stretching and C=C stretching modes, respectively. The regions of 1500–1000 and 1000–500 cm⁻¹ are assigned to in-plane =CH and out-of-plane =CH modes, respectively. This last region is very characteristic of PBD. The *cis*-1,4, *trans*-1,4 and vinyl structures give rise to sharp bands at 728, 966 and 911 cm⁻¹, respectively, and are thereby amenable to quantitative measurement [31].

The same absorptions also appear the ^{13}C NMR spectra of the PBD-0 and PBD-6 (Fig. 2): 129.3 ppm (a) and 27.4 ppm (b) associated with the allylic and the vinylic carbons of the *cis*-1,4-configuration; 129.9 ppm (c) and 32.7 ppm (d) assigned to the allylic and vinylic carbons of the *trans*-1,4-configuration; and 114.1 ppm (h); 142.5 ppm (g); 43.5 ppm (f); and 38.1 ppm (e) assigned to the terminal vinylic carbon, the non-terminal vinylic carbon, the tertiary carbon and the secondary carbon of the 1,2-vinylic configuration, respectively [3]. The spectra are not fully analyzed as the chains of mixed structure exhibit more complex spectra because of sequence effects [32].

No formation of oxidation products, such as ester group, carboxylic acid group, hydroperoxides, alcohols and ketones were observed, as found in the photo-oxidized PBD by De Paoli [3].

Although PBD experiences crosslinking during 6 months in the presence of air, the presence of oxidation products is absent according to the infrared spectroscopy and nuclear magnetic resonance spectroscopy for ^{13}C . Baba et al. [33] have shown that both reactions (oxidation and crosslinking) involve radical processes, so that crosslinking reactions can occur on the same time scale as oxidation. The conventional

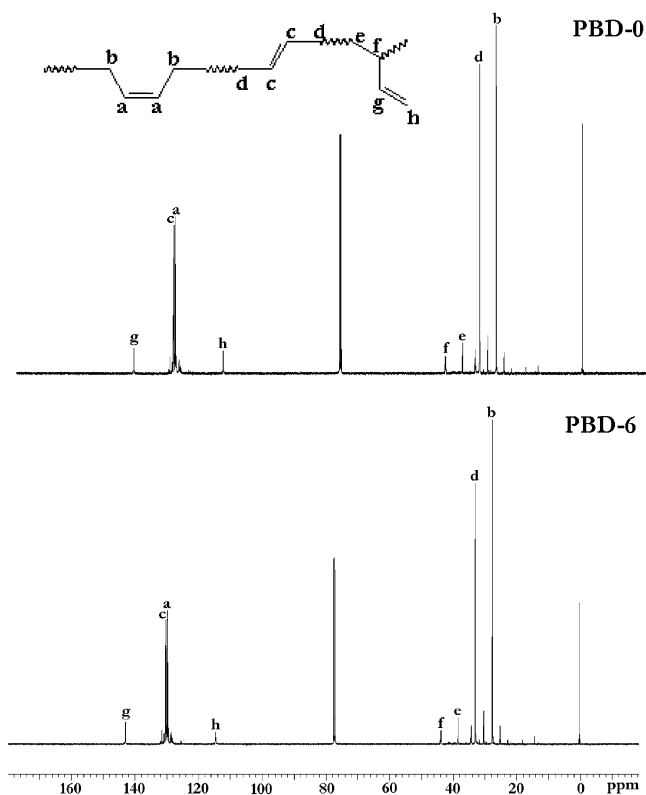


Fig. 2. ^{13}C NMR spectra of PBD-0 and PBD-6 showing the assignments.

analytical techniques such as FT-IR spectrometry used for the evaluation of the chemical changes that occur in polymeric materials upon ageing are not efficient enough to detect the crosslinking reactions.

3.2. Experiments with non-heated phases

Although from the infrared spectra of the PBD it is not possible to observe differences between the PBD samples, chromatographic differences were observed. Chromatographic parameters of columns prepared from non-heated stationary phases of PBD-0, PBD-3 and PBD-6, are given in Table 2. The increase in column efficiency (and %C)

Table 2
Chromatographic parameters of stationary phases prepared with PBD exposed to air for different periods, without thermal treatment

Time of use of PBD	Chromatographic parameters ^a				Percent carbon after column testing
	N/L^b	A_s^b	$k^{b,c}$	R_s^d	
0 day	24300 ± 1700	1.5	0.4	1.2	0.9
3 months	35200 ± 1600	1.4	0.6	2.0	1.1
6 months	78100 ± 1700	1.4	3.1	7.0	5.7

^a Chromatographic conditions: mobile phase, methanol: water (60:40, v/v); flow-rate, 0.2 ml min⁻¹; volume of injected sample, 5 μl; and detector, UV at 254 nm.

