Journal of Chromatography, 540 (1991) 145–155
Elsevier Science Publishers B.V., Amsterdam

CHROM. 22 853

Polymer-bound chiral polymers for use in enantiomer separations

TIHAMER HARGITAI, PER REINHOLDSSON and BERTIL TÖRNELL
Department of Chemical Engineering 2, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund (Sweden)
and
ROLAND ISAKSSON*
Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund (Sweden)
(First received July 10th, 1990; revised manuscript received October 2nd, 1990)

ABSTRACT

A new kind of chiral stationary phase was prepared by immobilization of the synthetic chiral polymer poly(N-acryloyl-S-phenylalanine ethyl ester) in macroporous polymer particles. Immobilization greatly improved the chromatographic performance of the chiral polymer almost without loss of selectivity. Rigid, macroporous particles were prepared by suspension polymerization of trimethylolpropane trimethacrylate. The chiral polymer was introduced into these particles by polymerizing the chiral monomer in their pore system. Immobilization was obtained by copolymerization with unreacted double bonds present in the matrix particles. Composite particles were prepared with up to 40% (w/w) of chiral polymers. The new materials, and materials prepared using alternative immobilization techniques, were evaluated for their use in chromatography with racemic compounds. The results suggest that enantioselectivity is dependent on the conformational freedom or flexibility of the chiral polymer.

INTRODUCTION

In this paper we report the preparation and chromatographic evaluation of a new kind of chiral stationary phase (CSP) which consists of a support of porous and rigid polymer particles to which the chiral selector, a flexible polymer, is grafted. The chirally selective polymer is grafted, *i.e.*, covalently bonded, by post-copolymerization of the functional monomer with residual double bonds of the premade support. With this technique, the chiral polymer is immobilized on the supporting matrix without the use of any cross-linking agent. This means that there is a high degree of flexibility of the immobilized polymer, which is important for chiral recognition (see below). The chromatographic properties of the CSP are governed by the premade support, prepared by suspension polymerization of trimethylolpropane trimethylacrylate (TRIM).

Although immobilization by grafting or adsorption of polymers to different kinds of silica supports is a commonly used technique [1–4], the preparation of CSPs by

0021-9673/91/$03.50

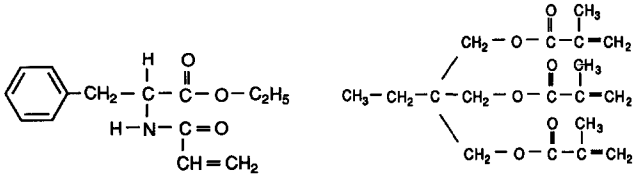
grafting synthetic chiral polymers to a macroporous polymer matrix has not, to our knowledge, been reported previously. The type of immobilization discussed in this paper can also be applied to other systems, such as the immobilization of polymer-bound catalytically active complexes, where the mechanical properties of the flexible functional polymer limits its applicability in column operations [5].

Chiral synthetic polymers have been successfully utilized as chiral selectors in liquid chromatographic separations of enantiomers [6]. The stereoselectivity of such polymers depends either on the chiral substituent (the primary structure) or on the conformation of the polymer molecules (the secondary structure), or on a combination of the two. Blaschke and Kraft [7] have prepared chiral stationary phases (CSPs) by suspension polymerization of chiral monomers, such as N-acryloyl-S-phenylalanine ethyl ester, in the presence of cross-linking agents. With this type of material, it has been shown that the enantioselectivity depends not only of the chiral monomer but also on the degree of cross-linking [8]. This led to the suggestion that the polymer network contained asymmetric cavities (chiral cavities) and that these were determinants of the enantiomeric selectivity. More recently, Blaschke [9] suggested that the chiral cavities are located in crystalline regions built up from polymer chains having a helical conformation. Okamoto *et al.* [10] introduced CSPs based on polymers that derive their chirality entirely from the helicity of the polymer chains. Chiral polymers of both types have been immobilized on small (5–10 μm) porous silica particles [1,4]. As far as chromatographic performance is concerned, these composite materials are superior to CSPs based on the unsupported polymers.

