

Transesterification of soybean oil catalyzed by alkylguanidines heterogenized on different substituted polystyrenes

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Abstract

1,5,7-Triazabicyclo[4.4.0]dec-5-ene and 1,1,3,3-tetramethylguanidine were heterogenized on different chloromethylated poly(styrene/divinylbenzene), as well as on linear polystyrene after introduction of a 'spacer-arm'. Furthermore, polymeric 2,3-dicyclohexylguanidines were synthesized by the reaction of 1,3-dicyclohexylcarbodiimide with *p*-(6-aminohexyl)polystyrenes. The guanidine-containing polymers were used in the transesterification of soybean oil with methanol in several consecutive catalytic cycles. The guanidines heterogenized on gel-type poly(styrene/divinylbenzene) with 1 meq Cl/g showed a slightly lower activity than their homogeneous analogous but reached the same high conversions after prolonged reaction time. On the other hand, they slowly leached from the polymers, allowing only nine catalytic cycles. The guanidines heterogenized on linear polystyrene with the use of a 'spacer-arm' were less active. Furthermore, they suffered substitution reactions during the recycling experiments to form inactive hexasubstituted guanidinium compounds.

Keywords: Guanidines; Polystyrenes; Spacer-arm; Transesterification; Vegetable oils; Leaching

1. Introduction

The transesterification of vegetable oils with methanol, producing glycerine and fatty acid methyl esters, is an important industrial process [1,2]. Sodium methoxide is the most active catalyst but not suitable for industrial use as it requires the total absence of water [3]. Industry normally uses sodium or potassium hydroxide or carbonate or a mixture of these compounds as catalyst, since they are relatively cheap and also very active. On the other hand, the oils should be acid-free and the alcohol anhydrous

(< 1% water) in order to avoid formation of soap and emulsions which make phase separation of the glycerine and the methyl esters difficult [4,5].

Guanidines also catalyze the transesterification of vegetable oils with methanol or ethanol, having the great advantage of not producing soaps of free fatty acids, even if unrefined oils are used, thus allowing an easy phase separation [6,7]. In a recent publication [8], we showed that substituted guanidines with a high intrinsic base strength are nearly as active as sodium hydroxide. In this paper, we report our results on the heterogenization of these guanidines on different types of chloromethylated poly(styrene/divinylbenzene)

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vinylbenzene) and linear polystyrene with the use of a 'spacer-arm'. The activity of these catalysts in the transesterification of soybean oil with methanol was evaluated in several consecutive cycles in order to understand the deactivation mechanism.

2. Experimental

2.1. Materials

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, Fluka, > 98%), 1,1,3,3-tetramethylguanidine (TMG, Aldrich, 99%) and 1,3-dicyclohexylcarbodiimide (DCCI, Aldrich, 99%) were used as purchased. Three different types of chloromethylated poly(styrene/divinylbenzene) were used: macroporous PS with 4.4 meq Cl/g (Rohm and Haas, A 27'), gel type PS with 4.15 meq Cl/g (Aldrich, 2% dvb, 200–400 mesh) and gel type PS with 1 meq Cl/g (Aldrich, 2% dvb, 200–400 mesh). The 'spacer-arm' was introduced by the reaction of linear polystyrene (Aldrich, average molecular weight 45,000) in nitrobenzene with 1,6-dibromohexane (Aldrich) in the presence of aluminum chloride, according to the procedure described by Tundo [9]. *p*-(6-Bromohexyl)polystyrene, PS-(CH₂)₆Br, was obtained in 35% yield, containing 1.35 meq Br/g.

