Molecular imprinting of flat polycondensed aromatic molecules in macroporous polymers

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(Received 24 December 1991)

2,6-Diaminoanthroquinone (DAAQ) has been used as a non-covalently bound template in order to generate shape-selective cavities in crosslinked porous polymers based on ethylene glycol dimethacrylate (EGDMA) and divinylbenzene (DVB). Dimethylsulphoxide was used as a solvent and porogen. When acrylic and methacrylic acid were employed to form a complementary binding site within the cavity, there was no evidence for selective resorption of DAAQ and hence no evidence for shape-selective cavity formation. However, when a monomer containing sulphonic acid groups was used in place of the polymerizable carboxylic acids, stronger interaction with DAAQ was achieved and shape-selective cavities within polymers were formed as indicated by the selective resorption of DAAQ by such polymers relative to analogous non-templated polymers. Similarly selective sorption of non-functional anthracene, with a similar framework to DAAQ, was also demonstrated, confirming the shape-selective nature of the cavities.

(Keywords: molecular imprinting; template polymers; shape-selective cavities; macroporous polymers)

INTRODUCTION

We have recently embarked on a research programme aimed at developing crosslinked polymers with anisotropic molecular cavities capable of selectively sorbing a flat polycondensed aromatic molecule from a mixture in solution, such that the sorbed species might be assayed quantitatively via linearly polarized infra-red spectroscopy. As a first objective in this, it has been necessary to develop the synthesis of appropriate macroporous polymers, using the templating technique pioneered by Wulff and his coworkers[1,2]. This involves the incorporation of a template molecule carrying at least two polymerizable groups into the macromolecular matrix, during polymerization, followed by chemical cleavage and washing out of the template species. A related approach in which the template is held by non-covalent forces has been developed by Andersson, Sellergren and Mosbach[3]. Important contributions have also been made by the groups of Shea[4], Neckers[5] and Sarhan[6].

In the main, templating of cavities within polymers has been utilized in the chromatographic resolution of enantiomers, where one particular optical isomer has been used as the template in preparing the polymer cavities[7]. Sugar derivatives[2] and amino acid derivatives[8] have received most attention, but recently Wulff's group reported on the separation of free sugars[9].

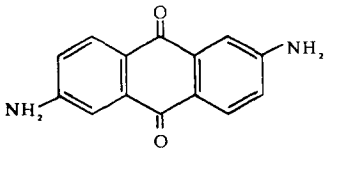
Attempts have also been made to utilize polymer cavities as the site for chemical reaction, hence approaching closely the mechanism of enzyme action. In this instance the template is chosen as a reaction transition state analogue[10], and here a close parallel emerges with the development of catalytic antibodies (abzymes)[11]. Other reactive groups have also been incorporated into polymer cavities[12].

We now report on our attempts to produce cavities employing a flat tricyclic condensed aromatic as the template. Shea and Sasaki[4] have previously used a *p*-vinylphenylbisketal derivative of 1,3-diacetylpyrene, but in our case we have utilized 2,6-diaminoanthraquinone (DAAQ), non-covalently bound to the incipient matrix by salt formation with acrylic acid (AA), methacrylic acid (MAA) or 2-acrylamido-2-methyl-1-propanesulphonic acid (AAMPSA).

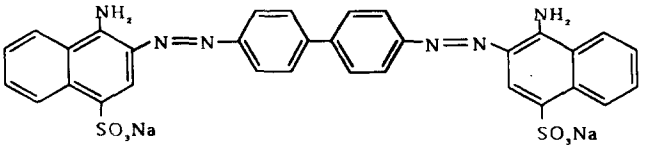
EXPERIMENTAL

Materials

Methyl methacrylate (MMA; BDH Chemicals Ltd), ethylene glycol dimethacrylate (EGDMA; Koch-Light Laboratories Ltd), styrene (ST; FSA Laboratory Supplies), divinylbenzene (DVB: 23.8% *p*-DVB, 56.8%



DAAQ



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0032-3861/93/010077-08

m-DVB, 10.5% *m*-ethylvinylbenzene, 8.2% *p*-ethylvinylbenzene; The Dow Chemical Co.), acrylic acid (AA; BDH Chemicals Ltd), methacrylic acid (MAA; Aldrich Chemical Co.) and 2-acrylamido-2-methyl-1-propanesulphonic acid (AAMPSA; Aldrich Chemical Co.) were all used as supplied.