EXPERIMENTAL

Chemicals

N-Acryloyl-S-phenylalanine ethyl ester (the chiral monomer) (Fig. 1) and phenylalanine ethyl ester (the chiral selector) were prepared according to the method described by Backmann [11]. The initiator α,α'-azobisisobutyronitrile (AIBN), the cross-linker divinylbenzene (DVB) (for synthesis), acryloyl chloride (for synthesis), sodium carbonate (98% pure) and dichloromethane (pro analysi) were purchased from Merck (Darmstadt, F.R.G.). Methacryloyl chloride (97% pure) was obtained from Fluka (Buchs, Switzerland), magnesium sulphate (puriss) from Kebo AB (Stockholm, Sweden) and L-phenylalanine (98.5% pure) from Janssen Chimica (Beerse, Belgium). Poly(vinyl alcohol) (PVAl), used as a suspension stabilizer, molecular weight 72 000 g/mol, hydrolytic grade 97.5–99.5 mol%, was purchased from Fluka.



chiral monomer TRIM

Fig. 1. Structures of the chiral monomer N-acryloyl-S-phenylalanine ethyl ester and trimethylolpropane trimethacrylate (TRIM).

Racemic benzoin was purchased from Merck and 1,3,5-tri-*tert.*-butylbenzene (TTB) from Fluka. Troeger's base was obtained from EGA-Chemie (Steinheim, F.R.G.). Enhexymal and chlorthalidone were purchased from Sigma (St. Louis, MO, U.S.A.). Methaqualone was a gift from Draco AB (Lund, Sweden). Mandelamide was prepared according to the method described by Blaschke [12]. The structures of the racemates are shown in Fig. 2.

All other chemicals were of at least analytical-reagent grade and used as received.

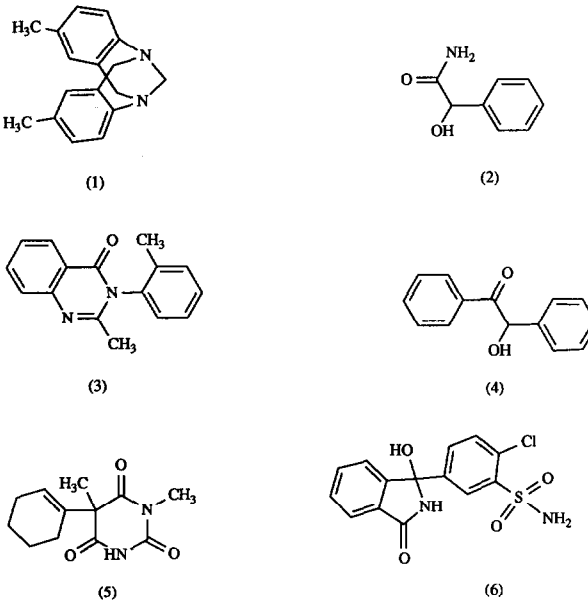


Fig. 2. Structures of the analytes: 1 = Troeger's base; 2 = mandelamide; 3 = methaqualone; 4 = benzoin; 5 = enhexymal; 6 = chlorthalidone.

Support particles

Large-size support particles, sieved to 40–100 μm, were prepared by suspension polymerization of TRIM (Fig. 1) as described elsewhere [13]. The pore volume of the particles, as determined by porosimetry (Poresizer 9310; Micromeritics, Norcross, GA, U.S.A.), was 0.77 cm^3/g, corresponding to a pore size range from 0.3 μm to 60 Å. The mean pore size was 500 Å. The toluene swelling of particles, as determined by the centrifugation method described by Pepper [14], was 3.4 g toluene/g dry particles.

Small-size TRIM particles (5–10 μm) were prepared in cooperation with Casco Nobel AB (Sundsvall, Sweden). The pore volume of the 5-μm TRIM particles was 0.49 cm^3/g, corresponding to a pore size between 0.3 μm and 60 Å (mean 250 Å). The toluene swelling was 4.5 g toluene/g dry particles.

Chromatographic evaluation

The standard chromatographic set-up consisted of a Beckman Model 110 B pump (Beckman, Altex Division, San Ramon, CA, U.S.A.), a Model 2158 Uvicord SD

UV detector (LKB, Bromma, Sweden) and a BBC SE 120 dual-channel potentiometric recorder (Brown Boveri Goerz Metrawatt, Vienna, Austria). Specific rotation was monitored with a Perkin-Elmer 141 M polarimeter, using a 1 ml/dm flow cell to establish the elution order of the enantiomers. The samples were injected with a Rheodyne (Cotati, CA, U.S.A.) Model 7120 injector equipped with a 20-μl loop.