2.2. Heterogenization of the guanidines on chloromethylated polystyrenes

The chloromethylated polystyrenes (5.2 meq Cl) were suspended in 100 ml of dry DMF under an argon atmosphere and then reacted with 3.0 g (26.1 mmol) of TMG or 1.45 g (10.4 mmol) of TBD in the presence of 0.3 g (1.8 mmol) of potassium iodide at 70°C for 60 h. The polymers were filtered and washed with methanol (2 × 50 ml), THF (2 × 50 ml) and acetone (2 × 50 ml). They were then suspended in 100 ml of 1,4-dioxane and reacted with 100 ml of 20% methanolic NaOH solution at room

temperature for 2.5 h. The guanidine-containing polymers 1–4 were washed with water until the washings were neutral and chlorine-free and dried at 70°C under reduced pressure to constant weight (about 8 h). The base content of the polymers was calculated from C/H/N analyses and determined by titration of 0.1 g of the polymer in 20 ml of dioxane with a 0.1 M HCl in methanol. The halogen content was determined as follows: a sample of 0.3 g of the polymer was reacted with an excess of anhydrous triethylamine under reflux temperature for 2 h. The polymer was filtered, washed with methanol and suspended in DMF. The mixture was stirred for 30 min and 4 ml of concentrated HNO₃ was added. After 2 h, the mixture was diluted with water and titrated by the Volhard method.

2.3. Heterogenization of the guanidines on linear *p*-(6-bromohexyl)polystyrene

The same procedure described before was used for the heterogenization of TMG on PS-(CH₂)₆Br and for the deprotonation of the supported guanidinium to form polymer 5. TBD was heterogenized on PS-(CH₂)₆Br using the procedure described by Iijima et al. [10]. Since TBD was used in excess, the TBD-containing polymer 6 was already obtained in its deprotonated form.

To prepare the heterogenized 2,3-dicyclohexylguanidine, PS-(CH₂)₆Br was first reacted with potassium phthalimide in DMF at 80°C for 36 h. The product was suspended in ethanol and reduced with 98% aqueous hydrazine under reflux for 6 h, producing PS-(CH₂)₆NH₂. Three grams of this polymer (3.27 meq N) were then reacted with 1.75 g (8.5 mmol) of 1,3-dicyclohexylcarbodiimide in *tert*-butanol under reflux for 96 h. The guanidine-containing polymer 7 was filtered, extracted with methanol in a Soxhlet apparatus for 4 h and dried under reduced pressure at 60°C.

PS-(CH₂)₆NH(CH₃) was obtained from PS-(CH₂)₆Br by reaction with an excess of

methylamine in CH_2Cl_2 at room temperature for 60 h. This polymer was reacted with 1,3-dicyclohexylcarbodiimide in the same way as described before, producing polymer **8**. The base content of the polymers was calculated from C/H/N analyses and determined by acid–base titration with 0.1 M HCl in methanol. The halogen content of the polymers was determined as described in 2.2.

2.4. Transesterification

A 100 ml two-necked flask was charged with 4.0 g (13.7 mmol, calculated from the average molecular weight of the fatty acid methyl esters) of soybean oil (Siméia Comercial, Brazil), 3.0 g (93.75 mmol) of methanol (Merck, 99%) and, typically, 5 mol% of supported guanidine. The mixture was vigorously stirred and refluxed at 70°C. The reaction was monitored by ^1H NMR spectroscopy (Bruker, 300 MHz). Normally, 1.5

Table 1

Composition of soybean oil and retention time of the resulting methyl esters

t_R (min)	Component	Content (%)
7.8	methyl palmitate (C16:0-OMe)	11.3
12.8	methyl stearate (C18:0-OMe)	3.4
15.1	methyl oleate (C18:1-OMe)	23.9
19.4	methyl linoleate (C18:2-OMe)	55.0
25.7	methyl linolenate (C18:3-OMe)	6.4

ml of the reaction mixture was removed every 60 min. The sample was filtered and the liquid phase washed three times with 2 ml of a saturated aqueous NaCl solution. The organic phase was separated by decantation, dried with anhydrous magnesium sulfate and submitted to NMR analysis in CDCl_3 using TMS as internal standard. The conversion of the soybean oil to a mixture of methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of the methyl esters) and 2.30 ppm (α -carbon CH_2 groups of all fatty acid derivatives).