Likewise, 2,6-diaminoanthraquinone (DAAQ; Aldrich Chemical Co.), anthracene (ATC; BDH Chemicals Ltd), Congo Red (CR; Aldrich Chemical Co.), dilauroyl peroxide (DLP; Fluka AG), *N,N,N',N'*-tetramethylethylenediamine (TMED; Fluka AG), pyridine (Py; Aldrich Chemical Co.) and hydrochloric acid (36%; BDH Chemicals Ltd) were all employed as supplied.

Dimethylsulphoxide (DMSO; Aldrich Chemical Co.) was dried over molecular sieves (4 Å).

Preparation of polymers

2,6-Diaminoanthraquinone (DAAQ) was weighed into a test tube and DMSO added. The mixture was shaken until all the DAAQ dissolved. An acidic monomer was added and dissolved, and then all other comonomers were likewise dissolved. Finally DLP was added and dissolved at 35°C. The solution was saturated with nitrogen before TMED was added (the final compositions of all polymerization mixtures are summarized in *Table 1*). Nitrogen was blown through the polymerization mixture until the first sign of polymerization (maximum time 10 min). Then the test tube was sealed with a rubber stopper and immersed for 24 h in a thermostated water bath (for the polymerization temperatures, see *Table 1*). After polymerization the test tube was broken and the polymer in the form of a solid block was separated.

Extraction and drying of polymers

Procedure EX1. Each polymer block was cut into the form of irregular particulates ~3–5 mm in size weighed (typically 7 g) into a conical flask (100 ml) and DMSO (10 ml/g polymer) added. The flask was equipped with a magnetic stirrer and a condenser, and was placed in a water bath thermostated at 50°C. After a defined time the DMSO in the flask was changed for a fresh portion and the extraction continued in the same way. The solvent was changed four times during a 48 h period at intervals ~4, 4, 16, 8, 16 h. Afterwards the polymer was separated and dried under reduced pressure (0.05 mmHg) at 70°C to constant weight.

Procedure EX2. Procedure EX1 was performed first using a mixture of DMSO (80 vol%) and pyridine (20 vol%). The polymer was then extracted with three portions of pure DMSO (10 ml/g polymer) for the periods 4, 4, 16 h respectively at 50°C with stirring. Extraction was continued with 0.1 M HCl in DMSO (20 ml/g polymer) for 24 h at room temperature, followed by three portions of DMSO (10 ml/g polymer) for the periods 4, 4, 16 h at 50°C with stirring. Finally the polymer was separated and dried in the same way as in the procedure EX1. With DVB-crosslinked polymers magnetic stirring was replaced by occasional shaking.

Procedure EX3. This was similar to EX1 but using eight portions of DMSO in time intervals 3, 16, 8, 24, 24, 64, 32, 43, 29 h (total extraction time 243 h). The course of the extraction was observed by u.v. spectrophotometry. Afterwards the polymer was separated and dried for 17 h under reduced pressure (0.05 mmHg) at 70°C. Then it was extracted for 6 h with DMSO (10 ml/g polymer) at 50°C under stirring, and dried again; and the whole extraction–drying cycle was repeated five times. The last drying step was carried out to constant weight of the polymer.

DMSO uptake measurements

Dry polymer (~0.5 g) was weighed with high precision into a pre-weighed dry glass sinter stick. The stick was

Table 1 Composition of polymerization mixtures

Polymer	Composition[a] of monomer mixture (g)											Polymerization temperature (°C)
	EGDMA	MMA	DVB	ST	AA	MAA	AAMPSA	DAAQ	DLP	TMED	DMSO	
I	4.80				0.083			0.127	0.103	0.033	5	35
II	4.92				0.084				0.100	0.037	5	35
III	4.80				0.077			0.124	0.101	0.038	7.5	35
IV	4.92				0.079				0.101	0.032	7.5	35
V	4.79					0.090		0.124	0.098	0.029	5	35
VI	4.91					0.096			0.102	0.035	5	35
VII	4.38	0.42			0.082			0.126	0.102	0.031	5	35
VII	4.48	0.44			0.076				0.104	0.029	5	35
IX	4.38	0.41			0.092			0.127	0.099	0.029	5	35
X	4.48	0.42			0.097				0.102	0.030	5	35
XI	4.66						0.225	0.126	0.109	0.030	5	35
XII	4.77						0.222		0.102	0.031	5	35
XIII			4.80		0.077			0.123	0.102	0.030	5	40
XIV			4.92		0.087				0.098	0.030	5	40
XV			4.38		0.080			0.127	0.107	0.029	5	40
XVI			4.48		0.082				0.105	0.029	5	40

