Pressure-Induced Binding Sites in Molecularly Imprinted Network Polymers

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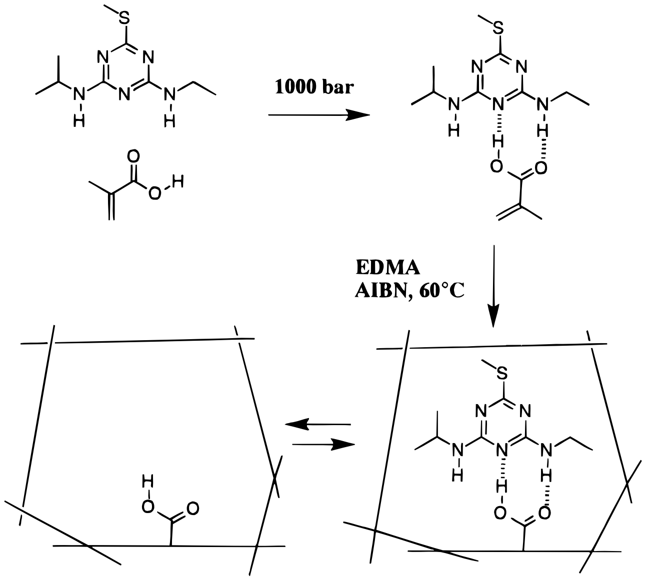
Received May 21, 1996[⊗]

ABSTRACT: Molecular imprinting in network polymers under high pressure was studied as a means of inducing selective binding sites for molecular recognition. Network polymers of methacrylic acid and ethylene glycol dimethacrylate were prepared in the presence of a template, atrazine or ametryn, by free radical polymerization at either 1 or 1000 bar in three different solvents. After washing, they were chromatographically evaluated for rebinding selectivity. In one case, a significantly stronger rebinding of the template to the polymer prepared at high pressure than to the polymer prepared at normal pressure was observed. On an ametryn-imprinted polymer prepared at 1 bar using 2-propanol as solvent, the capacity factor for ametryn was 2.3, whereas on a polymer prepared at 1000 bar the capacity factor was 3.2. The capacity factors of atrazine on these materials were 1.2 and 1.4, respectively. With atrazine as the template, no pressure effect was observed and the capacity factors were, within the experimental error, the same on the high-pressure and the normal-pressure materials. The polymers were characterized by porosimetry, swelling measurements, IR, and SEM. These data showed that the high-pressure polymers exhibited a more compact structure with lower pore volume, higher density, and higher swelling compared to the polymers prepared at normal pressure. The origin of the pressure effect on selectivity was discussed in terms of the monomer−template association tendency and in terms of polymer morphology.

Introduction

In molecular imprinting, preparation of cross-linked polymers in the presence of a template molecule results in materials with highly selective binding sites for small molecules.[1] The copolymerization of methacrylic acid with a cross-linking monomer in the presence of a basic template has proven to be a fruitful method. After removal of the template from the network material, binding sites with high complementarity toward the template are left behind. Ideally, all of the added template molecules should give rise to binding sites with similar affinity for the template.[2] This is of particular importance in high-performance analytical applications such as in chromatography[3] and chemical sensing.[4] The chances of achieving this would seem higher using templates covalently bound to the monomer, although this strategy requires a high-yielding splitting of the same bonds after polymerization.[5] In noncovalent molecular imprinting, free monomer and template exist in equilibrium with the monomer−template assemblies, resulting in a complex distribution of binding sites with different affinities for the template.[6] Ways to stabilize the monomer−template assemblies for a given template are therefore of interest.[7] We here previously investigated the influence of monomer concentration,[7] polymerization temperature,[7,8] and solvent[8] on the rebinding selectivity and affinity for the template exhibited by the corresponding polymers. In all cases, effects were seen in accordance with the law of mass action and thermodynamics. Thus higher monomer concentrations, lower polymerization temperature, and the use of noncompetitive solvents promoted high selectivity and affinity in the rebinding step. One remaining parameter to be investigated is the pressure of polymerization. The pressure effects on molecular associations are usually small and considerably smaller than the effects of temperature and solvent.[9] Nevertheless, the question whether the monomer template assemblies can be stabilized by high pressure and whether this in turn results in a detectable increase in affinity and selectivity of the resulting materials was of fundamental interest to us. In this report we describe the first example of the use of pressure in order to induce binding sites for molecular recognition (Scheme 1).