Table 2

C/H/N and halogen analyses of the guanidine-containing polymers before and after several uses

Polymer	C/H/N and halogen analyses ^a (%)	Residual Cl or Br content (meq/g)	Base content (meq/g polymer) from	
			C/H/N analyses	acid–base titration
1	C 71.0, N 6.8, Cl 3.3 (0)	0.93 (Cl)	1.62	0
	C 70.0, N 6.6, Cl 1.2, Br 12.0 ^b	1.50 (Br)	1.57	
2	C 71.0, N 8.3, Cl 3.1 (0)	0.87 (Cl)	1.98	0
	C 65.6, N 7.7, Cl 0.8, Br 13.9 ^b	1.74 (Br)	1.83	
3	C 86.9, H 7.5, N 2.2, Cl 1.7 (0)	0.50	0.51	0.49
	C 88.7, H 7.4, N 0.5, Cl 1.8 (8)			
4	C 88.0, H 7.4, N 3.8, Cl 0.3 (0)	0.08	0.91	0.89
	C 90.2, H 7.4, N 0.8, Cl 0.3 (8)			
5	C 84.5, H 7.0, N 1.2, Br 7.7 (0)	0.96	0.28	0.26
	C 84.4, H 7.0, N 1.0, Br 7.7 (3)			
6	C 82.9, H 7.5, N 3.1, Br 3.1 (0)	0.39	0.74	0.75
	C 86.0, H 7.7, N 1.3, Br 3.4 (4)			
7	C 83.4, H 7.6, N 3.4, Br 3.3 (0)	0.41	0.61	0.59
	C 85.7, H 7.7, N 2.9, Br 3.4 (1)			
8	C 88.0, H 7.8, N 3.0, Br 1.0 (1) ^c			
	C 86.1, H 7.7, N 2.5, Br 3.5 (5)			
	C 86.8, H 7.3, N 2.6, Br 2.8 (0)	0.35	0.38	0.38
	C 88.4, H 6.5, N 1.3, Br 3.1 (5)			

Base content calculated from the analytical data and determined by acid–base titration.

^a The number of relevant cycles is shown in parentheses.

^b After treatment of the polymer with excess of sodium methoxide/methanol solution and washings with 100 ml of 2 M NaBr solution. The introduced bromide is related to the presence of hexasubstituted guanidinium cations.

^c Obtained after treatment with 20% of methanolic KOH solution.

In the recycling experiments, the guanidine-containing polymers were filtered after 3 h of reaction time, washed with methanol (4×20 ml), n-hexane (3×20 ml), n-pentane (2×20 ml) and dried under reduced pressure at 60°C . After removal of approximately 0.003 g for elemental analysis, the supported guanidine was reused in the transesterification reaction. The solutions of the reaction products were analysed by ^1H NMR spectroscopy for determination of the conversions.

For analysis, the soybean oil was completely transesterified by the reaction of 4.0 g of the oil with 4.0 g of methanol and 0.2 g (5% w/w) of TBD at 70°C for 1 h. The methyl esters were dissolved in dry diethyl ether and analysed isothermally at 175°C using a Perkin Elmer Sigma 3B gas chromatograph equipped with a Silar 10C (10% cyanopropylsiloxane on Chromosorb W-HP) column and a flame ionization detector. For quantification, the same response

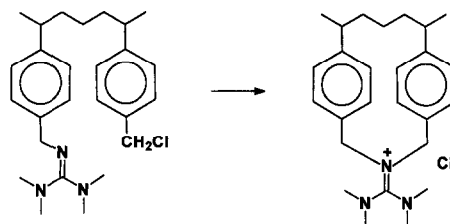


Fig. 2. Formation of hexasubstituted guanidinium in polymers 1 and 2.

factor was assumed for all methyl esters. The identity of the peaks was verified by analysis in a HP-5890II gas chromatograph equipped with a HP-1 column and coupled to a HP-5970B mass detector operated at 70 eV.