[a]EGDMA, ethylene glycol dimethacrylate; MMA, methyl methacrylate; DVB, commercial divinylbenzene; ST, styrene; AA, acrylic acid; MAA, methacrylic acid; AAMPSA, 2-acrylamido-2-methyl-1-propanesulphonic acid; DAAQ, 2,6-diaminoanthraquinone; DLP, dilauroyl peroxide; TMED, tetramethylethylenediamine; DMSO, dimethylsulphoxide

closed from underneath and DMSO (3 ml) added to the polymer. The stick was closed from above and left for 24 h at room temperature. The excess DMSO was filtered off and the interstitial volume of DMSO separated centrifugally (1000 rev min^{-1}). The weight of the polymer and the sinter stick was determined after centrifugation. The DMSO uptake value was then calculated using the equation:

$$DU = \frac{W_{spf} - W_{dp} - W_{df} - W_{sf}}{W_{dp}}$$

where DU (g DMSO/g dry polymer) is the DMSO uptake, W_{spf} (g) is the weight of the polymer plus the dry glass sinter stick after contact with DMSO and centrifugation, W_{dp} (g) is the weight of the starting dry polymer, W_{df} (g) is the weight of the dry glass sinter stick, and W_{sf} (g) is the DMSO uptake by the empty dry glass sinter stick.

Pore size measurements

Pore size data were obtained from mercury porosimetry using an Autopore II 9220 (Micromeritics Instrument Corporation, USA).

Sorption measurements

Calibration of u.v. spectrophotometer. A series of six solutions of each chromophore in DMSO in the concentration range 4–9 g l^{-1} was prepared. The solutions were diluted 200 times (50 μl to 10 ml of DMSO solution) and their u.v. and visible spectra were measured on a Shimadzu UV–Visible Recording Spectrophotometer UV-250 (Shimadzu Corporation, Japan) over the wavelength range 190–700 nm using 2 mm cells. Pure DMSO was used as the reference medium. Absorbances of the most significant absorption peaks were measured (for DAAQ $\lambda_{DAAQ} = 347$ nm, ATC $\lambda_{ATC} = 360$ nm, CR $\lambda^1_{CR} = 533$ nm, $\lambda^2_{CR} = 347$ nm, $\lambda^3_{CR} = 360$ nm) and plotted against the corresponding solution concentrations.

Standard sorption procedure. Approximately 0.1 g of each dried polymer was weighed with high precision into a 2 ml test tube and a sorption solution containing ~6.5–7.0 g l^{-1} of DAAQ or ATC and 6.5–7.0 g l^{-1} of CR (standard sorption solution) was added (1 g/0.1 g polymer). The test tube was sealed with a stopper and shaken for 24 h at room temperature. The supernatant solution was separated from the polymer with a syringe. In the case of DVB-based polymers, no shaking was used. With the sorption experiments at 50°C, no shaking was used, and the test tubes were placed in a thermostat. After sorption the contents of the test tubes were cooled to room temperature and the solutions were separated.

In determining the sorption concentration dependence, the standard sorption solution was diluted 10 and 100 times before addition to a test polymer, and a special sorption solution containing ~13 g l^{-1} of DAAQ and 13 g l^{-1} of CR was also prepared.

For the sorption time dependence, 50 μl samples of the sorption solution from a single sorption mixture were taken at specific time intervals.

Sorption by an extracted undried polymer. An extracted undried polymer was centrifuged in the same way as in the DMSO uptake experiments and weighed into a 2 ml test tube. The sorption solution was added (1 g/0.1 g dry polymer, the weight of which was calculated from its weight after centrifugation and its DMSO uptake value). The subsequent steps were the same as in the standard sorption procedure.

In all sorption measurements, samples of starting sorption solutions were taken as well and their concentrations measured.

U.v. spectrophotometric monitoring of sorption. A sorption solution was diluted 200 times and the u.v.–visible spectrum of such a solution was scanned. At least three samples from each sorption solution were prepared and measured, and the average concentration value was calculated. All experimental arrangements were the same as in the calibration measurements.

Concentration calculations. First the CR concentration in the sorption solution under test was read from the calibration curve using the absorbance value at the wavelength $\lambda = 533$ nm. Then the corresponding CR absorbance value at $\lambda = 347$ nm (in the case of DAAQ) or $\lambda = 360$ nm (in the case of ATC) was read from the calibration curve. Such an absorbance value was subtracted from the total absorbance value at $\lambda = 347$ nm (for DAAQ) or $\lambda = 360$ nm (for ATC) to get the absorbance due to pure DAAQ or ATC. Using this value, the DAAQ or ATC concentration in the sorption solution was read from the relevant calibration curve.