Scheme 1



Experimental Section

Materials. Triazine standards of 98−99% purity (ametryn (AME) and cyanazine (CYA), Chart 1) were obtained from Riedel-de Haen (Seelze, Germany). Methacrylic acid (MAA) and nicotine (NIC) were purchased from Aldrich, and ethylene glycol dimethacrylate (EDMA) was obtained from Fluka. The initiator azobis(isobutyronitrile) (AIBN) and atrazine (ATR, 98% purity) were obtained from Janssen. The solvents,

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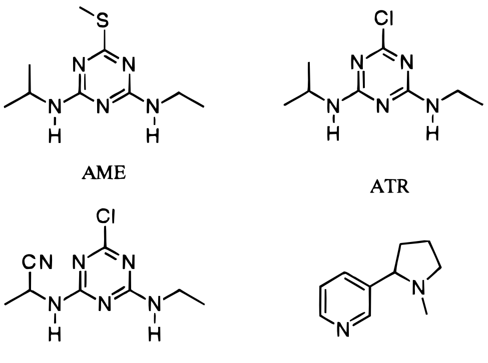
[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

Chart 1


AME ATR CYA NIC

acetonitrile (MeCN), methylene chloride (CH_2Cl_2), and 2-propanol, came from Merck, and the chromatographic evaluations were carried out using a Bischoff HPLC-pump, a Rheodyne injector, an LKB 2151 variable wavelength monitor as UV detector, and a Kipp and Zonen DB41 plotter. Pore and surface area analysis were performed by N_2 adsorption on a Micromeritics ASAP 2000 instrument using a 0.1−0.2 g sample of polymer (25−50 μm). The scanning electron micrographs were obtained at the University of Mainz electron microscope facility.

Polymer Preparation. A modified version of a previously described procedure was followed.[8] The polymers were labeled as shown in Table 1. P4 and P4hp were prepared as P3 and P3hp but using AME as template. To EDMA (20 mmol, 3.8 mL), MAA (4 mmole, 0.34 mL), and the triazine (1 mmol of ATR or AME) in the porogen (5.6 mL of CH_2Cl_2, MeCN or 2-propanol) was added AIBN (0.25 mmol, 40 mg). The mixture was transferred to a glass tube (14 mm i.d.). This was purged with nitrogen and placed in a thermostated water bath at 60 ± 0.2 °C (P1-P4). The high-pressure polymers (P1hp−P4hp) were prepared from the nitrogen-purged monomer mixture in a high-pressure steel autoclave immersed in a water bath thermostated at 60 ± 0.2 °C. The pressure was 1000 ± 30 bar. After 18 h the polymer block was crushed and the polymer grinded and sieved under water to a 25−50 μm particle size fraction.

Chromatographic Evaluation. The sieved polymers were slurry packed in MeCN/H_2O 1/1 (v/v) into 100 mm × 4.6 mm i.d. stainless steel columns. After having passed ca. 50 mL at a flow rate of 5 mL/min, the columns were equilibrated at 1 mL/min using acetonitrile/acetic acid 90/10 (v/v) as the mobile phase until a stable base line was reached. The flow rate was 1 mL/min and the UV detector wavelength 254 nm unless otherwise stated. The retention, k', was calculated as $k' = (t - t_0)/t_0$ where t_0 is the elution time of the void marker, acetone, which normally eluted as a sharp peak with a plate number, N, between 3000 and 5000 m^{-1}.

Polymer Density and Solvent Swelling Studies. Dry polymer (1 mL, 25−50 μm) was placed in a calibrated graduated glass cylinder and weighed. This gave the apparent dry density of the polymer. Excess solvent was then added, and the polymer was stirred in order to remove air bubbles. The cylinder was then tapped until no further settling was observed. The swelling given as volume of swollen polymer per volume of dry polymer was read after 12 h.