3. Results and discussion

The gas chromatographic analysis of the soybean oil is shown in Table 1. The average molecular weight of the methyl esters is $291.8 \text{ g} \cdot \text{mol}^{-1}$.

The structures of the guanidine-containing polymers are shown in Fig. 1. Their C/H/N and halogen analyses as well as their base content, calculated from the analytical data and determined by acid–base titration, are shown in Table 2.

The quantity of guanidine heterogenized on the different polymers is lower than the original content of functionalized groups. In polymers 1 and 2 the guanidine content, calculated from C/H/N analyses, is less than half of the chlorine content found in the starting polymers (PS with more than 4.0 meq Cl/g). Since the chloromethyl groups in these polymers are very close to each other, the guanidines react with two vicinal chloromethyl groups to form hexasubstituted guanidinium-containing polymers (Fig. 2). This inactivation reaction was verified treating the polymers with sodium methoxide and NaBr solution. The introduced bromide was related to the presence of the hexasubstituted guanidinium cation. Therefore, their base content,

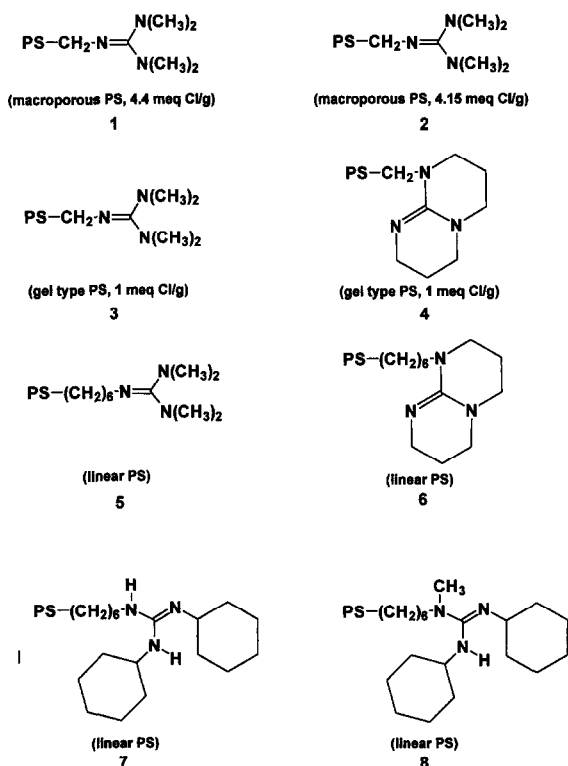


Fig. 1. Structures of the guanidine-containing polymers.

determined by acid–base titration, as well as their catalytic activity are negligible.

In polymers **3** and **4** this reaction is not possible due to the larger distance between the functional groups of the starting PS (1 meq Cl/g). In polymer **3** only half of the chlorine atoms have been substituted. On the other hand, the stronger nucleophile TBD substitutes 90% of the chlorine atoms in **4**. Similar results are observed for polymers **5** and **6**. In polymer **7**, approximately 70% (0.94 meq/g) of the original bromine atoms of PS-(CH₂)₆Br have been substituted by amino groups. However, only 65% of this function was converted to guanidine moieties. This percentage is lower in polymer **8**, probably due to the steric hindrance caused by the methyl group, in the reaction of PS-