RESULTS AND DISCUSSION

Preparation of polymers

A series of polymers was prepared (*Table 1*) to get information on how the compositions of polymerization mixtures influence the properties of the resulting polymers. Two types of polymers were prepared – polymers based on EGDMA and polymers based on DVB. These crosslinking bifunctional monomers represented the main component of all monomer mixtures. In some cases low levels of monomers as MMA or ST were added to try to optimize the polymer structure, but no thorough examination of the monomer/crosslink ratio was carried out. Monofunctional monomers containing acidic groups (AA, MAA, AAMPSA) were used in an attempt to form ionic bonds with the DAAQ template. DMSO was used as the solvent porogen because it was the only convenient one capable of dissolving DAAQ (see the next paragraph) in a sufficiently high concentration.

DAAQ was used as a model template molecule for the proposed later use of diaminodiazofluorene (DADAF). All monomer mixtures used contained 2.5 wt% of DAAQ, the solubility limit at room temperature being ~5 g of DAAQ in 100 g of DMSO. In the case of polymerization mixtures containing DVB (XIII, XIV, XV, XVI), even 2.5 wt% DAAQ was near the limit since DAAQ partly precipitated from the polymerization mixtures after the addition of monomers. For all template polymers, blank polymers (containing no DAAQ) were also prepared for comparative measurements.

A redox initiation system consisting of DLP and TMED was used to perform polymerization under mild conditions to allow the proposed later use of less stable template substances (DADAF).

Polymerizations of mixtures based on EGDMA were performed at 35°C for 24 h. They were rapid; the change from a solution to a gel form was observed 5–7 min after the addition of TMED under N_2. During the polymerization the transparency of the starting polymerization mixture did not change. A small volume contraction was observed. The polymers formed were hard and were difficult to cut into pieces.

Polymerizations of mixtures based on DVB were slower. They were performed for 24 h at 40°C. The first sign of polymerization occurred after ~2–3 h. The initial slightly turbid solution became totally opaque during the polymerization and a small volume contraction was observed. The polymers formed were fragile and it was possible to break them under mild shear.

Extraction of polymers

The extraction of polymers is a very important process; in principle, it releases the template molecule and creates the cavities capable of specific resorption of the template. It may also remove other materials from the polymer, e.g. residual monomers or oligomers, and initiator fragments. As DMSO satisfied such requirements best, it was used in all extraction procedures (these are summarized in *Table 2*). To improve the extraction process the temperature was raised to 50°C and the extraction mixture was stirred (stirring was not used in the case of DVB-based polymers because of their fragility).

In preliminary experiments it was found that extraction procedure EX1 did not release all the visible template despite the last portion of extractant remaining colourless. Surprisingly, after drying such polymers, contact with further DMSO released further visible levels of DAAQ. It seems that drying causes structural changes in the polymer, enabling further DAAQ to be released. Procedure EX3 was developed as a result of this observation.

As ionic or hydrogen-bonding interactions between the amino groups of DAAQ and the acidic groups of a polymer (carboxylic or sulphonic groups) were expected in the template polymers, any extraction procedure should not only facilitate the transport of DAAQ molecules from the polymer but also should break efficiently the chemical interaction. This might be achieved by use of a base stronger than the DAAQ amino groups, e.g. pyridine, in the extraction solvent. Such an extraction process would be important particularly in the case of polymers with sulphonic monomers because of the much higher acidity of sulphonic groups in comparison with carboxylic groups. A mixture of DMSO (80 vol%) and pyridine (20 vol%) was therefore used

Table 2 Physical characterization of extracted polymers

Starting polymer	Extraction procedure	Extracted polymer	Hg porosimetry			DMSO uptake ($g\,g^{-1}$)
			Total intrusion volume ($ml\,g^{-1}$)	Median pore diameter (μm)	Bulk density ($g\,ml^{-1}$)	
I	EX1	Ia	0.2657	0.0068	0.9865	0.998
I	EX3	Ib	0.4816[d]	0.0063	0.7867	1.144
I	EX3	Ib[e]	0.4261[a]	0.0062[a]	0.8309[a]	1.144
I	EX3[a]	Ic	0.2089	0.0057	0.8319	1.144
I	EX2	Id				1.025
II	EX3	IIa	0.2348	0.0065	1.0102	1.022
II	EX2	IIb				1.039
III	EX1	IIIa	0.4546	0.0075	0.8238	1.607
III	EX3[b]	IIIb	0.5268	0.0080	0.7637	1.624
IV	EX1	IVa	0.3410	0.0069	0.9118	1.528
V	EX1	Va				1.099
VI	EX1	VIa				0.994
VII	EX1	VIIa				1.069
VIII	EX1	VIIIa				1.007
IX	EX1	IXa				1.064
X	EX1	Xa				0.932
XI	EX1	XIa	0.4376	0.0072	0.8378	1.077
XI	EX2	XIb	0.3948	0.0072	0.8646	1.100
XII	EX1	XIIa	0.1244	0.0067	1.1337	0.185
XII	EX2	XIIb	0.1340	0.0072	1.1347	0.467
XIII	EX1[c]	XIIIa				3.247
XIV	EX1[c]	XIVa				1.499
XV	EX1[c]	XVa				2.960
XVI	EX1[c]	XVIa				2.720