^b Calculated for the naphthalene peak.

^c Column dead time was measured with uracil.

^d Calculated for the toluene–naphthalene pair.

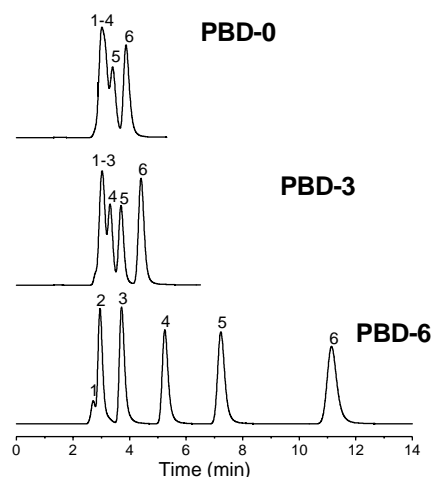


Fig. 3. Chromatographic behavior of non-heated stationary phases prepared with PBD-0, PBD-3 and PBD-6. Test mixture: (1) uracil; (2) acetone; (3) benzonitrile; (4) benzene; (5) toluene; and (6) naphthalene. Chromatographic conditions: mobile phase, methanol: water (60:40, v/v); flow-rate, 0.2 ml min⁻¹; volume of injected sample, 5 μl; and detector, UV at 254 nm.

with exposure of the polymer to air (O₂) inside the reagent bottle shows that air-modified forms of the reagent PBD are more rapidly adsorbed (immobilized) onto the silica surfaces than non-modified polymer molecules.

Fig. 3 shows the chromatographic behaviour of non-heated stationary phases prepared from PBD-0, PBD-3 and PBD-6, using methanol:water (60:40, v/v) as mobile phase. We can observe that only the PBD-6 stationary phase presented separation of all the compounds of the test mixture.

3.3. Experiments with heated phases

Table 3 shows chromatographic data obtained following the heating of samples of PBD-0 and PBD-3 at 100 °C in the presence of air or pure N₂. Heating either material in the presence of N₂ (absence of O₂) does not appear to alter the efficiencies of columns prepared from these stationary phases: in both cases the efficiencies obtained are similar to samples of PBD-0 that were not heated (Table 2). It is also seen that O₂, when present during the heat treatment, greatly improves (≈doubles) the efficiencies of the PBD-0 and PBD-3 stationary phases.

Table 4 gives the chromatographic results from PBD-6 samples following heating for different time periods at 100 °C, in air and in N₂. Heating in air for 1, 2 or 4 h gives similar high-efficiencies (70 000–79 000 plates m⁻¹). The other parameters (k , R_s and %C) are consistent with increases in stationary phase mass with heating time.

Heating in the absence of O₂ for 1, 2 and 4 h at 100 °C (Table 4) gave an unexpected result, an increase in efficiency with the increase of the time of heating. An impressive increase in efficiency (100 000 plates m⁻¹) was obtained after 4 h of heating.

Table 3

Chromatographic parameters of stationary phases prepared with PBD-0 and PBD-3 immobilized by thermal treatment at 100 °C for 1 h in air or for 4 h in an inert atmosphere (N₂)

Atmosphere	Time of use of PBD	Chromatographic parameters ^a				Percent carbon after column testing
		N/L ^b	As ^b	k ^{b,c}	Rs ^d	
Air	0 day	58400 ± 1200	1.8	1.5	3.9	7.0
	3 months	61500 ± 200	1.2	2.5	4.9	7.3
Inert (N ₂)	0 day	22900 ± 800	1.6	2.9	3.2	10.6
	3 months	24800 ± 300	1.6	3.3	3.4	11.0

^a Chromatographic conditions: mobile phase, methanol: water (70:30, v/v); flow-rate, 0.2 ml min⁻¹; volume of injected sample, 5 µl; and detector, UV at 254 nm.

^b Calculated for the naphthalene peak.

^c Column dead time was measured with uracil.

^d Calculated for the toluene–naphthalene pair.

Table 4

Chromatographic parameters of stationary phases prepared with PBD-6 immobilized by thermal treatment at 100 °C for different times in air or in an inert atmosphere (N₂)

Atmosphere	Time (h)	Chromatographic parameters ^a				Percent carbon after column testing
		N/L ^b	As ^b	k ^{b,c}	Rs ^d	
Air	1	76800 ± 1800	1.3	4.1	6.5	13.0
	2	74700 ± 1300	1.0	5.2	7.1	15.2
	4	71100 ± 300	1.3	8.8	8.1	16.4
Inert (N ₂)	1	53600 ± 2200	1.2	5.3	5.5	14.1
	2	76200 ± 700	1.7	5.6	7.0	15.2
	4	100000 ± 1800	1.1	7.6	8.8	18.6

^a Chromatographic conditions: mobile phase, methanol: water (70:30, v/v); flow-rate, 0.2 ml min⁻¹; volume of injected sample, 5 µl; and detector, UV at 254 nm.