Analytical columns were prepared by packing functionalized TRIM particles into stainless-steel columns (Skandinaviska GeneTec, Kungsbacka, Sweden) with a descending slurry-packing technique. The particles were allowed to swell in the packing solvent for about 2–4 h and then packed into the column with the chromatographic pump (Beckman Model 110 B) at a flow-rate of 2–10 ml/min and with a total packing volume of 200 ml. The chiral polymer gels (material E) were packed into glass columns (500 × 10 mm I.D.) (Pharmacia, Uppsala, Sweden) by pouring a swollen, well mixed and fairly thick gel suspension into the column. Two or three column volumes of the eluent were pumped through the column, in order to stabilize the bed and equilibrate it with the eluent, before chromatographic experiments were commenced. All CSPs were evaluated by chromatography with an organic mobile phase, usually *n*-hexane–dioxane (55:45, v/v) or pure toluene.

The capacity factor (k') was calculated as $(t - t_0)/t_0$, where t is the retention time of the sample peak and t_0 is the retention time of an unretained peak determined with 1,3,5-tri-*tert.*-butylbenzene [15]. The separation factor (α) measures the relative retention of the two antipodes, $\alpha = k'_2/k'_1$. The number of theoretical plates (N) was calculated as $N = 5.54(t/w_{1/2})^2$, where $w_{1/2}$ is the peak width at half-height. In cases where the UV trace showed only one peak, an alternative separation factor (α^*) was calculated by use of polarimetric data. The alternative retention times, t_1^* and t_2^*, were obtained from the extreme points, positive and negative, on the polarimetric trace.

Preparation of chiral stationary phases

The different CSPs discussed in this paper were prepared according to the following methods (A–E).

Method A: post-polymerization of chiral monomers in TRIM particles. The porous particles (2–10 g) were dispersed in 75–130 ml of water in a reactor vessel of a type described previously [16]. The chiral monomer and the initiator were dissolved in a given solution, the volume of which was equal to the toluene centrifugal swelling of the amount of TRIM particles used in the experiment. After being added to the particle suspension, the solution was drawn into the pore system of the particles by capillary action. The particles were allowed to swell for 2–4 h at 30–40°C. Before polymerization, the reactor vessel was repeatedly degassed and purged with nitrogen. Polymerization was performed at 80°C for about 4 h. The stirrer rate was kept between 200 and 400 rpm. The product (material A, Tables I and II) was first filtered off (sintered-glass filter) and then washed with an excess of toluene to eliminate any non-immobilized chiral polymer and unreacted monomer, and then washed with dioxane, acetone and diethyl ether and finally dried overnight at 60°C.

Methods B and C: post-polymerization of acrylic acid chloride (B) or methacrylic acid chloride (C) in TRIM particles, followed by reaction with phenylalanine ethyl ester. In a 250-ml glass vessel TRIM particles (10 g) were allowed to swell in a mixture of toluene (30 ml), monomer (50 ml, acryloyl or methacryloyl chloride) and initiator (0.75 g of AIBN). The mixture was repeatedly evacuated and flushed with nitrogen in

a 250-ml glass vessel. Polymerization was initiated by heating the glass vessel in a water-bath to 70°C. The product was then transferred under argon to a Soxhlet extractor and washed with an excess of dry tetrahydrofuran (THF) and then dried at room temperature, still in an atmosphere of argon.

To bond the chiral selector to the functionalized TRIM particles the phenylalanine ethyl ester (17.5 g) dissolved in toluene and pyridine (100 and 10 g, respectively) was added to a 200-ml reactor vessel [16] containing the functionalized TRIM particles (4.8 g). The reaction was allowed to proceed for 16 h at 60°C in a nitrogen atmosphere. The products were washed with large amounts of toluene, ethanol and water and dried at 60°C.

Method D: particles prepared by copolymerization of chiral monomers and TRIM monomers. Materials D were prepared by suspension copolymerization of toluene solutions of the chiral monomer and the TRIM monomer according to the method used for preparation of TRIM particles [13]. The amounts of monomers used in the experiments are given in Table II.