[a]Extracted without drying; process stopped after 243 h
[b]The extraction–drying cycle repeated only four times
[c]Extracted without stirring
[d]Large intrusion in the pore diameter range ~35 μm
[e]Intrusion–extrusion–intrusion measurement cycle

in extraction procedure EX2. To get polymers with cavities with acidic groups in the free acid form, pyridine-extracted polymers were subsequently washed with HCl/DMSO.

Attempts to measure quantitatively the course of extraction were unsuccessful because released with DAAQ was also some other u.v.-absorbing materials (probably monomers and oligomers) and the apparent yields of extractions were as a result higher than 100%. The results suggest, however, that even extraction process EX1 enables the release of most of the DAAQ from the template polymers (probably more than 80%). Finally polymers prepared with 60 vol% DMSO did seem to extract more quickly than those prepared with 50 vol% DMSO.

The influence of the extraction and drying process on the physical properties of polymers was observed visually and by measurements of DMSO uptake and by mercury porosimetry. The results are summarized in *Table 2*.

The EGDMA polymers with carboxylic acid comonomers (I–X) do not show any essential visual difference between template and blank polymers; there is no visible volume change nor change in their turbidity. All the dry samples disintegrated to smaller particulates after contact with DMSO. The effect was more intensive with template polymers yielding particles ~ 1–$2\ \mu m$ in size than with blank polymers yielding particulates ~ 2–4 mm in size. The DMSO uptake values are influenced essentially only by a larger amount of DMSO in polymerization mixtures (polymers IIIa, IIIb and IVa). This effect is also manifest in the Hg porosimetry data.

The EGDMA polymers with the sulphonic AAMPSA comonomer (XI, XII) can be somewhat different after extraction and drying depending on the composition of their initial monomer mixtures. When the DAAQ template is present (XI, XIa, XIb) the samples have a comparatively high porosity and DMSO uptakes, and lower values of bulk density irrespective of the extraction procedure used. The blank polymer (XII) is very different, however. Irrespective of the method of extraction (XIIa, XIIb) the polymer shows a much reduced DMSO uptake, lower total intrusion volume and higher bulk density. Why the exclusion of small amounts of the template, DAAQ, should cause such large changes is not at all clear, and we have no satisfactory explanation at the moment. In the present context, however, it is important that care be used in interpreting the sorption data from these blank polymers.

The polymers crosslinked with DVB and with acrylic acid present (XIIIa, XIVa, XVa, XVIa) all have a very large capacity for DMSO. The template polymer without styrene (XIII) has the highest DMSO uptake and its blank polymer (XIV) shows a significant decrease. There is also a change in appearance from absolutely non-transparent to slightly transparent.

Sorption properties of polymers

The DAAQ resorption behaviour of polymers was quantified by measurement of the concentration changes of components of sorption solutions. As polymers based on EGDMA and DVB swell in DMSO, it was necessary to devise an experimental procedure to eliminate the influence of swelling of polymers on concentration changes of sorption solutions. For this reason all the sorption solutions contained Congo Red (CR) in addition to DAAQ. Since these two compounds have different molecular sizes it was anticipated that the CR molecules would be 'size excluded' from the template cavities, and the change of the DAAQ/CR concentration ratio would be independent of the general concentration change caused by swelling and should reflect specifically the concentration change caused by DAAQ binding in the cavity. CR was chosen as a reference compound not only because of its shape and size but also because of its spectral behaviour. It absorbs in the visible spectral area where DAAQ does not, so that it is possible to measure the concentration of DAAQ and CR independently in a sorption solution. The concentration ratio between DAAQ and CR in a sorption solution is defined as:

$$\alpha = C_{DAAQ}/C_{CR}$$

To eliminate the influence of a possible non-specific sorption, the sorption behaviour of each template polymer was compared with the sorption behaviour of a corresponding blank polymer. The α values were measured for blank polymers as well, and the difference between the sorption behaviour of a template polymer and a corresponding blank polymer was defined as:

$$\beta = \alpha_{template}/\alpha_{blank}$$

If $\beta < 1$ the template polymer manifests specific DAAQ sorption, and $\beta = 1$ indicates no specific effects. The experiments with ATC were evaluated in the same way as with DAAQ.