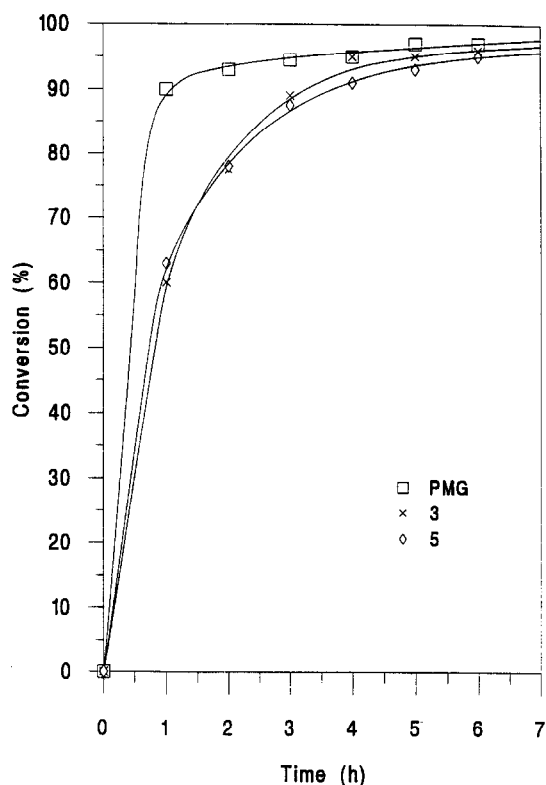


Fig. 3. Conversion of soybean oil as a function of time. Conditions: 3 mol% of PMG, 8.00 g (27.4 mmol) of soybean oil, 2.00 g (62.5 mmol) of methanol or 5 mol% of polymers **3** or **5**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C.

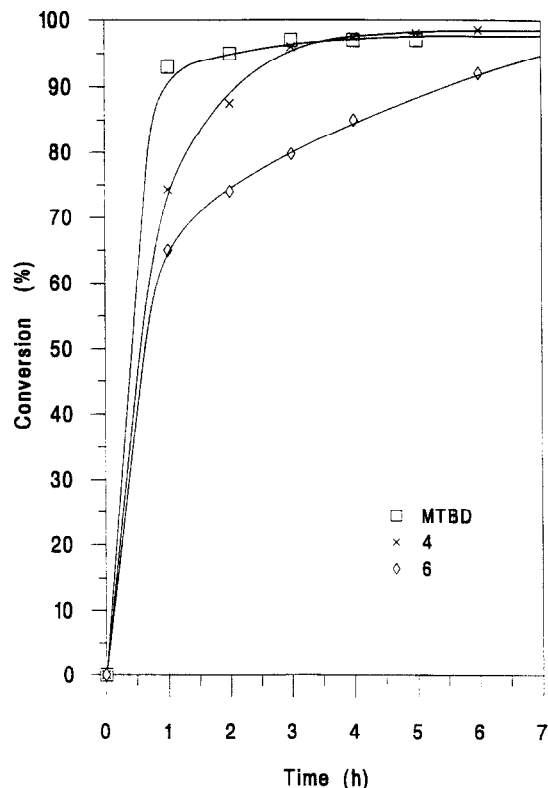


Fig. 4. Conversion of soybean oil as a function of time. Conditions: 3 mol% of MTBD, 8.00 g (27.4 mmol) of soybean oil, 2.00 g (62.5 mmol) of methanol or 5 mol% of polymers **4** or **6**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C.

(CH₂)₆NH(CH₃) with 1,3-dicyclohexylcarbodiimide (DCCI).

The catalytic activities of polymers **3** and **5** in the transesterification of soybean oil were compared with that of 1,1,2,3,3-pentamethylguanidine (PMG) in the homogeneous phase. The methanol/oil molar ratio was three times higher in the reactions using the guanidine-containing polymers in order to assure a low viscosity for the reaction mixture. PMG was used at only 3 mol% in contrast to the 5 mol% used with the heterogenized catalysts. Even so, we believe that the comparison of the catalytic activities gives important information on the behavior of the guanidine-containing polymers. The results are shown in Fig. 3.

The conversions after 1 h show that polymers **3** and **5** are less active than PMG. The lower activity is probably due to the hydrophobicity of the polymer chain which impedes diffusion of the methanol to the active sites. On the other hand, after 6 h the conversion is 95% for all three catalysts, showing that polymers **3** and **5** are as efficient as PMG.