^b Calculated for the naphthalene peak.

^c Column dead time was measured with uracil.

^d Calculated for the toluene–naphthalene pair.

Fig. 4 shows chromatograms obtained with PBD-6 using columns from thermal treatments in air (100 °C for 1 h) and in an inert atmosphere (100 °C for 4 h). In both cases all compounds of the same test mixture are separated, although for the treatment in an inert atmosphere (N₂), the analysis time was increased due to the increase of stationary phase mass. When these conditions were used for stationary phases prepared with PBD-0 and PBD-3 lower efficiency values were observed, especially for the treatment in presence of N₂ (Table 3). These results show that reaction of

PBD with air before the preparation of stationary phases is necessary to obtain columns that exhibit good chromatographic parameters, but that further oxidation, which occurs during thermal treatment in the presence of air, is not favorable.

3.4. Characterization of stationary phases

These results of chromatographic behaviour can be interpreted from the infrared spectra. The silica spectrum (Fig. 5)

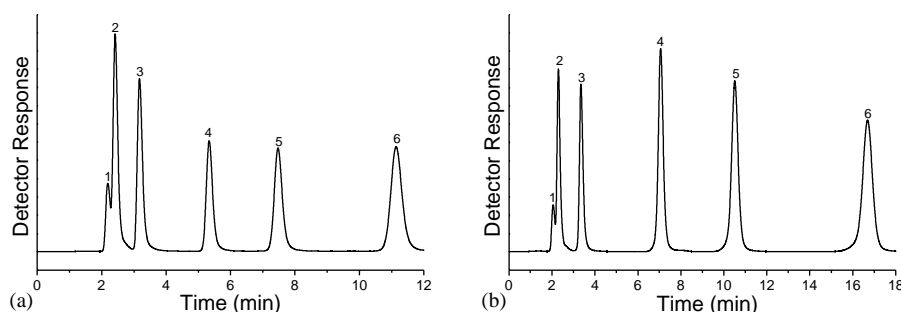


Fig. 4. Chromatographic behavior of PBD-6 stationary phases immobilized by thermal treatment at 100 °C (a) in air for 1 h (b) in an inert atmosphere (N₂) for 4 h. Test mixture: (1) uracil; (2) acetone; (3) benzonitrile; (4) benzene; (5) toluene; and (6) naphthalene. Chromatographic conditions: mobile phase, methanol: water (70:30, v/v); flow-rate, 0.2 ml min⁻¹; volume of injected sample, 5 µl; and detector, UV at 254 nm.

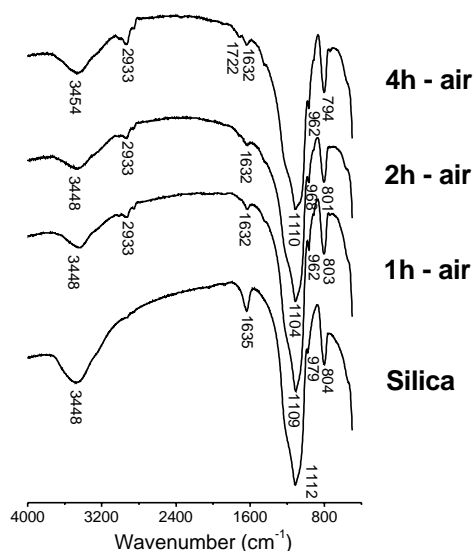


Fig. 5. IR spectra of silica and PBD stationary phases thermally immobilized (100 °C) in the presence of air for 1, 2 and 4 h.

shows a band at 3448 cm^{-1} , due to vibrations of the hydroxyl groups having a hydrogen bridge to physically adsorbed water. Another band, at 1112 cm^{-1} , is attributed to the siloxane groups and that at 979 cm^{-1} is assigned to the stretching vibration of free silanols [34]. The stationary phase spectra of samples heated in air for 1 and 2 h (Fig. 5) show characteristic bands of the PBD (Fig. 1) and silica, but for the stationary phase heated for 4 h, we can also observe a band at 1722 cm^{-1} . This band is characteristic of ketone formation [3,35], indicating that some oxidation of the PBD has taken place. For the non-heated stationary phase and the stationary phase heated in an inert atmosphere, we have not observed any alteration of the infrared spectra.

4. Conclusions

The immobilization of PBD in porous silica is a complex process, influenced by the level of oxidation and crosslinking of the PBD and the percent loading of the silica to produce columns that exhibit good chromatographic performance. The best stationary phase was obtained with the stationary phase using PBD-6 heated at 100 °C for 4 h in an inert atmosphere (N_2).