Method E: preparation of non-reinforced, cross-linked, chiral polymer gels by suspension polymerization. A toluene solution of the chiral monomer, 1 mol% of the initiator (AIBN) and 12 mol% of the cross-linker (DVB) (mol% with respect to moles of added chiral monomer) were suspended in a 5% (w/w) aqueous solution of PVA at 600 rpm. The weight ratio between chiral monomer and toluene was 1:2. Polymerization was performed in a nitrogen atmosphere in reactor vessels of the type mentioned above [16] at 80°C for 4–6 h. The gels were filtered off (using sintered-glass filters) and washed free from suspension stabiliser with hot water. To remove unreacted monomers and non-immobilized polymers, the product was washed first with ethanol, then acetone and finally toluene. The gels (material E) were used for chromatographic evaluation without further treatment.

Amount of immobilized polymer

The amount of immobilized chiral polymer and immobilized poly(acryloyl or methacryloyl chloride) was obtained by elemental analysis of nitrogen and chlorine. The results of these analyses were in agreement with the weight difference of the dried particles before and after functionalization.

RESULTS AND DISCUSSION

Immobilization of polymer to polymer particles

Polymerization of the chiral and achiral monomers in the pore system of TRIM particles resulted in irreversible binding of the corresponding polymers to the matrix particles. In this way composite particles containing up to 40% (w/w) functional polymers could be grafted onto the TRIM support without using any cross-linking agents. The amount of grafted polymer could also be easily varied by changing the concentration of the monomer phase.

It has been reported previously [17] that TRIM particles, depending on the polymerization conditions used, may contain unreacted double bonds in amounts corresponding to between 2 and 15% of the double bonds in the same weight of monomer. According to NMR and bromine addition data, the TRIM particles used here contained between 8 and 10 mol% of unreacted double bonds. Corresponding

analysis of the grafted TRIM particles showed that the amount had decreased to between 2 and 5 mol% [17]. These results strongly suggest that the functional polymers formed within the pore system of the TRIM particles were immobilized by copolymerization with residual double bonds in the matrix particles. The fact that the residual double bonds were accessible to copolymerization reactions is in agreement with the finding, from relaxation studies using solid-state NMR (cross polarization magic angle spinning NMR), that the double bonds had a high mobility [17].

Functionalization by copolymerization with residual double bonds present in the matrix particles is a simple operation which involves little risk of side-reactions that might affect the morphology or the chromatographic properties of the particles.

The observation that the amount of the grafted polymer could easily be varied in the range 10–40% (w/w) suggests that TRIM particles may be more suitable for functionalization by post-polymerization than particles prepared by copolymerizing styrene and divinylbenzene (S–DVB particles). For the latter type of particles, it has been reported that the amount of grafting is related to the degree of swelling. To obtain an abundance of grafting, S–DVB (particles) must be swollen using pure monomer or highly concentrated solutions of the monomer. It has also been reported that incomplete swelling or dilute monomer solutions yield materials with low amounts of grafted polymer [18].

In the present work, the functional polymer became located in the pore structure of the TRIM particles. Attempts to measure the penetration of polystyrene standards in the pore system indicated that, after functionalization by 40% chiral polymer, about half of the original pore volume was still accessible to polystyrene of molecular weight 10 800 g/mol, corresponding to a diameter of 60 Å [5].

Chiral separations

As can be seen in Table I, a number of different racemates could be separated into enantiomers on the CSP prepared according to method A. Results with different CSPs of the same type indicated that the enantioselectivity increased with an increase in the concentration of immobilized chiral polymer in the particles. Thus, the alternative separation factor (α^*) of mandelamide increased from 1.14 to 1.28 as the

TABLE I

SEPARATION OF ENANTIOMERS

Enantiomeric separations on 40–100-μm TRIM particles containing 25% (w/w) chiral polymer, prepared according to method A. Column: 350 × 8 mm I.D. Mobile phase: toluene. Flow-rate: 1.2 ml/min. Detection: UV (280 nm), polarimeter (365 nm).