Similarly, the catalytic activities of polymers **4** and **6** were compared with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD). The results are shown in Fig. 4. As observed for PMG, MTBD is more active than polymers **4** and **6**. On the other hand, polymer **4** gives, after 4 h, the same high conversion of 97% as observed for MTBD in homogeneous phase. Polymer **6** is not only less active but also less efficient, reaching a maximum conversion of 90% after 6 h.

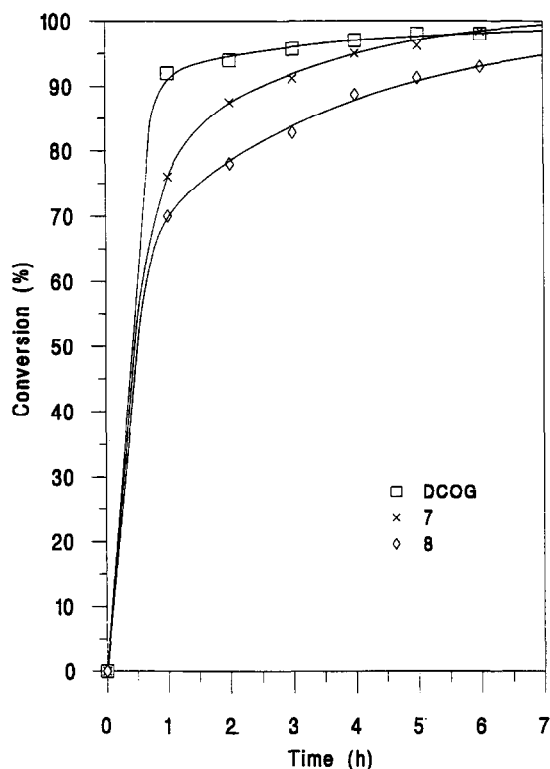


Fig. 5. Conversion of soybean oil as a function of time. Conditions: 3 mol% of DCOG, 8.00 g (27.4 mmol) of soybean oil, 2.00 g (62.5 mmol) of methanol or 5 mol% of polymers **7** or **8**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C.

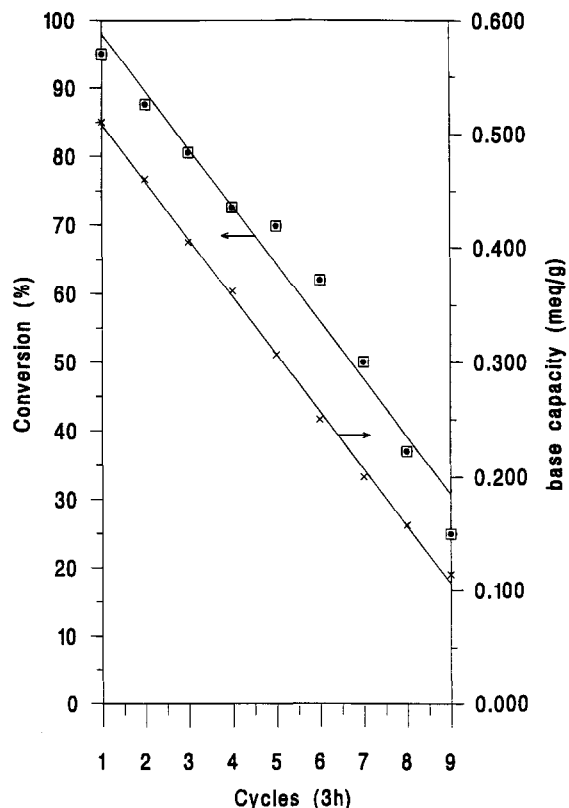


Fig. 6. Conversion of soybean oil and base capacity calculated from C/H/N analyses as a function of catalytic cycles. Conditions: 5 mol% of polymer **3**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C.

This result shows clearly that the 'spacer-arm' introduced in **6** does not improve the performance of the heterogenized catalyst.