The results of all sorption experiments with DAAQ/CR in DMSO solutions are summarized in *Table 3*. In all cases, except the last two entries, the α value of the starting solution falls during sorption, i.e. larger levels of DAAQ than of CR enter the polymers. This is true for blank polymers as well as template polymers and is probably a molecular 'sieve' effect. Selective sorption behaviour is reflected more realistically in the β value, which for polymers I–X and XIII–XVI is unity (± 0.01), i.e. no selective sorption of DAAQ into cavities is observed. All of these species use either acrylic or methacrylic acid as the potential source of the non-covalent binding site in the template, and it seems that the level of interaction of these monomers with the weakly basic aromatic $-NH_2$ groups in DAAQ may be too low to allow templating and cavity formation to occur.

Polymers XIa and XIb are significantly different. Their β values are less than unity and we are confident that the variation from unity lies outside the experimental error. These materials do indeed show a preference for the binding of DAAQ, which seems to be a cavity effect. In these cases the monomer AAMPSA was used to form the template and the interactions of the sulphonic acid group in this monomer with the amino groups in DAAQ would be expected to be much stronger than before. Significantly the blank polymers XIIa and XIIb were the ones mentioned earlier, which showed an anomalously large fall in their porosity relative to their respective template species XIa and XIb. In view of this, the molecular 'sieve' effect in these blanks might be expected to be higher than in the other polymers, i.e. the α_{blank} will be depressed (CR being size excluded). More structurally appropriate blank polymers would therefore be expected to have higher α_{blank} values, in which case the β values would have been even lower. The real selective sorption displayed by template polymers XIa

Table 3 Sorption data of polymers with DAAQ/CR/DMSO solution

Polymer	Blank polymer	Starting sorption solution			Sorption solution after sorption			
		DAAQ ($g\ l^{-1}$)	CR ($g\ l^{-1}$)	α	DAAQ ($g\ l^{-1}$)	CR ($g\ l^{-1}$)	α	β
Ia	IIa	6.660	7.080	0.9407	6.627	7.230	0.9166	1.011
Ib	IIa	6.660	7.080	0.9407	6.564	7.205	0.9110	1.005
Ic		6.660	7.080	0.9407	5.847	6.447	0.9069	
IIa	blank	6.660	7.080	0.9407	6.648	7.331	0.9068	
IIIa	IVa	6.660	7.080	0.9407	6.553	7.203	0.9098	1.003
IIIb	IVa	6.660	7.080	0.9407	6.519	7.173	0.9088	1.002
IVa	blank	6.660	7.080	0.9407	6.538	7.210	0.9068	
Va	VIa	6.720	7.060	0.9518	6.800	7.280	0.9341	1.011
VIa	blank	6.720	7.060	0.9518	6.820	7.380	0.9241	
VIIa	VIIIa	6.610	7.265	0.9098	6.687	7.453	0.8972	0.999
VIIIa	blank	6.610	7.265	0.9098	6.697	7.460	0.8977	
IXa	Xa	6.720	7.060	0.9518	6.700	7.250	0.9241	1.000
Xa	blank	6.720	7.060	0.9518	6.800	7.360	0.9239	
XIa	XIIa	6.500	6.890	0.9434	6.750	7.510	0.8988	0.971
XIIa	blank	6.500	6.890	0.9434	6.640	7.170	0.9261	
XIb	XIIb	6.720	7.060	0.9518	6.740	7.300	0.9233	0.982
XIIb	blank	6.720	7.060	0.9518	6.700	7.125	0.9404	
XIIIa	XIVa	6.610	7.265	0.9098	6.669	7.424	0.8983	1.011
XIVa	blank	6.610	7.265	0.9098	6.667	7.503	0.8886	
XVa	XVIa	6.610	7.265	0.9098	6.594	7.350	0.8971	1.013
XVIa	blank	6.610	7.265	0.9098	6.707	7.573	0.8856	

Table 4 Dependence of sorption data of the polymers XIa and XIIa on the sorption solution concentration[a]