Theoretical Background

The response of intermolecular associations in solution to pressure depends on the change in free volume ($\Delta V°$) upon association according to eq 1,[9,10] where K is

$$\left[\frac{\partial RT \ln K}{\partial P}\right]_T = -\Delta V° \qquad (1)$$

the association constant of the complex, R is the gas constant, T is the absolute temperature, P is the pressure, and $\Delta V°$ is the difference in volume occupied by the products and the reactants (reaction volume). If the association leads to a net decrease in volume ($\Delta V° < 0$), it follows that the association constant increases with increasing pressure. For instance, if $\Delta V° = -10$ cm^3/mol, K increases by a factor of 1.5 at 1000 bar and 60 at 10 000 bar, while if $\Delta V° = -20$ cm^3/mol, these factors are 2.2 and 3500, as is evident from the logarithmic dependence of K on P and $\Delta V°$ seen in eq 1.[10] Many weak solution complexes respond to pressure in this way although $\Delta V°$ is usually smaller. Thus in several electron donor−acceptor systems, high pressures cause a red shift in the charge transfer absorption band, indicating a stronger donor−acceptor interaction.[9] For hydrogen-bonded systems, the volume change depends on how close to a van der Waals contact the donor and acceptor approach in the complex, on the polarity of the complex compared to the free donor and acceptor, and on the polarity of the solvent.[10−12] In the association of phenol and diethyl ether in hexane, the change in free volume was estimated to be −6.1 cm^3/mol.[12] This resulted in an increase in the association constant from ca. 80 to 100 M^{-1} when the pressure was raised from 1 to 1000 bars. The association constant between phenol and dioxane in hexane (free volume change: −3 cm^3/mol) changed from 19 to 23 M^{-1} when the pressure was raised from 1 to 1500 bars.[13] Moreover, strongly bound complexes respond often less to pressure than weakly bound complexes.[11] In our previous report on the molecular imprinting of triazine herbicides, we found a correlation between pK_a values of structurally similar templates and the affinity and selectivity for the template in the rebinding to the polymer.[14] Considering the above factors, we chose to study the pressure dependence of the imprinting of two triazines (atrazine and ametryn), having different pK_a values, in three solvents (porogens) with different hydrogen-bonding capacities and polarities. For practical reasons these polymers were thermochemically initiated at 60 °C using AIBN as a free radical initiator.

Results

Polymer Structure and Morphology. The swelling, density, and specific swelling of the atrazine-imprinted polymers prepared using three different porogens at two pressures are seen in Table 1. The swelling and dry density were highest for the polymers prepared using CH_2Cl_2 as porogen (P1 and P1hp). Although the polymers were thermochemically initiated, this agrees with our previous observations on photochemically initiated polymers.[8] The polymers that shrunk the most upon drying (porogen: CH_2Cl_2 and $CHCl_3$) exhibited here the largest swelling, indicating a reversible swelling−shrinking process. Upon comparison of the materials prepared at 1 and 1000 bar the high-pressure polymers exhibited, with one exception (the density of the polymers prepared using CH_2Cl_2 as porogen), higher densities and higher swellings than those prepared at normal pressure. The pressure effect is more pronounced for the most swellable materials, as seen on the large difference in swelling between P1 and P1hp. The parallel changes in swelling and density (with the above exception) result in relatively small variations in the specific swelling among the materials. This indicates that the swollen state morphology of the materials varies less between the materials than the dry state morphology.

The results from nitrogen sorption porosimetry (Table 2) gave type IV isotherms, indicating mesoporosity.[15]

Table 1. Characterization of Atrazine-Imprinted Polymers Prepared at Different Pressures[a]

polymer	pressure (bar)	porogen	swelling[b] (mL/mL)	density[c] (g/mL)	specific swelling[d] (mL/g)
P1	1	CH_2Cl_2	2.22	0.57	3.89
P2		MeCN	1.42	0.34	4.18
P3		2-propanol	1.42	0.31	4.58
P1hp	1000	CH_2Cl_2	2.68	0.50	5.36
P2hp		MeCN	1.58	0.40	3.95
P3hp		2-propanol	1.50	0.34	4.41