The catalytic activities of polymers **7** and **8** were compared with 1,3-dicyclohexyl-2-(*n*-octyl)guanidine (DCOG). The results are shown in Fig. 5. Polymer **7** is less active than DCOG but reaches the same good conversion of 97% after 6 h. The additional methyl group in polymer **8** not only reduces the catalytic activity but also the efficiency of the catalyst, which can be explained by the lower symmetry of the guanidinium cation formed in the activation step [8].

All polymers were reused after filtration, washing and drying. The results obtained for polymer **3** in nine consecutive catalytic cycles are shown in Fig. 6. A permanent loss of base

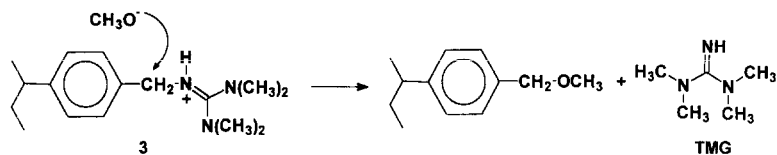


Fig. 7. Leaching of 1,1,3,3-tetramethylguanidine from polymer 3.

capacity and a parallel loss of catalytic activity of polymer **3** are observed. This loss of base capacity is explained by an attack of methoxide on the benzylic CH_2 groups, causing the leaching of 1,1,3,3-tetramethylguanidine (TMG) from the polymer, as shown in Fig. 7. Although this leaching seems to be significant, we were able to perform nine catalytic cycles with **3**, obtaining a total turnover number of 118, which is higher than the best turnover number observed in the homogeneous phase [8]. As shown in Fig. 8, TBD leaches in a similar way from polymer

4. However, after nine catalytic cycles, a total turnover number of 124 was obtained.

Polymers **5–8** behave very much alike in the recycling experiments but different than polymers **3** and **4**. As shown in Fig. 9, for polymer **7**, the base capacity calculated from C/H/N analyses decreases constantly, as also observed for polymers **3** and **4**. On the other hand, the catalytic activity drops sharply after the first cycle and remains low for four more cycles. This drastic loss of catalytic activity of poly-

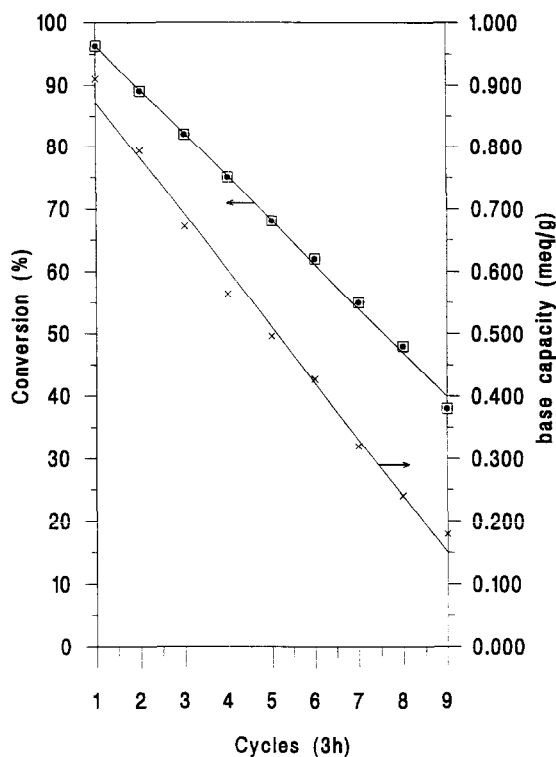


Fig. 8. Conversion of soybean oil and base capacity calculated by C/H/N analyses as a function of catalytic cycles. Conditions: 5 mol% of polymer **4**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C.