Substance	Amount (mg)	α^{*a}
Troeger's base	4	1.13
Methaqualone	5	1.12
Enhexymal	10	1.19
Benzoin	3	1.18
Mandelamide	10	1.14

[a] Calculated from the polarimetric data at the peak maximum.

amount of immobilized chiral polymer increased from 25 to 40% (w/w). In experiments with chlorthalidone on CSPs of type A, the separation factor increased from 1.33 to 1.40 as the amount immobilized chiral polymer increased from 33 to 40% (w/w). These values for chlorthalidone are slightly lower than the corresponding value of 1.50 (*cf.*, Table II) observed on a CSP of type E (non-reinforced, lightly cross-linked chiral gel). In this context it is noteworthy that experiments using a corresponding commercial silica-based stationary phase, HIBAR, prepacked column RT 250-4 (Merck), which according to elemental analysis contained 16% (w/w) of chiral polymer, gave a separation factor for chlorthalidone of 1.25, *i.e.*, a considerably lower value than those observed for the CSPs studied here.

Comparison of enantioselectivity between the different materials (A–E)

Results from the separation of chlorthalidone on CSPs prepared according to mehods A–E are summarized in Table II. As discussed in the previous section, the enantioselectivity of the CSP type A, containing 40% (w/w) of chiral polymer, is close to that of the unsupported gel E. With respect to other chromatographic properties, such as the permissible flow-rate and, with small particles, the height equivalent to a theoretical plate, supported materials of type A are much superior to the corresponding unsupported materials of type E.

TABLE II

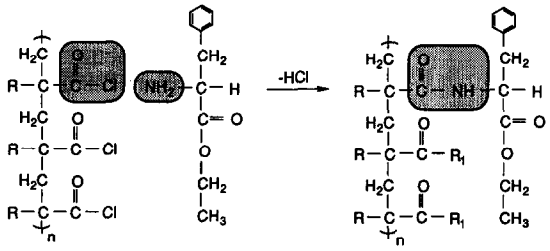
EVALUATION AND PREPARATION OF CSPs WITH CHLORTHALIDONE AS THE ANALYTE

Mobile phase: *n*-hexane–dioxane (55:45, v/v). Flow-rate: 0.3 ml/min. Detection: UV (254 nm).

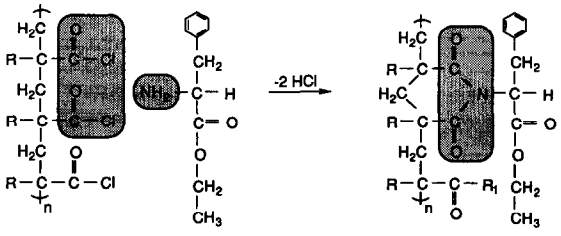
Starting material	Chiral selector	Preparation method	% (w/w) chiral	Separation factor (α)
TRIM particles	N-Acryloyl-S-phenylalanine ethyl ester	A	40	1.40
TRIM particles grafted with poly(acryloyl chloride)	S-Phenylalanine ethyl ester	B	38	1.18
TRIM particles grafted with poly(methacryloyl chloride)	S-Phenylalanine ethyl ester	C	38	–
TRIM monomer	N-Acryloyl-S-phenylalanine ethyl ester	D	20 42	– –
Cross-linker (DVB)	N-Acryloyl-S-phenylalanine ethyl ester	E	94	1.50

Compared with the chiral gels (material E), the chromatographic properties of material A, such as theoretical plate height, were greatly improved. The enantioselectivity of material A, when large amounts of chiral polymer are immobilized, is comparable to that of the soft gels (material E). The immobilized chiral polymers (material A) are probably mainly linear polymers. As mentioned above (material D), the more cross-linked the chiral polymer, the lower is the selectivity obtained. Some degree of "cross-linking" or "loop formation" of the formed chiral polymer was, of course, expected to occur between the growing polymer chains and the residual double bonds of the TRIM particles.

From Table II it can be seen that the separation factor of chlorthalidone on material B (α = 1.18) was lower than that obtained for material A (α = 1.40). Elemental analysis showed that 97% of the acid chloride groups of the poly(acryloyl chloride)-modified TRIM particles had reacted with the amino group of the phenylalanine ethyl ester. According to IR analysis, both amide and imide groups were obtained in the reaction between phenylalanine ethyl ester and poly(acryloyl chloride) (see Fig. 3). The structures of the chiral substituents in materials A and B are therefore not identical, which explains the observed difference in selectivity. It is possible, however, that other factors contribute to the differences observed. The imide groups not only lower the flexibility of the chiral polymer chain, but also reduce the number of possible conformations which might promote favourable interaction with the preferred enantiomer. Some difference in selectivity may also originate from the difference in tacticity of the polymers formed by polymerization of acryloyl chloride and N-acryloyl-S-phenylalanine. Differences in monomer polarity and bulkiness normally generate differences in tacticity. In the case of chiral polymers, it can be assumed that interactions between the growing polymer and the incoming chiral monomer may affect the steric structure of the polymer formed. The fact that no difference in selectivity was observed between CSPs of type A functionalized by polymerization at 20–80°C, and which would contain chiral polymers of different tacticity, indicates that tacticity is not a crucial factor in the present context.