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References

- [1] J.A. Brydson, *Rubbery Materials and Their Compounds*, Elsevier, London, 1988.
- [2] J. Guilment, L. Bokobza, *Vib. Spectrosc.* 26 (2001) 133.
- [3] M.A. De Paoli, *Eur. Polym. J.* 19 (1983) 761.
- [4] B. Schneider, D. Doskocilová, J. Stokr, M. Svoboda, *Polymer* 34 (1993) 432.
- [5] D. Doskocilová, J. Straka, B. Schneider, *Polymer* 34 (1993) 437.
- [6] W. Schnabel, G.F. Levchik, C.A. Wilkie, D.D. Jiang, S.V. Levchik, *Polym. Degrad. Stab.* 63 (1999) 365.
- [7] O. Chiantore, M.P.L. Di Cortemiglia, M. Guaita, G. Rendina, *Makromol. Chem.* 190 (1989) 3143.
- [8] M.P. Luda, M. Guaita, O. Chiantore, *Makromol. Chem.* 193 (1992) 113.
- [9] Y. Israeli, J. Lacoste, J. Lemaire, R.P. Singh, S. Sivaram, *J. Polym. Sci. A: Polym. Chem.* 32 (1994) 485.
- [10] C. Adam, J. Lacoste, J. Lemaire, *Polym. Degrad. Stab.* 24 (1989) 185.
- [11] G. Geuskens, Ph. Thiriaux, *Polym. Degrad. Stab.* 48 (1995) 371.
- [12] H. Figge, A. Deege, J. Köhler, G. Schomburg, *J. Chromatogr.* 351 (1986) 393.
- [13] M. Hanson, K.K. Unger, *J. Chromatogr.* 517 (1990) 269.
- [14] M. Hanson, B. Eray, K. Unger, A.V. Neimark, J. Schmid, K. Albert, E. Bayer, *Chromatographia* 35 (1993) 403.
- [15] N.P. Lopes, K.E. Collins, I.C.S.F. Jardim, *J. Chromatogr. A* 987 (2003) 77.
- [16] N.P. Lopes, K.E. Collins, I.C.S.F. Jardim, *J. Chromatogr. A* (2004) in press.
- [17] U. Bien-Vogelsang, A. Deege, H. Figge, J. Kohler, G. Schomburg, *Chromatographia* 19 (1984) 170.
- [18] J.R. Garbow, J. Asrar, C.J. Hardiman, *Chem. Mater.* 5 (1993) 869.
- [19] R.V. Arenas, J.P. Foley, *Anal. Chim. Acta* 246 (1991) 113.
- [20] Z.T. Jiang, D.Y. Zhang, Y.M. Zuo, *J. Liq. Chromatogr. Rel. Technol.* 23 (2000) 1159.
- [21] L. Sun, A.V. McCormick, P.W. Carr, *J. Chromatogr. A* 658 (1994) 465.
- [22] J. Li, P.W. Carr, *Anal. Chem.* 68 (1996) 2857.
- [23] J. Li, P.W. Carr, *Anal. Chim. Acta* 334 (1996) 239.
- [24] J. Li, P.W. Carr, *Anal. Chem.* 69 (1997) 2193.
- [25] D.H. Reeder, J. Li, P.W. Carr, M.C. Flickinger, A.V. McCormick, *J. Chromatogr. A* 760 (1997) 71.
- [26] J. Li, D.H. Reeder, A.V. McCormick, P.W. Carr, *J. Chromatogr. A* 791 (1997) 45.
- [27] J. Li, Y. Hu, P.W. Carr, *Anal. Chem.* 69 (1997) 3884.
- [28] K.E. Collins, A.C. Franchon, I.C.S.F. Jardim, E. Radovanovic, M.C. Gonçalves, *LC-GC* 18 (2000) 106.
- [29] M. Baba, J. Lacoste, J.L. Gardette, *Polym. Degrad. Stab.* 65 (1999) 421.
- [30] V. Giménez, J.A. Reina, A. Mantecón, V. Cádiz, *Polymer* 40 (1999) 2759.
- [31] D. Nava, T.R. Parada, E. González, N. Boscán, C. Cruz, *Spectrochim. Acta A* 52 (1996) 1201.
- [32] F.A. Bovey, L. Jelinski, P.A. Mirau, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, San Diego, CA, 1988.
- [33] M. Baba, J.L. Gardette, J. Lacoste, *Polym. Degrad. Stab.* 63 (1999) 121.
- [34] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.
- [35] A. Iraqui, D.J. Cole-Hamilton, *Polyhedron* 10 (1991) 993.