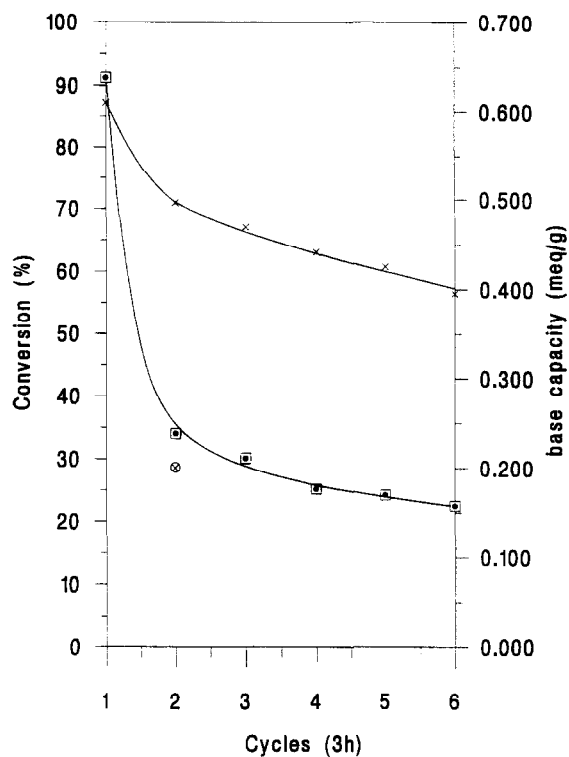


Fig. 9. Conversion of soybean oil and base capacity calculated by C/H/N analyses as a function of catalytic cycles. Conditions: 5 mol% of polymer **7**, 4.00 g (13.7 mmol) of soybean oil, 3.00 g (93.75 mmol) of methanol, 70°C. \otimes base capacity determined by titration.

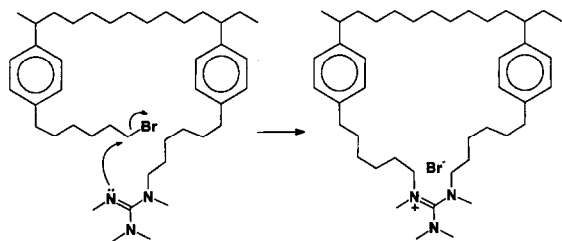


Fig. 10. Reaction of the heterogenized guanidine of polymers 5–8 with unreacted 6-bromoheptyl substituents.

mers 5–8 after the first catalytic cycle was explained by titration with 0.1 M HCl, which shows that the real base capacity drops as sharply as the catalytic activity after the first cycle (separate point in Fig. 9). This significant loss of base capacity with only a minor loss of nitrogen content of these polymers is explained by the reaction of the heterogenized guanidines with unreacted 6-bromoheptyl substituents, as shown in Fig. 10. This reaction forms hexasubstituted guanidinium cations which are not active. Similar reactions were observed for polymers 1 and 2, which were prepared from a PS with a high content of chlorine atoms. On the other hand, polymer 7 recovers its catalytic activity after treatment with an excess of 20% methanolic KOH solution, which removes the Br^- ions (after treatment, the bromine content drops to 1%, Table 2), producing 90% of methyl esters in a subsequent transesterification reaction. The ‘spacer-arm’ allows the reaction of the heterogenized guanidine with functional groups which are further away. They are, therefore, not appropriate for this type of catalyst. The total turnover number obtained with catalysts 5–8 in six catalytic cycles, was only around 40.

4. Conclusions

Alkylguanidines can be easily heterogenized on chloromethylated polystyrenes. When the PS

has a high chlorine content, hexasubstituted guanidinium cations (which are not active) are formed directly. With a chlorine content around 1 meq Cl/g, transesterification catalysts are obtained which are nearly as active as their homogeneous analogues. These catalysts may be recycled but the guanidines leach slowly from the polymers due to attack of the methoxide anions. Introduction of a spacer-arm between the polystyrene and the guanidine is not recommended as the deactivation of the catalyst by reaction of the guanidines with functional groups which are further away on the polymer chain occurs.

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