Formation of amide bonds



Formation of imide bonds

Fig. 3. Formation of amide and imide bonds between the chiral selector and immobilized poly(acryloyl or methacryloyl chloride). R = H (material B) or CH_3 (material C). R_1 = amide or imide bonds.

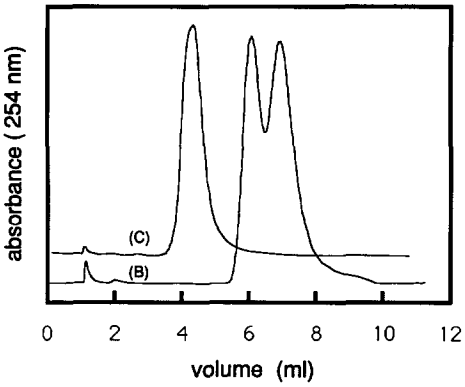


Fig. 4. Separation of chlorthalidone on 5-μm TRIM particles containing 38% (w/w) chiral polymer. Materials B and C were prepared according to Table II. Column, 100 × 4.6 mm I.D.; mobile phase, *n*-hexane–dioxane (55:45, v/v); flow-rate, 0.3 ml/min; detection, UV (254 nm).

The chromatograms in Fig. 4 show a comparison between CSPs of type B and C. It is obvious that material C did not show any enantioselectivity with respect to chlorthalidone. In this instance, the turnover of acid chloride groups and the ratio between amide and imide substituents were the same as in material B. This means that substitution of the acrylic acid backbone in material B for a methacrylic acid backbone in material C had a dramatic effect on chiral selectivity. Disregarding the possible effect of tacticity differences, the decrease in selectivity must be ascribed to the presence of methyl groups on the methacrylate residues. For steric reasons, a methacrylate polymer is much less flexible than the corresponding acrylate polymer. This is reflected by the large difference in glass transition temperature between poly(methyl methacrylate) and poly(methyl acrylate), *i.e.*, 105 and 10°C, respectively. The lack of selectivity of material C is probably due to the effect of the backbone methyl groups which, first, decrease the flexibility of the chiral polymer, thereby reducing the possibility of its chiral substituents adopting conformations favourable to chiral recognition, and second, might exert steric hindrance to access by the analyte to the chiral substituent.

Material D (Table II), which is a fairly highly cross-linked copolymer between the chiral polymer and TRIM, did not show any enantioselectivity with respect to chlorthalidone. Materials D and E differ with respect to the degree of cross-linking and type of cross-linker. Material C probably contains fairly short sequences of chiral monomer residues, fixed between stiff cross-links. This would obviously reduce the possibility of chiral substituents interacting selectively with the enantiomers of chlorthalidone. The results obtained with material D are in agreement with the findings of Blaschke and Donow [8], who reported that the selectivity of cross-linked chiral gels decreased with increase in the degree of cross-linking.

Column efficiency

The CSPs prepared by post-polymerization of chiral monomer in TRIM particles can be used at high flow-rates, even with particle sizes as small as 5 μm. The maximum flow-rate is well above that corresponding to optimum resolution. No leakage of chiral polymer was observed with prolonged usage.