Template polymer *Blank polymer*	Starting sorption solution			Sorption solution after sorption			
	DAAQ ($g\ l^{-1}$)	CR ($g\ l^{-1}$)	α	DAAQ ($g\ l^{-1}$)	CR ($g\ l^{-1}$)	α	β
XIa	0.0657	0.0708	0.9280	0.0670	0.0644	1.0404	1.080
XIIa				*0.0659*	*0.0684*	*0.9635*	
XIa	0.653	0.695	0.9396	0.676	0.737	0.9172	0.998
XIIa				*0.656*	*0.714*	*0.9188*	
XIa	6.500	6.890	0.9434	6.750	7.510	0.8988	0.971
XIIa				*6.640*	*7.170*	*0.9261*	
XIa	12.80	13.72	0.9329	13.10	14.56	0.8997	0.980
XIIa				*13.02*	*14.18*	*0.9182*	

[a]24 h, room temperature

and XIb is therefore likely to be stronger than their β values suggest. Both of these species originate from polymer XI and differ only in the extraction procedure used to remove the template. The results suggest that there is little difference in the effectiveness of the two procedures (EX1 and EX2).

Concentration and time dependence of selective sorption by template polymers XIa and XIb

Some preliminary experiments suggested that the sorption properties of polymer XIa might be dependent on the concentration of the initial DAAQ/CR solution. As a result, four sorption solutions were investigated, and the results are summarized in *Table 4* and plotted in *Figure 1*. These show that for solutions above ~2 g DAAQ/l the β value is constant (~0.97) and that selective sorption by cavities is operative. Below this

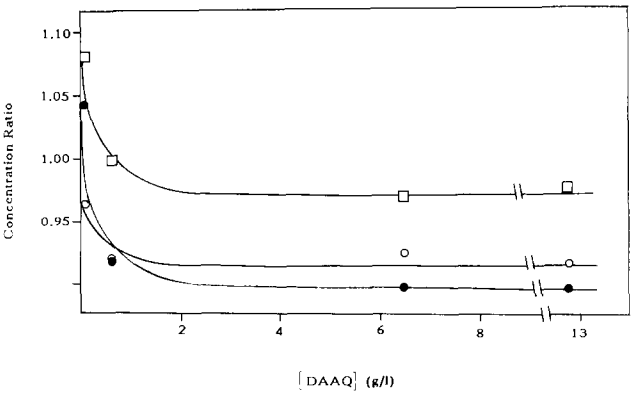

Figure 1 Dependence of sorption properties of polymers XIa and XIIa on the concentration of the sorption solution: (●) α_{XIa}; (○) α_{XIIa}; (□) β

concentration, however, background effects dominate, and the influence of the cavity is lost.

Preliminary experiments also indicated that sorption effects might be time-dependent, and so this parameter was investigated in more detail using template polymer XIa and blank XIIa. The results are summarized in *Table 5* and plotted in *Figures 2* and *3*. Initially the β value is ~ 0.96, implying significant selective binding of DAAQ in cavities. However, on prolonged contact with the sorption solution, the β value rises steadily until all selective interactions *seem* to disappear ($\beta \rightarrow 1$). Closer examination of the separate α values shows that the main component is a steady fall in the α_{blank} value. Indeed, looking at the individual DAAQ and CR concentrations (*Figure 3*), it can be seen that neither of these vary much with the template polymer XIa over 70 h. However, both concentrations rise substantially in the case of the blank polymer XIIa, that for CR rising the more steeply, and accounting for the fall in α_{blank} and the rise in β. Indeed, a close examination shows both concentrations falling slightly over the first 5 h before rising more dramatically. Why there is such a big difference between the behaviour of blank polymer XIIa and template species XIa is not clear, but again this is one of the samples that shows a very low inherent porosity when the template is omitted from the polymerization. It might be that initially this blank polymer exhibits relatively low uptake of all components, but that over a much longer timescale progressive (solvent) swelling does occur with a consequential rise in the external concentration of both DAAQ and CR. The earlier sorption data were collected after 24 h contact with solutions, and significantly the data in *Figure 3* are relatively flat over this time period. The longer timescale changes therefore do not influence the previous conclusions drawn about selectivity.

Table 5 Dependence of sorption data of the polymers XIa and XIIa on the time of sorption[a]

Template polymer *Blank polymer*	Sorption time (h)	Sorption solution after sorption DAAQ ($g\,l^{-1}$)	CR ($g\,l^{-1}$)	α	β
XIa	0.5	6.710	7.430	0.9031	0.966
XIIa		*6.540*	*6.960*	*0.9451*	
XIa	1	6.660	7.380	0.9024	0.970
XIIa		*6.550*	*7.040*	*0.9304*	
XIa	2	6.680	7.400	0.9027	0.966
XIIa		*6.440*	*6.890*	*0.9347*	
XIa	4	6.670	7.460	0.8941	0.960
XIIa		*6.270*	*6.730*	*0.9316*	
XIa	8	6.640	7.380	0.8997	0.957
XIIa		*6.480*	*6.890*	*0.9405*	
XIa	24	6.750	7.510	0.8988	0.971
XIIa		*6.640*	*7.170*	*0.9261*	
XIa	48	6.700	7.440	0.9005	0.993
XIIa		*6.990*	*7.710*	*0.9066*	
XIa	72	6.720	7.340	0.9155	1.024
XIIa		*9.320*	*10.420*	*0.8944*	