[a] The polymers were prepared at 60 °C, using the solvents, and at the pressures given in the table and as described in the Experimental Section. IR (KBr) (P1) 1155 (s), 1263 (s), 1388 (m), 1478 (m), 1638 (w), 1734 (s), 2958 (m), 3500 (vb); (P1hp) 1157 (s), 1264 (s), 1388 (m), 1460 (m), 1638 (w), 1738 (s), 2958 (m), 3441 (vb); (P2) 1157 (s), 1258 (m), 1388 (m), 1458 (m), 1638 (w), 1730 (s), 2961 (m), 3425 (vb); (P2hp) 1157 (s), 1256 (m), 1385 (w), 1456 (w), 1638 (w), 1730 (s), 2957 (w), 3428 (vb); (P3) 1159 (s), 1258 (m), 1385 (w), 1456 (w), 1636 (w), 1730 (s), 2957 (w), 3447 (vb); (P3hp) 1157 (s), 1258 (m), 1385 (w), 1456 (w), 1636 (w), 1730 (s), 2953 (w), 3439 (vb); (P4) 1157 (s), 1258 (s), 1385 (w), 1476 (m), 1638 (w), 1730 (s), 2960 (w), 3450 (vb); (P4hp) 1157 (s), 1258 (m), 1385 (w), 1456 (w), 1638 (w), 1730 (s), 2957 (w), 3453 (vb). Anal. Calcd for P1 N, 0.26; Cl, <0.3. Anal. Calcd for P1hp: N, 0.29; Cl, <0.3. Anal. Calcd for P3: N, 0.29; Cl, <0.3. Anal. Calcd for P3hp: N, 0.17; Cl, <0.3. [b] Swelling in acetonitrile given as an average of two measurements with a spread of less than 5%. [c] Apparent dry density of the polymers. [d] Swelling divided by apparent density.

Table 2. Pore Analysis of the Imprinted Materials Used in Table 1

polymer	pressure (bar)	porogen	surface area[a] (m^2/g)	pore diameter[b] (Å)	pore volume[c] (mL/g)
P1	1	CH_2Cl_2	236 (17)	52	0.24
P2		MeCN	320 (58)	136	0.85
P3		2-propanol	275 (35)	97	0.77
P1hp	1000	CH_2Cl_2	68 (0)	63	0.11
P2hp		MeCN	310 (12)	101	0.75
P3hp		2-propanol	181 (0)	162	0.79

[a] Determined using the BET model[15] on a five-point linear plot. Values in parentheses refer to the micropore surface area determined from a t-plot using the Harkins−Jura average thickness.[15] [b] BJH adsorption average pore diameter (4 × pore volume/surface area)[15] of pores between 17 and 3000 Å. [c] BJH cumulative adsorption pore volume of pores between 17 and 3000 Å.

As in our previous study, the hysteresis loops were unclosed with a desorption branch that leveled off either below or above the adsorption branch. This effect increased with the swellability of the material and was previously explained by shrinkage of the polymer when subjected to increasing pressure at the liquid nitrogen temperature.[8] We have therefore based the calculations of average pore diameter and cumulative pore volume on the adsorption branch. As expected, the materials that swelled the most (P1 and P1hp) exhibited the lowest surface areas, pore diameters, and pore volumes. It should be noted that these are considerably larger than the corresponding materials prepared by photochemical initiation which were essentially nonporous. Furthermore, in agreement with the swelling data, the most swellable materials were most affected by polymerization pressure. Thus both surface area and pore volume were much lower in the material prepared using CH_2Cl_2 at 1000 bar (P1hp) than the corresponding material prepared at 1 bar (P1). The pressure effect on the other materials was considerably smaller, although it must be added that the sorption data for P2, P3, and P3hp indicate the existence of a large volume of pores over 1000 Å not included in the nitrogen adsorption experiment.

The scanning electron micrographs clearly show the different morphologies of the materials (Figure 1). In agreement with the pore analysis, the polymers prepared at higher pressure were more compact, again with the most pronounced effect seen when comparing P1 and P1hp. While P1hp shows a smooth surface, P1 exhibits a rough surface with clearly visible pores. Further, in agreement with the swelling and pore analysis, the difference between the normal- and the high- pressure materials becomes less pronounced in the order P1, P2, P3. The existence of macropores (>1000 Å) is confirmed by the pictures of P2, P2hp, P3, and P3hp.

Polymer Affinity and Selectivity for the Template. The polymers were packed in chromatographic columns and evaluated in the chromatographic mode using acetonitrile as the mobile phase. Three structurally similar triazines and a reference compound, nicotine, were injected separately on the column and the capacity factors, a measure of the solute retention, determined using acetone as the void marker. Selectivity factors were also calculated with reference to the capacity factor of the template.