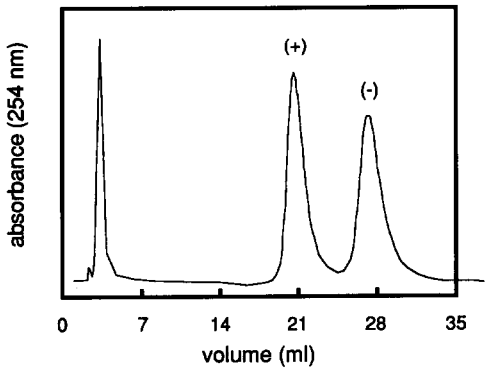


Fig. 5. Separation of chlorthalidone on 7-μm TRIM particles containing 33% (w/w) chiral polymer, prepared according to method A. Column, 250 × 4.6 mm I.D.; mobile phase, *n*-hexane–dioxane (55:45, v/v); flow-rate, 0.8 ml/min; detection, UV (254 nm). Separation factor (α) = 1.33.

The efficiency of the columns, expressed as the theoretical plate number (N), was determined with chlorthalidone as reference. As expected, low values of N were obtained for the chiral columns prepared from large particles. The plate number of the antipodes was N = 1500/m for CSPs based on the 40–100-μm TRIM particles and N = 900/m for the unsupported chiral polymer gel, prepared according to method E. The plate number can be increased by decreasing the particle size. Thus, from experiments with chlorthalidone on a CSP of type A containing 33% (w/w) of chiral polymer functionalized on 7-μm TRIM particles, the plate number was calculated to be 5500/m (Fig. 5).

CONCLUSION

It has been demonstrated that column materials for chiral separation in the form of two-component particles can be prepared by grafting a selective, highly swollen chiral polymer to the pore system of rigid polymer particles. The new column materials, which contain large amounts (at least 40%, w/w) of the functional component, combine the good mechanical and hydrodynamic properties of the supporting TRIM particles with the high capacity and selectivity of the corresponding unsupported chiral polymeric gels (Blaschke gels).

The immobilization technique described is based on polymerization of the chiral monomer in the pore system of TRIM particles. Functionalization occurs by copolymerization between the functional monomer and residual double bonds present in the particles. This is a simple procedure which does not require any pretreatment of the TRIM particles. The enantioselectivity of materials prepared according to this technique is higher than that of the corresponding silica-based materials.

The techniques described can be used in the preparation of column materials for other applications, where a flexible functional polymer is required to be supported on mechanically rigid particles.

ACKNOWLEDGEMENTS

This work was supported by grants from the Swedish National Board for Technical Development. The kind cooperation of the late Mr. S. Porrvik of Casco Nobel, Sweden, is gratefully acknowledged.

REFERENCES

1 G. Blaschke, W. Bröker and W. Fraenkel, *Angew. Chem., Int. Ed. Engl.*, 9 (1986) 25.
2 H. Engelhardt, H. Löw, W. Eberhardt and M. Mauss, *Chromatographia*, 27 (1989) 535.
3 K. Saigo, Y. Chen, N. Kubota, K. Tachibana, N. Yonezawa and M. Hasegawa, *Chem. Lett.*, (1986) 515.
4 Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata and R. Noyori, *J. Am. Chem. Soc.*, 103 (1981) 6971.
5 P. Reinholdsson, A. Nikitidis and C.-A. Andersson, in preparation.
6 Y. Okamoto and R. Aburatani, *Polym. News*, 14 (1989) 295.
7 G. Blaschke and H.-P. Kraft, *Makromol. Chem. Rapid Commun.*, 1 (1980) 85.
8 G. Blaschke and F. Donow, *Chem. Ber.*, 108 (1975) 1188.
9 G. Blaschke, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 13.
10 Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada and H. Yuki, *J. Am. Chem. Soc.*, 101 (1979) 4763.
11 W. Backmann, *Thesis*, Rheinischen Friedrich-Wilhelms Universität, Bonn, 1978, p. 23.
12 G. Blaschke, *Chem. Ber.*, 107 (1974) 232.
13 P. Reinholdsson, T. Hargitai, R. Isaksson and B. Törnell, *Angew. Makromol. Chem.*, submitted.
14 K. W. Pepper, *J. Appl. Chem.*, 1 (1951) 124.
15 J. N. Kinkel, W. Fraenkel and G. Blaschke, *Kontakte (Merck)*, 1 (1987) 3.
16 H. Nilsson, C. Silvergren and B. Törnell, *Eur. Polym. J.*, 14 (1978) 737.
17 T. Hjertberg, T. Hargitai and P. Reinholdsson, *Macromolecules*, 23 (1990) 3080.
18 A. Guyot and M. Batholin, *Prog. Polym. Sci.*, 8 (1982) 277.