[a]Composition of the starting sorption solution: DAAQ, 6.500 $g\,l^{-1}$; CR, 6.890 $g\,l^{-1}$; $\alpha = 0.9434$; room temperature

Table 6 Sorption data of polymers with ATC/CR/DMSO sorption solution[a]

Template polymer *Blank polymer*	Sorption solution after sorption ATC ($g\,l^{-1}$)	CR ($g\,l^{-1}$)	α	β
XIa	6.172	7.203	0.8569	0.974
XIIa	*6.082*	*6.910*	*0.8802*	
XIb	6.042	7.207	0.8384	0.969
XIIb	*5.955*	*6.882*	*0.8653*	

[a]Composition of the starting sorption solution: ATC, 6.400 $g\,l^{-1}$; CR, 6.679 $g\,l^{-1}$; $\alpha = 0.9595$; 24 h; room temperature

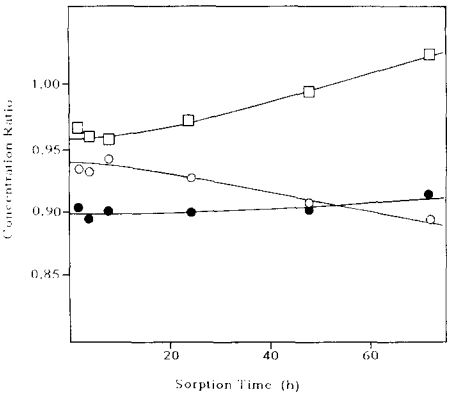

Figure 2 Dependence of the sorption properties of polymers XIa and XIIa on the time of sorption: (●) α_{XIa}; (○) α_{XIIa}; (□) β

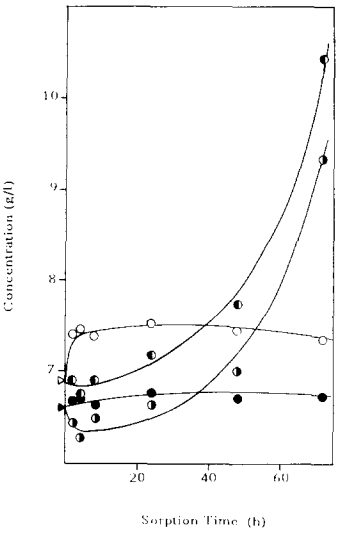

Figure 3 Dependence of the sorption properties of polymers XIa and XIIa on the time of sorption: (●) [DAAQ], polymer XIa; (◑) [DAAQ], polymer XIIa; (○) [CR], polymer XIa; (◐) [CR], polymer XIIa; (▶) $[DAAQ]_{initial}$; (▷) $[CR]_{initial}$

Sorption of anthracene

Previous work on polymer template cavities has shown that two factors contribute to the specificity of the sorption: (i) the cavity shape; and (ii) the presence of chemical groups in the cavity complementary to the groups on any potential sorbate (e.g. the original template). In our own work the longer-term objective is to sense non-functional aromatic compounds, and it was of interest therefore to investigate whether the cavities formed using DAAQ as a template might also show selective binding of anthracene (ATC), a neutral

molecule with a shape and size similar to the central unit of DAAQ. The results are shown in *Table 6*. Both polymers XIa and XIb exhibit β values below unity and of similar magnitude to those for DAAQ for these polymers. This suggests that indeed ATC is sorbed as selectively as DAAQ itself, i.e. the cavity shape is a dominant factor.

CONCLUSIONS

Use of 2,6-diaminoanthraquinone (DAAQ) as a non-covalently bound template molecule does not allow the formation of shape-selective cavities in crosslinked porous polymers when acrylic and methacrylic acid are employed as the incipient complementary binding site within the cavity. However, shape-selective cavities are formed when a monomer containing sulphonic acid groups is used in place of the carboxylic acids. The cavities so formed resorb DAAQ selectively relative to blank polymers with no cavities, and in addition the non-functional molecule, anthracene, with a similar molecular framework, is selectively sorbed to the same extent as DAAQ.

ACKNOWLEDGEMENT

We acknowledge the receipt of a research assistantship for JL from the SERC.

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