Comparing the atrazine-imprinted materials prepared using different porogens (Table 3) confirmed the results of our previous observations.[8] Thus the affinity and selectivity in the rebinding step decrease with increasing hydrogen-bonding capacity of the porogen, which is in the order CH_2Cl_2, MeCN, 2-propanol. We intrepret this as the result of destabilization of the monomer template assemblies due to the higher polarity of the solvent as well as due to the stronger solvation of the free monomer and template. Furthermore, the polymer dry state morphology and swelling appear to have little influence on the selectivity in view of the different morphologies and swellings of P1 and P1hp.

Comparing the materials prepared at the two pressures yielded no pronounced differences. Thus the capacity factors were roughly the same on the 1000 bar polymers as on the 1 bar polymers. We then compared normal- and high-pressure polymers prepared using ametryn as the template. This template is known to give binding sites with higher affinities and selectivities for the template.[14] 2-Propanol was used as the porogen since the structure and morphology of the corresponding materials appear to be less influenced by pressure. A significant effect of the pressure applied during polymerization on the affinity and selectivity for ametryn is seen (Table 4). The capacity factor for ametryn was ca. 30% higher on the polymer prepared at 1000 bar than on the one prepared at normal pressure at a sample load of 100 nmol and ca. 40% higher when the same comparison was done at a sample load of 10 nmol. The retention of the other triazines and of the reference increased as well, but not to the same extent. This is shown by the relative retentions of these compounds, which are lower on the 1000 bar polymer than on the one prepared at normal pressure. The enhanced retention induced by pressure was lost upon aging and thermal treatment of the materials. Thus, after a months storage of the materials, retention of the other triazines and the reference increased relative to the retention of ametryn. Heating the polymers at 60 °C in the dry state affected the 1000 bar polymer the most, where, overall, lower capacity factors were observed. This effect was also observed for P1hp.

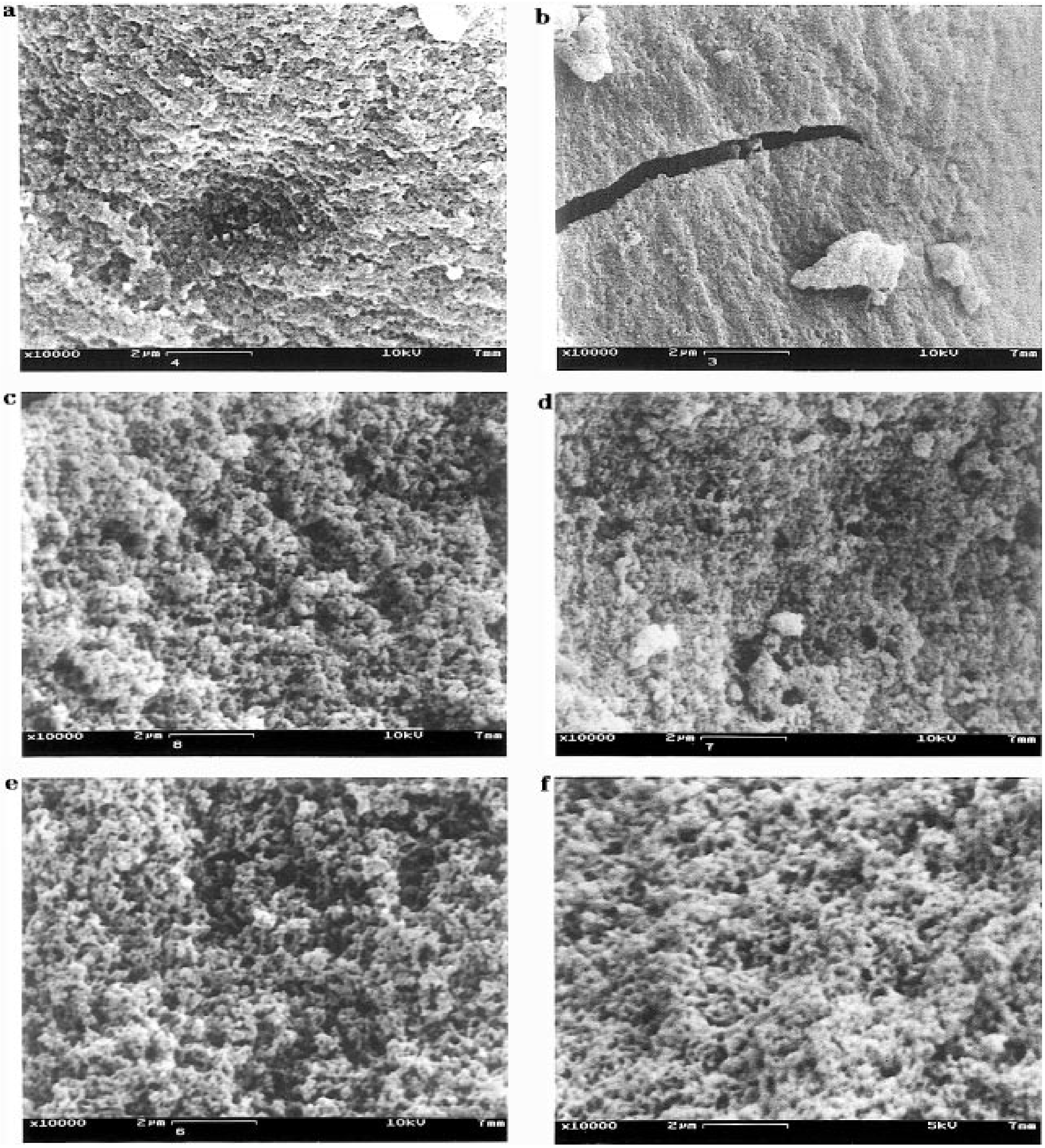


Figure 1. Scanning electron micrographs of (a) P1, (b) P1hp, (c) P2, (d) P2hp, (e) P3, and (f) P3hp photographed at 10000× magnification. The micrographs were reduced to 70% for publication.

Discussion

Polymer Structure and Morphology. The differences in swelling between the materials may have several causes. First it appears to be unrelated to the number of unreacted double bonds since the infrared spectra showed the intensities of the C=C stretch at 1638 cm^{-1} to be similar for the normal- and high-pressure materials. This agrees, furthermore, with our previous CP-MAS-NMR results showing that the number of unreacted double bonds was less than 10% in polymers prepared using THF as the porogen.[8] Rather, it is related to the heterogeneity of the cross-link density, which in turn will affect the rigidity of the chains linking the agglomerates or microspheres together during phase separation.[16–18] For instance, in a poor solvent, agglomeration will be promoted, leading to the formation of dense cross-linked microspheres where the phase separation occurs when the microspheres precipitate, giving a relatively open pore structure with strong links between the microspheres. Such materials exhibit permanent porosity and low swelling. Instead, using a good solvent, intermolecular cross-links are favored and a material is obtained that is built up of loosely linked grains of solvent-swollen gel particles. These materials exhibit low pore volume and high swelling. In view of the higher swelling of the 1000 bar polymers compared to the 1 bar polymers, it appears that applying a high pressure during polymerization has the same effect on swelling as using a porogen which more efficiently solvates the growing polymer chains. This would be the result if solvation of the polymer chains is associated with a comparably large $-\Delta V°$. However, a high pressure is known to affect polymerizations in a number of ways, which makes it difficult to

Table 3. Chromatographic Retention of Triazines on the Atrazine-Imprinted Polymers Used in Table 1[a]

			ATR		AME		CYA		ref[b]	
polymer	pressure (bar)	porogen	k'	k'/k'_{ATR}	k'	k'/k'_{ATR}	k'	k'/k'_{ATR}	k'	k'/k'_{ATR}
P1	1	CH_2Cl_2	6.6	1	4.5	0.68	2.7	0.41	4.2	0.64
P2		MeCN	3.3	1	2.3	0.70	1.1	0.34	3.9	1.16
P3		2-propanol	1.3	1	2.1	1.6	0.6	0.46	5.1	3.9
P1hp	1000	CH_2Cl_2	6.8	1	4.1	0.61	2.6	0.38	4.3	0.63
P2hp		MeCN	3.4	1	2.6	0.76	1.2	0.35	n.d.	n.d.
P3hp		2-propanol	1.2	1	2.1	1.8	0.5	0.44	5.5	4.6

[a] The chromatographic evaluation was done using acetonitrile as the mobile phase, as described in the Experimental Section. [b] The reference was nicotine.

Table 4. Chromatographic Retention of Triazines on Ametryn-Imprinted Polymers Prepared at Different Pressures[a]

		AME		ATR		CYA		ref	
polymer	pressure (bar)	k'	k'/k'_{AME}	k'	k'/k'_{AME}	k'	k'/k'_{AME}	k'	k'/k'_{AME}
P4[b]	1	1.8	1	0.75	0.41	0.25	0.14	1.6	0.86
P4hp[b]	1000	2.4	1	0.94	0.40	0.24	0.10	1.6	0.70
P4[c]	1	2.3	1	1.2	0.50	0.44	0.19	1.6[d]	0.68
P4hp[c]	1000	3.2	1	1.4	0.44	0.63	0.20	1.6[d]	0.50

[a] The chromatographic evaluation was done using acetonitrile as the mobile phase, as described in the Experimental Section. The polymers were prepared at 60 °C, using 2-propanol as the porogen, and at the pressures given in the table. The capacity factors (k') are averages of two injections where the spread for k' values over 1 was less than 5%. Capacity factors less than 1 are associated with a larger error due the error in t_0. [b] Results from runs at a sample load of 100 nmol and at a flow rate of 1 mL/min. [c] Results from runs using columns packed with a particle size fraction of <25 μm and at a flow rate of 0.2 mL/min. The sample load here was 10 nmol. [d] Due to low sensitivity, the capacity factors at the 100 nmol sample load have been used in the calculations.

ascribe the changes in polymer structure to one single factor.[10] Firstly, high pressure applied during free radical polymerization commonly results in an increased rate of polymerization as well as higher molecular weights. This has been ascribed to the large negative $\Delta V°$ associated with the formation of covalent bonds in the propagation step. For instance, in the polymerization of methyl methacrylate in benzene, a $\Delta V°$ of -19 cm^3/mL was calculated.[19] The increased polymerization rate may naturally affect the quality of the binding sites as well as the buildup of the pore structure. Secondly, the increase in solvent and monomer viscosity expected at high pressures is also likely to influence the gelation process prior to phase separation.[16] Third, several cases have been reported where high pressures induce cyclopolymerizations.[10] This could be a contributing factor to the higher swellings observed for the 1000 bar polymers. Finally, an increase in the proportion of isotactic linkages has been reported for the high-pressure polymerization of methyl methacrylate.[20] This could also affect the quality of the binding sites.

Polymer Affinity and Selectivity for the Template. Enhanced retention was observed mainly for ametryn when comparing the retentions on ametryn-imprinted polymers prepared at 1000 and 1 bar using 2-propanol as porogen (Table 4). Since this effect was not observed on the corresponding atrazine-imprinted material (Table 3), it is specific for the properties of the template. Ametryn (pK_a = 4.1) is more basic than atrazine (pK_a = 1.7) and is thus expected to interact more strongly with methacrylic acid.[14] This leads to the formation of binding sites with a higher affinity and selectivity for the template. Upon further comparison of the atrazine (P3, P3hp) and the ametryn materials (P4, P4hp), the atrazine-imprinted materials show no selectivity for atrazine, as seen by the similar capacity factors for atrazine obtained on P3 and P4. However, ametryn was more retained on the ametryn materials than on the atrazine materials. A certain level of selectivity thus appears to be necessary in order for the pressure effect to be significant. The reason why no pressure effect was observed for P1 and P2 is unclear. It is known, however, that when the polarities of the associated and dissociated complex are different, the polarity of the solvent may to a large extent influence the pressure effect.[9,10]

Conclusions

In molecular imprinting there is a need for additional techniques to increase affinity and selectivity in the rebinding of template to the polymer binding sites. We have shown here that molecular imprinting at high pressures can result in enhanced retentions of the template. It is believed that pressure-induced stabilization of the monomer−template assemblies contributes to the pressure effect observed. The intrepretation is, however, complicated by the fact that no pressure effect was observed for the atrazine-imprinted materials. Nevertheless, high-pressure polymerization may be a feasible technique in order to enhance selectivity in molecular imprinting, particularly when monomer−template complexation is weak and associated with a large decrease in volume.

Acknowledgment. This work was supported by the National Bank of Sweden Tercentenary Foundation and by a postdoctoral fellowship (C.D.) from the graduiertenkolleg of supramolecular chemistry at the University of Mainz. We wish to thank Professor Bernhard Wolf at the University of Mainz for valuable assistance and fruitful discussions. The valuable advice from Professor William Pirkle, University of Champaigne−Urbana, IL, is also greatfully acknowledged.

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MA960745I